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Synthesis, characterization and properties of functional star and dendritic block copolymers of ethylene oxide and glycidol with oligoglycidol branching units

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ABSTRACT

Well-defined, four-arm star block copolymers of ethylene oxide and glycidol were prepared via controlled anionic polymerization using protected glycidol. The length of the poly(ethylene oxide) block was varied from DP = 10 to 50, while the length of the short polyglycidol block remained nearly constant, at DP = 4–6. Star block copolymers with hydroxyl groups at the ends of the arms after conversion to the corresponding alkoxides were used as multifunctional macroinitiators for the sequential polymerization of ethylene oxide and protected glycidol. After deprotection, the branched block copolymers of ethylene oxide and glycidol had narrow molar mass distributions and multiple hydroxyl groups (up to 200) at the peripheries. The structure and functionality were determined using size exclusion chromatography with a light scattering detector and nuclear magnetic resonance spectroscopy. The thermal properties of the synthesized copolymers were also investigated, as well as the hydrophilic dye uptake to the hydrophobic phase containing copolymers.

1. Introduction

Poly(ethylene oxide)s with branched structures are very attractive because their properties are similar to linear poly(ethylene oxide) (i.e., biocompatible, non-toxic, water soluble, etc.[1,2]) while also having the advantages of branched polymers. Compared to linear polymers, branched macromolecules have lower viscosity, lower hydrodynamic volume, a higher number of end groups in the molecule (which are mostly hydroxyl groups in the case of ethylene oxide polymers) and higher ability to entrap low molecular compounds. Some branched polymers of ethylene oxide with different active end groups are commercially available, mostly in the form of star polymers.

Linear polymers of glycidol [3] and copolymers with ethylene oxide [4], as well as branched polymers [5] and copolymers of glycidol [6], have been extensively investigated over the last 20 years, through the application of different kinds of polymerization and branching strategies.

The presence of several or tens of active groups in the molecule and the branched structure makes such polymers very interesting and broadens their range of potential applications [7], including such applications as cross-linking agents, polymers for the preparation of functional surfaces, drug conjugates and soluble supports for liquid-phase organic synthesis. The investigation of new methods of synthesis of well-defined multifunctional water-soluble polymers is significant, especially for polymers containing the hydrophilic, biocompatible poly(ethylene oxide) chains.

To synthesize branched poly(ethylene oxide), the use of a branching agent is necessary. Several methods have been reported in the literature for the generation of branching points in the poly(ethylene oxide) chain. Depending on the method, star polymers, hyperbranched polymers or polymers of more sophisticated chain structure can be obtained [8–10]. The most frequently used method for the preparation of the stars with poly(ethylene oxide) arms is the initiation of the polymerization of ethylene oxide using multifunctional alcoholates, known as the core-first method. The most frequently applied initiators are trimethylolpropane, pentaerythritol, di(trimethylolpropane), dipentaerythritol, calixarene or other alcoholates, which yield stars with three, four, six, or more arms [11–14]. Similar stars were obtained using the arm-first method [15–17], and different terminating agents such as multivalent chlorides, iodides and hexachlorocyclotriphosphazene. Homo- and hetero-arm star polymers of ethylene oxide and glycidol were synthesized by applying the multi-step process and using diepoxides as the branching agent [18].

Another type of branched polymers with poly(ethylene oxide) chains is core–shell polymers, which have a more complex, multifunctional core (mostly hydrophobic) and a shell consisting of

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poly(ethylene oxide) [19–22]. For this kind of polymer, both methods can also be applied: either the initiation of ethylene oxide polymerization with active sites on the core, or the conjugation of earlier prepared poly(ethylene oxide) chains with the multivalent core. Using the coupling method, one chain end group of the poly (ethylene oxide) must be protected. In this case, the number of arms can reach several dozen or more.

For the synthesis of hyperbranched polymers with poly(ethylene oxide) chains, multi-step processes are required. Branched or hyperbranched architectures can be created with the use of a low molar mass agent connected to the end of the linear chains, which causes branches in the next step [9,10,23]. The branching agent can be introduced either as the terminator of the former polymerization step or as the modification of the end group after the termination of the polymerization. In some cases, the authors used highly toxic osmium compounds [8b,10,23,24].

Another method for branching the poly(ethylene oxide) chain is copolymerization with another monomer (oxiranes) containing a functional group that, after modification, may serve as the initiating site [6]. The copolymerization of the mixture of monomers may be more complicated due to the different reactivities of ethylene oxide and substituted oxiranes [25]. The sequential copolymerization leads to more defined structures, but the full conversion of very reactive ethylene oxide can be easily obtained.

The application of the controlled steps of the synthesis might be the only way to obtain polymers of controlled and desired molecular architectures, dimensions and molar masses.

In our previous paper [6], we reported the preparation of pompom like polymers of ethylene oxide using hydroxyl groups in the short polyglycidol blocks as the initiating sites to create branches. The grafting efficiency of the short glycidol blocks (5–8 units) is very high. We estimated that after the grafting process of such short polyglycidol blocks with the ethylene oxide, there were no hydroxyls derived from the glycidol unit.

In this paper, we report the synthesis of multifunctional star and dendritic copolymers of ethylene oxide and glycidol with the possibility of controlling the molar mass, dimension, compactness of the molecule and functionality of the shell using two methods: for star preparation, polymerization of ethylene oxide with the use of a multifunctional initiator, and for the preparation of dendritic polymers, the grafting of the polyglycidol blocks at the ends of the prepared star block copolymers.

2. Experimental section

2.1. Materials

Ethylene oxide (Fluka) was stored over calcium hydride and distilled directly before polymerization. Dimethyl sulfoxide (DMSO) (POCh, Gliwice) was distilled over calcium hydride, stirred with barium oxide for several days under argon, and then distilled into an ampoule equipped with a Rotaflo glass-Teflon valve. Pentaerythritol (Aldrich) was crystallized from water and dried under high vacuum for several days. 1-Ethoxyethyl glycidyl ether (EGlE) was obtained according to Fitton [26], distilled several times under reduced pressure, stored over calcium hydride and distilled directly before polymerization. Potassium *tert*-butoxide (Merck) and calmagite (Aldrich) were used as received.

