

# Dextran-Based Block Copolymers: Synthesis and Self-Assembly in Solution

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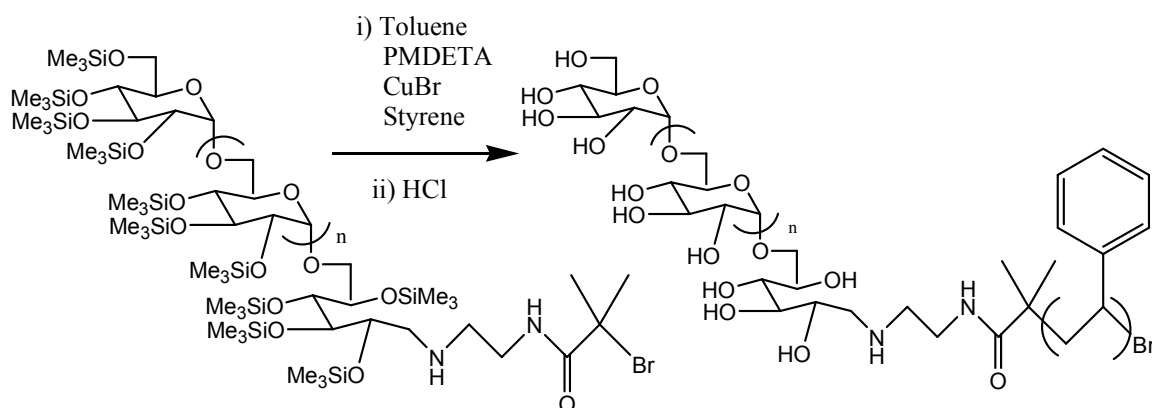
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Naturally occurring polysaccharides such as cellulose, dextran, etc... are an abundant source of raw materials that attract an increasing interest due to their biodegradability and renewable character. A convenient and classical means to tailor the physicochemical properties of these natural macromolecules is to modify their backbone by graft copolymerisation. A number of applications have thus been developed from such graft copolymers but seldom as nanodevices or nanosystems.

An attractive route to obtain nanostructures with well-defined morphologies is to let block copolymers to self-assemble in a selective solvent, but the synthesis of polysaccharide-based block copolymers has so far presented challenging difficulties. In this work, we describe the first synthesis of dextran-*b*-polystyrene diblock copolymers from a dextran-based ATRP macroinitiator and the preliminary results of the self-assembly of such diblocks in water.

Dextran is a highly water-soluble polysaccharide composed of  $\alpha$ -D-glucopyranosyl units mainly linked by (1 $\rightarrow$ 6) bonds and exhibiting a low degree of branching. The first step in our synthetic endeavor was to introduce an appropriate ATRP site at the anomeric extremity of a commercial dextran of  $M_n = 6600 \text{ g}\cdot\text{mol}^{-1}$ . This terminal anomeric aldehyde was subjected to reductive amination, using a specifically designed coupling agent fitted with  $\omega$ -amino and  $\alpha$ -tertiary bromide groups. Before growing the polystyrene (PS) block by ATRP from the tertiary bromide-ended dextran, the OH groups of the latter were silylated to make it soluble in regular organic solvents.

Next, styrene was polymerized from the corresponding silylated dextran-based ATRP macroinitiator. ATRP experiments were carried out in toluene using CuBr/PMDETA as catalyst. Five diblock copolymers whose  $DP_n$  of the PS block ranged from 5 to 775 were synthesized from the same dextran-based precursor and characterized by SEC using THF as eluent. Finally, these (silylated dextran)-*b*-PS block copolymers were readily desilylated under acidic conditions (Scheme 1), affording the targeted amphiphilic dextran-*b*-PS block copolymers.



Next, the self-assembling properties in water of these diblock copolymers were investigated. Block copolymers with the smallest content in PS could be directly dissolved in water at  $\sim 90^\circ\text{C}$ . The nanoparticles thus formed adopted a micelle-like spherical shape with a diameter of 56

nm, as determined by dynamic light scattering (DLS) and 50 nm from atomic force microscopy (AFM). Samples with larger contents in PS could not be directly transferred in water; they were first dissolved in a DMSO/THF mixture before slowly substituting water for the organic phase, the latter being totally removed by dialysis. For instance, a sample with a 87% content in PS exhibited a vesicular morphology as seen by Transmission Electron Microscopy (TEM). DLS and static light scattering measurements on the same sample afforded a ratio of 1 for  $R_g/R_H$ , thus confirming the formation of a vesicle.

The self-assembly in water of other diblock copolymers led to a variety of stable morphologies (vesicles ovoides, etc.) whose size strongly depended on the overall composition.