Controlled Nanopores by Supramolecular Assembly of End-Functionalized Dendrimer and Homopolymer Blend

Giyoung Song,[†,#] Ju Eun Kim,[‡,#], Suk Man Cho,[†] Seong Ik Jeon,[‡] Hui Joon Park,[∥] June Huh,[§] Cheol-Hee Ahn,[*,‡] Cheolmin Park[*,†]

[†] G. Song, S. M. Cho, Prof. C. Park[*]
Department of Materials Science and Engineering, Yonsei University, Seoul, 120-749, Korea
e-mail: cmpark@yonsei.ac.kr

[‡] J. E. Kim, S. I. Jeon, Prof. C. Ahn[*]
Department of Materials Science and Engineering, Seoul University San 56-1, Gwanak_599 Gwanak-ro, Seoul, 515-744, Korea
e-mail: chahn@snu.ac.kr

[∥] Prof. H. J. Park
Division of Energy Systems Research, Ajou University, 206 World cup-ro, Suwon 443-749, Korea

[§] Prof. J Huh
Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Korea

< Experimental Section & Supporting information S1-S6 >

Experimental Section

Materials and film preparation

Three different end-functionalized polystyrene with sulfonic acid (SPS) were purchased from Polymer Source, Inc. (Doval, Canada) with molecular weights of 17 (SPS1), 10.5 (SPS2), and 31.5 (SPS3) kg mole^{-1} and polydispersity indexes (PDIs) of 1.07, 1.12, and 1.10, respectively. Various blend solutions with various molecular weights of SPSs and aminated poly(ethylene oxide) dendrimers (APEO-Gs) with its stoichiometric compositions in benzene solvent **(Table 1)** were prepared. Thin films were

subsequently prepared from 1 and 2 wt% of solutions by spin coating (SPIN 1200 Midas-system, Korea) with 4000 rpm on Si wafer.

APEO-G dendrimer synthesis

APEO-G1, APEO-G2, and APEO-G3 dendrimer were synthesized using anionic ring-opening polymerization of ethylene oxide (EO) as schematically shown in **Figure 1**. In brief, EO was introduced into an ampoule and diluted with anhydrous THF. The solution was stirred at room temperature for 30 min and stoichiometric amount of diphenylmethyl potassium (DPMK) (1.76 mmol) was then added. Polymerization was carried out at 40 ^{o}C for 72 h to produce Generation 0 PEO (G0). In order to introduce branch points at the terminal end of linear G0 PEO, tetrabutylammonium bromide (0.03 g, 0.09 mmol) and NaOH (0.36 g, 9.00 mmol) were dissolved in 2 mL water and G0 PEO (4.5 g, 0.90 mmol) in 3 mL anhydrous THF was added. Allyl bromide (0.78 mL, 9.00 mmol) was introduced after 30 min at 50 ^{o}C and the reaction was continued for 24 h to obtain allylated G0. Allylated G0 (4.00 g, 0.80 mmol) and N-methylmorpholine-N-oxide (0.56 g, 4.80 mmol) in 4.5 mL acetone and 4.5 mL distilled water were introduced. 0.2 mL of 2.5 % OsO_4 solution in *tert*-butanol was added and the reaction was continued at room temperature for 24 h to obtain polymers with two hydroxyl groups at the terminal end. G0 precursor with two hydroxyl group ends was freeze dried from 1,4-dioxane under high vacuum system for the growth of next generation. Synthesis of G1 followed the same procedure of G0 using living anionic polymerization. Introduction of branch points in each generation was obtained by allylation and dihydroxylation as mentioned previously. Synthesis of G2 and G3 were carried out in dimethyl sulfoxide (DMSO) with DPMK with the concentration around 30 % of hydroxyl moles. The reaction was proceeded at 40 ^{o}C for 72 h to produce G2 and G3 as schematically shown in **Figure 1a**.