2.2. Measurements

2.2.1. Gas chromatography

Gas chromatography was used to determine the residual monomer content in the reaction mixture. A gas chromatograph VARIAN 3400 with the J&W Scientific DB-5 (30 m × 0.32 mm) column was used.

2.2.2. Size exclusion chromatography (SEC-MALLS)

The molar masses and dispersities of the polymers were determined using gel permeation chromatography with a refractive index detector and a multiangle laser light scattering detector. Analyses of polymers with protected polyglycidol blocks were performed in THF at 35 °C using a set of columns (Polymer Standard Service (PSS): SDV $1 \times 10^5 + 1 \times 10^3 + 2 \times 10^2$ Å), a differential refractive index detector (Δn-1000 RI Dr Bures) and a multiangle laser light scattering detector (DAWN EOS from Wyatt Technologies). Polymers with protected and unprotected polyglycidol blocks were analyzed in DMF (5 mmol/L solution of LiBr) at 45 °C using a set of columns (Polymer Laboratories and Polymer Standard Service: 2 × PL MIXED-C + 1 × Gram 100 Å), a differential refractive index detector (Δn-2010 RI Dr Bures) and a multiangle laser light scattering detector (DAWN HELEOS from Wyatt Technologies). The results were evaluated using Astra software from Wyatt Technologies and WINGPC software from PSS.

2.2.3. NMR

NMR spectra were recorded on a VARIAN Unity-Inova spectrometer operating at 300 MHz for ^{1}H. Tetramethylsilane was used as an internal reference.

2.2.4. DSC

Differential scanning calorimetry measurements were performed using a Mettler-Toledo DSC 822 e calorimeter with a heating rate of 10°/min. The glass transition temperature, degree of crystallinity and melting point were determined from the second heating thermogram. The heat of fusion of 100% crystalline PEO (196.8 J/g) was applied from [34]. Calibration was performed using indium and zinc standards.

2.2.5. MALDI-ToF

MALDI-ToF analyses were performed on a Bruker Reflex III spectrometer equipped with a 337 nm N_2 laser and 20 kV acceleration voltage. The samples were prepared by mixing methanolic solutions of PENT$(PEO_{10}$-*b*-$PGl_6)_4$ and dihydroxybenzoic acid (DHB) as matrix (ratio 20:5), AgTFA was also added (ratio 20:5:1) for the case of PENT$(PEO_{30}$-*b*-$PGl_6)_4$.

2.3. Preparation of star block copolymers of ethylene oxide and glycidol (PENT$(PEO_n$-b-$PGl_m)_4$)

2.3.1. Polymerization

Pentaerythritol (0.326 g, 2.4 mmol) was introduced into an ampoule equipped with glass-Teflon valves and dried over high vacuum for two days. It was then dissolved in 15 mL of dry DMSO, and all DMSO was removed under reduced pressure. Pentaerythritol was dissolved in 25 mL of dry DMSO and a solution of potassium *tert*-butoxide (94 mg, 0.84 mmol) in 10 mL DMSO was added. After 1 hour, almost all the DMSO and formed *tert*-butyl alcohol were removed at 30 °C under reduced pressure. The residue was dissolved in 25 mL of DMSO, and a solution of freshly distilled ethylene oxide (4.8 mL, 4.23 g, 96.0 mmol) in 20 mL of DMSO was added. Polymerization was carried out at 45 °C for 24 hours. After this time, the reaction mixture was cooled down to room temperature, and a small sample was taken out to estimate the conversion of the monomer using the GC method and for ^{1}H NMR and SEC-MALLS measurements. After 24 hours, the conversion was complete. 1-Ethoxyethyl glycidyl ether (EGlE) (8.60 g, 59 mmol) was added to the living poly(ethylene oxide) solution, and the polymerization was carried out at 60 °C for the next 24 hours. The GC measurements confirmed the absence of monomer in the reaction mixture.

After polymerization, DMSO was removed under reduced pressure, and the crude star block copolymer of ethylene oxide and EGlE was analyzed by SEC-MALLS and ^{1}H NMR.

Preparation of PENT(PEO$_n$-*b*-PEGlE$_m$)$_4$ of different monomer compositions was conducted according to this procedure by changing the ratio of the reagents.

2.4. Deprotection of polyglycidol block

The crude PENT(PEO$_n$-*b*-PEGlE$_m$)$_4$ copolymer (2 g) was dissolved in acetone (20 mL), and then a solution of oxalic acid (0.9 g, 10 mmol) in acetone (10 mL) was added. The solution was stirred, and deionized water (30 mL) was slowly added to keep the mixture homogeneous. The mixture was stirred for 30 minutes, and then sodium hydrogen carbonate (2.6 g, 31 mmol) was carefully added. Acetone and water were removed under reduced pressure, and the residual polymer was dissolved in 25 mL of water and desalinated using ion exchange resins. Then, water was removed under reduced pressure, and the very viscous, colorless, transparent polymer (1.2 g) was dried under high vacuum (1×10^{-6} mbar) at 50 °C for several days.

