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High molecular arborescent polyoxyethylene with hydroxyl containing shell

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Abstract

Arborescent polyoxyethylene of high molar mass (2×10^5 g/mol) and narrow molar mass distribution was synthesized in a three-stage process. In the first stage a triblock copolymer of ethylene oxide (central block, DP ca. 90) and 2,3-epoxypropanol-1 (short flanking blocks, DP ca. 5) was synthesized. The potassium alcoholate derived from this copolymer was used to initiate the polymerization of ethylene oxide and the subsequent addition of protected glycidol (1-etoxyethyl glycidyl ether). After deprotection the short polyglycidol blocks were used as branching units for the next generation. Repeated step by step process leads to the 'pom-pom like' branched polyoxyethylene macromolecules enriched with the reactive hydroxyl groups in the outer shell. The branched structure of the obtained polymers was evidenced by the size exclusion chromatography and NMR spectroscopy.

Keywords: Hyperbranched polymers; Poly(ethylene oxide); Anionic polymerization

1. Introduction

Poly(ethylene oxide), the polymer of the simplest oxirane, has found many applications, amongst them biological and biomedical [1–4]. In many cases the control of the molar mass and a high content of the functional groups is necessary.

When the attempted degree of polymerization of ethylene oxide does not exceed ca. 500, the anionic polymerization of this monomer is living and allows to control the molar masses and to synthesize linear polymers of well defined functionality [5,6]. The polymerization using calcium or strontium catalysts, leading to much higher molar masses, is not living, so that neither controlled functionality nor controlled molar masses may be obtained [7,8].

The syntheses of the star-like branched or hyperbranched PEO may help to overcome these difficulties. In spite of the higher molar mass the degree of the polymerization may be controlled, when arms of the star or branches of the tree are generated using living techniques. The content of the functional groups may be much higher, then in the case of the linear analogues of comparable molar mass, as each arm may be terminated with a proper function. Also the limited length of the PEO chains between the branching points may prevent their crystallization, which is of importance for solid polymer electrolytes [9,10].

Much attention has been paid to the synthesis of non-linear poly(ethylene oxides). Stars have been synthesized using both the arm first and the core first methods. In the first case, polyoxyethylene chains were connected with a proper multi-functional core [11,12]. The 'core first' approach attempts to obtain PEO stars using the polymerization of the ethylene oxide initiated by the active centers of the preformed core. The living anionic polydivinylbenzene, first described by Lutz [13] is probably most frequently used.

Penczek [14] described the use of the anionic polymerization of diepoxides for the formation of the core. Other cores were also used, amongst them carbosilanes [15], PAMAM dendrimers [16] and others. In some cases, the star arms may be branched to yield arborescent polymers.

Gnanou [17] multiplied the active centers using a

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dioxane derivative of halogenoesters [18]. Since Frey et al. ([19], for review, see [20]) have perfected the polymerization of glycidol to densely and regularly branched polyols this process and this polymer have been used extensively to produce multi-arm polyether star or arborescent polymers. Hyperbranched polyglycidol was used to initiate the polymerization of oxiranes of different philicity [21,22]. Random hyperbranched copolymers of glycidol and other oxiranes were also described [23].

Here we want to describe an approach to synthesize an arborescent poly(ethylene oxide) of 'pom-pom like' structure using the living polymerization techniques and the chain branching properties of glycidol.

2. Experimental

2.1. Materials

Poly(oxyethylene) diol of $M_n = 4000$ g/mol (Fluka) was purified by precipitation in *n*-heptane and dried under vacuum. Ethylene oxide (Fluka) was dried several days over CaH_2 and distilled. 2,3-Epoxypropanol-1 (glycidol) (Fluka) was dried over molecular sieves and distilled two times under reduced pressure. Racemic 1-etoxyethyl glycidyl ether, further referred to as glycidol acetal, was synthesized from glycidol and ethyl vinyl ether as described by Fitton [24]. Dimethyl sulfoxide was dried over CaH_2, distilled under reduced pressure and dried over BaO. Potassium *tert*-butoxide (Fluka), cesium hydroxide (Aldrich) and oxalic acid (Fluka) were used as received.

Linear poly(ethylene oxide) of $M_n = 160,000$, $M_w/M_n = 1.70$ was kindly supplied by Prof. Christo Tsvetanov, Institute of Polymers, Bulgarian Academy of Sciences in Sofia.

2.2. Polymerization of glycidol initiated with PEO cesium dialcoholate

All polymerizations were carried out under dry nitrogen or using standard high-vacuum technique.

