Supporting Information

Robust Nanocoatings Based on Ionic Silicones

Agnieszka Puciul-Malinowska, Szczepan Zapotoczny

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland

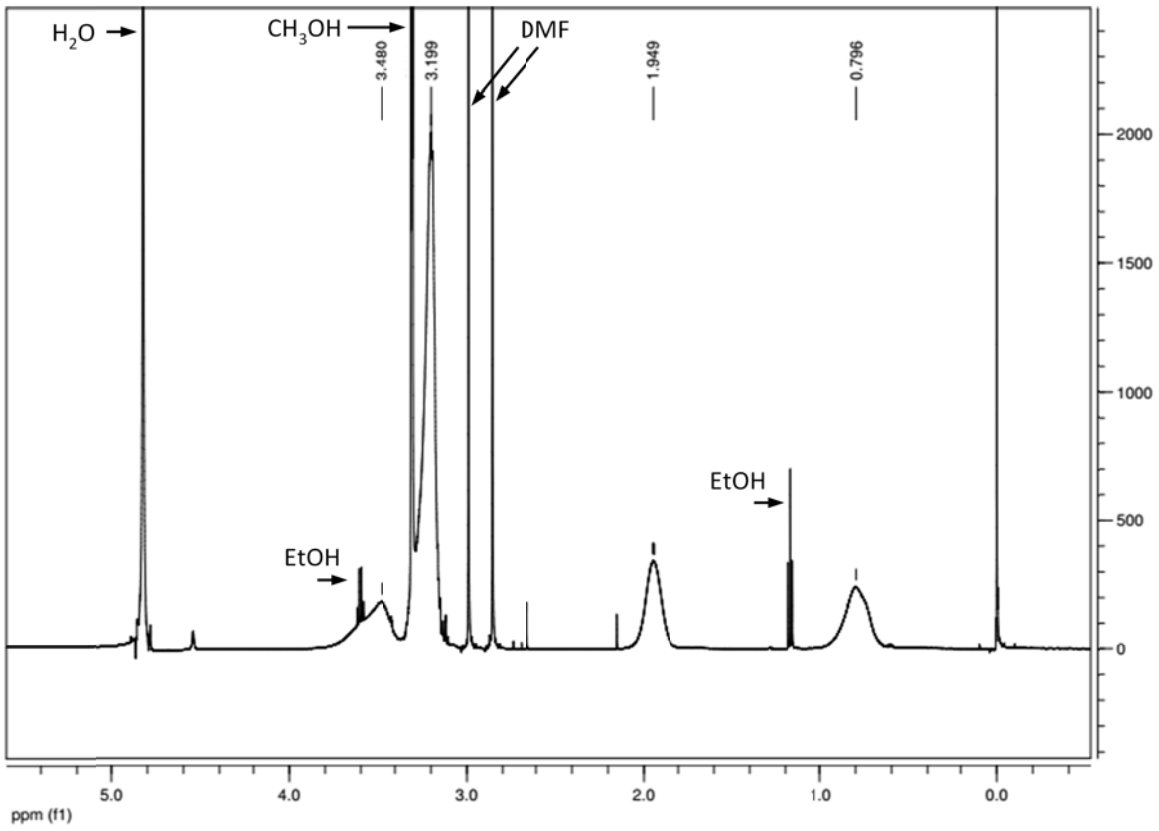

Figure S1. The ^{1}H NMR spectrum of PQS (signals of residual solvents are indicated).

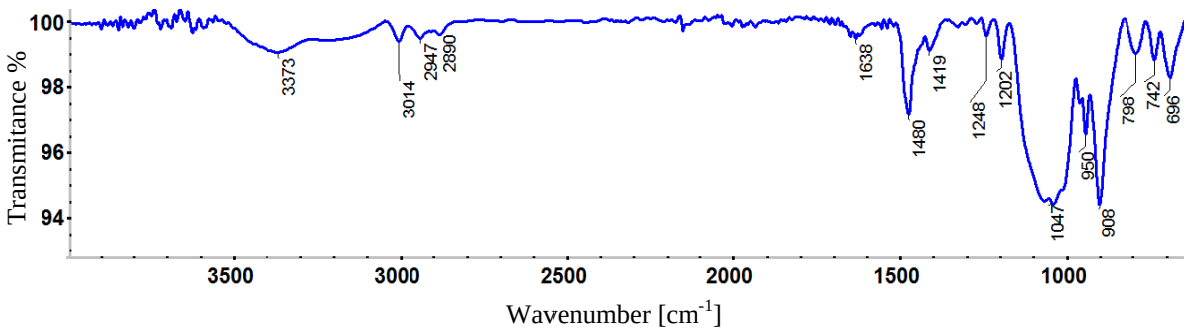

Figure S2. The IR spectrum of PQS.

