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

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Calcul of the degree of functionalization from proton NMR integrations

The degree of functionalization ($f$) was calculated by using the following equation:

$$f(\%) = \frac{\text{Integration from 0.91 to 1.62 ppm in Figure 1D}}{\text{theoretical integration for 100% functionalization from 0.91 to 1.62 ppm}} \times 100\% = \frac{24.79}{30 + 8} \times 100\% = 65\%,$$

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:

$$\frac{n_{SG1}}{n_{diethylphosphate}} = \frac{m_{\text{polymer}} / (M_{n,dex-SG1} \times f + M_{n,dex-NH2} \times (1 - f))}{m_{\text{diethylphosphate}} / M_{\text{diethylphosphate}}} = \frac{I_{NMR,SG1}}{I_{NMR,diethylphosphate}}$$

$$\frac{n_{SG1}}{n_{diethylphosphate}} = \frac{0.011 / (363f + 2698)}{0.0055 / 138} = \frac{I_{NMR27 \text{ ppm}}}{I_{NMR8 \text{ ppm}}} \Rightarrow f = 0.61$$
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 (%) = \[ \frac{\text{Integration}_{\text{TMS}}}{(27 \times \text{Integration}_1)} \times 100\% \].
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: $r_S = 0.489$, $r_{MMA} = 0.493$