Carbohydrate Polymers 83 (2011) 1174–1179

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Easy access to amphiphilic glycosylated-functionalized polystyrenes

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ARTICLE INFO

Article history:
Received 21 June 2010
Received in revised form 31 August 2010
Accepted 14 September 2010
Available online 25 September 2010

Keywords:
Amphiphilic polymer
Atom transfer radical polymerization (ATRP)
Polystyrene
Oligosaccharides
Self-assembly

ABSTRACT

A new route for the synthesis of amphiphilic functionalized polymers based on polystyrene and glycosidic part is described. They were obtained in a three steps procedure combining atom transfer radical polymerization (ATRP), nucleophilic substitution and reductive amination without the need of protection and deprotection steps of the glycosidic part. This process allows the easy synthesis of polystyrenes functionalized by glucose, maltose, maltotriose and dextran. According to the end groups characterization by ^{1}H NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and the study of the molar masses evolution by size exclusion chromatography, the structures are very well-defined. These amphiphilic polymers were shown to self-associate in aqueous solvent leading to micelles formation as attested by dynamic light scattering measurements.

1. Introduction

Oligo- and polysaccharides are important macromolecules in living systems, showing their multifunctional characteristics in the construction of cell walls, energy storage, cell recognition and their immune response. The combination of oligo- or polysaccharides with synthetic or derived from renewable resources polymers opens a novel class of materials (Ouhib et al., 2009; Spain, Gibson, & Cameron, 2007; Voit & Appelhans, 2010).

Some examples of block copolymers composed of hydrophobic block as polystyrene and hydrophilic blocks based on polysaccharides such as amylose, cellulose or dextran have been previously described in literature using different synthetic methodologies (Bosker et al., 2003; Haddleton & Ohno, 2000; Hernandez, Soliman, & Winnik, 2007; Houga, Le Meins, Borsali, Taton, & Gnanou, 2007; Liu & Zhang, 2007; Loos et al., 2005; Loos & Müller, 2002; Loos & Stadler, 1997; Narumi et al., 2006; Van der Vlist & Loos, 2007). Linear polymers with saccharidic segments are synthesized by coupling techniques (before or after polymerization) and by phosphorylase-catalyzed enzymatic polymerization. Loos et al. described the synthesis of copolymers of polystyrene and amylose by reductive amination or hydrosilylation using an amino-functionalized PS prepared via living anionic polymerization. In a second step, *in vitro* enzymatic polymerization was used to extend the amylose block by reaction with α-D-glucose-1-phosphate in the presence of potato phosphorylase (Loos et al., 2005; Loos & Müller, 2002; Loos & Stadler, 1997). The synthesis of polystyrene–polysaccharides diblock copolymers by reductive amination between dextran or maltoheptaose and a commercially available amino-terminated polystyrene with an average molar mass M_w equal to 12,300 g/mol was described and their interfacial behaviors were studied (Bosker et al., 2003).

Using controlled radical polymerization, different copolymers using a glyco-derived macroinitiator with a peracetylated oligosaccharide residue were prepared (Haddleton & Ohno, 2000; Narumi et al., 2006). More recently, the synthesis of block copolymers comprising dextran and polystyrene obtained by ATRP after the covalent attachment of an ATRP-initiating moiety onto the anomeric position of the silylated polysaccharide was described (Houga et al., 2007).

In the present communication, we demonstrate the synthesis of functional polymers based on the combination of a synthetic

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doi:10.1016/j.carbpol.2010.09.018

polymer (polystyrene) with a biofunctional moiety (glucose, maltose, maltotriose or dextran). To obtain such materials, we used a new strategy based on the combination of ATRP, nucleophilic substitution and reductive amination.

2. Experimental part

2.1. Materials and reagents

Styrene (99%, Aldrich) was stirred over CaH_2 and distilled prior to use. Copper (I) bromide (CuBr, 98%, Aldrich), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA, 99%, Fluka), ethyl 2-bromoisobutyrate (98%, Aldrich), D-(+)-glucose (99%, Acros), D-(+)-maltose monohydrate (99%, Fluka), maltotriose hydrate (95%, Aldrich), dextran (obtained by enzymatic synthesis, $M \approx 1500$ g/mol, Fluka), pyridine (SDS), acetic anhydride (99%, Acros), 1,6-diaminohexane (99.5%, Acros), dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetic acid and methanol were used as received. MilliQ water (Millipore) was used for all the experiments.