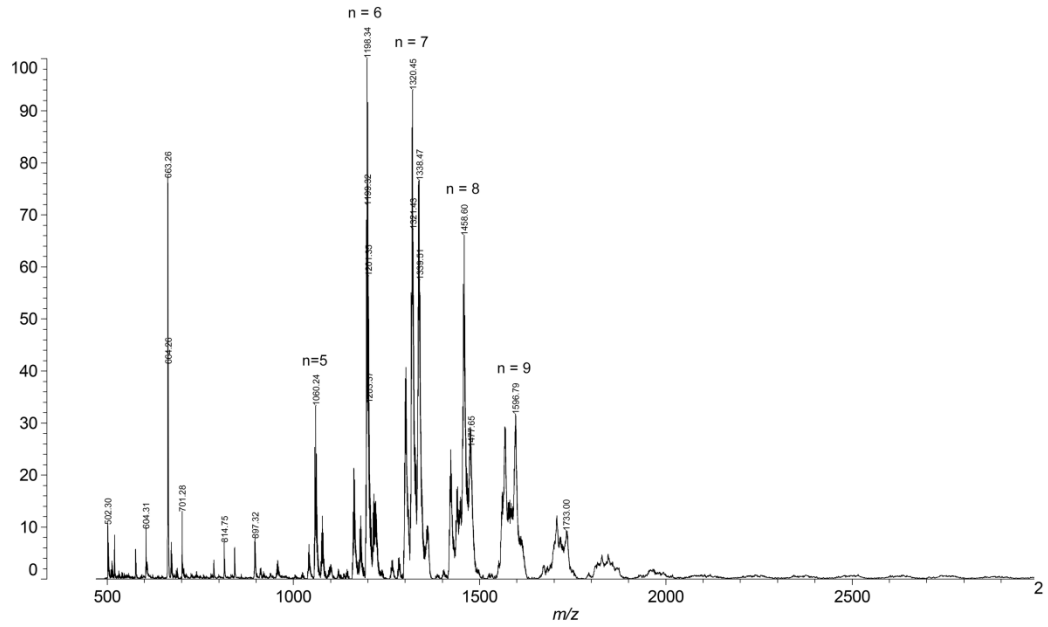

Figure S3. The MALDI-TOF MS spectrum of PQS. Estimated numbers of mers (n) that can be assigned to the peaks are indicated.

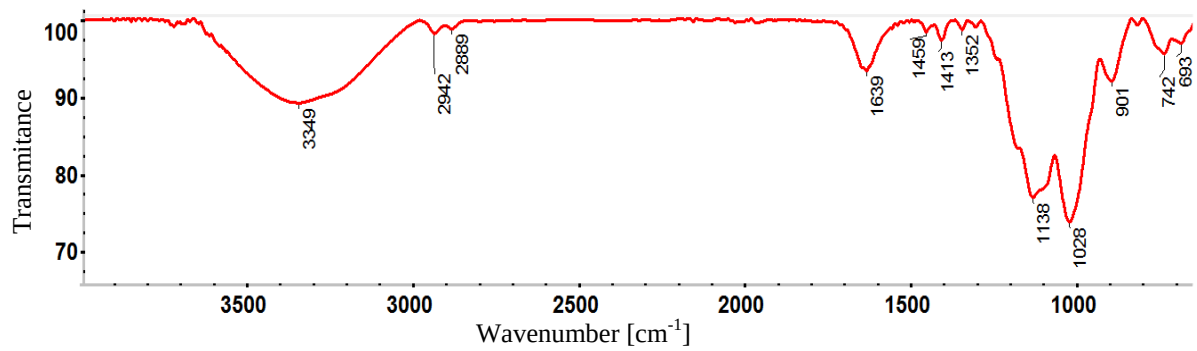

Figure S4. The IR spectrum of SPOS.

