Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of amphiphilic diblock copolymers derived from renewable dextran by nitroxide mediated polymerization: towards hierarchically structured honeycomb porous films

*Senbin Chen, Marie-Hélène Alves, Maud Save and Laurent Billon**

Université Pau & Pays Adour, CNRS, UMR 5254 – IPREM – Equipe de Physique et Chimie des Polymères, 2 avenue du Président Angot, Pau, F-64053, France.

Corresponding author: laurent.billon@univ-pau.fr

Calcul of the degree of functionalization from proton NMR integrations

The degree of functionalization (*f*) was calculated by using the following equation: *f* (%) = [Integration $_{\text{from 0.91 to 1.62 ppm in Figure 1D}}$ / theoretical integration for 100 % functionalization $_{\text{from 0.91 to 1.62 ppm}}$] × 100% = [24.79 / (30 + 8)] × 100% = 65 %, where 30 and 8 are the protons of SG1 (**Figure 1A**) and hexylenediamine (**Figure 1C**) from 0.91 to 1.62 ppm, respectively.

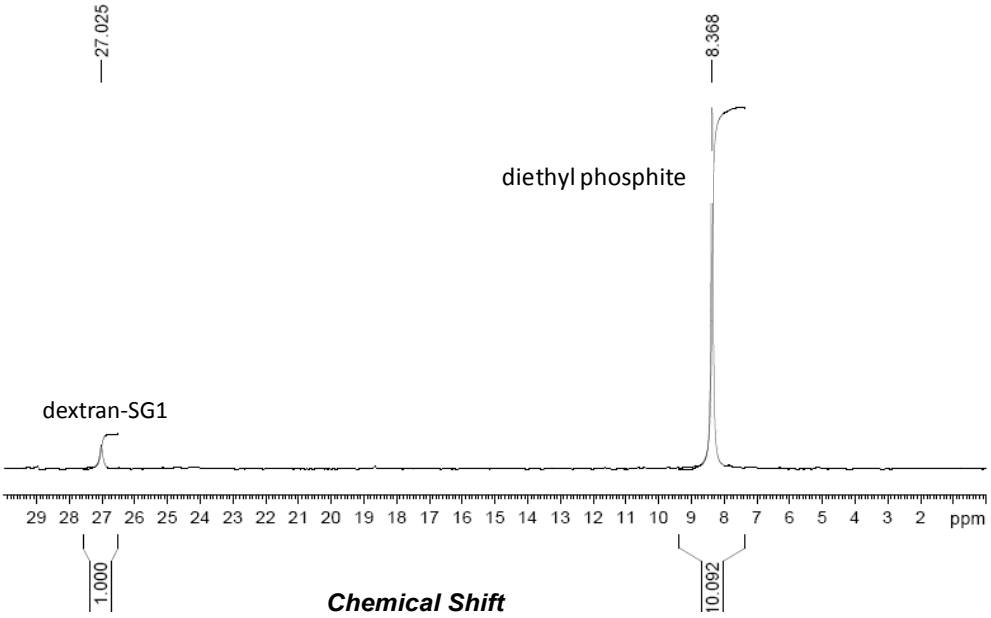

Figure S1. ^{31}P NMR of mixture of dextran-SG1 (11 mg) and diethyl phosphite (5.5 mg) in DMSO-d_6 at 25°C, the functionality (*f*) was calculated by using the following equation:

$$\frac{n_{SG1}}{n_{diethylphosphite}} = \frac{m_{polymer} / (M_{n,dext-SG1} * f + M_{n,dext-NH2} * (1-f))}{m_{diethylphosphite} / M_{diethyl\ phosphite}} = \frac{I_{NMR,SG1}}{I_{NMR,diethylphosphite}}$$

$$\frac{n_{SG1}}{n_{diethylphosphite}} = \frac{0.011 / (363f + 2698)}{0.0055 / 138} = \frac{I_{NMR,27\ ppm}}{I_{NMR,8\ ppm}} \Rightarrow f = 0.61$$