2.2. Synthesis of ω-bromo-PS precursor (PS-Br)

A Schlenk apparatus dried under vacuum was charged with ethyl 2-bromoisobutyrate (0.34 g, 1.74×10^{-3} mol), CuBr (0.25 g, 1.74×10^{-3} mol), PMDETA (0.36 mL, 1.74×10^{-3} mol), and styrene (20 mL, 0.174 mol) under argon atmosphere. The reaction mixture was degassed by three-pump-thaw cycles and backfilled with argon and stirred at room temperature for 10 min. After polymerization at 100 °C during 35 min, the reaction medium was dissolved in CH_2Cl_2 and passed through a column of neutral alumina to remove the copper salts. PS-Br was precipitated from methanol, filtered, washed with methanol and dried under vacuum: 4.9 g of PS-Br, conversion: 27%, M_n th = 2800 g/mol, M_n exp = 2870 g/mol and $M_w/M_n = 1.11$.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30–6.35 (–Ph), 4.5 (–*CH*(Ph)–Br), 3.6 (–*CH*$_2$–OCO), 2.3–1.3 (–*CH*$_2$–*CH*–), 1.2–0.9 (–*CH*$_3$) ppm.

2.3. Synthesis of ω-amino-PS (PS-NH_2)

Polystyrene with bromine end groups (3.5 g, 1.3×10^{-4} mol, M_n = 2870 g/mol) was dissolved in DMF (30 mL) and 1,6-diaminohexane (1.56 g, 1.3×10^{-3} mol) was added. After stirring for 72 h at 30 °C, the polymer was precipitated in cold methanol, washed with methanol, filtered and dried under vacuum. The precipitation was repeated twice.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30–6.35 (–Ph), 3.6 (–*CH*$_2$–OCO), 3.3-3.05 (–*CH*–NH–*CH*$_2$–), 2.65 (–*CH*$_2$–NH$_2$), 2.3–1.3 (–*CH*$_2$–*CH*–), 1.2–0.9 (–*CH*$_3$) ppm.

2.4. Synthesis of sugars-functionalized polymers (PS-sugar), general procedure for PS-maltotriose

Amino-functionalized polystyrene (0.5 g, 1.9×10^{-4} mol, M_n = 2870 g/mol) and maltotriose (0.95 g, 1.9×10^{-3} mol) were dissolved in 10 mL of a mixture of DMF and CH_3COOH (9/1 vol.%). The reaction mixture was heated at 50 °C for 1 h. Then, $NaBH_3CN$ (0.12 g, 1.9×10^{-3} mol) was added. After stirring for 72 h at 50 °C, the polymer was precipitated in MeOH/water (9/1 vol.%), washed with a large amount of MeOH/water (9/1 vol.%), filtered and dried.

^{1}H NMR (600 MHz, d_6-DMSO): δ = 7.30–6.35 (–Ph), 5.5, 5, 4.8, 4.5, 3.7-3 (*CH*, O*H* sugar), 2.3–1.3 (–*CH*$_2$–*CH*–), 1.2–0.9 (–*CH*$_3$) ppm.

2.5. Acetylation of amphiphilic polymers

Sugar functionalized-polystyrene (10 mg) was dissolved in pyridine (1 mL) and acetic anhydride (2 mL). After stirring for 48 h at room temperature, the solvents were evaporated and the polymer dried.

2.6. Preparation of the micelles

Amphiphilic copolymer (PS-maltotriose, 10 mg) was dissolved in DMSO (1 mL). Then, water (10 mL) was added at a constant rate (drop by drop) under vigorous stirring. The resulting micellar dispersion was analyzed after further stirring for at least 1 h

2.7. Characterizations

^{1}H NMR spectra were recorded at room temperature using a Bruker AVANCE II 600 MHz spectrometer. $CDCl_3$, D_2O and d_6-DMSO were used as deuterated solvents (10 mg/0.6 mL).