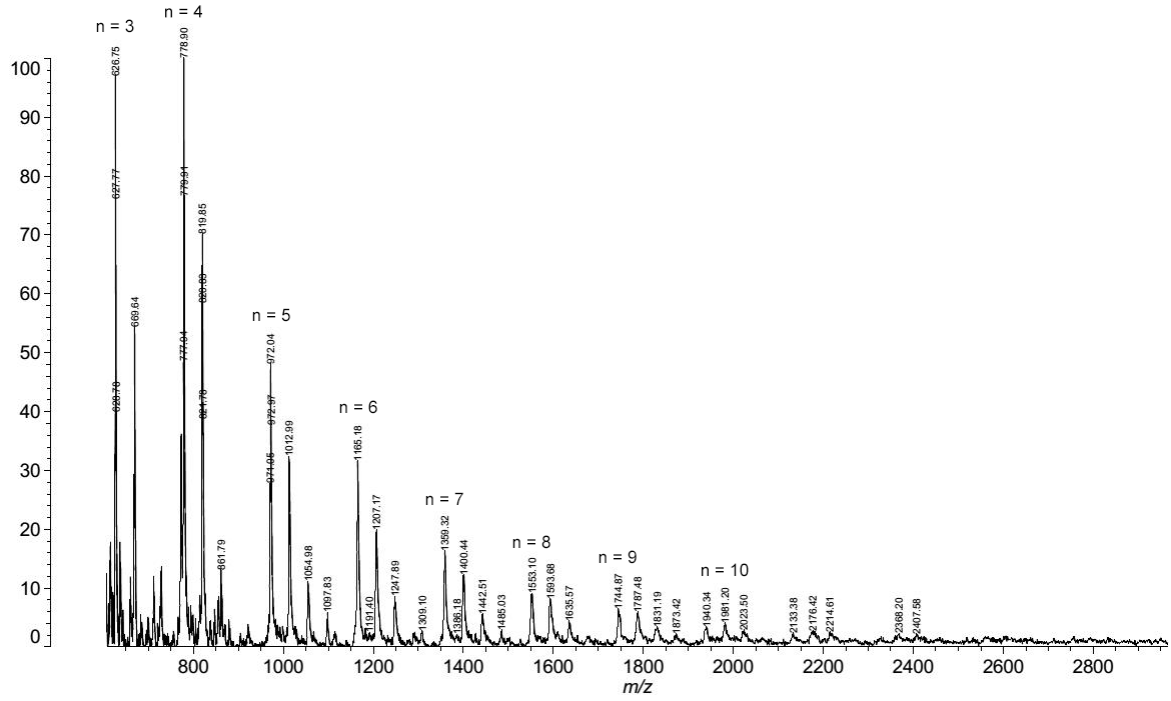

Figure S5. MALDI-TOF results for SPOS. Estimated numbers of mers (n) that can be assigned to the peaks are indicated.

Calculations of the degree of substitution of PQS

The calculations of the degree of substation (DS) of PQS were based on ^{1}H NMR spectrum (Figure S1) and the results of the elemental analysis presented in the main text.

Taking into account integration of the signal of the methyl protons at 3.2 ppm (I_{methyl}) and all methylene protons at 3.48, 1.95, 0.80 ppm ($I_{methylene}$), DS may be determined as (eq. 1):

$$DS = (6 \cdot I_{methyl}/9 \cdot I_{methylene}) \cdot 100\% \quad (1)$$

The experimentally found carbon to nitrogen weight ratio $(C/N)_{ex}$ for PQS was taken for the calculation of DS using the following equation:

$$(C/N)_{ex} = (6 \cdot 12 \cdot DS + 3 \cdot 12 \cdot (100\text{-}DS))/14 \cdot DS \quad (2)$$

that results in:

$$DS = 3600/(14 \cdot (C/N)_{ex} - 36) \quad (3)$$

The calculated DS value using eq. 3 was found to be ca. 110% that is unphysical. However, this must be the result of some residual DMF (evidenced in the NMR spectrum – Fig. S1) that could not be totally removed from ionic PQS and this residual solvent contributed to higher relative nitrogen content (lower C/N value).

The topography of [PQS/SPOS]$_{10}$ film in water

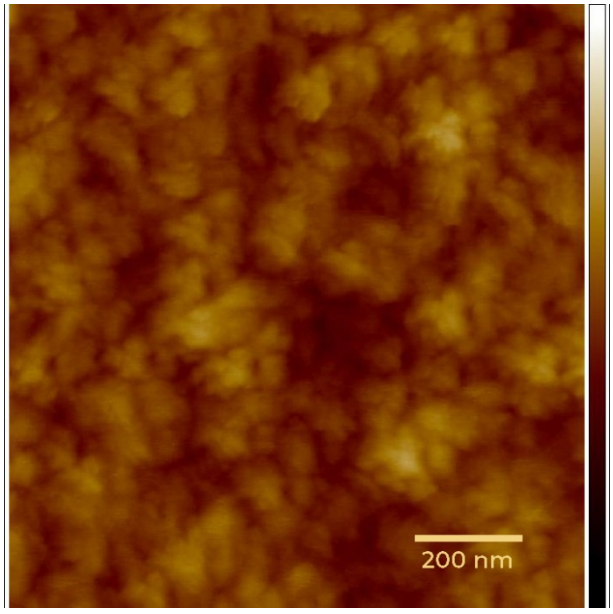

Figure S6. The AFM image (1 μm x 1 μm) of [PQS/SPOS]$_{10}$ in water. Z scale – 50 nm. The RMS roughness was found to be 2.9 nm.