2.5. Preparation of dendritic copolymers of ethylene oxide and glycidol (PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$)

The star copolymer PENT(PEO$_n$-*b*-PGl$_m$)$_4$ was dissolved in deionized water and dialyzed for one week (water was changed twice daily) using a Spectra/Por dialysis membrane (MWCO 1000). The water solution of the copolymer was filtered using a 0.45 μm syringe filter, and water was removed under reduced pressure. The copolymer was dried under high vacuum at 50 °C several days. The dry copolymer (1.429 g) was introduced into an ampoule equipped with glass-Teflon valves and dried over high vacuum for two days. Then DMSO (20 mL) was added, and after the dissolution of polymer, the solution was stirred for 1 hour. Then all DMSO was removed under reduced pressure. The polymer was dissolved in a new portion of DMSO (25 mL), and a solution of potassium *tert*-butoxide (123.5 mg, 1.1 mmol) in 11.6 mL DMSO was added. After several minutes, almost all of the DMSO was carefully evaporated under reduced pressure, while still being stirred to eliminate the formation of a polymer film on the solution surface and reactor walls. A new portion of DMSO (20 mL) and freshly distilled ethylene oxide (4.8 g, 5.4 mL, 109 mmol) in 12 mL DMSO were added. Polymerization was carried out at 45 °C for 4 hours and at 55 °C for 22 hours. The reaction mixture was cooled down, and a small sample was taken out for GC, ^{1}H NMR and SEC-MALLS measurements. The conversion of ethylene oxide was complete. Protected glycidol (EGlE) (10.075 g, 69 mmol) was added, and the polymerization was carried out at 65 °C for 48 hours. After polymerization, a small sample of the reaction mixture was taken out to confirm the complete conversion of the monomer (GC). DMSO was removed from the reaction mixture under reduced pressure, and the crude copolymer was analyzed by ^{1}H NMR and SEC-MALLS methods.

The preparation of dendritic copolymers with different monomer compositions was conducted according to the procedure described, with different ratios of reagents.

The deprotection of the polyglycidol block and purification of the dendritic copolymers were performed according to the method described for star copolymers.

2.6. Investigations of the phase transfer of calmagite to solutions of (PENT(PEO$_n$-b-PGl$_m$))$_4$ and PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$ copolymers in methylene chloride

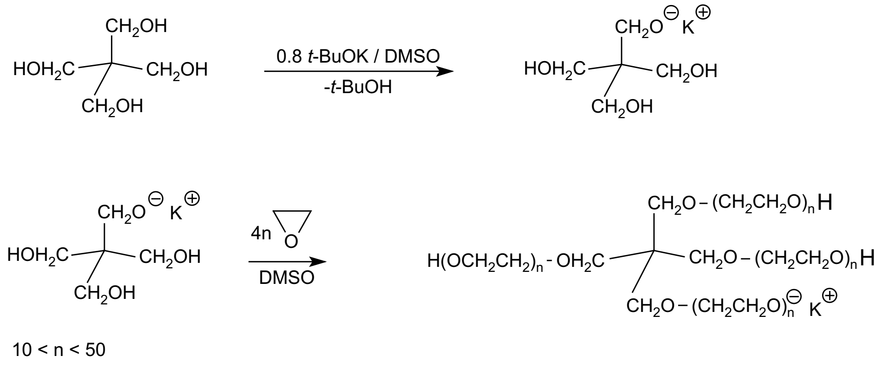
Solutions of synthesized star and dendritic block copolymers with a concentration of 1.25 g/L were prepared in small screw-thread vials (10 mL) with leak-proof caps equipped with a stirrer bar. After the addition of 50 mg of calmagite, the solutions were stirred for 48 hours. Colored solutions were filtered using a 0.45 μm syringe filter, and the absorbance was measured in a 1 mL cuvette at 520 nm. The concentration of calmagite in the solutions was estimated using calibration based on water solutions and UV–vis absorbance, using the same procedure.

3. Results and discussion

3.1. Preparation of the star copolymers (PENT(PEO$_n$-b-PGl$_m$)$_4$)

The synthesis of the star copolymers (PENT(PEO$_n$-*b*-PGl$_m$)$_4$) is the preliminary step towards the preparation of multifunctional dendritic copolymers. The controlled structure of synthesized star block copolymers and their purity are essential for the next step, since they were used as the multifunctional macroinitiators for obtaining the final dendritic polyoxiranes.

Three star block copolymers (PENT(PEO$_n$-*b*-PGl$_m$)$_4$) were obtained by sequential anionic ring-opening polymerization with the use of pentaerythritol as the tetra-functional initiator (Scheme 1). The pentaerythritol was converted to its alcoholate using potassium *tert*-butoxide. To avoid precipitation of the alcoholates, only up to 20% of all hydroxyl groups were ionized. The preparation of pentaerythritol alcoholate and the polymerization were carried out in dimethyl sulfoxide (DMSO). After the addition of potassium *tert*-butoxide to the solution of pentaerythritol, almost all the DMSO was distilled off to remove the *tert*-butyl alcohol formed. The GC analysis of the hydrolyzed sample of the initiator solution, which was taken from the reactor directly before the polymerization, indicates the absence of *tert*-butyl alcohol in the initiating system. Traces of alcohol have to be carefully removed from the reaction mixture to prevent initiation by these species.



Scheme 1. First stage of the synthesis of dendritic block copolymers – synthetic route of star poly(ethylene oxide).

The polymerization of ethylene oxide was carried out at 45 °C for 24 hours. The conversion of the monomer was complete (GC). Then protected glycidol (EGlE) was added to the reaction mixture, and polymerization was carried out at 60 °C for the next 24 hours. The total conversion is necessary to obtain the regular block copolymer. After removal of the solvent, the polymer was treated with oxalic acid to recover the hydroxyl groups of the polyglycidol blocks (Scheme 2).

Three different star block copolymers were prepared with average DP values for the poly(ethylene oxide) block of 10, 30 and 50 and average DP values for the polyglycidol block in the range 4–6 per arm. In all the cases, the conversion of monomers after each step was complete in order to obtain regular blocks. The details are summarized in Table 1.

