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Polymer 44 (2003) 5067–5074

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Synthesis of functionalized multiarm poly(ethylene oxide) stars

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Received 7 February 2003; received in revised form 20 April 2003; accepted 18 June 2003

Abstract

Six arm poly(ethylene oxide) (PEO) stars carrying either 6 pyridyl or 12 hydroxyl groups at their periphery were synthesized using an arm-first approach. To this end, two novel α,ω-heterodifunctional PEO's, namely α-ketal,ω-hydroxy and α-pyridyl,ω-hydroxy PEO's were synthesized and, after the deprotonation of their hydroxyls, deactivated onto hexachlorocyclophosphazene which served to build the core. Quaternization of the stars containing six outer pyridyl groups created positive charges at their periphery while the acidic treatment of stars carrying terminal ketal rings afforded six arm PEO stars with 12 peripheral hydroxyls. The latter compound was subsequently deprotonated and used to polymerize ethylene oxide by a classical core-first approach. This resulted in the formation of highly branched PEO's also referred to as dendrimer-like PEO stars which consisted of a first generation of six PEO arms and a second generation of 12 hydroxy-ended PEO branches.

Keywords: Poly(ethylene oxide); Stars; Hexachlorocyclophosphazene

1. Introduction

Among branched structures, star polymers containing a precise number of arms have attracted a specific attention that was fuelled by the necessity to understand how branching affects the overall properties of polymers in solution or in the melt [1]. In contrast, interest in star-like and branched systems based on poly(ethylene oxide) (PEO) is mainly motivated by their potential for application in biomedical and pharmaceutical areas [2–4]. This is due to the specific properties of PEO such as its chemical stability, water solubility, non-toxicity, and resistance to recognition by the immune system. In addition, the arrangement of PEO chains into a branched architecture is expected to provide better performance as compared to linear PEO counterparts in these applications [2–4]. On the other hand, PEO stars also find increasing interest as high loading soluble support for liquid-phase organic synthesis [5].

Methodologies for synthesizing PEO stars are limited and each of them has its merits and drawbacks. PEO stars can be obtained either by linking a given number of linear chains to a central core following an arm-first method [5–13] or by growing branches from a multifunctional initiator via a core-first approach [14–20]. Alternatively, one can homopolymerize or copolymerize PEO-based macromonomers to low degrees of polymerization and generate structures—also called polymacromonomers—that exhibit a star-type behavior [21–23].

'Core-first' approaches to PEO stars rest on the use of either carbanionic initiating cores [15,16] or precursors containing a precise number of hydroxyl groups [17–20] to initiate the polymerization of ethylene oxide. Unsurprisingly, PEO stars grown from multicarbanionic precursors derived from homopolymerization of a divinylic monomer were shown to exhibit a rather large fluctuation in size and functionality [15]. Naraghi et al. though, reported that control over the star functionality could be improved upon substituting poly(diisopropenylbenzene) for poly(divinylbenzene) as divinylic monomer [16]. In contrast, multihydroxylated compounds used in a deprotonated form to grow PEO branches in multiple directions generally afford better defined star samples [15,17–20]. For instance,

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doi:10.1016/S0032-3861(03)00521-4

Comanita et al. and Knischka et al. chose carbosilane-based dendrimers [18] and hyperbranched polyglycerols [19], respectively, to derive core-first PEO stars containing a high number of arms. The solutions to prevent the multiple propagating alkokides from aggregating have also been discussed in these papers.

In the arm-first approach, a fractionation step is generally required to separate linear chains—used in excess—from star-shaped species exhibiting the expected number of arms. For example, 6 and 12 arm PEO stars have been prepared by deactivating linear PEO chains onto a cyclophosphazene core [5–7]. Likewise, Merrill and coll. [8] have coupled up to 32 arms of PEO chains to a third generation poly(amidoamine) dendrimer while Fréchet and coll. [9] have attached short PEO chains to a polyether dendrimer. Multiarm PEO stars have also been prepared by complexation of a ω-bipyridyl PEO to a metallic core based on a transition metal [12,13].

More recently, Lapienis and Penczek have generated starlike PEO's by an 'in-out' method: a bis-epoxide was, indeed, reacted with an ω-hydroxy PEO under basic conditions to form multi-oxanionic cores which were then used to initiate the polymerization of ethylene oxide [14]. Other branched architectures such as dendrimer-like polymers [20] hyperbranched polymers [24] or hydrogels [25] all based on PEO have also been derived.

