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Amphiphilic core-shell PEO stars by Williamson etherification reaction

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Summary

Star copolymers of M_n varying between 20 000 and 80 000, containing a hydrophobic branched poly[p-(chloromethyl)-styrene] core and hydrophilic polyether shell, were synthesized. The core was obtained via atom transfer radical polymerization of p-(chloromethyl)styrene. Some of the chlorine groups in the core were reacted with living polyether macroanions, yielding amphiphilic star structures in the Williamson etherification reaction.

Introduction

Star polymers, macromolecules with many arms emanating from a common central point or object, are subject of numerous investigations both because of their unusual behavior in the solution and in the condensed phase, which differs strongly from that of the linear macromolecules, and because of their potential applications (for review, see [1, 2, 3]). The synthetic routes to such polymers have been recently reviewed [2, 4, 5, 6]. They consist in most cases in the initiation of the living polymerization of arms by a multifunctional initiator ("core first") or by termination of the living polymerization of the arms by a proper multifunctional terminating agent ("arm first"). Also "mixed" methods are applied, which combine both approaches.

Amphiphilic star macromolecules contain in their structure both hydrophobic and hydrophilic segments. An example of such structure are stars consisting of a hydrophobic polystyrene core and hydrophilic polyether shell [7]. Such structures have been obtained, in most cases by a combination of the living polymerization of styrene or divinylbenzene with living polymerization of the oxirane [8, 9, 10].

Here, we want to describe a facile route to such polymers by the termination of the living polyether macroanions with branched chlorinated polystyrene core.

Experimental

Materials:

p-(chloromethyl)styrene (Aldrich) was distilled under reduced pressure prior to use.
CuBr and 4,4'-dimethyl-2,2'bipyridine (biPy) were used as received.
THF was refluxed over Na/K alloy.
Poly(ethylene glycol) monomethyl ethers (Aldrich, M_n – 750, 2000, 5000) were precipitated from THF in hexane and dried.
NaH (Aldrich) was washed with dry THF and dried under reduced pressure.
Ethoxy ethyl glycidyl ether was synthesized from 2,3-epoxypropanol-1 (glycidol) according to Fitton et al [11] and fractionated under reduced pressure prior to use. A fraction with purity exceeding 99.8% (GC) was used.

Polymer syntheses

Poly[p-(chloromethyl)styrene] was synthesized via atom transfer radical polymerization of p-(chloromethyl)styrene in bulk using CuBr (1 mol% of the monomer) and biPy (3 mol% of the monomer) at 130°C, as described by Matyjaszewski [12].

Course of the etherification reaction

For all star polymers the same procedure was used.
NaH (0.0393 g, 1.6 x 10^{-3} mol, 5 times the molar amount of the poly(ethylene glycol) monomethyl ether used) was suspended in 10 mL dry THF under nitrogen. Polystyrene M_n=900000 was added as standard. 3.3 x 10^{-4} mol poly(ethylene glycol) monomethyl ether (0.2459 g of M_n=750, 0.6557 g of M_n =2000 and 1.6393 g of M_n=5000) dissolved in 10 mL dry THF was added and the suspension was stirred for 24 h at room temperature. The temperature was raised to 50°C and a solution of 0.1 g poly[p-(chloromethyl)styrene] in 5 mL dry THF was added. At regular intervals of time samples of the reaction mixture were taken and injected into SEC chromatograph. Integration of the signals of the unreacted poly(ethylene glycol) monomethyl ether and of the polystyrene standard yielded the amount of the reacted polyether.

Synthesis of the star polymers with PEO arms

NaH (5 times of the molar amount of the poly(ethylene glycol) monomethyl ether used) was suspended under nitrogen in 10 mL dry THF. Poly(ethylene glycol) methyl ether (amount which enabled full conversion, i.e. 2.3 x 10^{-3} mol of M_n=750, 1.9 x 10^{-3} mol of M_n=2000 or 1.2 x 10^{-3} mol of M_n=5000) were dissolved in 90 mL dry THF and poured into NaH/THF mixture. The reaction was carried out at room temperature. After 24 h, mixture was heated to 50°C and solution of poly[p-(chloromethyl)styrene] (1g) in THF (30 mL) was added. Stirring was continued for 4 h at 50°C**.** The mixture was poured into 5% HCl to deactivate excess of NaH. The solution was neutralized and the solvents evaporated. The polymer was dissolved in water and desalinated using ion exchange resins. Water was evaporated, the polymers dissolved in THF, precipitated in n-hexane and dried.