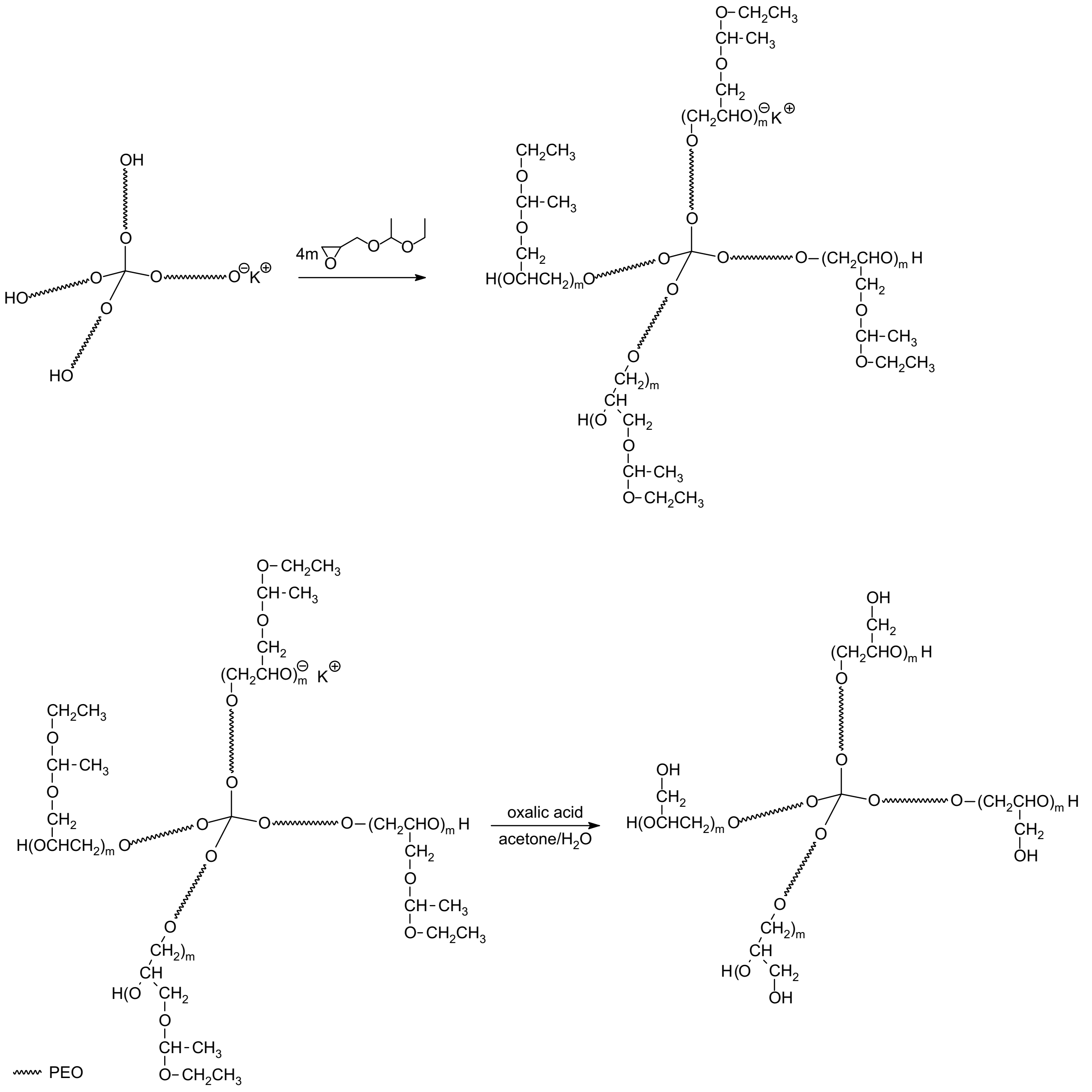
Table 1
Four-arm star block copolymers (PENT(PEO$_n$-*b*-PGl$_m$)$_4$).

	$DP_{EO}:DP_{Gl}$[a] for arm	M_n[a]	$DP_{EO}:DP_{Gl}$[b] for arm	M_n[b]	M_n/D	
					SEC-MALLS	MALDI-ToF
1	10.0:6.2	3720	10.0:6.1	3600	5100/1.11	3670/1.06
2	30.6:5.7	7200	28.8:5.5	6800	8200/1.01	7370/1.03
3	50.6:4.3	10 320	51.9:4.4	10 570	9200/1.01	–

[a] Average values calculated from the feed ratio.
[b] Average values estimated from ^{1}H NMR spectra.

Polymers were analyzed after each step of the synthesis using SEC-MALLS and ^{1}H NMR. Molar masses were estimated using the SEC-MALLS. The refractive index increment values (d*n*/d*c*) for the block copolymers were calculated from weight ratios and the d*n*/d*c* values of each homopolymer. The weight ratios for the star block copolymers were calculated from the ^{1}H NMR spectra. Some polymers were also analyzed using mass spectrometry (MALDI-ToF).

Molar masses measured after each step of the synthesis agree well with the average values obtained from the feed ratios. In all the cases, the dispersity of the molar mass is very low. Molar masses



Scheme 2. Second stage of the synthesis of star block copolymers: polymerization and deprotection of the polyglycidol block.

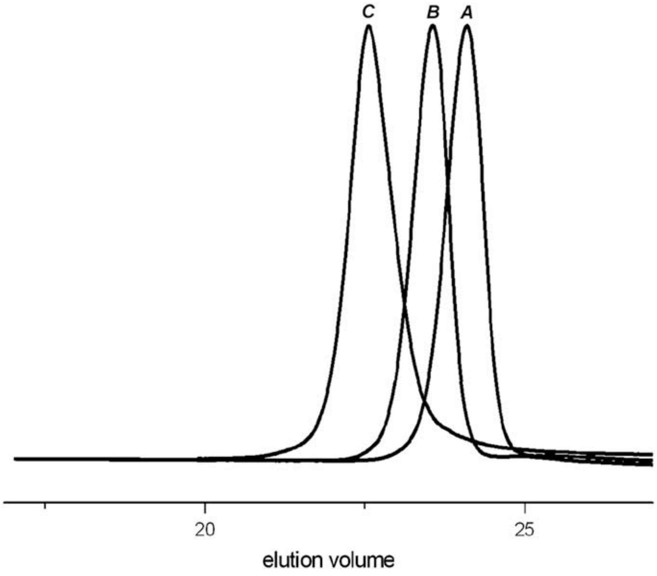


Fig. 1. Chromatograms of four-arm star copolymers: A – PENT(PEO$_{30}$)$_4$, B – PENT(PEO$_{30}$-*b*-PEGlE$_6$)$_4$, C – PENT(PEO$_{30}$-*b*-PGl$_6$)$_4$; (RI traces) DMF/5 mmol LiBr, 45 °C.

determined from SEC-MALLS are slightly different than those calculated from the feed ratio and estimated by another method (^{1}H NMR and MALDI-ToF). The differences are higher for low molar mass copolymers. Chromatograms of the star polymer and copolymers obtained after each step with DP = 30 for the poly(ethylene oxide) block (entry 2 in Table 1) are shown in Fig. 1.