This contribution reports the use of novel precursors for the synthesis of arm-first PEO stars carrying peripheral functional groups. Both arm-first and core-first methods were also combined to derive PEO-based dendrimer-like stars consisting of a first generation of six PEO arms and a second generation of 12 additional PEO blocks.

2. Experimental section

2.1. Materials

Ethylene oxide (Fluka) was transferred from a steel tank into a three neck flask, dried over sodium at −40 °C for 3 h, then distilled into a graduated burette. Dimethylsulfoxide was purified by distillation over calcium hydride into a Schlenk apparatus prior to use. 4-Hydroxymethyl pyridine (**1**) was used as received. 5,5-Dimethyl-2-hydroxymethyl-1,3-dioxane (**5**) was prepared as previously reported [20]. A THF solution of diphenylmethylpotassium (DPMK) was prepared according to a procedure reported earlier [26] and transferred into a burette. The concentration of this solution was then verified through titration with a known amount of acetanilide dissolved in DMSO until the appearance of a persistent red-orange color.

2.2. Preparation of α,ω-heterodifunctional PEO's

The synthesis of heterodifunctional PEO's was achieved using hydroxymethyl pyridine or 5,5-dimethyl-2-hydroxymethyl-1,3-dioxane as initiators for the anionic polymerization of ethylene oxide. In a typical experiment, 1.18 g (10.8 mmol) of hydroxymethyl pyridine were dried in a 500 mL flask under vacuum for 3 h before adding 190 mL of freshly distilled DMSO. Over a period of 3 h, 5.7 mL (3.24 mmol) of a DPMK solution in THF were slowly added until a light yellow color was obtained. To the above solution, 19 mL of ethylene oxide (0.38 mol) were introduced. The reaction mixture was initially stirred at room temperature for at least 24 h and then heated to 40 °C for 48 h. The polymerization was quenched upon addition of 1 mL of methanol and the resulting polymer was recovered by three successive precipitations in diethyl ether (yield = 89%).

In the case of 5,5-dimethyl-2-hydroxymethyl-1,3-dioxane (**5**), 720 mg (4.86 mmol) of the latter compound was freeze-dried overnight from a dioxane solution and then dissolved in 100 mL of distilled THF. The initiator was deprotonated with 6.7 mL (3.84 mmol) of a DPMK solution followed by reaction with 10 mL of ethylene oxide (0.20 mol). After the polymerization was terminated, the final product was isolated following the same procedure as described above (yield = 96%). Additional data are provided in Table 1.

Table 1
Molecular features of α,ω-heterodifunctional PEO's and the corresponding end-functionalized hexaarm PEO stars

Compound	$M_{\mathrm{n\ theo}}$ [a] (g mol^{-1})	$M_{\mathrm{n\ SEC}}$ [b] (g mol^{-1})	$M_{\mathrm{n\ NMR}}$ [c] (g mol^{-1})	PDI [b]
2	2000	2050	2100	1.04
3	12 300	8270	[d]	1.23
4	13 150	4890	[d]	1.10
6	2340	2000	2300	1.09
7	13 500	10 400	[d]	1.05
8	13 260	10 100	[d]	1.08
9	24 000 [a]	17 000	21 000 [e]	1.14

[a] Theoretical molar mass based on the monomer to the OH precursor molar ratio for 100% conversion in the case of **2** and **6**. For star species (**3**, **4**, **7** and **8**) the theoretical molar mass is equal to 6 × (molar mass of the linear precursor) + the molar mass of the core, assuming the stars contain 6 arms. For the dendrimer-like species **9**, the theoretical molar mass is equal to: $M_{\mathrm{n\ PEO\ \mathbf{9}}} = (M_{\mathrm{n\ PEO\ \mathbf{8}}}) + (44 \times [\mathrm{EO}]/[\mathrm{PEO}\ \mathbf{8}] \times \mathrm{conv(EO)}\%)$; this corresponds to $M_n = 1000\ g\ mol^{-1}$ for each PEO branch in the second generation for 10% conversion of EO.

[b] Molar masses determined by SEC equipped with a RI detector using THF as the eluent (calibration with PEO standards).

[c] Molar masses determined by ^{1}H NMR in $CDCl_3$ (see text).

[d] Molar masses of PEO star derivatives were not determined by ^{1}H NMR due to the absence of protons characteristics to the core.

