

Microscopic Characterization of IBM Star Polymers at High-Temperature for Water Membrane Applications

Jae-Young Cho¹, Jonathan Le¹, Young-Hye Na², Mohtada Sadrzadeh³ and Andrew Myles¹

¹. National Research Council CANADA - Nanotechnology Research Centre, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

². IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120, USA

³. Department of Mechanical Engineering, 10-367 Donadeo Innovation Centre for Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada

The star polymers have attracted considerable attention in recent years since their high areal density generate a thin and stable coating on various membrane surfaces through a self-assembly process for better antifouling properties of ultrafiltration system [1-3]. However, the structural stability of star polymer coating with membranes at high temperature is not fully understood until now. In this study, various cutting edge microscopic characterization methods, such as scanning electron microscopy (SEM), Focused Ion Beam (FIB), high-temperature transmission electron microscopy (HT-TEM) and high-temperature atomic force microscopy (HT-AFM) were used for complete understanding of structural changes for star polymers at high temperature (80°C).

Two different concentrations (0.1 and 0.01%) of star polymers in water were prepared and used for this study. For the SEM and TEM studies, samples were prepared by depositing a droplet of solution on a carbon-coated 400-mesh copper TEM grid, the excess solution was blotted after 10 s. The staining of samples for TEM was performed by depositing one droplet of a 2% uranyl acetate solution for 120 s. The grid was then blotted and dried. For HT-AFM study, two different polyethersulfone membranes (Phase Inversion Polyethersulfone – PI-PES and Commercial Polyethersulfone – Com-PES) with star polymers were prepared by dip-coating technique for 30mins and drying in the air. SEM images were obtained without negative staining, at an accelerating voltage of 5 kV and 10 μ A and a working distance of 5-8 mm on high resolution Hitachi S-4800 cold field emission SEM. TEM imaging was carried out on JEOL 2200 FS TEM – 200 kV Schottky field emission instrument equipped with an in-column omega filter. Bright field TEM images were acquired using energy filtered zero loss beams (slit width 10ev). HT-AFM images were obtained using a Digital Instruments/Veeco Instruments MultiMode Nanoscope IV AFM, equipped with a J scanner, along with high-temperature attachment. To verify HT-AFM results, HT-TEM imaging was performed by Hitachi-9500H environmental TEM with elevating temperature till 80°C. In addition, FIB (Zeiss NVision 40) were used to identify the location of star polymer from the surface of membrane by dip coating.

As shown in Fig.1a, SEM image of star polymers shows the round shape of particles. To understand the detail structure of the individual star polymer, TEM images of stained star polymers were acquired by Jeol 2200fs TEM which has in-column filter for enhancing contrast of organic structures (Fig.1b). Measured average particle size was around 23.41 nm, however its standard deviation was high (6.85nm). It seems that this difference is generated by the changes of the shape of star polymers on the carbon film surface of TEM grid when it dried, which can be affected by surface interactions between star polymers (hydrophobic core and hydrophilic arms) and carbon film surface. Two different membranes with star polymers were characterized by FIB and AFM, as shown Fig. 2. Star polymers showed relatively uniform size distribution and were well dispersed on the surface of membranes. Also, star polymers

were found till 500nm thick from the surface in the Com-PES membrane, however, only few star polymers were found in PI-PES membrane (Fig 2a and b). At 80°C, PI-PES membrane was stable for HT-AFM imaging however, Com-PES membrane were unstable, coated star polymers on both membranes showed a good thermal stability at high temperature (Fig 2c). No significant structural changes of star polymers, such as aggregation, swallowing and shrinking, were not found in both samples which shows the good agreement with HT-TEM study (Fig. 1c).

In summary, two different membranes, PI-PES and Com-PES coated by star polymers were successfully characterized by SEM, TEM, FIB, HT-AFM and HT-TEM: star polymers have a size that ranged 15-40nm since it has different shapes on the carbon film surface of TEM grid. HT-AFM and HT-TEM studies revealed the thermal stability of star polymer on the different membranes: it was found that its shape and size of star polymer were very stable at 80°C.