Cesium alcoholate of poly(oxyethylene) diol 4000 g/mol was prepared as described previously [25] by reacting poly(oxyethylene) diol with CsOH in water and subsequently removing water by the azeotrope distillation with benzene. The initiator (1.1 mmol, 4.67 g) was dissolved in DMSO (5 ml) and after heating to 90 °C a solution of glycidol in DMSO (2.8 ml 50 wt%) was added at a rate of 0.01 ml/min using a syringe pump. The polymerization was completed after 10 h, as indicated by the gas chromatography. DMSO was removed under vacuum and the crude product was dissolved in $CHCl_3$ and fractionated by stepwise addition of *n*-hexane.

2.3. Synthesis of block copolymer of ethylene oxide and glycidol

Triblock copolymer consisting of central oxyethylene block and two glycidol acetal (ethoxy ethyl glycidyl ether) side blocks was prepared as described before [25] using 11.4 g (2.67 mmol) of PEO cesium dialcoholate and 4.48 g (30.7 mmol) of glycidol acetal. Hydroxyl groups in the polyglycidol blocks were recovered by hydrolysis of the prepared poly(ethoxy ethyl glycidyl ether)-block-poly(oxyethylene)-block-poly(ethoxy ethyl glycidyl ether) in acetone/water solution using oxalic acid. After hydrolysis acetone was removed, the water solution was neutralized and desalinated with ion exchange resins. Water was removed under reduced pressure, the obtained polymer dissolved in THF, precipitated in *n*-heptane and dried at room temperature under vacuum.

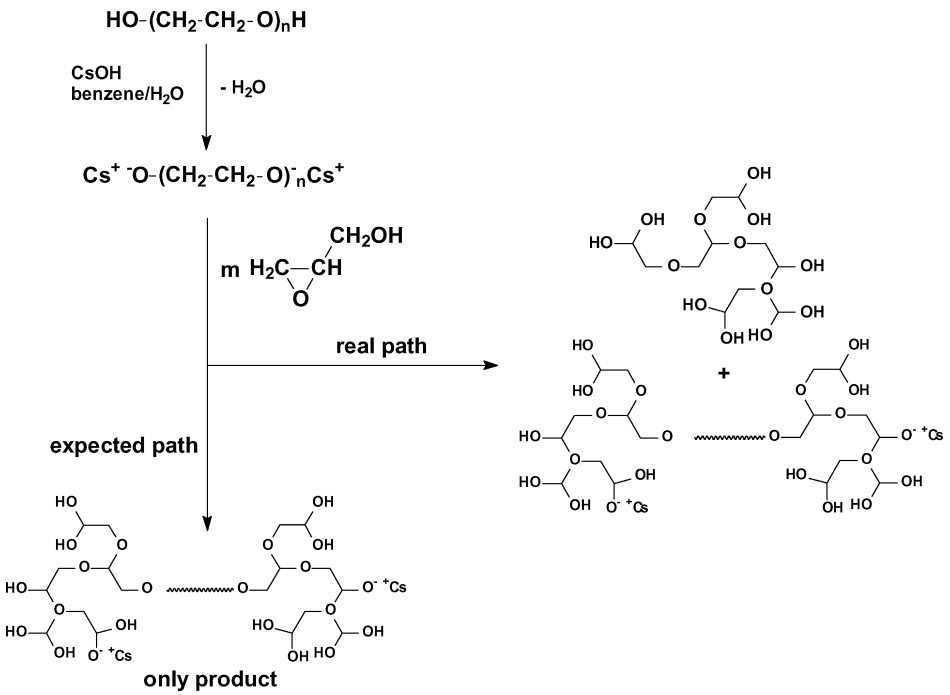
2.4. Synthesis of branched poly(oxyethylene) polymers

The triblock copolymer of oxirane and glycidol (0.8 g, 0.164 mmol) was introduced into a reactor equipped with magnetic stirrer and dried 2 days under vacuum, then dissolved in DMSO (10 mL). Almost all DMSO was evaporated under vacuum to remove adventitious water; another portion of DMSO (10 ml) was added and stirred until the macroinitiator has dissolved. Then 0.057 g (0.509 mmol) of potassium *t*-butoxide in 10.5 ml DMSO was added under stirring. *t*-Butanol formed and almost all DMSO were removed i.v. and the residue was dissolved in 20 ml DMSO. Solution of 3.96 g ethylene oxide (90 mmol) in 14 ml DMSO was added and the polymerization was carried out at 50 °C during 24 h. The reaction mixture was cooled down and samples for GC, SEC and NMR measurements were taken under nitrogen. 1.72 g glycidol acetal (11.8 mmol) was added under nitrogen from calibrated vial equipped with PTFE valves and the polymerization was carried out at 60 °C. After 24 h full monomer conversion was obtained, as indicated by the gas chromatography. DMSO was removed under reduced pressure and the polymer was hydrolyzed to remove the protective groups of glycidol acetal and purified as described above.