[e] The following expression was used: $M_{\mathrm{n\ NMR}} = (44 \times m \times 12) + 13\,260$, where m is the degree of polymerization of PEO arms of the second generation determined as follows. $I_{3.5\ \mathrm{ppm}}/I_{0.91\ \mathrm{ppm}} = (45 \times 4H + 8H \times m)/3H$, where $I_{3.5\ \mathrm{ppm}}$ and $I_{0.91\ \mathrm{ppm}}$ is the intensity of the peak due to the protons of EO units and the intensity of the peak due to the protons of the CH_3 group of the branching entity, respectively (see Fig. 3); 45 in this case corresponds to the degree of polymerization of PEO arms of the first generation.

2.3. Synthesis of six arm PEO stars

The coupling reaction for forming multi-arm PEO was carried out as follows. The α,ω-difunctional PEO (5×10^{-4} mol) was freeze-dried from a dioxane solution overnight prior to being dissolved in 100 mL of distilled THF. The hydroxyl groups were fully deprotonated through slow addition of 0.9 mL (5.1×10^{-4} mol) of a DPMK solution in THF. In another burette, 30 mg of hexacyclophosphazene (8.6×10^{-5} mol) was dissolved in 50 mL of distilled THF and slowly introduced into the deprotonated precursor solution. The reaction was carried out for 24 h at room temperature and then terminated with 2–3 mL of methanol to remove any residual alkoxides. The product was precipitated in diethyl ether, re-dissolved in CH_2Cl_2, and re-precipitated twice (yield = 77%). Characterizations by ^{1}H NMR and by SEC are shown in Figs. 1–4 (see also Table 1).

2.4. Purification of the arm-first PEO stars by selective extraction

The recovered PEO stars (2 g) were first completely dissolved in toluene (200 mL). To this solution, *n*-heptane was added dropwise while stirring, with an interval of 5 min for every 1 mL of *n*-heptane, until the mixture turned slightly cloudy. Upon heating, a clear solution was obtained. This solution was allowed to cool to room temperature resulting in the formation of a white precipitate that was isolated through filtration, washed with the toluene–heptane mixture, and then collected and dried under vacuum.

2.5. Chemical modification of arm-first PEO stars

2.5.1. Synthesis of the dodecahydroxy six-arm PEO star

To a THF solution (200 mL) of the hexaketal six arm PEO star (3 g 2.2×10^{-4} mol), 2 mL of concentrated (35%) aqueous hydrochlorid acid were added. The reaction mixture was stirred overnight at room temperature. After concentration, the solution was poured into 10-fold of cold diethyl ether and the white solid material was dried under vacuum (yield = 95%). The cleavage of the ketal rings was checked by ^{1}H NMR (see Fig. 3).

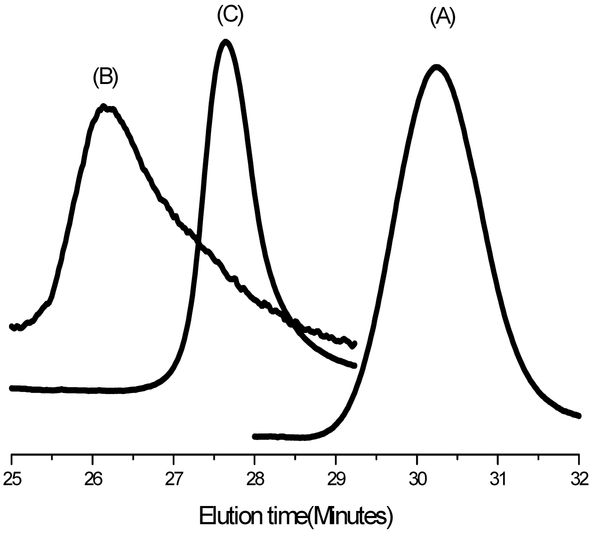


Fig. 2. SEC traces (Solvent: THF, RI detector) of (A) the α-pyridyl,ω-hydroxy PEO **2**, (B) the 6-armed pyridyl-ended PEO **3** and (C) the 6-armed pyridinium-ended PEO **4**.

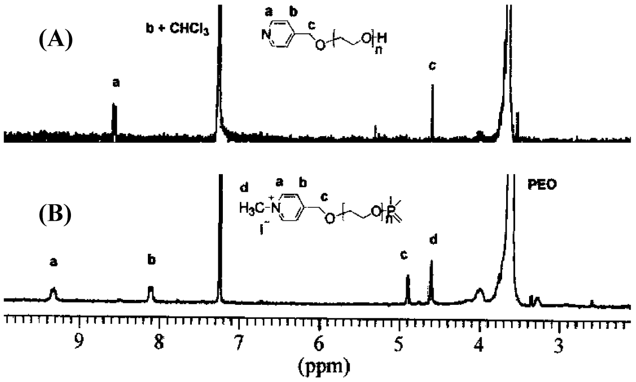


Fig. 1. ^{1}H NMR ($CDCl_3$; 200 MHz) spectrum of (A) the α-pyridyl,ω-hydroxy PEO **2** and (B) the 6-armed pyridinium-ended PEO **4**.