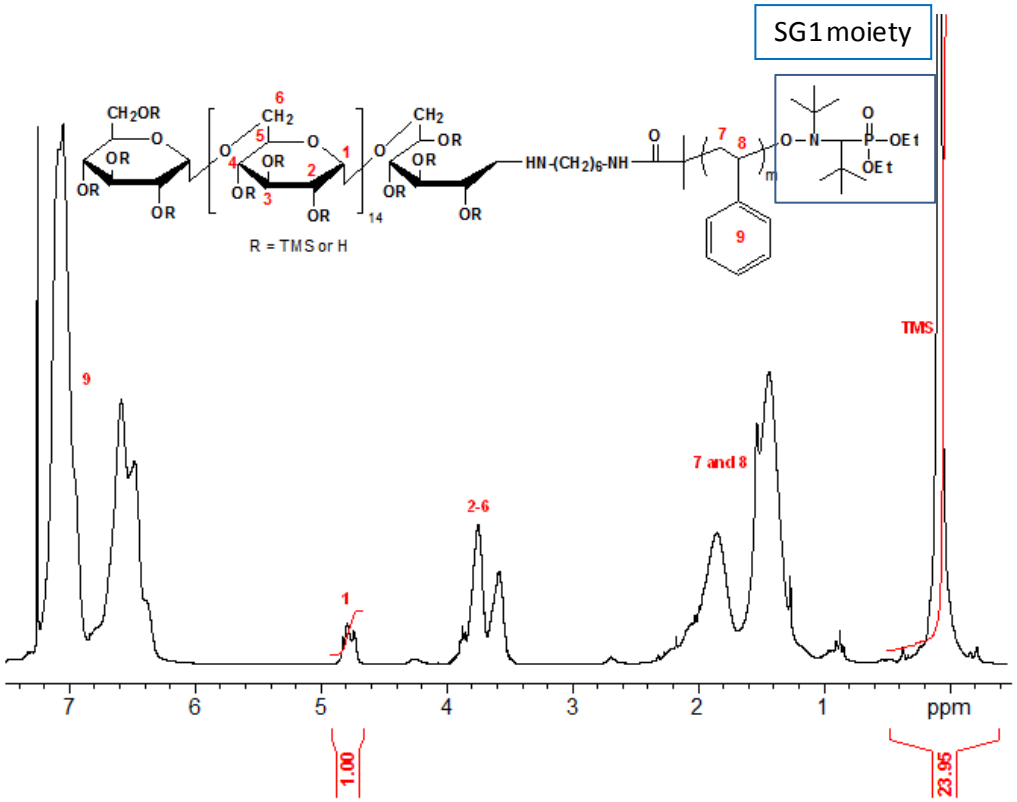

Figure S2. ^{1}H NMR of partial (88.7%) silylated dextran-*b*-PS in $CDCl_3$ at 25°C, the silylation degree (SD) was calculated by using the following equation: SD (%) = [Integration $_{TMS}$ / (27 × Integration $_{1}$)] × 100%.

Calculation of respective degree of polymerization of styrene (*n*) and MMA (*m*) units in dextran-*b*-P(MMA$_m$-*co*-S$_n$) copolymers from proton NMR integrations (*I*) (see Figure 3 of article for assignment of NMR peaks):

$$n = \frac{I_3}{5}$$

$$m = \frac{I_{1,2,4,5} - (I_3/5) \times 3 - [(I_g/15) \times 0.625 \times 38]}{5}$$

The value of 0.625 corresponds to the average value of dextran-SG1 chain end functionality and value of 38 corresponds to the 38 protons of SG1 chain end.

The fraction of styrene in the final copolymer was calculated as follows:

$$F_S = \frac{n}{n+m}$$

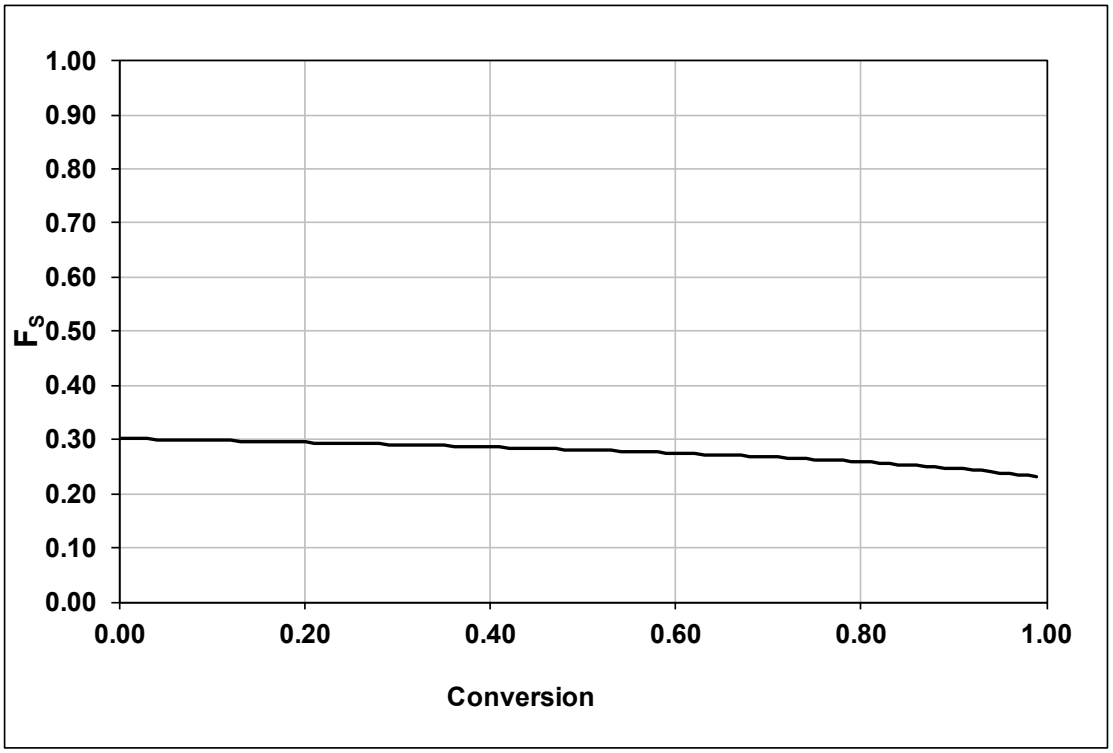

Figure S3. Theoretical average composition of styrene (F_S) in a P(S-*co*-MMA) copolymer starting with $f_S = 0.23$ and using values of reactivity ratio of: $r_S = 0.489$, $r_{MMA} = 0.493$