The polymers (PS-Br and PS-NH_2) were analyzed by MALDI-TOF MS performed using a PerSeptive Biosystems Voyager Elite (Framingham MA, USA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm – 3 ns pulse), a delayed extraction and a reflector. It was operated at an accelerating potential of 20 kV in reflector mode. The MALDI-TOF mass spectra represent averages over 512 consecutive laser shots (3 Hz repetition rate). The polymer solutions (2–5 g L^{-1}) were prepared in THF. The matrix, 1,8-dihydroxy-9[10H]-anthracenone (dithranol), was also dissolved in THF (25 g L^{-1}). A 10 μL portion of the polymer solutions was mixed with 20 μL of the matrix solution. A sodium iodide solution (10 μL of a solution at 20 g L^{-1} in THF) was finally added to favour ionization by cation attachment. 1 μL of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Standards (polystyrene derivatives of known structure (M_n = 1500 and 3280 g/mol) purchased from Polymer Standards Service) were used to calibrate the mass scale using the two point calibration software 3.07.1 from PerSeptive Biosystems.

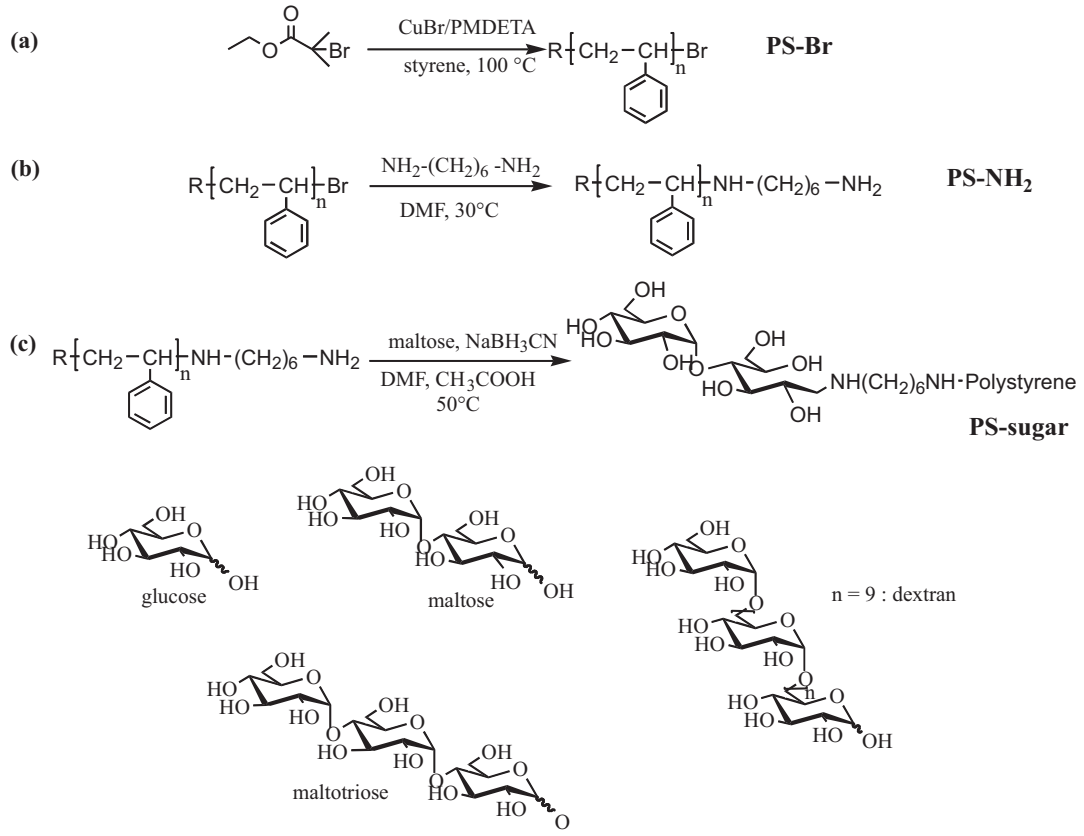
The polymer molar masses were determined using size exclusion chromatography (SEC) with tetrahydrofuran as eluent (1 mL/min) at room temperature. This apparatus was equipped with a refractive index detector (Waters 410) and two ViscoGEL™ columns (7.8 × 300 mm, type GMH_{HR}-H mixed bed) provided by Viscotek. The molar masses were determined with a calibration curve based on polystyrenes standards using the NTeqGPC V6.4.04 program software from hs GmbH.