The next generations of the hyperbranched PEO were synthesized in the same way using the polymer of the previous generation as a multi-functional macroinitiator. To avoid precipitation of the macroinitiator from the solution only up to 10% of all hydroxyl groups were ionized.

2.5. Measurements and characterization

Size-exclusion chromatography measurements were performed in tetrahydrofurane (THF) using PSS-SDV 5 μ columns: 10^5, 10^3, 2×100 Å or in *N*,*N*-dimethylformamide (DMF) with 5 mmol/l KBr using a set of PSS GRAM 10 μ columns: 10^3, 10^2 and 30 Å. All chromatograms were



Scheme 1. Attempted 'one pot' synthesis of branched PEO.

obtained at 1 ml/min. Differential refractometer from WGE Dr Bures was used as concentration detector and the molar masses were determined using the DAWN multi-angle laser light scattering detector (MALLS) from Wyatt Technology Corporation and their Astra software. Where calibration with polymer standards was applied, the software WINGPC for PSS company was used.

NMR spectra were measured at 300 MHz (^{1}H) or 75 MHz (^{13}C) using a Varian Unity spectrometer.

The contents of primary and secondary hydroxyl groups in obtained polymers were estimated from intensities of signals at $\delta = 4.2–4.6$ ppm (CH_2) and $\delta = 5.2–5.4$ ppm (CH) (for glycidol block) and $\delta = 4.4$ ppm (CH_2 of the PEO end groups) in the ^{1}H NMR ($CDCl_3$) spectra of the corresponding trichloroacetyl urethanes obtained in the reaction with trichloroacetyl isocyanate [26].

Gas chromatograms were run on the VARIAN 3400 chromatograph equipped with FID detector and column DB 5 J&W Scientific with diameter 30 m × 0.32 mm.

3. Results and discussion

Two strategies of the synthesis of hyperbranched

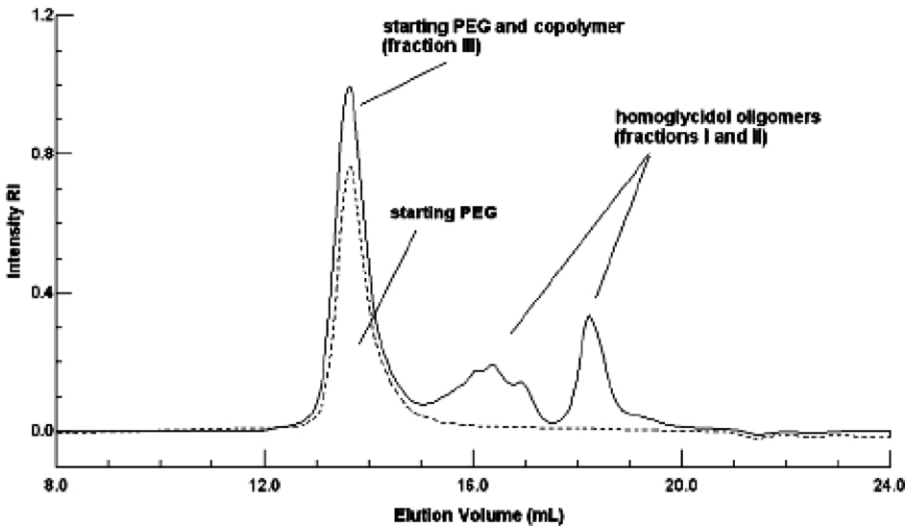
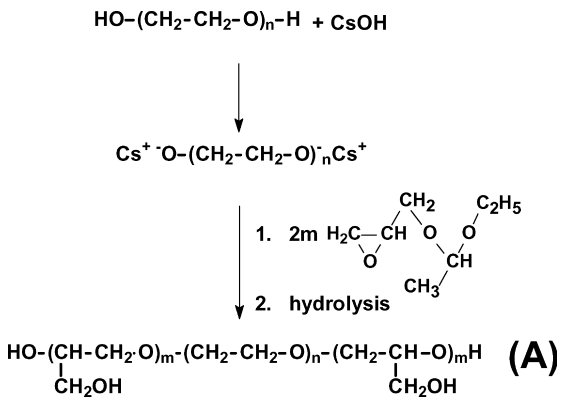


Fig. 1. GPC traces of the product of the polymerization of glycidol initiated with polyethylene glycol cesium dialcoholate; product (solid line) and starting PEO 4000 (dotted line) (solvent: DMF containing 5 mmol/l KBr).