Introduction of amino group at the focal point of G1, G2, and G3 dendrimer was performed using the same following procedure. Allyl group was introduced to the focal point of dendrimer of each generation with the same allylation reaction employed at the activation of the terminal end groups. Allyl

terminated dendrimer and cysteamine hydrochloride (3.0 equiv. of hydroxyl group) were reacted using 2,2-dimethoxy-2-phenylacetophenone (0.04 equiv. of hydroxyl group) as photo-initiator in methanol and dichloromethane (1/1, v/v) in a 50 mL 2-neck round bottom flask. The reaction mixture was stirred for 30 min and exposed to the UV light (λ_{exc} = 365 nm) for 1 h. The organic layer was dried over anhydrous magnesium sulfate and condensed solution was precipitated into excess amount of cold diethyl ether to produce amine functionalized dendrimer, APEO, with 80 % yield as shown in **Figure 1b**.

Each PEO dendrimer was characterized using ^{1}H NMR and GPC analysis and the shift of peak molecular weight in GPC traces confirmed the successful synthesis of dendrimer without the presence of any impurities. The molecular weight and polydispersity of dendrimer is shown in **Supporting information 1**. Allylation and dihydroxylation step was examined through ^{1}H NMR analysis. Allyl peak shown between 5.0 and 6.0 ppm was compared to the methyl groups next to the terminal hydroxyl groups of the dendrimer and the allyl peaks completely disappeared as dihydroxylation reaction proceeded, which supported the successful activation steps for the growth of the next generation dendrimers. Amine functionalization at the focal point of each dendrimer was also confirmed using ^{1}H NMR and the data of APEO-G1, APEO-G2, and APEO-G3 NMR spectra are shown in **Supporting information 2.**

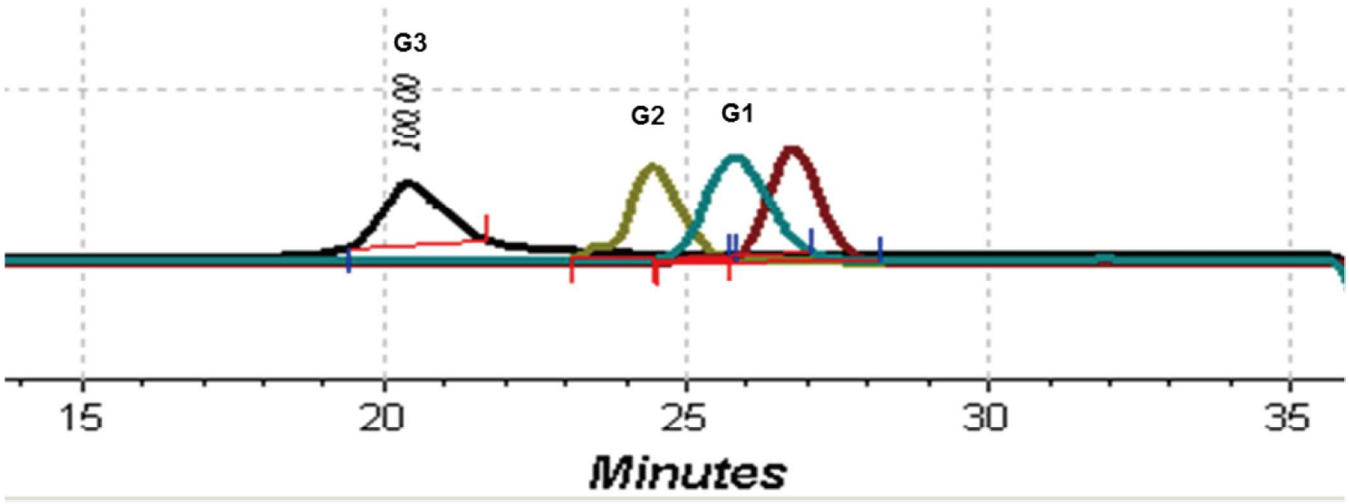
Supramolecular assembled porous film preparation

To fabricate nanoporous thin films, solvent annealing was performed. The thin films were placed in a chamber containing a mixture of saturated water (vapor pressure at 25 °C: 24 mmHg) and benzene (vapor pressure at 25 °C: 95 mmHg) vapor with a water volume fraction of 0.2 for an hour. The environment outside the chamber was maintained at 25 °C and 20 % humidity. Due to the interaction of end groups, sulfonate and aminate, polymer chain ends were connected ionically, and nanoporous thin films having different pore sizes were produced under the given solvent conditions. To selectively

remove the APEO chains by the dissociation of the bond between sulfonic acid and the amine, the films were subsequently washed by ethanol, a selective solvent to APEO.