Nanoparticle sizes were determined by photon correlation spectroscopy using the Zetasizer Nano particle analyzer (nano-ZS, ZEN3500) from Malvern. Measurements were performed at 25 °C after dilution in water or in DMF; data treatment was done with the Dispersion Technology Software (DTS) from Malvern.

3. Results and discussion

Our approach to prepare glycosylated-functionalized polystyrenes is based on a three steps procedure presented on Scheme 1:

(a) the synthesis of well-defined ω-bromo-terminated polystyrene by atom transfer radical polymerization (PS-Br)
(b) the transformation of the halogen end groups of these polymers into primary amino functions by nucleophilic substitution with a diamine (PS-NH_2)
(c) the coupling of different mono and oligosaccharidic molecules (as glucose, maltose, maltotriose and dextran) by reductive amination (PS-sugar).



Scheme 1. Reaction pathway for the synthesis of amphiphilic glycosylated polystyrenes in three steps (ATRP (a), nucleophilic substitution (b) and reductive amination (c)) and glycosidic molecules used in the third step.

3.1. Synthesis of amino-functionalized polystyrenes

Atom transfer radical polymerization (ATRP) is one of the most successful methods to polymerize styrenes, (meth)acrylates and other monomers in a controlled fashion, yielding polymers with narrow polydispersities and with molar masses predetermined by the molar ratio of consumed monomer to introduced initiator. ATRP is widely used for the preparation of functional polymers, polymer architectures and surface modification (Kamigaito, Ando, & Sawamoto, 2001; Matyjaszewski & Xia, 2001).

In the first step, ω-bromopolystyrenes denoted PS-Br were prepared. Ethyl 2-bromoisobutyrate was used as initiator for the ATRP of styrene. The polymerizations were performed in bulk at 100 °C with CuBr/PMDETA (1/1) as a metal/ligand complex according to classical conditions. As low molar masses PS samples were targeted to compensate the hydrophilic part, the chemical modification of the chain ends was easily monitored by ^{1}H NMR. Two PS-Br samples with average molar masses equal to 2870 and 4500 g/mol were synthesized on a large scale. The theoretical and experimental molar masses were in good agreement and narrow molar masses distributions ($M_w/M_n < 1.15$) were obtained. The presence of the initiating moiety and the bromine end group were confirmed by ^{1}H NMR (Fig. 1a).

The second step was synthesis of amino-functionalized PS, denoted PS-NH_2. Some groups previously reported studies concerning end-functionalized ATRP-derived polymers by nucleophilic substitutions. Indeed, the replacement of halogen ends groups of either polystyrene or poly(methyl acrylate) by hydroxyl functions, using either ethanolamine or 4-aminobutanol was described (Coessens & Matyjaszewski, 1999a, 199b). The same methodology was used for the synthesis of asymmetric stars, miktoarm stars and dendrimer-like (co)polymers (Francis, Lepoittevin, Taton, & Gnanou, 2002; Lepoittevin, Matmour, Francis, Taton, & Gnanou, 2005): the bromo end groups of PS chains obtained in the first step were derivatized into twice as many bromoisobutyrates in order to obtain ω,ω′-bis(bromo)-PS chains that was used for the second polymerization step. We followed a similar strategy as the aforementioned to introduce primary amino groups at the ω-end of our PS chains. 1,6-Diaminohexane reacted in large excess with PS-Br in DMF, solvent which promoted nucleophilic substitution reaction at 30 °C for 72 h. The effective formation of PS-NH_2 was confirmed by ^{1}H NMR spectroscopy (Fig. 1a and b). No noticeable side reactions occurred. Indeed, the *CH*(Ph)–Br signal at 4.5 ppm totally disappeared and a new one assignable to the –*CH*$_2$–NH_2 appears at 2.65 ppm showing the quantitative conversion of PS-Br into PS-NH_2.

