

## Electronic supplementary information (ESI)

for

# **Polyaniline films doped with ladder-type sulfonated polyphenylsilsesquioxane and unusual dependence of their electrical conductivity on temperature**

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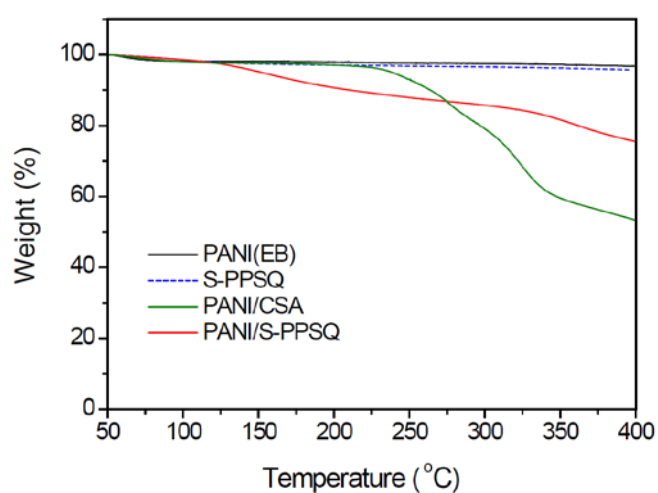
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## 1. Synthesis of S-PPSQ

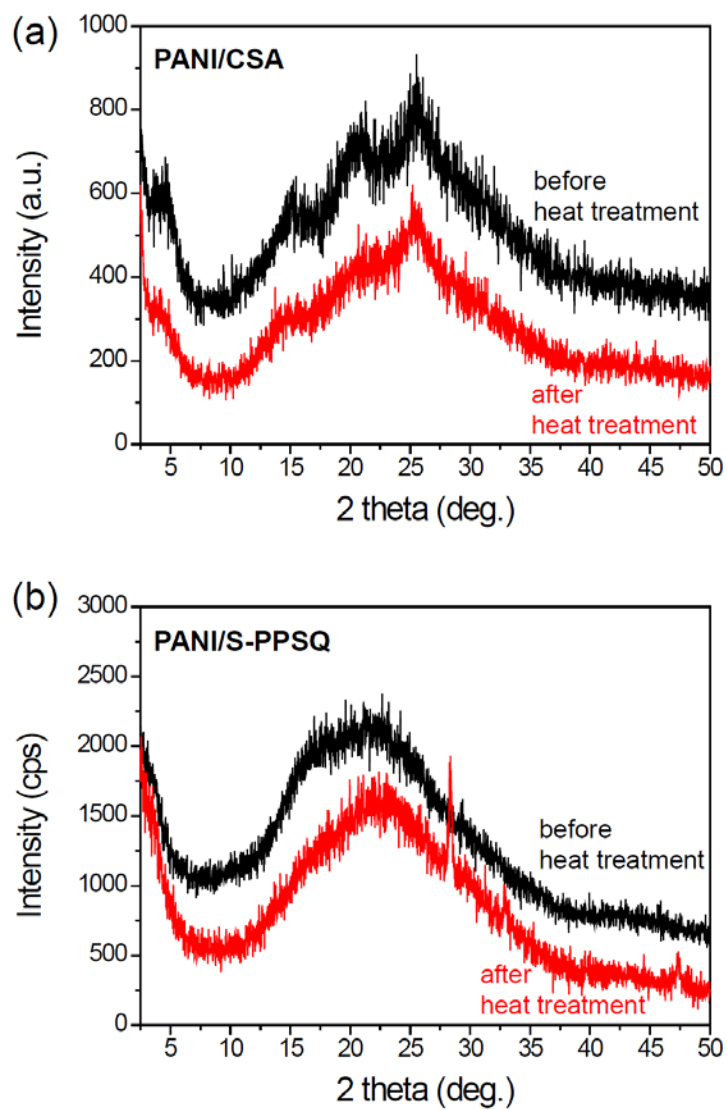
*Polyphenylsilsesquioxane (PPSQ)*: In a 1 L round-bottomed flask, deionized water (24 g, 1.33 mol) and a base catalyst were charged and stirred for 10 min. Dry tetrahydrofuran (THF) (40 g, 0.56 mol) was then added and the mixture was stirred for an additional 30 min. After this, trimethoxyphenylsilane (79.32 g, 0.4 mol) was added dropwise via syringe under atmospheric N<sub>2</sub> and the reaction solution was stirred for 36 h at room temperature. After this time, the crude was divided into a colorless and a white phase. The crude white viscous product was obtained by decantation of the colorless solvent mixture. The crude white viscous product was dissolved in methylene chloride (150 mL) and extracted with deionized water (200 mL) for 2 h. The water was removed and the methylene chloride solution was dried overnight with MgSO<sub>4</sub> and then filtered to remove the solid. Methylene chloride was removed using a rotary evaporator at 40 °C and a final white powder (49.1 g, yield = 95%) was obtained after vacuum drying at 40 °C.