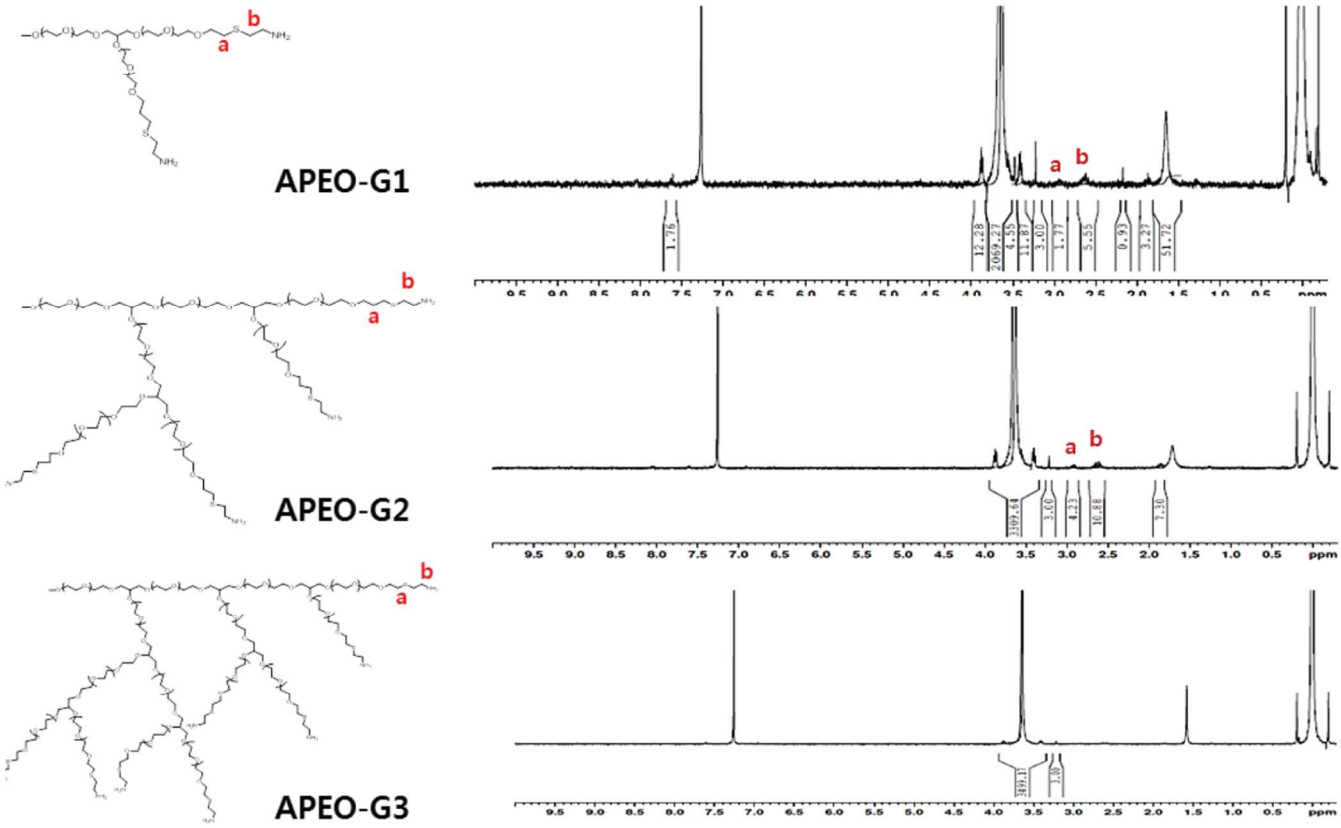
Characterization

The supramolecular-assembled nanostructures in the film samples were observed using tapping mode atomic force microscopy (AFM) (Nanoscope IVa Digital Instruments) with height and phase contrast, field emission scanning election microscopy (FESEM) (JEOL S4800), and optical microscopy (OM) (Olympus BX 51M) in bright field. X-ray photoelectron spectra (XPS) were measured with a K-alpha (Thermo VG, UK) at room temperature using a monochromatic Al X-ray source at 12 kV and 3 mA. The sample analysis chamber of the XPS instrument was maintained at a pressure of 2.9×10^{-9} mb. The pore size distribution analysis from the AFM images was done by using the *ImageJ* program. Grazing-incidence small angle X-ray scattering (GISAXS) was employed to characterize the structure of blend films on 3C beamline at Pohang Accelerator Laboratory in Korea. The measurements were performed with a wavelength of 1.2081 **Å** and the sample-to-detector distance (SDD) of 4 m having grazing incidence angle 0.15°. Two-dimensional GISAXS patterns were recorded by using MAR165.