In addition, the efficiency of functionalization was confirmed by analysis of PS-Br and PS-NH_2 by MALDI-TOF mass spectrometry. The spectrum of PS-Br is presented in Fig. 2a. A single distribution is observed with a peak-to-peak mass increment of 104 g/mol, corresponding to the molar mass of styrene. This series of peak can be attributed to the following chemical structure: initiator-(styrene)$_n$–CH=CH–(C_6H_5), Na^+, experimental and calculated molar masses being in good agreement. Elimination of HBr occurred during MALDI-TOF characterization as previously observed (Pascual et al., 2001). The MALDI-TOF spectrum of PS-NH_2 is presented in Fig. 2b. The previous distribution corresponding to PS-Br was totally vanished and two distributions appeared. The main distribution perfectly matches the expected structure: initiator-(styrene)$_n$–NH–(CH_2)$_6$–NH_2, Na^+. The second distribution with a shift of 28 g could be attributed to a side reaction occurring during MALDI-TOF characterization with some traces of residual DMF present in the sample: initiator-(styrene)$_n$–NH–(CH_2)$_6$–NH–(C=O)–H, Na^+.

Double substitution reaction leading to dimer product could be completely avoided by using a large excess of 1,6-diaminohexane (1/10 molar ratio). No trace on SEC with higher molar mass was observed.

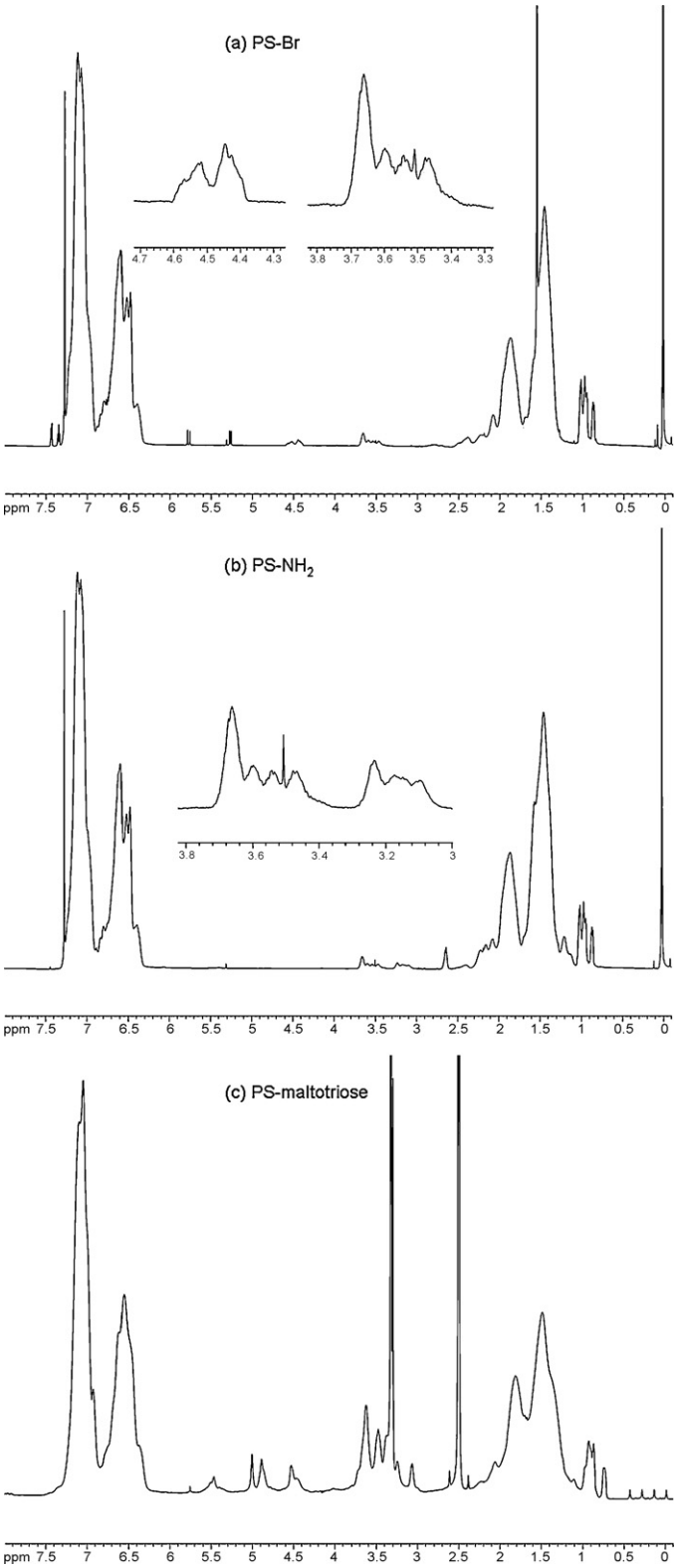


Fig. 1. ^{1}H NMR spectra of (a) PS-Br precursor ($CDCl_3$), (b) PS-NH_2 ($CDCl_3$) and (c) PS-maltotriose (d_6-DMSO).

