**Supporting Information** 

## **Manipulating Glass Transition Behavior of Sulfonated Polystyrene**

## by Functionalized Nanoparticle Inclusion

Sung-Kon Kim,<sup>a†</sup> Ngoc A. Nguyen,<sup>b†</sup> Jeong Jae Wie,<sup>\*c</sup> and Ho Seok Park<sup>\*d</sup>

<sup>a</sup>Department of Materials Science and Engineering and Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

<sup>b</sup>Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716,

USA

<sup>c</sup>Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

<sup>d</sup>School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon 440-746, Gyeonggi, Republic of Korea

<sup>†</sup> **Author Contributions** These authors contributed equally to this paper.

\* **Corresponding Authors** \*E-mail: wie@mit.edu, phs0727@skku.edu



Figure S1. <sup>1</sup>H NMR spectra of sPS in DMSO-*d*<sub>6</sub> at room temperature.

The solubility of sPS was tested in different solvents as shown in Table S1. The hydrophilicity of sPS was raised upon the increase in the degree of sulfonation as shown by water soluble sPS-2 h (DS=26.2%) and sPS-3 h (DS=37.6%) at 80 °C. Meanwhile, water was not capable of dissolving neither PS nor sPS-1 h (DS=18.5%) at constant conditions. Amphiphilicity of sPS samples were tested by a non-polar solvent, THF and by a polar solvent, methanol that is representative non-solvent for hydrophobic PS. Among three synthesized sPS, the sPS-3 h had the highest DS and hydrophilicity and was utilized to prepare nanocomposites for the dispersion study of nanoparticles in sPS matrices.

Samples	Dichloro- methane	Hexane	THF	DMF	Water	Ethanol	Methanol
PS	++	-	++	++	-	-	-
sPS (18.5%) <sup>a</sup>	-	-	++	++	-	++	++
sPS (26.2%) <sup>a</sup>	-	-	++	+	+	++	++
sPS (37.6%) <sup>a</sup>	-	-	++	+	+	++	++

Table S1. Solubility of sulfonated polystyrene (sPS) in different solvents

<sup>*a*</sup> Degree of sulfonation. ++, soluble at RT; +, soluble on heating (80 °C); -, not soluble

Thermal stability of sPS nanocomposites was investigated by TGA and isothermal measurements were carried out at 100 °C for 2 h prior to temperature ramp tests to remove absorbed moisture. Temperature dependent weight loss of the nanocomposites were measured at a temperature ramp rate of 10 °C/min. Thermal stability and residual weights of neat sPS was extensively investigated by a number of studies and known to strongly depend on the degree of sulfonation, and the results for the sPS-3 h agreed with literature.<sup>1</sup> Onset degradation temperature,  $T_{OD}$ , was defined at the temperature for 5 wt% initial weight loss. The  $T_{OD}$  of neat sPS was 261.7 °C due to the degradation of (-SO<sub>3</sub>H) groups in phenyl rings while the nanocomposites had  $T_{OD}$  values range from 279.6 to 295.5 °C upon nanoparticle inclusion.



Figure S2. Thermal stability of sPS nanocomposites

## References

1. Devrim, Y.; Erkan, S.; Bac, N.; Eroglu, I. International Journal of Hydrogen Energy 2009, **34**.