The average degree of polymerization was calculated from the ^{1}H NMR spectra, which were recorded after the conversion of the hydroxyl groups of the star polymer or copolymer to trichloroacetyl urethane derivatives (see Fig. 2). In the case of the poly(ethylene oxide) star, the only primary hydroxyl groups are at the end of the arms. After polymerization of protected glycidol, each arm has a secondary hydroxyl group at the end, and the primary hydroxyls disappear. Deprotection of the glycidol block maintains the secondary group at the end of the arm, and the primary hydroxyl groups derived from the glycidol units are recovered. The DP of the arm in the star polymer PENT(PEO$_n$)$_4$ was determined from the ratio of the intensity of the signal derived from the ethylene oxide units to the intensity of the signal derived from the primary end group. In the case of the star copolymer PENT(PEO$_n$-*b*-PEGlE$_m$)$_4$, the ratio of comonomers can be estimated using characteristic signals from protons of the 1-ethoxyethoxy group (CHCH_3 and also CH$_2$CH_3), and the sum of signals derived from the polyether backbone of glycidol and ethylene oxide units. The ratio of primary to secondary hydroxyl groups in the star block copolymer after deprotection is equal to the DP of the glycidol block of the arm. The estimated DP values of poly(ethylene oxide) and polyglycidol blocks before and after deprotection are almost the same. The DP values estimated after deprotection are summarized in Table 1.

3.2. Preparation of branched copolymers of ethylene oxide and glycidol (PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$)

The star block copolymers obtained had average numbers of hydroxy groups between 22 and 28 per molecule (entries 3 and 1 in Table 1, respectively) and were used as multifunctional macroinitiators

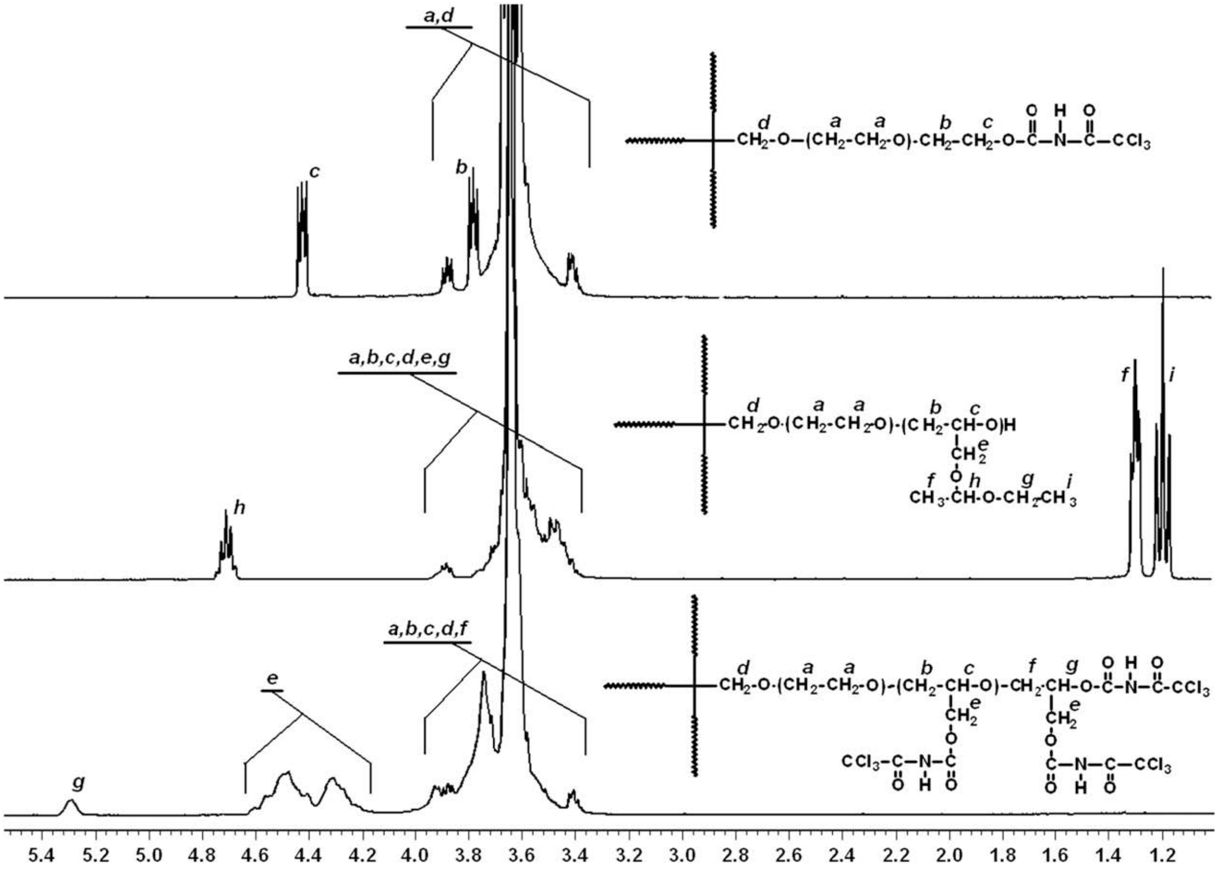
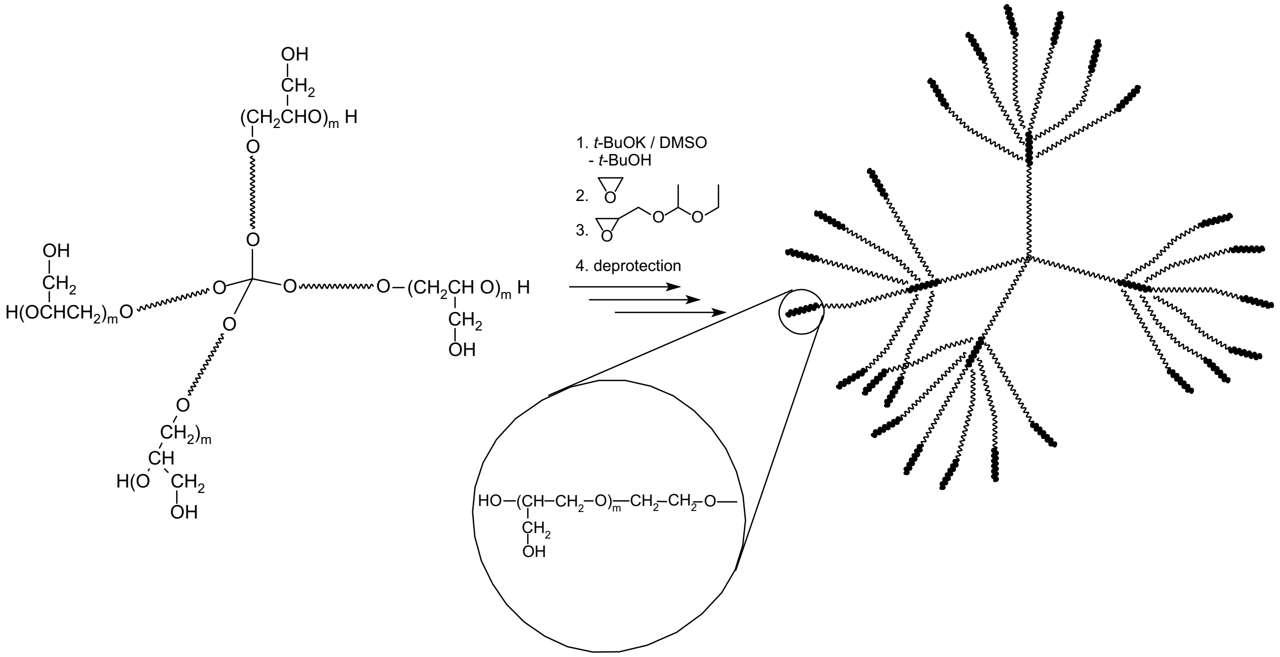