2.5.2. Synthesis of the hexapyridinium six-arm PEO star

The hexapyridyl six arm PEO star (0.28 g, 2.27×10^{-5} mol) was first dissolved in dry acetonitrile. To the above solution, 1 mL of methyl iodide was added and the reaction mixture was stirred at 80 °C for 48 h. After

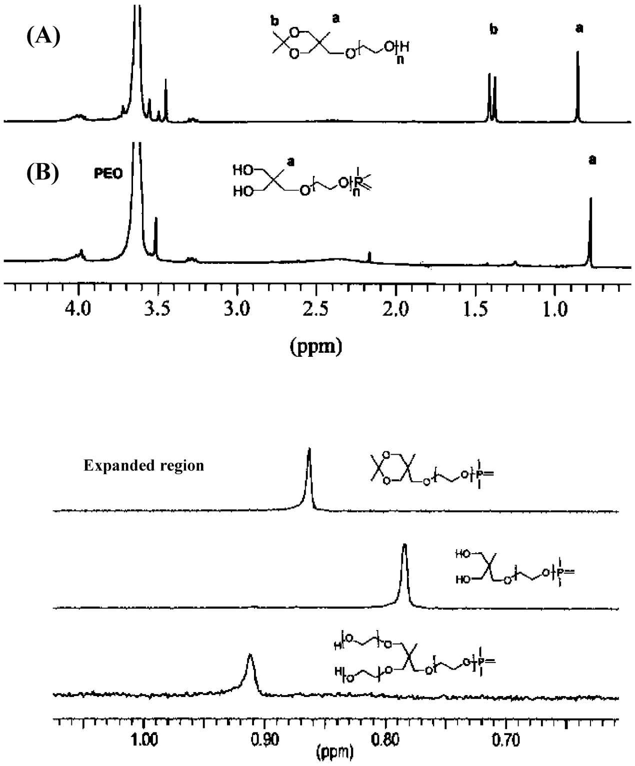


Fig. 3. ^{1}H NMR spectrum ($CDCl_3$; 200 MHz) of (A) the α-ketal,ω-hydroxy PEO **6** and (B) the 6-armed dodecahydroxy-ended PEO **8**.

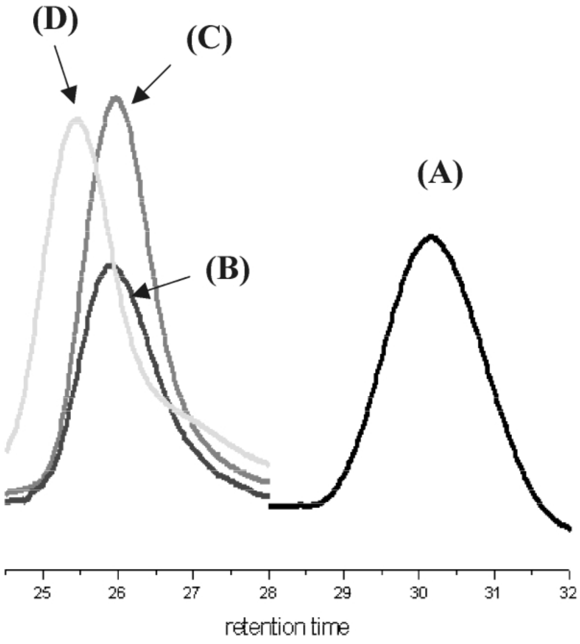


Fig. 4. SEC traces (Solvent: THF, RI detector) of (A) the α-ketal,ω-hydroxy PEO **6**, (B) the 6-armed ketal-ended PEO **7**, (C) the dodecahydroxy-ended PEO **8** and (D) the dendrimer-like star PEO **9**.

concentration, the polymer was recovered by two successive precipitations in diethyl ether (yield = 80%). The quaternization of the pyridyl groups was confirmed by ^{1}H NMR (see Fig. 1).