Scheme 2. Synthesis of the triblock copolymer of ethylene oxide and glycidol.

oxyethylene polymers with glycidol branching of controlled structure were designed and verified.

3.1. Method 1. 'One pot' approach: formation of the branches by the polymerization of unprotected glycidol initiated with alcoholate end groups of the polyoxyethylene macromolecule

First method we attempted is shown in Scheme 1. The polymerization of glycidol is initiated with a PEO macroinitiator. After completed, ethylene oxide is introduced into the system. Its polymerization could be expected to produce branches, as each hydroxyl group should initiate the polymerization of EO due to the fast exchange of protons. The repetition of this procedure should yield branched PEO macromolecules.

This method could be successful only if the transfer reaction of the active chain end to hydroxyl group in glycidol is absent or is very slow comparing with the chain propagation. To minimize the transfer reaction the monomer was added slowly, as described by Frey [19,27] and discussed later by Bharathi and Moore [28].

To synthesize a hyperbranched macromolecule of polyoxyethylene the poly(ethylene glycol) $M_n = 4000$ g/mol was chosen and its cesium dialcoholate was used as a macroinitiator for the polymerization of glycidol. Polymerization was carried out in DMSO with a very slow glycidol addition (0.01 ml/min) at 90 °C. The SEC indicates that the product consists of three fractions, two low molecular ones (fraction I and II) and the third of the retention time almost the same as the retention time of the starting PEO (Fig. 1).

On the preparative scale it was easy possible to separate two fractions: a fraction soluble in THF and a fraction insoluble in this solvent. Homopolymers of EO are soluble in THF, at least when a minimal molar mass exceeded, the polymers of glycidol are not. The SEC analysis of the fractions indicates that the THF soluble fraction is fraction III and the THF insoluble fraction is a mixture of the SEC fractions I and II. The ^{1}H NMR spectra of the mixture of fractions I and II are identical with the spectra of branched polyglycidol. The ^{1}H NMR spectrum of fraction III shows that it consist mostly of PEO and contains only a few percent of glycidol.

It indicates that only a small amount of glycidol is added to poly(ethylene glycol) chain and the chain transfer reactions in this process are present or even dominating. The formed homopolymer of glycidol would initiate the polymerization of ethylene oxide in the next steps and finally yield a mixture of the homopolymers of glycidol and the expected copolymer. We were not able to find conditions for the suppression of the chain transfer and a clean synthesis of the copolymer using the approach described above.

3.2. Method 2. Formation of the branches by the polymerization of protected glycidol initiated with alcoholate end groups of the growing polyoxyethylene macromolecule and subsequent deprotection

A clean synthesis of the dendritic polymer makes the suppression of the chain transfer reaction to monomer necessary. This may only be achieved if the hydroxyl group of glycidol is protected. The use of several protecting groups has been described. Fitton [24] reported the acetalization of the hydroxyl group of glycidol to 1-etoxyethyl glycidyl ether. The anionic polymerization of this monomer is possible [29], is close to living [30] and may be used to obtain block copolymers of ethylene oxide and glycidol in a well-controlled way [25].

The synthetic route is presented on Scheme 2. A

Table 1
Molar masses, molar mass distributions and polymerization degrees of blocks of obtained arborescent copolyethers

Initiator	Product of the polymerization after deprotection							
	M_n [a]	$\overline{DP}_{EO}$ [a,b]	$\overline{DP}_{Gl}$ [a,b]	M_n [c]	M_w/M_n [c]	$\overline{DP}_{EO}$ [b,d]	$\overline{DP}_{Gl}$ [b,d]	Product
Cesium dialcoholate of PEO 4000	4850	90	5.8	5000	1.10	94	5.9	A
Potassium alcoholate of A, degree of ionization ca. 8%	33,180	39	5.2	33,000	1.04	37	5.5	B
Potassium alcoholate of B, degree of ionization ca. 8%	195,340	37	4.3	203,000	1.03	36	4.5	C

[a] Calculated from the feed ratio.
[b] $\overline{DP}$ of block grown in each generation.
[c] Measured by SEC–MALLS.
[d] Estimated from SEC–MALLS and ^{1}H NMR.