Fig. 2. ^{1}H NMR (CDCl$_3$, 300 MHz) spectra of four-arm stars: A – PENT(PEO$_{30}$)$_4$ after reaction with trichloroacetyl isocyanate, B – PENT(PEO$_{30}$-*b*-PEGlE$_6$)$_4$, C – PENT(PEO$_{30}$-*b*-PGl$_6$)$_4$ after reaction with trichloroacetyl isocyanate.



Scheme 3. Synthetic route for the preparation of dendritic block copolymers (PENT[(PEO_n-*b*-PGl_m)–(PEO_o-*b*-PGl_p)$_{m+1}$]$_4$).

for the synthesis of dendritic, highly functional copolymers of ethylene oxide and glycidol.

The star block copolymer was carefully purified to remove the impurities that were generated during the deprotection step (see Experimental section). The purity of the macroinitiator is essential due to the low concentration of initiating species on the macromolecule (lower than 40 mmol/L) and their lower reactivity compared to low molar mass initiators.

After drying, the copolymers were dissolved in DMSO and ionized using a solution of potassium *tert*-butoxide. As in the synthesis of star copolymers, *tert*-butyl alcohol was removed by evaporation under reduced pressure together with the first part of DMSO, and after the addition of a new portion of DMSO, the solutions were used to initiate the polymerization of ethylene oxide. Because of the strong aggregation of the obtained alkoxides, which leads to gels insoluble in DMSO, the addition of potassium *tert*-butoxide and the evaporation of DMSO must be done very carefully (see Experimental section).

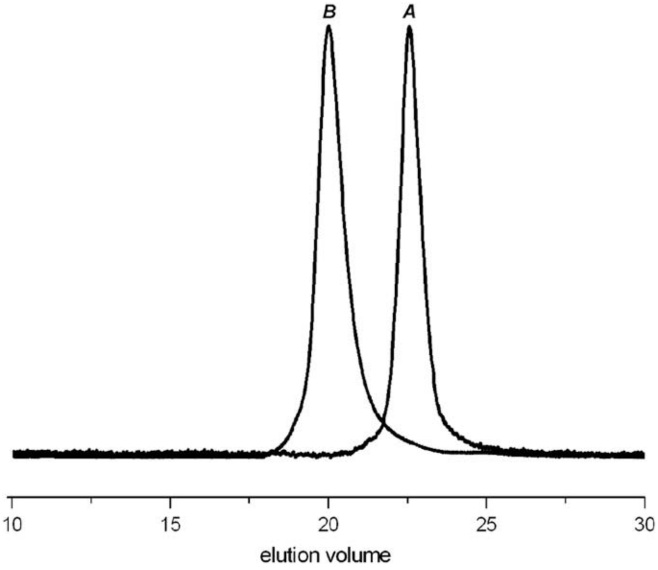


Fig. 3. Chromatograms of four-arm star (macroinitiator) and dendritic block copolymer: A – PENT(PEO_{30}-*b*-PGl_6)$_4$, B – PENT[(PEO_{30}-*b*-PGl_6)–(PEO_{30}-*b*-PGl_8)$_7$]$_4$; (RI traces) DMF/5 mmol LiBr, 45 °C.

The initiation in such an inhomogeneous system leads to a broad molar mass distribution and a mixture of different structures of branched copolymers, and unreacted macroinitiator can remain after the polymerization. The ionization degree cannot be higher than 10–15% of all hydroxyl groups in the system.

Prepared solutions of ionized star block copolymers were used for the polymerization of ethylene oxide, and after all the ethylene oxide was consumed, the protected glycidol was added (Scheme 3). After polymerization, the crude product obtained by the evaporation of DMSO under reduced pressure was treated with oxalic acid to recover the hydroxyl groups of the glycidyl block, according to the procedure described in Experimental section.