2.6. Synthesis of dendrimer-like PEO

To a THF solution (100 mL) of the dodecahydroxylated six arm PEO star (0.4 g, 3.02×10^{-5} mol), 0.51 mL (2.9×10^{-4} mol) of DPMK was added. This yielded a slightly cloudy solution which was allowed to stir overnight. Ethylene oxide (4 mL, 7.8×10^{-2} mol) was added and the reaction mixture was stirred at room temperature for 24 h, then at 35 °C for 48 h. The polymerization was quenched with a few drops of methanol. After concentration, the polymer was precipitated in diethyl ether (yield = 10%).

2.7. Characterization

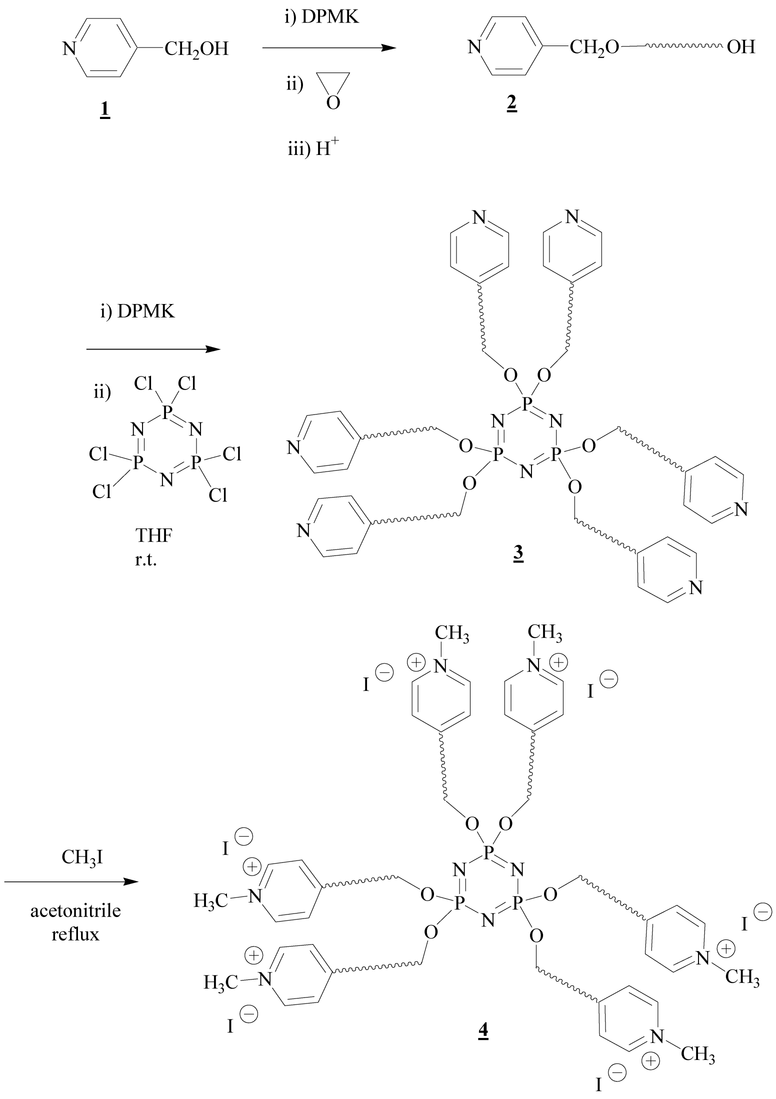
NMR spectra were obtained using a Bruker AC200 NMR spectrometer. Apparent molar masses of PEO stars were determined using a size exclusion chromatography apparatus equipped with a Varian refractive index detector connected to three TSK columns (G4000HXL, G3000HXL, G2000HXL) and using tetrahydrofuran as the eluent (flow rate: 1 mL/min) at 25 °C. A JASCO 875 UV/VIS absorption detector was also part of the instrumentation and proved useful in this study to detect samples comprising the pyridyl moiety. Calibration was performed using linear PEO standards (Tosoho).

