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Supporting Information

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Oriented Perforated Nanoporous Lamellar Organosilicates Templated from Topologically Unsymmetrical Dendritic-Linear Block Copolymers

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Materials.

2,2-Bis(hydroxymethyl) propionic acid was obtained from Aldrich and used without further purification. Dowex 50W-X2 ion exchange resin was obtained from Aldrich and used after a simple methanol rinse, and DMAP (Aldrich) was used as received. The 4-(dimethylamino)pyridinium p-toluensulfonate (DPTS) was prepared according to literature procedure.

2,2' Bis (hydroxymethyl) propionic acid acetonide was prepared according to literature procedure. 2,2'-Bis(hydroxymethyl)propionic acid (Bis-MPA) (200 g, 1.491 mole, FW = 134,13), 2,2-dimethoxypropane (232,4 g, 2.232 mole, FW = 104.15), and p-toluenesulfonic monohydrate (p-TSA) (10g, 52.5 mmol, FW = 190.22) were mixed together in 1L of acetone. The mixture was stirred for 5H, until the mixture turns clear. The p-TSA was neutralized by adding a solution of NH_4OH/EtOH 1/1 v/v. The salt was filtered and the acetone was evaporated. The product was then dissolved in CH_2Cl_2 and washed three times with 200 mL of water. The combined organic phases were dried over $MgSO_4$ and concentrated to yield a crystalline white powder. ^{1}H-NMR ($CDCl_3$): δ 1.18

(s, 3H, -CH_3), 1.38 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 3.64 (d, 2H, -$COCH_2$-, J = 11.9 Hz), 4.16 (d, 2H, -$COCH_2$-, J = 11.9 Hz). ^{13}C-NMR ($CDCl_3$) : δ 18.4, 22.3, 24.9, 41.7, 65.8, 98.3, 180.1

Acetonide-2,2' bis (hydroxymethyl) propionic anhydride (bis MPA anhydride) was prepared according to literature procedures. Acetonide-2,2'-bis(methoxy)propionic acid (50.0 g, 287 mmol, FW = 174.19 g.mol^{-1}) was stirred in CH_2Cl_2 (200ml). N,N'-Dicyclohexylcarbodiimide (DCC) (29,61 g, 143 mmol, FW = 206.33 g.mol^{-1}) was added to the mixture, and stirring was continued for 48h at room temperature. The reaction was run to completion as monitored by ^{13}C-NMR. This was determined by the disappearance of the acid carbonyl carbon corresponding to Acetonide-2,2'-bis(methoxy)propionic acid at 178 ppm. The dicyclohexyl urea was filtered off and the solvent evaporated. The viscous residue was diluted in 1L of hexane cooled to –78°C by dry ice and stirred until a white solid formed. The mixture was filtered through a glass filter and the product was dried under vacuum to afford **1** as a white powder. ^{1}H-NMR, ($CDCl_3$): δ 1.21 (s, 6H, -CH_3), 1.36 (s, 6H, -CH_3), 1.41 (s, 6H, -CH_3), 3.66 (d, 4H, J = 12 Hz, -CH_2O), 4.18 (d, 4H, J = 12 Hz, -CH_2O). ^{13}C-NMR ($CDCl_3$): δ 17.83, 21.75, 25.72, 43.83, 65.85, 98.56, 169.68.

General procedure for the functionalization of hydroxyl-functional polyethylene oxide with the acetonide protected bis MPA (PEO 5k/g-1 (act). The procedures used to prepare the dendritic-linear hybrids were developed by Frechet.[i] Monomethyl ether PEO, Mn = 4800, (8.34g, 1.66 mmol) was dissolved in 50 mL methlene chloride/pyridine (90/10) solvent mixture. To this solution, bis MPA anhydride 1.70g, 5.06 mmol) was added along with DMAP (0.19g, 1.51 mmol) and the mixture stirred overnight. Methanol (8 mL) was added and allowed to stir for 5 h to quench excess anhydride and the polymer was precipitated in 1L of ether. ^{1}H NMR ($CDCl_3$) δ = 1.22 (s, 3H, CH_3), 1.34 (s, 6H, CH_3),1.39 (s, 6H, CH3), 3.36 (s, 3H), 3.44 (m,)3.65 (bs,-CH_2), 3.67 (d, 4H,-CH_2), 4.15 (d, 4H,-CH_2), 4.25 (t, -CH_2). ^{13}C-NMR ($CDCl_3$) δ 19.01, 23.43, 24.58, 42.19, 59.38, 64.22, 66.27, 69.34, 70.91, 71.31,72.67, 98.37, 174.45.

General procedure for the deprotection of the acetonide protecting groups. Approximately 2 teaspoons of Dowex 50WX2 was added to a solution of acetonide functional **PEO 5k/g-1 (act)** in 150mL of MeOH. The mixture was stirred at 55°C and the deprotection was followed with ^{13}C NMR until complete disappearance of peaks unique to the acetonide group occurred (i.e., the quaternary carbon at 98 ppm and/or the methoxy carbon at 23 ppm). Once the reaction was complete, usually 3-5 hours, the resin was removed by and washed with MeOH. The filtrate was concentrated to give the deprotected product as a white crystalline solid. ^{13}C-NMR ($CDCl_3$) δ 17.50, 50.40, 59.40, 63.73, 76.89, 70.78, 70.93, 72.29, 77.18, 77.49, 77.81, 176.20.