The products obtained after each step (polymerization of ethylene oxide and protected glycidol) were investigated using SEC-MALLS and ^{1}H NMR. The molar masses of the dendritic copolymers were estimated using d*n*/d*c* values calculated from the monomer ratios and d*n*/d*c* values for polyglycidol and poly(ethylene oxide). Chromatograms of the star copolymer (macroinitiator) and deprotected dendritic copolymer with DP = 30 for the poly(ethylene oxide) block are shown in Fig. 3.

Table 2
Dendritic block copolymers (PENT[(PEO_n-*b*-PGl_m)–(PEO_o-*b*-PGl_p)$_{m+1}$]$_4$).

Polymer	Macroinitiator	M_n[a]	M_n/D SEC-MALLS	Number of hydroxyl groups per molecule[a]	Number of hydroxyl groups per molecule[b]
4A	Entry 1 in Table 1	16 500	18 000/1.02	29	28
4B	Entry 1 in Table 1	29 500	33 700/1.01	209	210
5A	Entry 2 in Table 1	42 700	46 000/1.05	27	26
5B	Entry 2 in Table 1	54 500	55 800/1.01	192	180
6A	Entry 3 in Table 1	58 600	58 000/1.01	21	22
6B	Entry 3 in Table 1	70 400	67 100/1.01	182	180

Series A – polymers after polymerization of ethylene oxide; series B – polymers after polymerization of protected glycidol and hydrolysis.

[a] Average values calculated from the feed ratio.

[b] Average values estimated from ^{1}H NMR spectra.

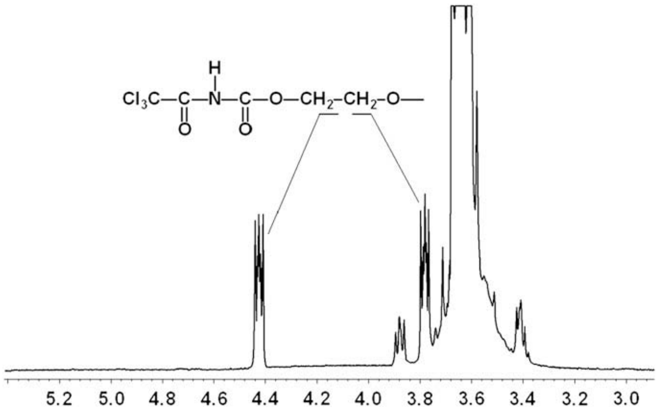


Fig. 4. ^{1}H NMR (CDCl$_3$, 300 MHz) spectra of dendritic block copolymer (PENT[(PEO$_{30}$-b-PGl$_6$)–(PEO$_{30}$)]$_4$) after the polymerization of ethylene oxide and reaction with trichloroacetyl isocyanate.

The number of hydroxyl groups was calculated from the ^{1}H NMR spectra of the trichloroacetyl urethane derivatives of the branched copolymers. The details are summarized in Table 2.

The dendritic copolymers (PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$) have very similar macromolecular structure and functionality but different lengths of poly(ethylene oxide) blocks, which are the linear chains between the branching points. The lengths of the poly(ethylene oxide) blocks determine the molar mass, dimension and compactness of the branched macromolecule. The average degrees of the poly(ethylene oxide) blocks were 10, 30 and 50, respectively, for polymers in the 4A and 4B to 6A and 6B series in Table 2. The functionality is almost the same (from 183 to 205) since the average degrees of the polyglycidol blocks in the prepared copolymers are very similar (5–8). The number of hydroxyl groups in branched copolymers depends on the length of the polyglycidol block in the star copolymer, which was used as the macroinitiator, and the length of the polyglycidol block in the shell, and this can be calculated by the equation:

$$F = 4 \times (\mathrm{DP_{st}} + 1) \times (\mathrm{DP_{shell}} + 1)$$

where $\mathrm{DP_{st}}$ – degree of the polyglycidol block in the star block copolymer, and $\mathrm{DP_{shell}}$ – degree of the polyglycidol block in the shell of the dendritic block copolymer.

The number of hydroxyl groups in the polyglycidol block exceeds the DP of the polyglycidol block because the end units contain two hydroxyl groups – primary and secondary. We found that both groups are active in the initiation of the polymerization of ethylene oxide, because after this step, only primary hydroxyl groups at the end of poly(ethylene oxide) blocks are present. This can be seen in the ^{1}H NMR spectra obtained for the trichloroacetyl urethanes of the dendritic copolymers. After reaction with trichloroacetyl isocyanate, only characteristic peaks of the primary hydroxyl derivatives of ethylene oxide end units are visible at 4.42 and 3.78 ppm (see Fig. 4).

3.3. *Thermal properties of star block and dendritic block copolymers of ethylene oxide and glycidol*

The four-arm star PENT(PEO$_n$-b-PGl$_m$)$_4$ and dendritic block copolymers (PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$) were investigated using differential scanning calorimetry. The glass transition temperatures and melting temperatures are listed in Table 3. In the temperature range from −60 to 120 °C, no temperature effects (T_g or T_m) were observed for any of the investigated copolymers, which could be attributed to the short polyglycidol blocks.

For copolymers of star and dendritic structure with an average DP = 10 for the PEO blocks, no melting point was observed. The polymers were amorphous and did not crystallize during after several weeks even at low temperature (−20 °C). Poly(ethylene oxide) blocks of DP = 10 form an amorphous phase and are too short to crystallize. The more branched structure slightly lowers the T_g of the poly(ethylene oxide) phase. This effect is stronger for copolymers of PEO block DP = 30, where the difference between the T_g of the poly(ethylene oxide) block in star and in dendritic copolymers of the same block length and composition rises to 7.6°. For copolymers of PEO block DP = 50, the T_g is almost independent of the microstructure of the copolymer. The difference between the degree of crystallinity of the PEO blocks in star and dendritic copolymers is also stronger for copolymers of PEO block DP = 30.

In contrast to the copolymer with PEO block DP = 10, polymers with DP = 30 and 50 crystallize very easily. The T_m changes in almost the same way as observed for the PEO blocks attached to different polymer backbones, where T_m depends on the length of the PEO blocks [27,28]. The melting temperature increases with increasing DP of the PEO blocks and is significantly lower than the melting temperatures reported in literature for PEO oligomers with similar DP values [29].