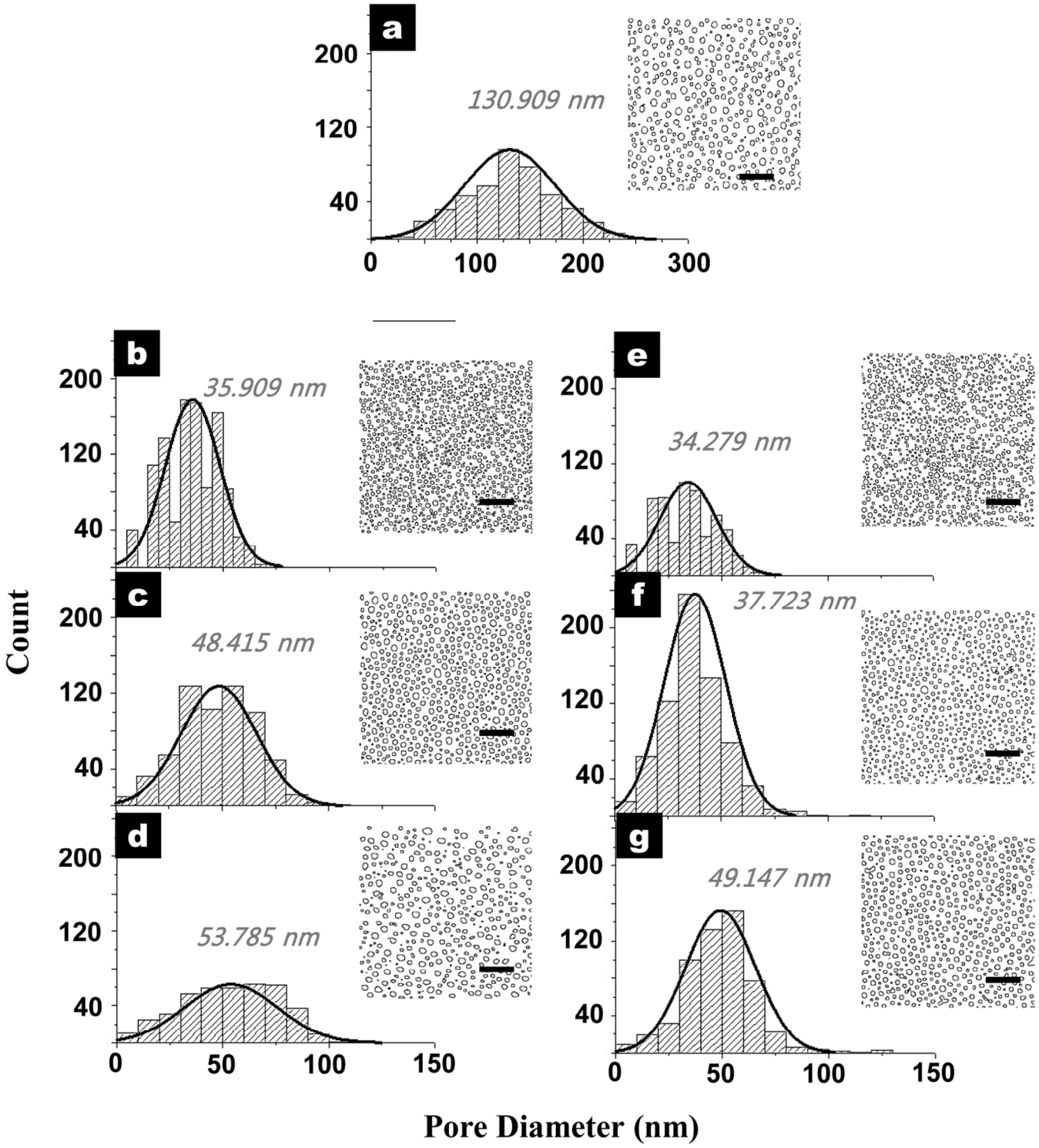


G1 – M_n 21,000, M_w/M_n=1.03
G2 – M_n 43,000, M_w/M_n=1.02
G3 – M_n 78,000, M_w/M_n=1.06