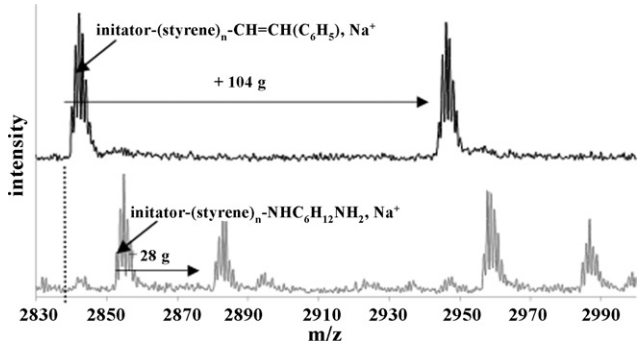


Fig. 2. MALDI-TOF mass spectra of PS-Br (a) and PS-NH_2: M_n = 2870 g/mol, M_w/M_n = 1.11; initiator: $CH_3CH_2OCOC(CH_3)_2$.

3.2. Reaction with oligosaccharidic molecules by reductive amination

By reductive amination, covalent attachment of carbohydrates was accomplished via reaction between the amino-functionalized polystyrenes and the aldehydic groups of sugars in the presence of a reducing agent ($NaBH_3CN$) to reduce the unstable imines to secondary amines. Previously, we have studied this reaction for the grafting of glycosidic molecules on primary amino-functionalized surfaces of nanoparticles and polymer fibers (Bech, Meylheuc, Lepoittevin, & Roger, 2007; Lepoittevin, Masson, Huc, Haut, & Roger, 2006). This reaction was performed at 50 °C during 48 h in a mixture of DMF and acetic acid, DMF being both good solvent of hydrophobic polystyrene and hydrophilic sugar molecules. Oligosaccharides used in this study were glucose, maltose, maltotriose and dextran with a molar mass closed to 1500 g/mol and narrow molar mass distribution.

The synthesized polymers (denoted PS-glucose, PS-maltose, PS-maltotriose and PS-dextran) were precipitated in methanol/water mixture (9/1 vol.%). A white precipitated was formed which was purified by large washing to remove residual sugar molecules. The glycosylated polymers were characterized by ^{1}H NMR using d_6-DMSO a good solvent for both PS and oligosaccharidic groups. Fig. 1c shows the appearance of new signals between 5.5 and 4 ppm and closed to 3.5 ppm assignable to the protons of the sugars groups.

In addition, the amphiphilic polymers were characterized by size exclusion chromatography. Non-acetylated glycosylated polymers have a poor solubility in regular organic solvents as THF, solvent used for SEC characterizations. Therefore, acetylation of alcohol sugars functions was conducted by reaction with acetic

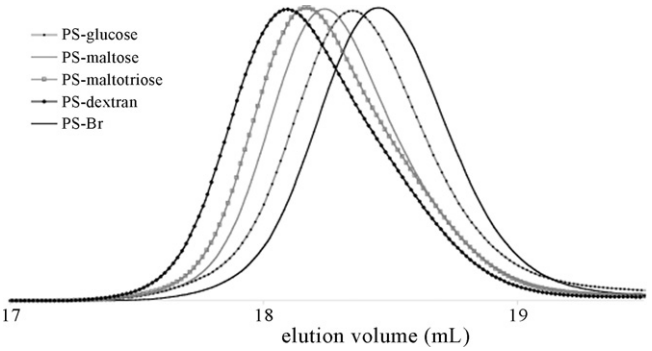


Fig. 3. Size exclusion chromatograms of PS-Br precursor and acetylated sugar functionalized polystyrenes (RI response, calibration curve based on polystyrenes standards): PS-Br precursor M_n = 2870 g/mol, M_w/M_n = 1.11; PS-glucose; PS-maltose; PS-maltotriose and PS-dextran.