The architecture of the block copolymer also influences the melting point. More developed structures (from star to dendritic copolymer) reduce the melting temperature, and the changes are greater for shorter PEO blocks.

3.4. *Phase transfer properties of star PENT(PEO$_n$-b-PGl$_m$)$_4$ and dendritic PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$ block copolymers*

The uptake of the hydrophilic model compound to an organic hydrophobic phase containing synthesized star and dendritic copolymers was investigated. The model compound calmagite is a dye that is soluble in both water and hydrophilic organic solvents (DSMO, DMF) and insoluble in hydrophobic solvents. Water solutions of calmagite are of red wine color, with a maximum UV absorbance at 602 nm.

Two different methods for investigating the phase transfer properties are commonly used [30–33]: the solid–liquid and the liquid–liquid phase transfer methods. The liquid–liquid method is usually more effective, but it sometimes causes problems, especially

Table 3
Thermal properties of star PENT(PEO$_n$-b-PGl$_m$)$_4$ and dendritic block copolymers PENT[(PEO$_n$-b-PGl$_m$)–(PEO$_o$-b-PGl$_p$)$_{m+1}$]$_4$.

Average DP of PEO blocks	10		30		50	
Polymer[b]	1	4B	2	5B	3	6B
T_g [°C]	−41.5	−42.6	−45.0	−52.6	−53.0	−53.1
Degree of crystallinity of PEO blocks [%]	–	–	39	31	41	40
T_m [°C]	[a]	[a]	32.4	27.0	36.0	34.8
T_m of linear PEO[c]	8.0		37.0		>53.0	
% Weight content of PEO	49.4	48.6	75.7	74.7	87.5	80.9

[a] Melting point not observed.
[b] Polymers are characterized in Tables 1 and 2.
[c] Data for oligomers PEO of DP 9, 23 and 45 from Ref. [29].

Table 4
Phase transfer properties of star PENT(PEO$_n$-*b*-PGl$_m$)$_4$ and dendritic PENT[(PEO$_n$-*b*-PGl$_m$)–(PEO$_o$-*b*-PGl$_p$)$_{m+1}$]$_4$ copolymers.

Polymer[a]	M_n[b] [g/mol]	$c_c/c_p \times 10^2$	n_c/n_p [mol/mol]	Weight content of PEO [%]
1	3720	0.99	0.10	49.4
2	7200	5.31	1.08	75.7
3	10 320	13.65	3.15	87.5
4B	29 500	0.80	0.66	48.6
5B	55 800	1.60	1.95	74.7
6B	67 100	4.26	6.70	80.9
Linear PEO 10 000	10 000	8.10	1.80	100.0

c_c – concentration of soluble calmagite; c_p – concentration of the polymer (1.25 g/L); n_c/n_p – number of calmagite molecules per one copolymer molecule.

[a] Polymers are characterized in Tables 1 and 2.

[b] Average values calculated from the feed ratio.

when the polymer is soluble in two phases and forms stable emulsions. Synthesized star and dendritic copolymers are soluble in water and halogenated hydrocarbons, and calmagite is insoluble in hydrophobic organic solvents. Therefore, the solid–liquid method and methylene chloride were used. The uptake of calmagite into the methylene chloride phase, which contained the synthesized star and dendritic copolymers, was investigated by estimating the maximum concentration of calmagite soluble in the copolymer solution. The concentration of calmagite was measured by UV–vis spectroscopy. Since calmagite is not soluble in methylene chloride and calibration in this solvent is not possible, absorption measurements yield only relative values. To estimate the dye concentration in the polymer solutions, water solutions of calmagite at different concentrations were used for calibration. The ratio of the relative concentrations of calmagite transferred to star and dendritic copolymer solutions to the copolymer concentration and the estimated average number of dye molecule per polymer molecule are summarized in Table 4. For each polymer, the concentration in methylene chloride was 1.25 g/L.

The most effective uptake of calmagite was observed for the star copolymer with the higher DP of ethylene oxide blocks. Copolymer of more developed structure (6B) with the higher hydroxyl group content and almost the same content of ethylene oxide units uptakes only one-third the amount of their star precursor. For all star and dendritic copolymers, the longer poly(ethylene oxide) blocks increase the calmagite uptake, and the rise is higher for stars than for dendritic copolymers. The linear homopolymer PEO of a similar molar mass to the star copolymer with PEO blocks DP = 50 is less effective and uptakes only 60% of the amount of its branched analogue.

On the other hand, the calculated average number of calmagite molecules per one copolymer molecule is highest for dendritic copolymers with the longest polyethylene blocks. This effect is probably related to the insolubility of the strongly hydrophilic shell containing polyglycidol blocks in methylene chloride, while the poly(ethylene oxide) blocks are very soluble in this solvent. Many hydrophilic blocks on the shell of the branched block copolymer aggregate in a hydrophobic solvent, and this decreases the access to the core of the ethylene oxide blocks. Star block copolymers contain only four blocks of polyglycidol, so the aggregation effect is not so strong and does not block the core responsible for the solubilization of the hydrophilic dye.

4. Conclusions

Three star block copolymers of ethylene oxide and glycidol were synthesized by the sequential anionic controlled polymerization of ethylene oxide and protected glycidol. After deprotection, the hydroxyl groups of the polyglycidol blocks were used to prepare branched block copolymers with a hydrophilic polyglycidol shell and a branched core derived from the poly(ethylene oxide) blocks. The synthesized star and dendritic block copolymers have low dispersity and well-defined structure. The star and branched copolymers with the lowest DP = 10 of ethylene oxide do not crystallize, in contrast with copolymers with poly(ethylene oxide) DP = 30 and 50.

The uptake of hydrophilic dye (calmagite) to a methylene chloride solution of synthesized star and branched block copolymers was investigated. The length of the poly(ethylene oxide) block is the main factor determining the dye uptake to a methylene chloride solution.

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