*Sulfonation of Polyphenylsilsesquioxane (S-PPSQ)*: Sulfonated PPSQ was prepared by reaction of PPSQ (M<sub>w</sub>: 10,000 g/mol, M<sub>n</sub>: 4,700 g/mol, PDI: 2.13) with chlorosulfuric acid. First, PPSQ was dried in a vacuum oven at 50 °C for 24 h. PPSQ and methylene chloride were placed in a three-neck reaction vessel equipped with a reflux condenser at room temperature. The PPSQ solution was mixed using a magnetic stirrer to obtain a homogeneous solution. Chlorosulfuric acid was carefully added as a sulfonation agent to the PPSQ solution at room temperature (PPSQ : chlorosulfuric acid = 1:1.2 molar ratio). The homogeneous PPSQ/chlorosulfuric acid mixture was magnetically stirred and refluxed for 12 h at 60 °C. Once the reaction was complete, the mixture was carefully added into a large excess of isopropyl alcohol (IPA) under continuous stirring. The precipitate was filtered and washed many times with IPA and methanol to achieve a neutral pH. Finally, the sulfonated PPSQ was dried for 24 h at 40 °C and overnight at 100 °C under vacuum. In FT-IR spectrum of S-PPSQ shown in Figure 5a, the strong broad absorption peak at 3700-2600 cm<sup>-1</sup> corresponds to O-H vibrations in -SO<sub>3</sub>H groups as well as absorbed humidity. The content of water in the synthesized

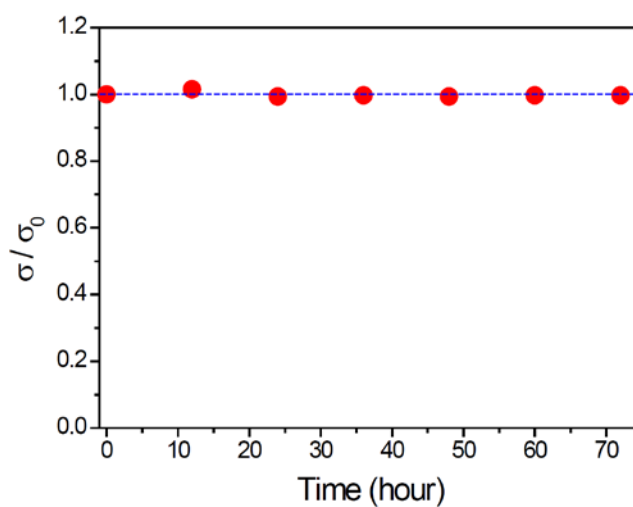
S-PPSQ is about less than 2.5 %, determined by the initial weight loss (< 2.5 % at 150 °C) in thermogravimetric analysis (TGA) measurement (see Figure S1 in ESI).



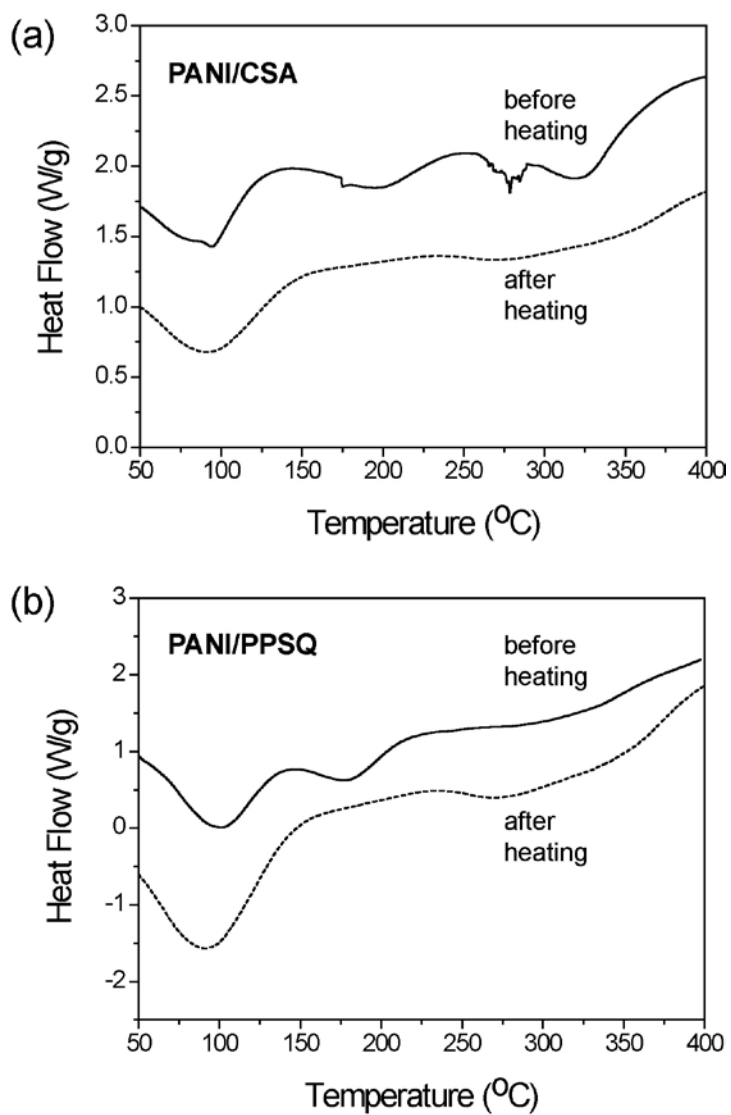
**Figure S1.** TGA curves of PANI (EB) powder, S-PPSQ powder and PANI/CSA and PANI/S-PPSQ films prepared in *m*-cresol.



**Figure S2.** X-ray diffraction (XRD) patterns of (a) PANI/CSA and (b) PANI/PPSQ before and after heat treatment at 150 °C for 10 h.



**Figure S3.** Change of relative electrical conductivity as a function of time at a heat treatment temperature of 120 °C. The electrical conductivity of PANI/S-PPSQ films was measured by the four-line method at room temperature.



**Figure S4.** DSC thermodiagrams (10 K/min scan rate): (a) PANI/CSA film and (b) PANI/PPSQ film before and after heat treatment at 150 °C for 10 h.