Supporting Information

Morphological Transformation During Cross-linking of a Highly Sulfonated Poly(phenylene sulfide nitrile) Random Copolymer

So Young Lee,^{*a*} Na Rae Kang,^{*b*} Dong Won Shin,^{*a*} Chang Hyun Lee,^{*d*} Kwan-Soo Lee,^{*e*} Michael D. Guiver,^{*b,c*} Nanwen Li,^{*b*} and Young Moo Lee*^{*a,b*}

TEM morphology of ESPSN60 and ESPSN70 membranes

Additional cross-sectional nanophase-morphologies of ESPSN60 and ESPSN70 membranes were obtained by using TEM measurement. ESPSN60 (a) and ESPSN70 (b) produced largely featureless morphologies, indicating a random distribution of ionic groups (dark phase) within the polymer matrix (bright phase), similar to that of ESPSN50. Therefore, the degree of sulfonation of ESPSN membranes did not influence the morphological changes before thermal crosslinking.



Fig S1. TEM images of (a) ESPSN60 and (b) ESPSN70 precursors.

Presence of crystallinity

Evidence for any crystallinity in the membranes was examined by wide angle X-ray diffraction spectroscopy (WAXS) and 2D-small-angle X-ray scattering pattern (2D-SAXS). As shown in Fig. S2a, the membrane before and after cross-linking did not show any evidence of a crystalline peak above 20 degrees of the 2θ value. In addition, the 2D-SAXS in Fig. S2b provided a deeper insight into the 3D morphologies. All ESPSN50 and XESPSN membranes exhibited isotropic amorphous halos without any distinctive crystalline images, like those of Nafion[®] and conventional random copolymers^{1,2}



Fig. S2. (a) Wide-angle X-ray diffraction patterns of ESPSN50 and XESPSN60. (Wide-angle X-ray diffractometer (D/MAX-2500, Rigaku, Japan) operating in the 20 range of 5–80 ° with a scan rate of 5 min⁻¹) and (b) 2D-SAXS patterns of ESPSN50 and all XESPSN.

Effect of thermal annealing and crosslinking in XESPSN polymers

Thermal annealing experiments on non-crosslinkable SPSN60 membrane treated at 120 °C and 250 °C, respectively, for 100 minutes were compared with those for ESPSN60 samples at 120, 200, 220, and 250 °C, to determine the effect of annealing and/or crosslinking on the phase separation of the polymer, since the T_g of ESPSN60 was 205 °C. AFM was used to visualize any phase changes upon thermal annealing of the membranes.

Fig. S3, shows a change of surface morphologies of SPSN60 occurs after thermal annealing treatment. SPSN60-120°C membrane shows relatively featureless morphology indicating homogeneous distribution of hydrophilic domains (dark region) within the hydrophobic phase (bright region). However, after thermal annealing at 250 °C, SPSN60-250 °C membrane exhibits the formation of hydrophilic spheroidal clusters with an average size of 8-10 nm.



Fig. S3 AFM morphologies of (a) SPSN60-120 °C, dried at 120°C in a vacuum oven, and (b) SPSN60-250 °C, dried at 120 °C in a vacuum oven and then thermally treated under vacuum at 250 °C for 100 min.

Fig. S4 shows AFM images of ESPSN60 polymer membrane containing ethynyl groups as a function of thermal curing temperature from 200 to 250 °C. Note that the T_g of ESPSN60 is 205 °C, as shown in Fig. 2a. Phase separation behavior of ESPSN60 membrane is obvious at annealing temperature above T_g but below the ethynyl group cross-linking, which usually occurs around 250 °C as shown in Fig. 2b. Well-ordered phase separation behavior of ESPSN60 appears to be dominated by ethynyl phenol group crosslinking at thermal curing temperatures of 250°C. In other words, as shown in Fig. S4 (a)-(d), ESPSN60-200°C membrane(b) shows relatively featureless morphology like that of ESPSN60-120°C membrane(a). However, at temperatures above T_g of the base polymer, from 220 to 250°C, distinctive surface morphology changes emerge. ESPSN60-220°C membrane(c) shows the formation of small hydrophilic clusters of 6-8 nm in size. At temperatures in the cross-linking region, ESPSN60-250°C membrane(d) (Fig. S4d) shows pronounced worm-like morphology composed of 13-15 nm bi-continuous hydrophilic and hydrophobic networks, corresponding to TEM images in Fig. 3(c).

These observations demonstrate that morphological transformation is to some extent associated with thermally induced molecular rearrangement, where the driving force would be thermal annealing of ESPSN main chains,⁴¹ in addition to thermal cross-linking of ethynyl terminal groups. During the thermal treatment at 250 °C, ESPSN experienced thermal annealing leading to the self-aggregation of both hydrophilic and hydrophobic moieties.



Fig. S4. (a) AFM morphology of ESPSN60-120 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven, (b) ESPSN60-200 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven followed by treatment at 200 $^{\circ}$ C for 100 min under vacuum, (c) ESPSN60-220 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven followed by treatment at 220 $^{\circ}$ C for 100 min under vacuum, (d), ESPSN60-250 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven followed by treatment at 250 $^{\circ}$ C for 100 min under vacuum, (d), ESPSN60-250 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven followed by treatment at 250 $^{\circ}$ C for 100 min under vacuum, (d), ESPSN60-250 $^{\circ}$ C, dried at 120 $^{\circ}$ C in a vacuum oven followed by treatment at 250 $^{\circ}$ C for 100 min under vacuum, (d),

Small-angle X-ray scattering (SAXS) measurement of ESPSN50 and XESPSN membranes.

Small-angle scattering (SAXS) profiles of ESPSN50 and XESPSN membranes were obtained by using a Cu K_{α} radiation ($\lambda_i = 1.54$ Å) source of rotating anode type (Rigaku, Japen, operated at 40 kW) at 50% RH and ambient temperature. The X-ray beam was collimated with a system of three pinholes. The distance between sample and detector was varied from 0.1 to 3 m. q and 20 represent the momentum transfer (accessible range: 0.03-0.5 Å⁻¹) and total scattering angle, respectively.

SAXS profiles of ESPSN and XESPSN exhibit strong scattering maxima (q_{max}) which are attributed to the ionic aggregation of their hydrophilic domains. The SAXS patterns are different from the typically featureless ones observed for conventional random copolymers. In addition, their q_{max} values are similar to those (0.1-0.2 Å⁻¹) of Nafion[®] membranes.^{3,4} The inter-domain distance of ESPSN50 became wide from 4.48 to 6.28 nm after the thermal conversion into XESPSN50. This behavior is of interest to us and needs further detailed studies in the future.



Fig.S5. SAXS patterns of ESPSN50 and all XESPSN membranes (a) at accessible range of 0.01 $\text{\AA}^{-1} < q < 0.14$ \AA^{-1} (b) accessible range of 0.03 $\text{\AA}^{-1} < q < 0.5$ \AA^{-1} .

References

- 1. B. P. Ladewig, R. B. Knott, A. J. Hill, J. D. Riches, J. W. White, D. J. Martin, J. C. Diniz da Costa, and G.O. Lu, *Chem. Mater.*, 2007, **19**, 2372-2381.
- 2. M. K. Mistry, N. R. Chouhury, N. K. Dutta, and R. Knott, *Langmuir*, 2010, 26, 19073-19083.
- 3. T. D. Gierke, G. E. Munn and F. C. Wilson, J. Polym. Sci.: Polym, Phys, Ed., 1981, 19, 1687-1704.
- 4. G. Gebel, Polymer, 2000, 41, 5829-5838.