Synthesis of living anionic poly(ethoxy ethyl glycidyl eter)

Potassium tert-butoxide (0.1745 g, 1.6 x 10^{-3} mol) was dissolved in 2 mL dry THF, the reactor was cooled to –50°C and a solution of 3.7376 g (2.56 x 10^{-2} mol) ethoxy ethyl glycidyl ether in 2 mL dry THF was added. The polymerization was carried out at 60˚C for 17 hours to the full conversion of the monomer, checked by gas chromatography.

Synthesis of poly(ethoxy ethyl glycidyl ether) star polymer
Solution of 5.338g (2.3 x 10^{-3} mol) living poly(ethoxy ethyl glycidyl eter) in 6 mL THF was added to a solution of poly[p-(chloromethyl)styrene] (1g) in THF (20 mL). The reaction was carried out at 50˚C for 4 h. The solvent was evaporated, the polymer dissolved in water, desalinated and precipitated as described before.

Reaction of potassium t-butoxide with branched poly[p-(chloromethyl)styrene]
Potassium tert-butoxide (0.5441g, 4.8 x 10^{-3} mol, twice the amount of the Cl groups of the core) was dissolved in 20 mL dry THF. A solution of 0.3697g poly[p-(chloromethyl)styrene] in 20 mL dry THF was added to the reactor.

Measurements

NMR
The ^{1}H NMR spectra of poly[p-(chloromethyl)styrene] were recorded at 500 MHz in $CDCl_3$ using a Brucker AM spectrometer. The ^{1}H NMR spectra of the star polymers were measured at 300 MHz in $CDCl_3$ or D_2O using Varian Unity spectrometer.

Size exclusion chromatography
The molecular weights and the polydispersities of obtained products were determined by SEC using 3 x PlGel Mixed C 30 cm and guard columns with differential refractive index detector Schambeck 2000 (Schambeck GmbH) and a multiangle light scattering detector DAWN EOS of Wyatt Technologies. Measurements were performed in THF as the solvent at 30°C with a nominal flow rate of 1 ml/min. Results were evaluated using the ASTRA software from Wyatt Technologies.
Refractive index increments in THF were determined independent for all obtained polymers.

Results and discussion

Synthesis of poly[p-(chloromethyl)styrene] using CuBr/biPy

The atom transfer radical polymerization of p-(chloromethyl)styrene was first reported by Matyjaszewski [12] and later discussed in details by Frechet [13]. The action of the ATRP mechanism in the case of this monomer should lead to a branched product (fig. 1), as the p-(chloromethyl)styrene may act as an “inimer” - monomer (styrenic double bond) and initiator (abstraction of the chlorine and generation of the CH_2 radical):
The ^{1}H NMR spectrum of the polymer obtained (fig. 2) indicates branching, as evidenced by the presence of the signals of the Ph-CH-Cl protons at δ=4.7 ppm.
The determination of the degree of branching is not straightforward. Frechet [13] analysed the structure very exactly, using NMR and light scattering and varying the synthetic conditions. According to the method he developed, the “minimal percent of linearity” in our polymer is 39%.

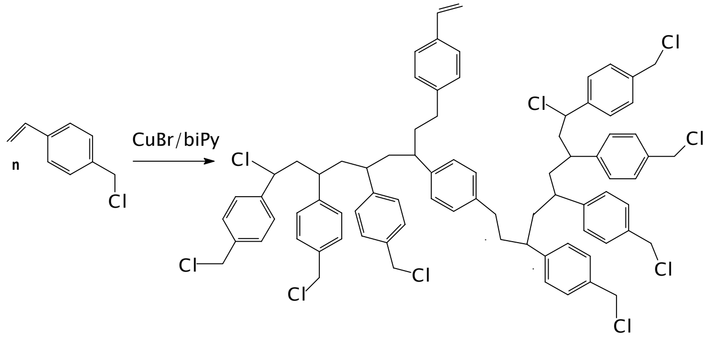

Fig. 1. Possible structure of the poly[p-(chloromethyl)styrene] obtained via ATRP

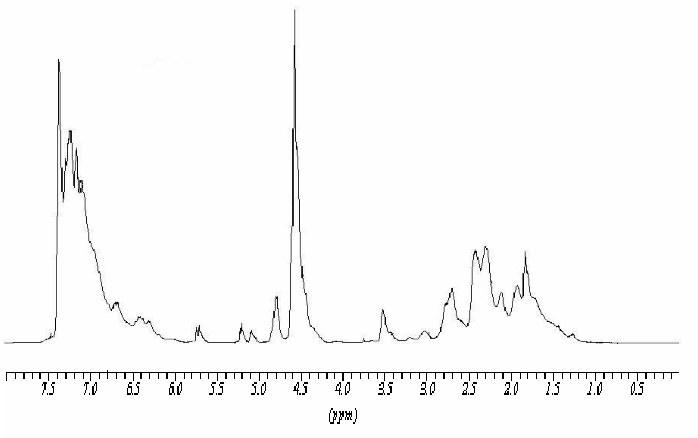

Fig. 2. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the poly[p-(chloromethyl)styrene] obtained via ATRP

The molar mass of the obtained polymer, measured by the SEC-MALLS in THF, is ca. 1400 with M_w/M_n=1.38.