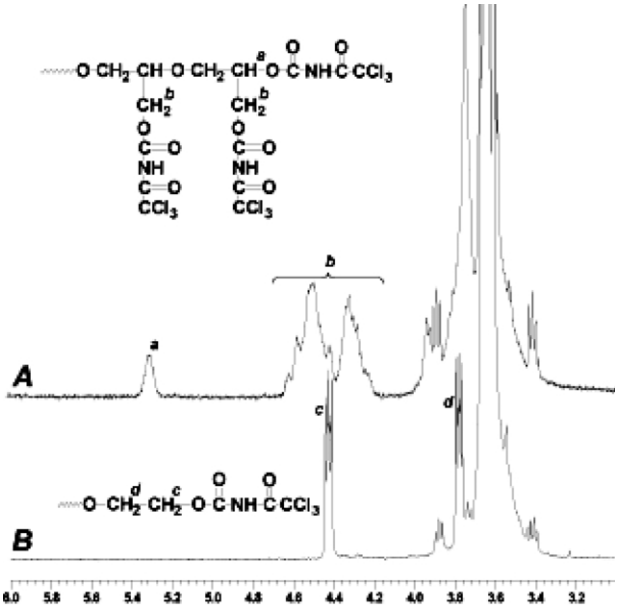


Fig. 2. ^{1}H NMR of the trichloroacetyl urethane derivatives of the polymer A, Table 1 (upper trace) and polymer B in Table 1 before glycidol acetal addition (lower trace) (300 MHz, $CDCl_3$).

polyglycidol-block-PEO-block-polyglycidol containing a PEO central block of $DP_n = 90$ flanked with two polyglycidol blocks of $DP_n = 6$ each was obtained in the first step (Table 1, product A).

The proof of the structure was delivered by the SEC and ^{1}H NMR.

The ^{1}H NMR proves the presence of the glycidol units (Fig. 2, trace A), while the SEC (Fig. 3, trace A) indicates a monomodal molar mass distribution, thus confirming their incorporation.

The length of the polyglycidol blocks was determined by the ^{1}H NMR analysis after the polymer has been reacted with trichloroacetyl isocyanate [26]. The signals of the methine and methylene groups of the obtained urethanes are distinctly different from each other and from the CH_2 group in the urethane of the PEO block end group (Fig. 2). The average molar mass estimated from CH and CH_2 signals of

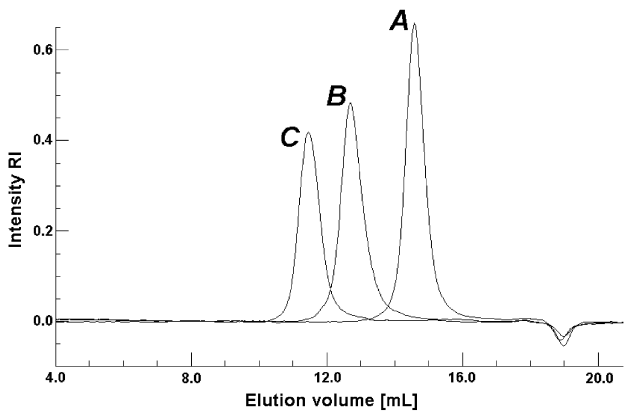
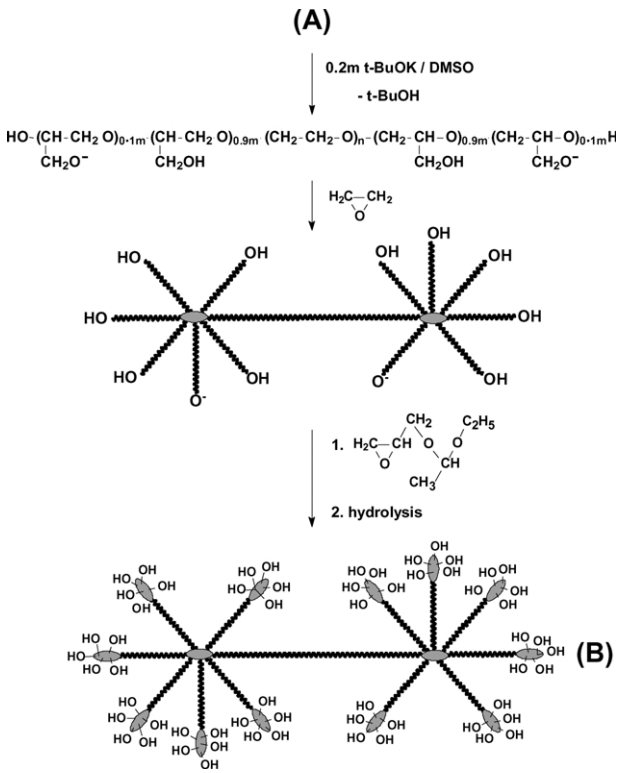


Fig. 3. SEC traces of the polymers A, B and C from Table 1 (solvent: DMF containing 5 mmol/l KBr).