Table 1
Molecular characteristics of PS-Br precursors and acetylated PS-sugar.

Entry	PS-Br precursor		Acetylated PS-sugar		
	$M_{n\,SEC}$[a] (g/mol)	M_w/M_n	Sugar	$M_{n\,SEC}$[a] (g/mol)	M_w/M_n
1	2870	1.11	Glucose	3150	1.12
2	2870	1.11	Maltose	3560	1.10
3	2870	1.11	Maltotriose	3720	1.11
4	2870	1.11	Dextran	3960	1.13
5	4500	1.15	Glucose	4960	1.12
6	4500	1.15	Maltose	5420	1.12
7	4500	1.15	Maltotriose	5600	1.12
8	4500	1.15	Dextran	6240	1.07

[a] Determined by SEC in THF (calibration with PS standards).

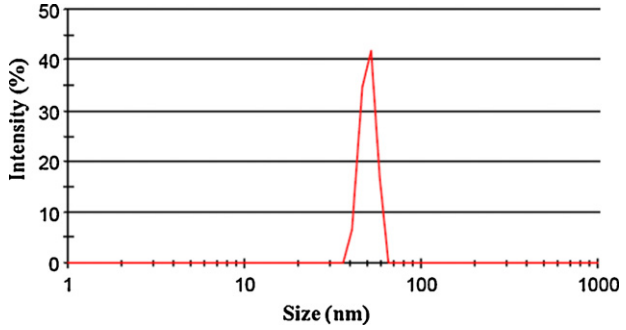


Fig. 4. Particle size distribution (diameter) of PS-maltotriose micelles obtained by dynamic light scattering.

anhydride in pyridine. This reaction is quantitative. Fig. 3 shows the evolution of molar masses for polystyrenes functionalized with glucose, maltose, maltotriose and dextran. Table 1 summarizes the data for two different series of sugar-functionalized polystyrenes.

The SEC traces of the glycosidic-functionalized PS were monomodal with no residual PS-Br precursor and shifted toward a lower elution volume attesting the formation of macromolecular species with higher molar masses. Elution volumes decrease as increasing the molar masses of the saccharidic fragment covalently grafted. In addition, the polydispersity indexes remained below 1.15 indicating that grafting of glycosidic molecules occurred very efficiently. This synthetic procedure combining ATRP (none drastic purifications compared with ionic polymerizations) and reductive amination realized easily in a good solvent of both polystyrene and glycosidic block could be extent on a large scale. It is important to note that this new synthetic procedure allows to obtain amphiphilic polymers without the need of protection and deprotection steps of the glycosidic block in opposition with most of the study reports in the literature (Haddleton & Ohno, 2000; Li & Zhang, 2008; Narumi et al., 2006).

The amphiphilic character of glycosylated PS was confirmed by preliminary study showing micelles formation by self-association. Amphiphilic copolymers are of great interest for nanotechnological applications because of their potential in forming well-defined morphologies in bulk, in solution or at interfaces (Joncheray et al., 2007). Indeed, micelles were formed after solubilization of the amphiphilic polymer in small volume of DMSO by addition of a large volume of water under rapid stirring. For example, dynamic light scattering measurements of the amphiphilic PS-maltotriose (run 3 in Table 1) show the formation of nanoparticules with a diameter of about 50 nm and narrow size distribution (Fig. 4). For the sake of comparison, the hydrodynamic radius (R_H) of PS-maltotriose in a good solvent (DMF) is equal to 2.5 nm. Systematical study about the self-assembly in water of such amphiphilic polymers according to different parameters (polymer composition, sugar chain length and effect of solvent) will be the subject of a forthcoming work.

4. Conclusion

Different amphiphilic oligosaccharide-functionalized polystyrenes were successfully synthesized in a large scale using an easy three steps procedure combining ATRP of styrene and chain ends modifications (nucleophilic substitution followed by reductive amination with glucose, maltose, maltotriose or dextran). Thus, the present work provides a facile route to obtain well-defined polystyrenes with an oligosaccharide residue without the need of protection and deprotection steps of the saccharidic block. First investigation of the self-assembly in water of such functionalized polystyrenes led to micelles formation. This synthesis may offer the opportunity to prepare a large range of various molecules to study the behavior of these amphiphilic copolymers at the interface.

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