Elemental analysis indicates 73.6 % C, 6.11% H, 18.05% Cl and 2.24% N.

There is some elimination of chlorine, as also observed by Frechet [13]. The content of nitrogen evidences the presence of the 4,4'-dimethyl-2,2'-bipyridine, used as ligand. No purification of the polymer could eliminate the nitrogen, which indicates that the biPy is covalently bound to the polymer chain. The molar mass of the polymer and the nitrogen content indicate that there is approximately one bipirydyl moiety per poly[p-(chloromethyl)styrene] macromolecule.

Synthesis of the star polymers

The reaction of the polyether macroanion, regardless whether obtained by the ionization of the hydroxyl group in the reaction of the poly(ethylene glycol) monomethyl ether with NaH or generated in the course of the living anionic polymerization of the ethoxy ethyl glycidyl ether initiated with t-BuOK, proceeds smoothly, according to the schema shown on figure 3.

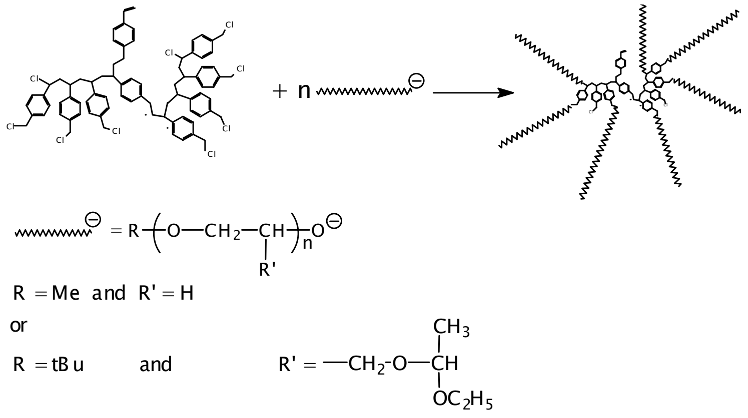

Fig. 3. Reaction of the branched poly[p-(chloromethyl)styrene] with polyether macroanions leading to star polymers

However, the measurements of the reacted amount of polyether macroanions by the SEC indicate that not all of the chlorine atoms undergo the etherification (fig. 4).

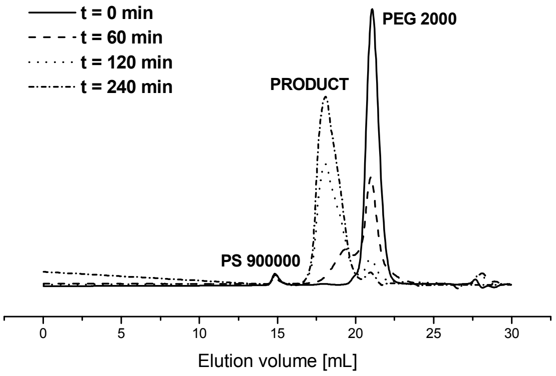

Fig. 4. SEC traces of the reaction mixture of poly[p-(chloromethyl)styrene] with the macroanion of poly(ethylene glycol) monomethyl ether

The fraction of the chlorine atoms which may be etherified depends upon the molar mass of the etherifying PEO macroanions and varies between 20 and 30% (table 1). The higher the molar mass of the PEO, the lesser this fraction. This is probably due to the steric hindrance caused by the attached PEO arms. Moreover, THF, the reaction medium, is a poor solvent for poly(ethylene oxide). The quality of THF as the solvent for PEO deteriorates with increasing molar mass of the PEO [14]. This causes the attached longer polyether chains to collapse into dense coils, which “cover” the core from the attack of the incoming chains.

Table 1. Results of the etherification of poly[p-(chloromethyl)styrene] with the polyether macroanions

Run	Macroanion used*)	% of etherified Cl groups
A	PEG_{750}	32
B	PEG_{2000}	27
C	PEG_{5000}	18
D	$Poly(AcGl)_{2300}$	34
E	$t\text{-}BuO^-$	crosslinked product

*) PEG – poly(ethylene glycol) monomethyl ether, Poly(AcGl) – poly(ethoxy ethyl glycidyl ether), indices denote the molar masses

Molar masses of obtained star polymers – evidences for core coupling

Table 2 contains the measured molar masses and polydispersion indices of the obtained star polymers.