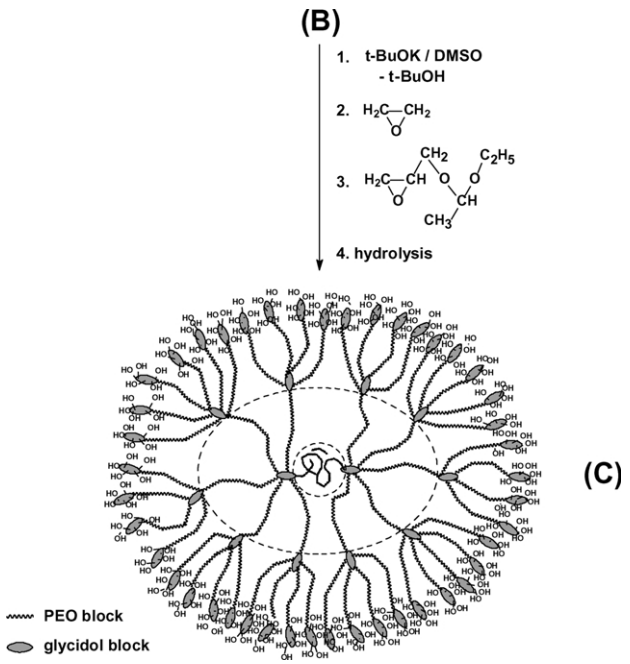
Scheme 3. Synthesis of the 'pom-pom like' PEO second generation (product B in Table 1).

polyglycidol block in ^{1}H NMR spectra (4900 g/mol) agrees well with the value calculated from the feed ratio (4850 g/mol) and from the SEC measurements (5000 g/mol) (Table 1). This polymer was used as the macroinitiator to obtain the second generation of the branched polymer.

The next step of the synthesis was the ionization of the hydroxyl groups of the glycidol blocks using potassium *tert*-butoxide to obtain multi-functional macroinitiator. We found that when the degree of the ionization is less then 10% of all hydroxyl groups the solution of such alcoholate in DMSO is homogeneous. This polymer was used as initiator of the ethylene oxide polymerization. Polymerization proceeded smoothly with almost full conversion of the monomer within few hours at 40 °C. After completion the monomeric glycidol acetal was introduced into the system to generate the branching groups. The expected product should have a structure of two six-arm oxyethylene stars with glycidol acetal shell linked by oxyethylene chain (Scheme 3).

The molar mass of the obtained product after hydrolysis of acetal groups measured by SEC–MALLS was 33,000 g/mol while from feed ratio 33,180 g/mol were calculated. The average degree of polymerization of the glycidol blocks estimated from NMR measurements (5.50) agrees well with calculated from feed (5.25).

In order to obtain the next shell of the branched oxyethylene macromolecule (third generation) an approach similar to the previous procedure was used. The ionization of more than 10% of the product B in Table 1 leads to a gel



Scheme 4. Synthesis of the 'pom-pom like' PEO third generation.

insoluble in DMSO, soluble in water. When applying a lower ionization degree of 8% the solution of the macroinitiator was homogenous. This initiator was used to form the grafted linear oxyethylene chains. Again, living oxyethylene chains were terminated by the addition of glycidol acetal forming short poly(glycidol acetal) blocks. After hydrolysis of acetal groups the glycidol blocks create the outer shell of the macromolecule enriched with hydroxyl groups (Scheme 4).

SEC indicates that the elution volume of the polymers obtained in each generation decreases (Fig. 3).

3.3. Characterization of branched structures by SEC coupled with the light scattering detection (MALLS) and NMR

The determination of the molar masses of highly branched polymers by the SEC is not straightforward. The calibration with narrow standards cannot be applied, as no standard of known molar mass and of narrow molar mass distribution mimicking the exact topology of the studied macromolecules exists. Absolute methods of detection are to be used. Even then, the separation efficiency might create a problem, as the columns frequently do not separate properly such branched macromolecules [31].