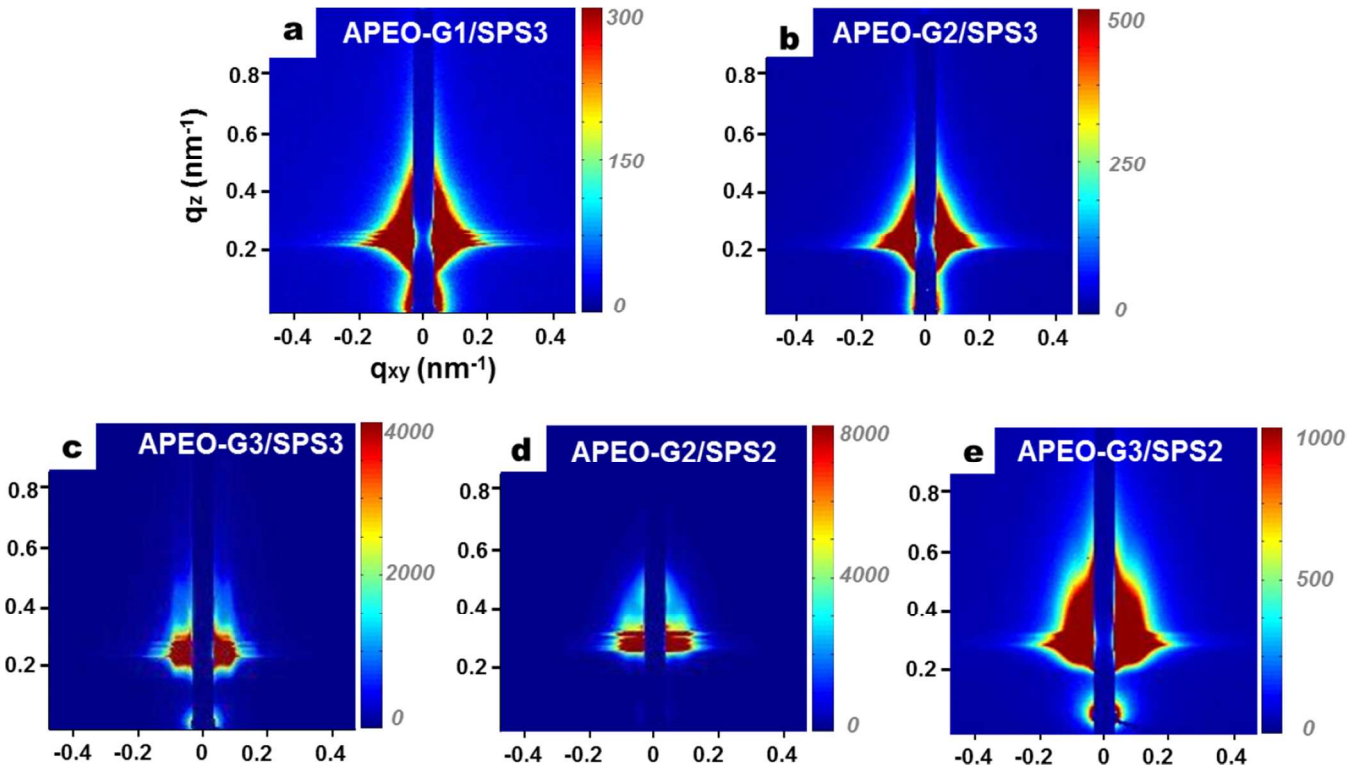
Supporting Information S1. GPC traces of APEO-G1, APEO-G2, APEO-G3



