

# Polymer and Colloid Highlights

Division of Polymers and Colloids

A Division of the Swiss Chemical Society

## Introducing a Reversible Linkage to Block Copolymer Self-Assembly: Towards Controlling Nanopore Chemistry

Jingyi Rao, Swati De, and Anzar Khan\*

\*Correspondence: Dr. A. Khan, Institut für Polymere, ETH Zürich, CH-8093 Zürich, Tel.: +41 44 633 6474, E-mail: anzar.khan@mat.ethz.ch

**Keywords:** Block copolymer self-assembly · Dynamic covalent chemistry · Nanoporous membranes

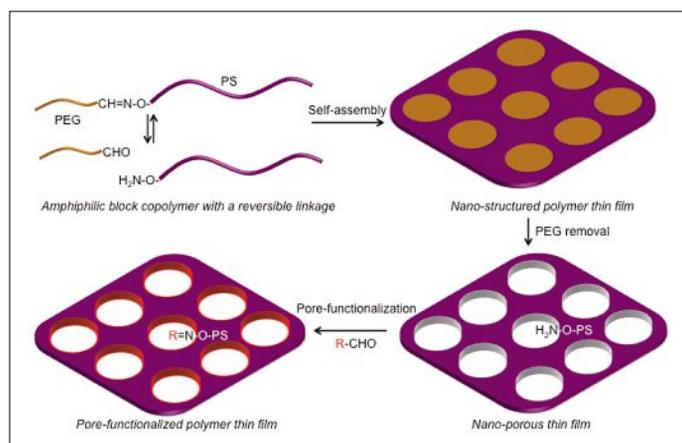
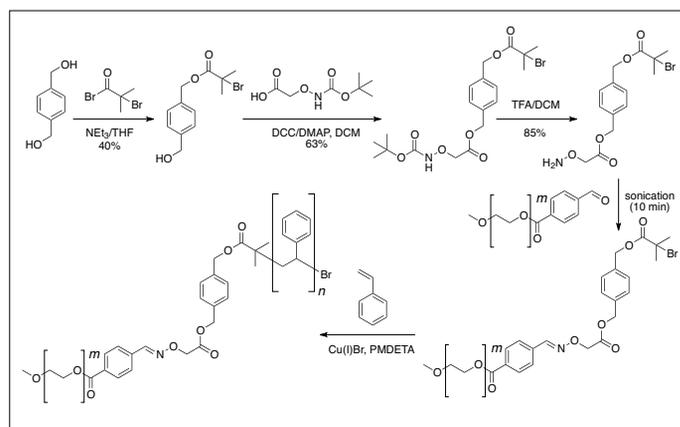


Fig. 1. Schematic representation of nanostructured thin film formation from self-assembly of dynamic covalent diblock copolymer, subsequent step of pore formation due to the reversibility of the copolymer linkage, and tentative graphic representation of the functionalized-pore.

Block copolymer self-assembly<sup>[1]</sup> has shown remarkable potential towards preparation of highly ordered nanoporous membranes.<sup>[2]</sup> In this approach, covalently connected yet chemically dissimilar polymer blocks phase separate into ordered nanostructures with length scales on the order of ten to a hundred nanometres. Selective removal of the minor phase from these nanostructured polymer thin films affords nanoporous membranes. Such membranes have found use in surface patterning, templated nanomaterial synthesis, separation, filtration, catalysis, sensing, and drug delivery applications. The far-ranging applicability and performance of these porous materials will further enhance if the surface of the nanopore can carry chemically reactive functionalities that can be altered under ambient conditions. So far, strategies for covalent chemical functionalization of the nanopores in highly ordered porous thin films remains undeveloped. To this end, we designed and synthesized a diblock copolymer featuring incompatible blocks, unsymmetrical block lengths, and a reversible copolymer linkage (Fig. 1 and Scheme 1).<sup>[3]</sup> Self-assembly of this copolymer results in nanostructured thin films exhibiting highly ordered cylindrical morphology (Fig. 2). Removal of the nanosized cylinders by reversing the dynamic covalent – oxy-imine – linkage then affords ordered nanoporous membranes that contain chemically reactive oxy-amine functionalities. Covalent and non-covalent



Scheme 1.

membrane-functionalization were carried out both by re-establishing imine bonds with fluorescent organic molecules and *via* forming metal complexes.

Received: May 7, 2012

- [1] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.  
 [2] C. J. Hawker, T. P. Russell, *MRS Bull.* **2005**, *30*, 952.  
 [3] J. Rao, S. De, A. Khan, *Chem. Commun.* **2012**, *48*, 3427.

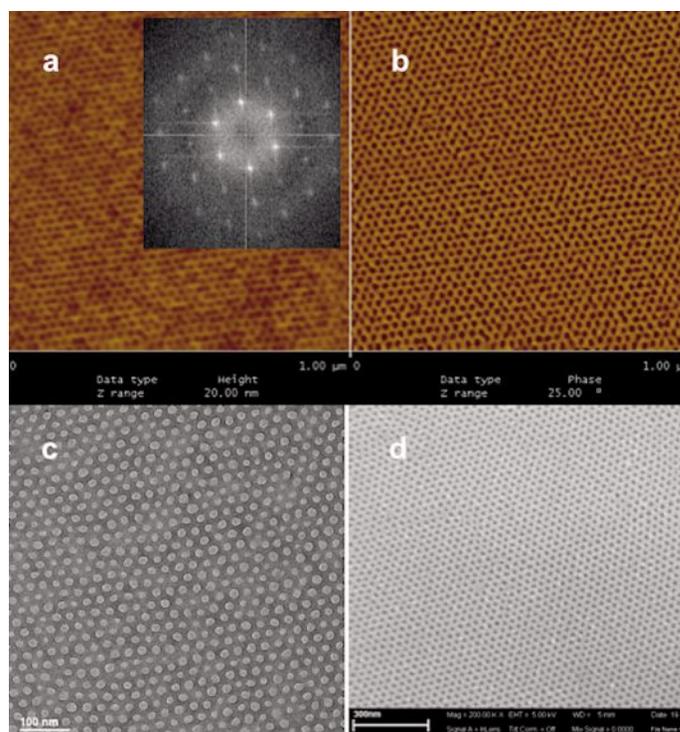


Fig 2. AFM height (a) and phase (b) images (1  $\mu\text{m} \times 1 \mu\text{m}$ ) of the thin film. Inset shows the corresponding Fourier transform. TEM (c, scale bar = 100 nm) and SEM (d, scale bar = 300 nm) images of the thin film after removal of the PEG cylinders.

**If you are interested in submitting a new highlight, please contact:**

Prof. A. Dieter Schlüter, Institut für Polymere, ETH Zürich  
 E-mail: dieter.schluter@mat.ethz.ch, Tel.: +41 44 633 63 80