References:

- [1] VY Lee, K Havenstrite, M Tjio, M McNeil, HM Blau, RD Miller, and J Sly, *Adv. Mater.* **23** (2011), p. 4509.
- [2] J Diep, A Tek, L Thompson, J Frommer, R Wang, V Piunova, J Sly and Y-H La, *Polymer* **103** (2016), p. 468.
- [3] JM. Ren, TG McKenzie, Q Fu, EHH Wong, J Xu, Z An, S Shanmugam, TP Davis, C Boyer and GG Qiao, *Chem. Rev.* **116** (2016), p. 6743.
- [4] The authors acknowledge funding from National Research Council CANADA, University of Alberta and Government of Alberta.

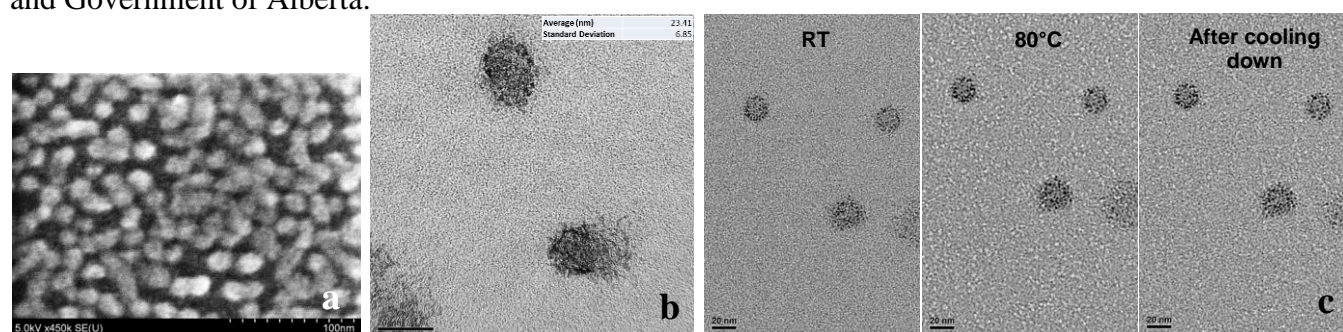


Figure 1. Electron microscopy images of IBM star polymers: a) SEM b) TEM and c) HT-TEM.

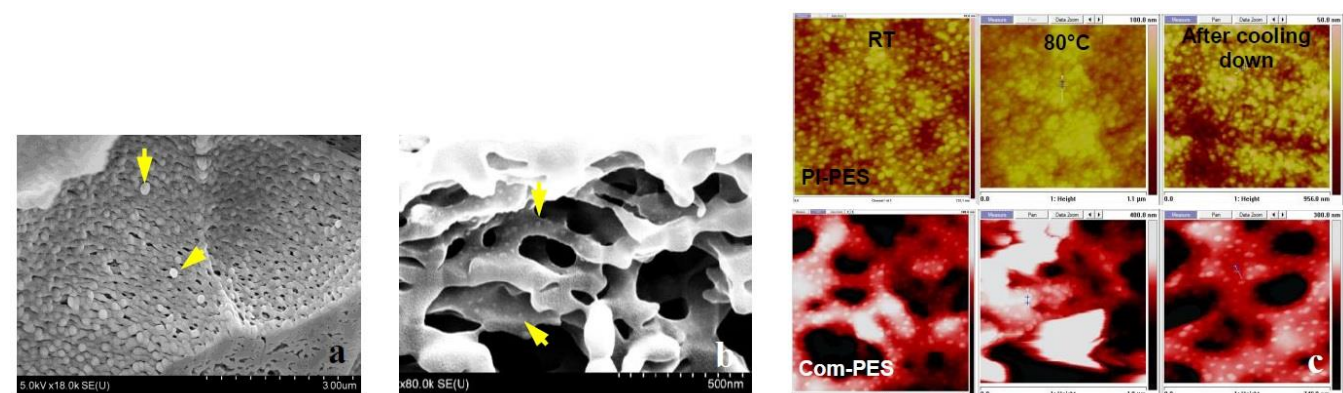


Figure 2. Water membranes with star polymer coating: FIB cross-sectional images of a) PI-PES and b) Com-PES membranes, and c) HT-AFM images (yellow arrows indicate star polymers).