Throughout this work we used multi-angle laser light scattering detection for the SEC measurements. This detection yields reasonable values, provided that the refractive index increments of the polymers to be separated are known and there is no significant distribution of the composition in the case of copolymers.

The studied systems are formally copolymers of glycidol and ethylene oxide. The content of glycidol is rather low (16–18% weight). To obtain a correct refractive index of our copolymers we estimated it from the weight ratio of the comonomers and refractive indexes of polyglycidol in DMF (0.056 l/g) and poly(ethylene oxide) in DMF (0.044 l/g), determined by independent measurements. In our calculation we used the increment value so estimated to 0.046.

It is difficult to prove the correct separation efficiency of the columns themselves. A plot of the determined molar mass versus elution volume may serve as an indication. If it is linear or at least monotonously decreasing, the separation is probably correct. As seen in Fig. 4, this is the case in our systems.

There are several indicators confirming the non-linear, branched structures of the obtained high molar mass branched poly(ethylene oxide).

Except for the linear polymer A, the molar masses measured using the calibration with the linear PEO standards are always lower, than the molar masses determined using an absolute molar mass detector (the on-line multi-angle laser light scattering detector). The ratio of these both values varies from 0.72 for the 'second generation' polymer B to 0.39 for the highly branched polymer C.

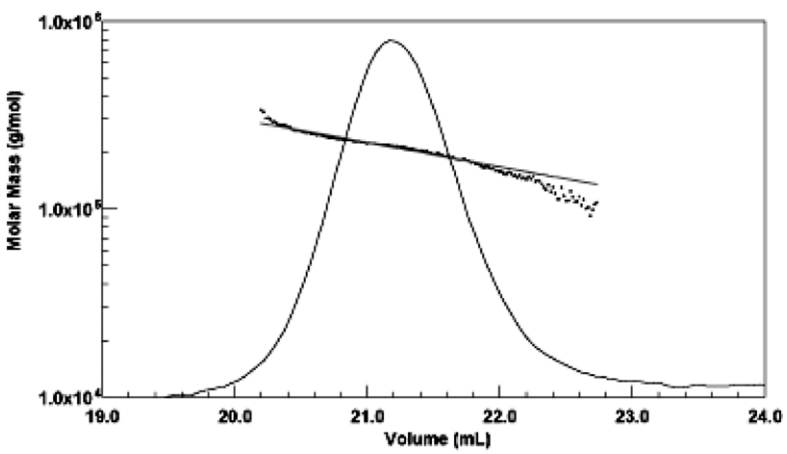


Fig. 4. Molar mass versus elution volume for the polymer C in Table 1.

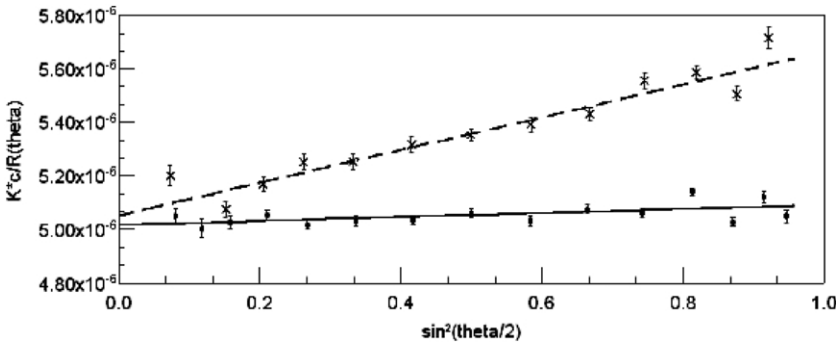


Fig. 5. Zimm plots for the 200,000 g/mol chromatographic slices of linear (dashed line) and branched (polymer C in Table 1) (solid line) poly(ethylene oxide).

This indicates that the polymers B and C have a much smaller hydrodynamic radii then their linear counterparts of the same molar mass and confirms their branched structure. The 'compactness', for which the ratio $M_{\mathrm{nSEC-calibr}}/M_{\mathrm{nSEC-MALLS}}$ may serve as a qualitative measure, is for the polymer C much higher, than for the polymer B, according to what may be expected from their synthesis. A similar relationship between the 'true' molar masses and the molar masses determined using SEC and the calibration with linear standards has been observed for many other branched macromolecules [13,32–34].