3. Results and discussion

To access end-functionalized PEO stars by the ‘arm-first’ method, one primarily requires α,ω-heterodifunctional PEO precursors; therefore, appropriate initiators are to be designed to this end. Specifically, we report herein the synthesis of ω-hydroxy PEO carrying at their ω-end either a pyridyl group or two protected hydroxyls. Attempts to synthesize other α,ω-heterodifunctional PEO’s were described in the literature. For instance, Schlaad and coll. [27] deprotonated α-methylbenzyl cyanide with a phosphazene-based nucleophile (t-BuP$_4$) to trigger the anionic polymerization of ethylene oxide. As a result, α-cyano,ω-hydroxy-heterodifunctional PEO’s were obtained and subsequently converted into α-amino,ω-hydroxy PEO’s by treatment with LiAlH$_4$. In an earlier report, Mosquet and coll. [28] employed aminoethanol as a precursor to anionically polymerize ethylene oxide and finally obtained α-amino,ω-hydroxy-heterodifunctional PEO’s. In our case, a pyridine functional group could be introduced at the ω-end of PEO chains through the use of hydroxymethyl-pyridine **1** as the initiator (Scheme 1). Dimethylsulfoxide (DMSO) was chosen as solvent of polymerization instead of tetrahydrofurane (THF) due to a better solubility of hydroxymethyl-pyridine in the former solvent. The extent of deprotonation of the hydroxyl group of **1** by a solution of diphenylmethyl potassium (DPMK) was restricted to 30%, in order to prevent the aggregation of propagating alkoxides [17] and their transfer to DMSO from occurring [29]. Under such homogeneous conditions, the exchange between dormant OH groups and active alkoxides ($R_{\text{exch.}} = k_{\text{exch.}}[\text{O}^-][\text{OH}]$) [30,31] was rapid enough—with respect to the rate of polymerization ($R_p = k_p[\text{O}^-][\text{M}]$)—for the PEO chains to grow under controlled conditions from precursor **1**.

An α-ketal,ω-hydroxy PEO (PEO **6** in Scheme 2) was synthesized through the use of 2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (**5**) as a precursor. The latter compound was thoroughly deprotonated with DPMK before being used for by the anionic polymerization of ethylene oxide, which was carried out, in this case, in THF medium.

The results shown in Table 1 indicate that the experimental molar masses determined by NMR (see below) match the expected values and that the molar mass distribution determined by SEC is very narrow; this attests that the polymerization of ethylene oxide occurred in a living and controlled manner. Characterization of PEO **2** and PEO **6** by ^{1}H NMR confirmed their expected structure, as documented by the assignment of the peaks appearing in Figs. 1(A) and 3(A), respectively. The M_n values of these samples could be calculated upon comparing the integration of the protons of either the pyridyl moiety or the methyl group of the ketal ring, for PEO **2** and PEO **6** respectively, with that of the protons belonging to ethylene oxide units. NMR thus provided the necessary evidence that these PEO chains were quantitatively labeled with the expected pyridyl and ketal ring, respectively.

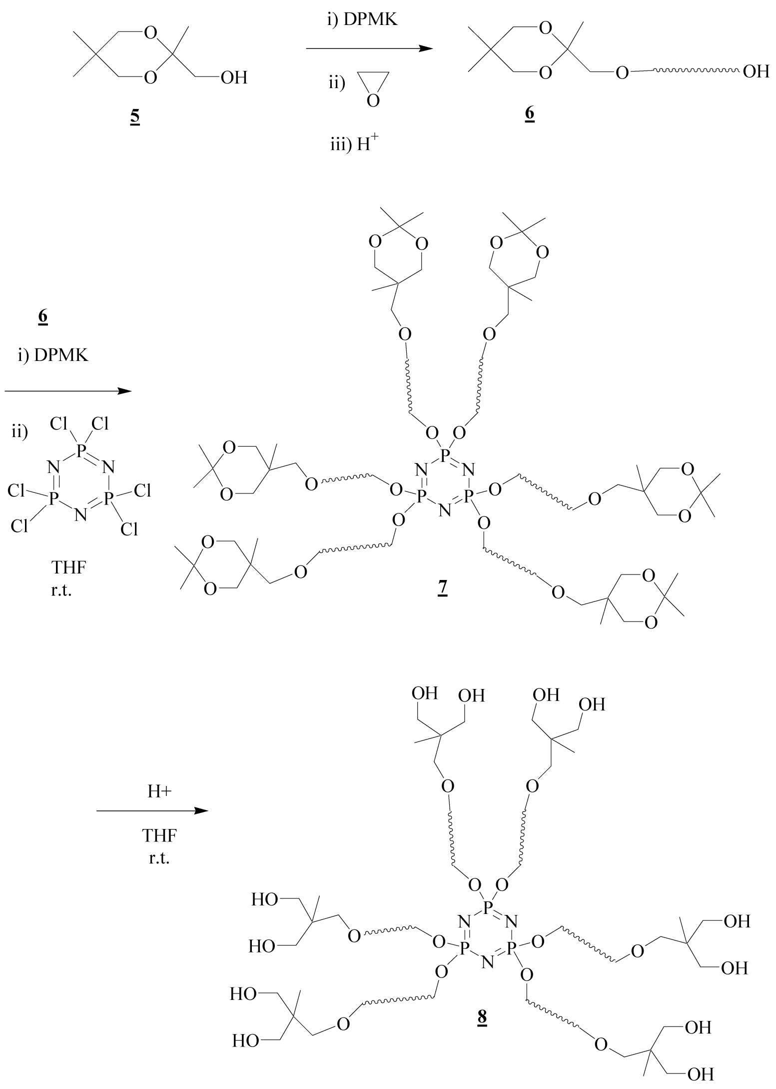


Scheme 1. Synthesis of six arm PEO stars with pyridyl and pyridinium end groups.