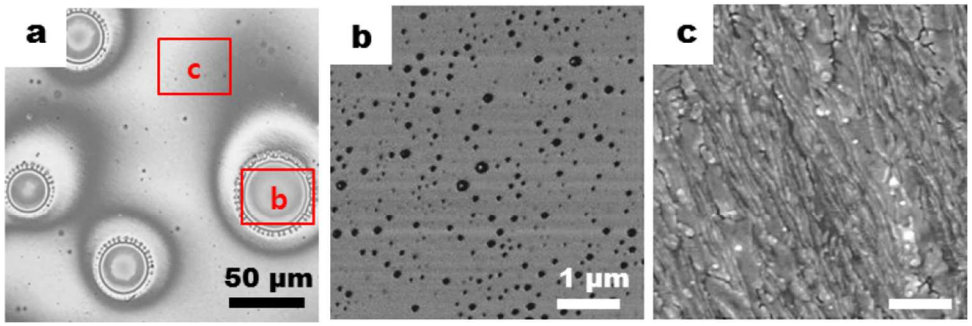
Supporting Information S2. NMR analysis of APEO-G1, APEO-G2, APEO-G3



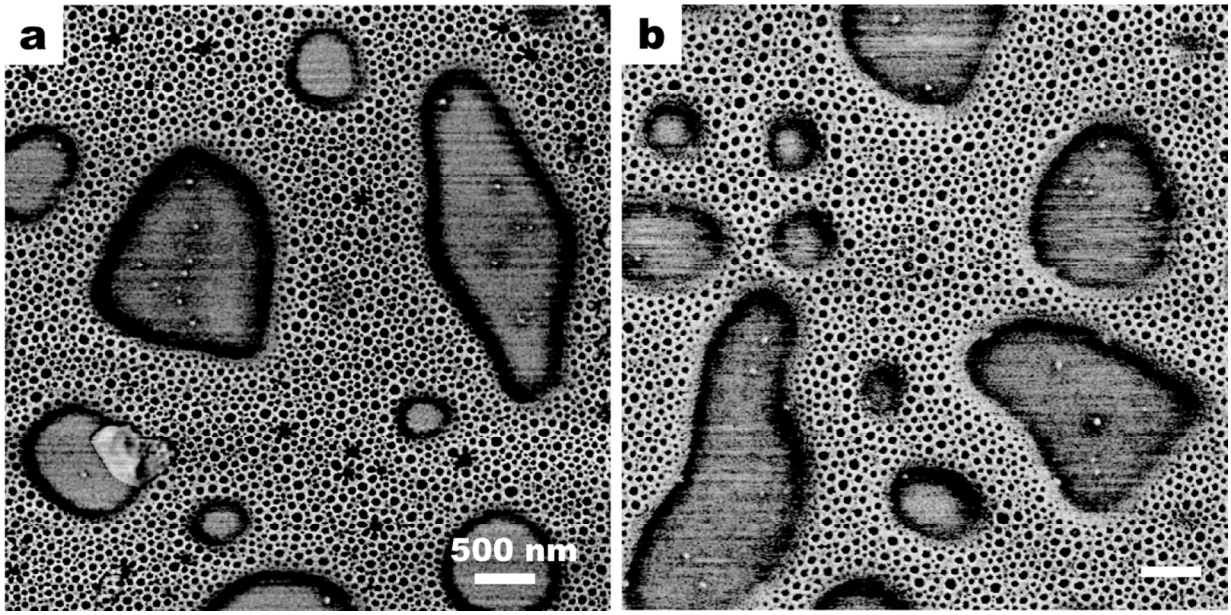
Supporting Information S3. Pore size distributions (normal) calculated by *ImageJ.* of a) APEO-G1/SPS3 (scale bar: 1 μm), b-d) APEO-G2 with SPS1, 2, and 3, and e-g) APEO-G3 with SPS1, 2 and 3 respectively. (scale bar: 400 nm)



Supporting Information S4. 2D-GISAXS patterns of blend films of a) APEO-G1/SPS3, b) APEO-G2/SPS3, c) APEO-G3/SPS3, d) APEO-G2/SPS2 and e) APEO-G3/SPS2.



Supporting Information S5. TM-AFM images of macrophase-separated blend films of a) APEO-G1/SPS1, where circular droplets with supramolecular assembled nanostructures (b) were embedded in APEO dendrimer rich matrix films with the characteristic semi-crystalline structures (c).



Supporting Information S6. TM-AFM images in height mode of a) APEO-G2/SPS2 and b) APEO-G3/SPS2 films were prepared from 1 wt% blend solution with respect to the solvent showing bilayer, insufficiently covered supramolecular assembled film on APEO-G dendrimer bottom layer.