The polymer C of third generation has a molar mass high enough that the radius of gyration may be determined by the light scattering (anisotropic scatterer) using the Zimm formalism.

Fig. 5 shows the Zimm plots for the 200,000 g/mol slice of the hyperbranched polymer (polymer C in Table 1) and the Zimm plot for the same molar mass slice of a linear poly(ethylene oxide) of broad molar mass distribution ($M_{\mathrm{n}} = 160,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.70$). The radius of gyration determined for the branched PEO at 200,000 g/mol is 10.2 ± 1.3 nm, whereas for the linear PEO of the same molar mass 24.7 ± 2.4 nm are obtained. The ratio of the radii of gyration of 0.41 indicates that the polymer C (entry 3 in Table 1) has a very dense structure, which confirms multiple branching.

3.4. Contents of hydroxyl groups and number of branches

The number of PEO arms introduced in each generation should be equal to the number of the hydroxyl groups in the starting macroinitiator, if all hydroxyl groups initiate the polymerization of ethylene oxide.

The full consumption of the hydroxyl groups is confirmed by the ^{1}H NMR spectra of the urethanes (Fig. 2). It may be seen that after the polymerization of ethylene oxide initiated with alcoholate derived from the polyglycidol blocks, all the signals originating from the hydroxyl groups of the polyglycidol units disappear and only primary hydroxyl groups of the added poly(oxyethylene) are observed. Polymerization of glycidol acetal initiated with the alcoholates generated at the end of the oxyethylene outer sphere blocks gave after the hydrolysis both, primary and secondary hydroxyl groups, characteristic of the polyglycidol block, with the ratio well agreeing to the calculated from the feed. This fact indicates that within the limits of the accuracy of the NMR method all hydroxyl groups (primary of both blocks and secondary of the glycidol block end) are active in the chain initiation and growing processes.

To calculate the number of branches the number of the hydroxyl groups has to be known. It may be calculated from their content, determined from ^{1}H NMR, and the molar mass.

The number of the hydroxyl groups in the shell of the hyperbranched polyoxyethylene molecule formed in each stage can be calculated from the formula:

$$N_{(\mathrm{OH})} = 2\prod_{i=1}^{p}(\overline{\mathrm{DP}}_i + 1) \quad (1)$$

where p is the number of the acetal polymerization reaction carried out in the process (the generation number) and DP_i is the average degree of polymerization of glycidol in each

Table 2
Molar masses of the obtained polyethers measured using SEC with absolute molar mass detection (MALLS) and using the calibration with linear PEO standards

Polymer (cf Table 1)	M_{n}		
	SEC–MALLS	Calibration with linear standards	$\frac{M_{\mathrm{nSEC-calibr}}}{M_{\mathrm{nSEC-MALLS}}}$
A	5000	5000	1.0
B	33,000	24,000	0.72
C	203,000	80,200	0.39

Table 3
The contents of the hydroxyl groups and branches

Product	M_n[a]	Average number of hydroxyl groups[b] per molecule		Number of branches	
		Calculated[c]	From ^{1}H NMR	Calculated[c]	From ^{1}H NMR
A	5000	13.5	13.8	–	–
B	33,000	84	89	13.5	13.8
C	203,000	446	487	84	89

[a] Measured by SEC–MALLS.
[b] Primary and secondary.
[c] Calculated from feed ratio.

reaction stage. Values calculated from the ^{1}H NMR agree with the values calculated from the feed ratio (Table 3).

The number of branching units is less than the number of hydroxyl groups because outer shell consists of short glycidol blocks having several hydroxyl groups, which cannot be considered as branches. However, they are potential branches for the next generation. The contents of branches can be calculated according to formula 2

$$N_{(\text{branches})} = 2\prod_{i=1}^{p-1}(\overline{\text{DP}}_i + 1) \quad (2)$$

The values are presented in Table 3.

4. Conclusions

Glycidol may be used as an agent generating branches in the polymerization of ethylene oxide. If the hydroxyl group of this monomer, which otherwise causes extensive chain transfer, is properly protected, the combination of the living anionic polymerization of this monomer and of ethylene oxide yields densely branched PEO macromolecules of molar mass up to 2×10^5 g/mol and narrow molar mass distribution, enriched with hydroxyl groups in the outer sphere. The branched structure of the obtained polymers is evidenced by the NMR spectroscopy. The elution volumes of the obtained polymers in the SEC and the radii of gyration, determined from SEC coupled with light scattering detection, are much smaller than of their linear counterparts, which confirms the dense, compact structure of obtained branched macromolecules.

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