The synthesis of functionalized arm-first PEO stars was subsequently accomplished by deactivating PEO **2** and **6** on phosphonitrilic chloride trimer ($N_3P_3Cl_6$), also referred to as hexachlorocyclophosphazene, serving here as the core of the targeted stars (Schemes 1 and 2). The key to the successful reaction between $N_3P_3Cl_6$ and oxanionic chains of PEO [32] is the formation of very stable phosphorous–oxygen bonds by substitution of the six highly reactive chlorine atoms [5–7]. Unreacted linear chains were easily removed from such samples by fractionation using a mixture of toluene and heptane (see Section 2).

The coupling reaction was monitored by SEC which clearly showed a shift towards the higher molar mass of the linear precursor peak (see Figs. 2 and 4). However, a tail in the low molar mass area was observed in the SEC trace of the six-ended pyridyl PEO star **3**. This was attributed to the affinity of this compound for the support of the chromatographic columns. SEC characterization of the same sample after modification of its pyridyl groups (see below) supported this hypothesis. Characterization of products **3** and **7** by ^{13}C and ^{1}H NMR indicated the absence of free hydroxyl groups. Moreover, the presence of a singlet at 18.5 ppm in the ^{31}P NMR spectrum of each compound confirmed the integrity of the inorganic cyclotriphosphazene core. These data thus confirmed that the six chlorine atoms of the core were completely substituted and that well-defined PEO stars were formed.

A subsequent treatment of the pyridyl-terminated compound **3** with methyl iodide in refluxing acetonitrile yielded the hexaarm pyridium-terminated PEO star **4** (Scheme 2), as evidenced by ^{1}H NMR spectroscopy. The change in the chemical shift of the pyridyl protons (Fig. 2) is, indeed, an excellent tool to probe the extent of the quaternization step. On the other hand, the SEC profile of this positively charged PEO differed from that of its neutral pyridyl-ended precursor; despite the only slight increase in molar mass due to the introduction of six methyl groups, the PEO star **4** exhibited a lower hydrodynamic volume than its



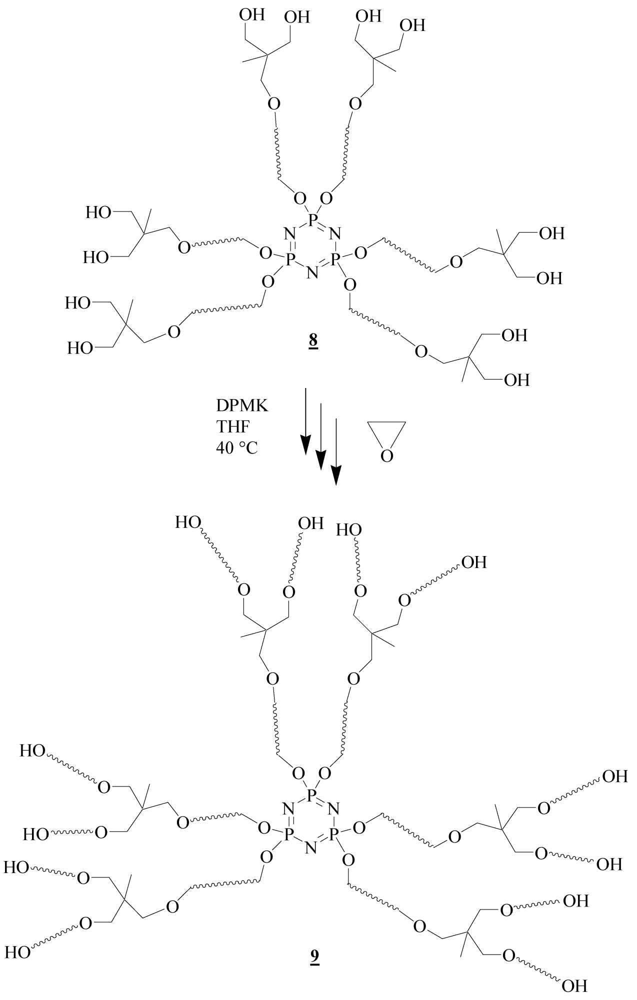
Scheme 2. Synthesis of six arm PEO stars with hydroxy end groups.

neutral precursor **3**. Work is currently in progress to quaternize the pyridyl moieties with species that can afford materials with self-associating properties.