Table 2. Molar masses of obtained star polymers

	Calculated[1]	Measured[2]			
Run	M_{calc}	M_n	M_w/M_n	Number of coupled cores	Number of arms
A	3849	24 900	3.12	6.5	19
B	6799	37 800	1.94	5.6	15
C	10 261	69 000	1.71	6.7	12
D	9100	71 000	1.87	7.8	26

[1] Based upon the molar mass of the core, molar mass of the polyether and amount of the polyether consumed in the etherification (see table 1)
[2] Based upon SEC–MALLS measurements

The determination of the molar masses of polymers of unusual topology (stars and highly branched macromolecules) is a challenging task. The difficulties are due to the imperfections of the chromatographic separation and difficulties in the absolute molar mass detection. Even chemically homogenous branched polymers are frequently not properly separated in the SEC columns [15, 16]. In addition, in the case of amphiphilic macromolecules, which contain the segments of very different philicity, the distribution of the chemical composition changes the overall interactions with the solvent, thus disturbing the relationship between the hydrodynamic volume and the molar mass. Even if the chromatographic separation is proper, the detection of the molar mass in the eluent slices causes problems. No proper calibration standards exist, so that “absolute” methods are to be used. Light scattering coupled with SEC is an absolute method, however, the changes in the composition of the amphiphilic polymer change also the refractive index increment, which may severely disturb the measured molar mass values [17]. Therefore great caution has to be exercised when interpreting the molar mass data for the amphiphilic star polymers.

Being aware of these limitation one has to state however, that the measured molar masses of obtained stars are several times higher then the values calculated basing upon the molar mass of the core poly[(p-chloromethyl)styrene] and the amounts and molar masses of the polyethers used in the etherification (table 2). The possible errors of the measurements cannot account for this discrepancy. The necessary condition for the correct molar mass determination by SEC, the linearity of the molar mass versus elution volume plot is well fulfilled for all measured samples (fig. 5).

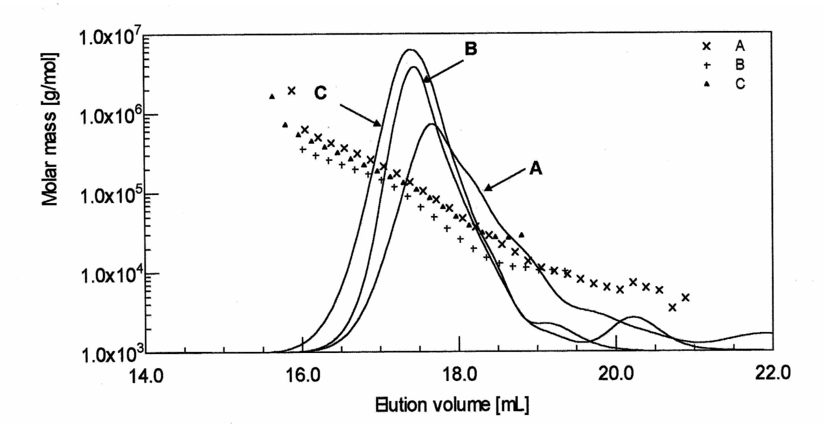

Fig. 5. Elution traces (RI signal) and molar mass versus elution volume plots for polymers A – C in table 2.

Therefore it has to be assumed that the etherification leading to the formation of star polymers is accompanied by the coupling of the core macromolecules. A possible reason could be the linking of the core molecules by diols, which may be present in the commercial samples of the poly(ethylene glycol) monomethyl ethers [18]. To account for this, living poly(ethoxy ethyl glycidyl ether) macroanions were used for etherification. It is known that the anionic polymerization of ethoxy ethyl glycidyl ether proceeds without any significant chain transfer, leading to polymers with well defined end group functionality [19]. The results (table 2, entry D) indicate a coupling of core molecules also in this case. Moreover, when potassium tert-butoxide is used in a model etherification reaction (table 1, entry E), only crosslinked product is obtained. Another, most likely explanation is due to the presence of a diamine, the 4,4’-dimethyl-2,2’bipyridine, covalently bound to the poly[p-(chloromethyl)-styrene], as indicated by the results of the elemental analysis. The quaternization of both nitrogen atoms in the 4,4’-dimethyl-2,2’bipyridine by the chloromethyl groups of the polymer is most probably responsible for the observed coupling of the cores. A similar behavior of poly[(p-chloromethyl)styrene was reported by Frechet, who studied polymer modification reactions on chloromethylated polystyrene and observed crosslinking when he attempted to introduce amino groups into these polymers [20].

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