Determination of glass transition temperatures of thin film

The ellipsometric measurements were conducted for the 10 bilayers film ([PQS/SPOS]$_{10}$) in 0.01 M NaCl and in pure water using the spectroscopic ellipsometer equipped with a liquid cell. The measurements were performed during heating the liquid from room temperature to ca. 40°C) (see Figure S). The thicknesses of the films were subsequently determined and plotted as relative thickness (with respect to the height at 25°C) versus temperature (Figure S7). It appeared that the growth of the film thickness with temperature was only negligible up to certain temperature and significantly increased above it (27-28°C for both

studied solvents). Such observed structural changes of the films may be related to glass transition and the temperatures determined at cross sections of the respective trend lines (see Figure S7), as glass transition temperatures (T_g).

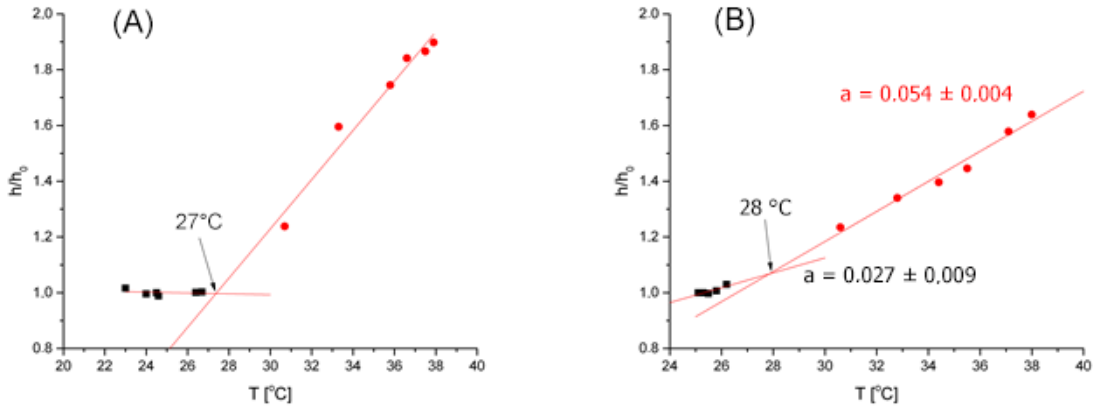

Figure S7. Changes of the relative thickness (h_0 – thickness at 25°C) of the $[PQS/SPOS]_{10}$ with temperature as determined using spectroscopic ellipsometry in 0.01 M NaCl (A) and pure water (B). The intersections of the trend lines indicate the T_g values. The slopes (a) of the trend lines together with respective standard deviations (from linear regression) are also presented (B).

Stability of the $[PQS/SPOS]_{10}$ film

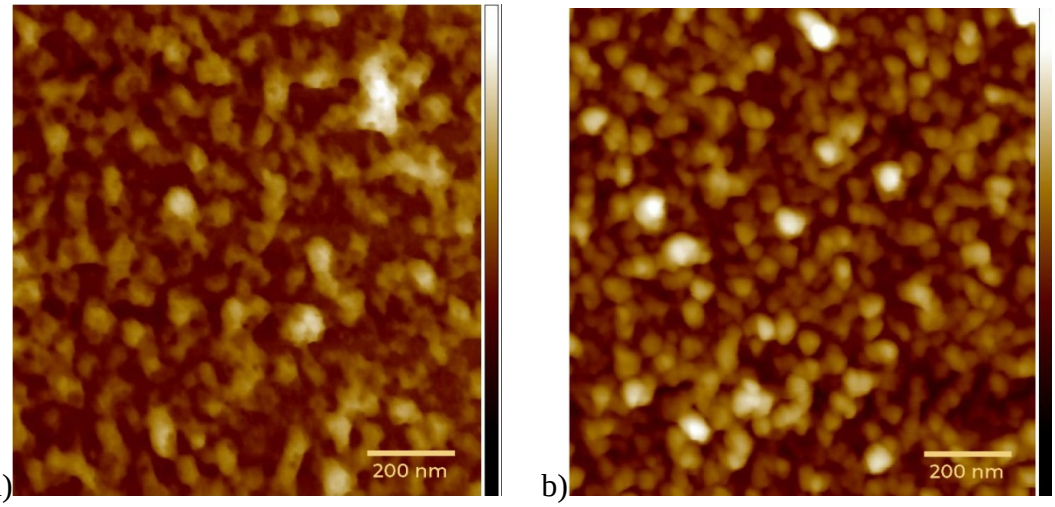

Figure S8. AFM topography images (1 µm·1 µm scan size) of $[PQS/SPOS]_{10}$ films after 12h treatment with water (a) and (b) 0.01M NaCl solution at 60 °C (z scale – 70 nm).