As for the PEO star containing six ketal protecting groups, it was treated under acidic conditions to readily produce a dodecahydroxy-ended PEO star. The quantitative deprotection of hydroxyl groups was confirmed by ^{1}H NMR which showed the disappearance of the methyl protons of the ketal and the (re)appearance of the hydroxy protons at 4.8 ppm (Fig. 3). In addition, the resonance of the methyl protons of the branching point is entirely shifted downfield upon transformation of the six ketal rings into the 12 hydroxy chain ends (see expanded region of Fig. 3). This hydrolysis did not affect the SEC profiles of the star compounds since those obtained before and after cleavage proved superimposable (Fig. 4).

Finally, this dodecahydroxy PEO star, after deprotonation with a solution of DPMK was used as multifunctional initiator to anionically grow 12 additional PEO branches by the core-first approach. The polymerization of ethylene oxide was carried out in THF, deprotonating about 80% of the hydroxyl groups of **8**. This caused to some extent the aggregation of the alkoxides formed, but the reaction mixture became entirely homogeneous upon monomer addition after a few hours. A so-called dendrimer-like star was isolated (Scheme 3). The terms ‘dendrimer-like star’ refer to polymeric structures that share with regular dendrimers some of their features such as a precise number of branching points and outer functions in all molecules, the presence of a central core, but that differ from the latter by the macromolecular size of their generations [20,33].

Fig. 3 shows an expanded window (0.5–1 ppm) of ^{1}H NMR spectra of the compounds **8** and **9** before and after the growth of the second generation of PEO chains. In this region, the methyl group a of the branching entity could be easily assigned and its location was used to probe the initiation of polymerization. Indeed, upon addition of a few ethylene oxide units, the resonance of these methyl protons



Scheme 3. Synthesis of a dendrimer-like star PEO.

is shifted upfield. Moreover, no residual signal at the original position of the macroinitiator **8** was detected after polymerization. This allows to conclude that all the 12 hydroxyls, after their partial deprotonation ($<80\%$), simultaneously initiated the polymerization of ethylene oxide. From the knowledge of the M_n of the star precursor **7** and **8**, the M_n of **9** could be estimated by ^{1}H NMR (see Table 1). As discussed above, the rapid exchange of protons between propagating alkoxides and dormant hydroxyls—as compared to the rate of polymerization of ethylene oxide—is essential for the chains to grow at the same rate.

The SEC traces of the four polymers **6**, **7**, **8** and **9** obtained after precipitation in diethyl ether (Fig. 4) unambiguously show the growth of additional PEO arms from the dodecahydroxy PEO **8**. After ethylene oxide polymerization, indeed, the SEC traces shifted to the higher molar mass region. However, a shoulder was observed in the low molar mass region of the SEC trace. This side peak is attributable to the presence of linear PEO chains that might have been well initiated by protic impurities—active under alkoxide—contained in the improperly dried PEO precursors. In spite of this minor drawback, this synthetic strategy based on the combination of both arm-first and core-first methods allowed to tailor dendrimer-like PEO's. Optimization of the synthesis of dendrimer-like PEO's and investigation of both their solution and crystalline properties are currently in progress.

4. Conclusion

This paper describes the synthesis of end-functionalized poly(ethylene oxide) stars from readily accessible precursors. Both the number and the nature of the terminal groups in these stars could be varied. For instance, incorporation of peripheral charges was easily accomplished through the quaternization of pyridyl-end groups. More complex PEO-based such as dendrimer-like stars were also derived by combination of the arm-first and the core-first methodologies. This synthetic strategy allowed us to target the generations of PEO arms of different size. The hydrophilic branched materials prepared in this way combine many advantages, such as the presence of terminal functional groups, facile preparation, and core stability.

Acknowledgements

The authors are grateful to the National Institute of Health (USA) and the French Ministry of Higher Education and Research for support of this research.

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[32] Living oxanions deriving from PEO's **2** and **6** could have been directly deactivated onto $N_3P_3Cl_6$ without isolating the α-ω-hydroxy PEO intermediates. Isolation of the latter species was simply accomplished for characterization purpose.

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