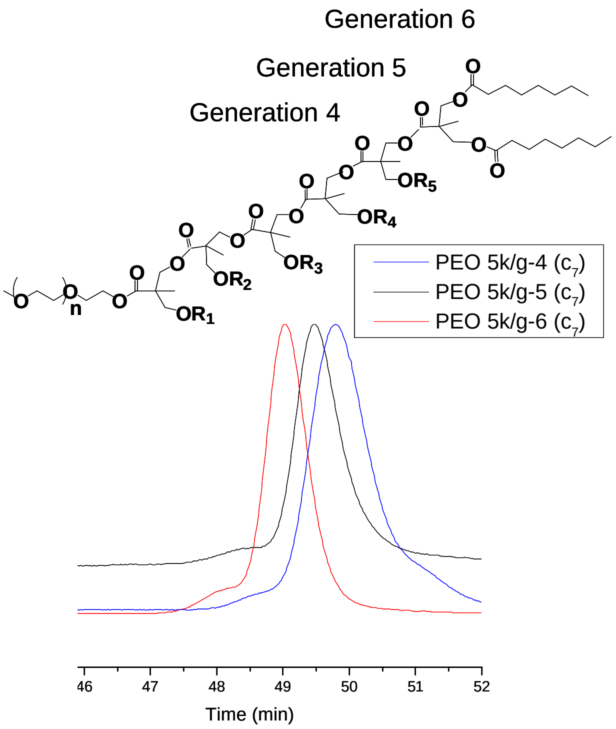
General procedure for the modification of the surface functional end-groups on the dendron. A dendritic linear hydrid having a PEO block length of 4,800 g/mol with a 4th generation dendron having 16 hydroxyl groups (1.00g, 0.13 mmol) was dissolved in CH_2Cl_2 together with heptanoic acid (0.48g, 3.69 mmol). To this solution DCC (0.59g, 2.86 mmol) was added followed by DPTS (0.30g, 0.96 mmol) and DMAP (0.16g, 1.31 mmol) and allowed to stir overnight. The solid byproducts were removed by filtration and the polymer solution was isolated by precipitation. The polymer was then purified by dialysis (methanol). ^{1}H NMR ($CDCl_3$) δ = 0.78-0.82 (br, 55H), 1.14- 1.20 (br, 165 H), 1.49-1.57 (br, 37H), 2.10-2.23 (br, 22H), 3.42(s, 3H0, 3.57-3.59 (br, 300H), 4.15-4.23 (br, 38H). ^{13}C-NMR ($CDCl_3$) δ = 14.41, 18.87, 22.86, 25.18, 29.15, 31.82, 34.38, 46.71, 65.21, 70.95, 99.98, 104.16, 173.50.

Shown in Figure s-2 are the SEC chromatograms of the 4-6th generation copolymers that clearly demonstrate monomodel, narrowly dispersed products are obtained.

Measurements

Size-exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5 µm Waters columns (300 X 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, 10^6 Å) were used with THF as eluant. The SEC results were calibrated with polystyrene standards. The thermophysical properties (Tg) were recorded on a Perker-Elmer DSC-7. ^{1}H NMR spectra were recorded in a solution with a Bruker AM 250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer using the solvent carbon signal as an internal standard.

Film thicknesses and refractive indices were measured using a Filmetrics F20 thin-film optical spectrometry system. Dielectric constants values were measured using a capacitance bridge with an HP 4192A impedance analyzer using a metal insulator semi-conductor structure. Film densities were obtained using a x-ray reflectomer (Panlytical, X-Pert pro MRD) with a ceramic x-ray tube. X-rays of the wavelength of 1.54Å (Cu $K_{?\,1}$) were monochromated with a 4-bounce monochromator (Ge(220)).

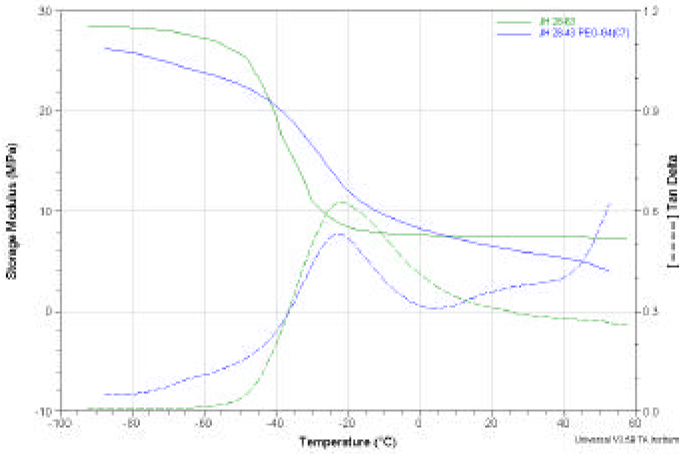


Small angle x-ray scattering (SAXS) Experiments:

The experiments were performed at the LB-4-2 beamline at the Stanford Synchrotron Radiation Laboratory (SSRL). X-rays having energies of 8.98 keV, (wavelength of 1.381Å) were used with a gas chamber detector. The samples were positioned with the substrate normal coinciding with the incident beam. In order to reduce attenuation from the silicon, ~0.5-0.8 µm films were processed on double-sided polished wafers having thicknesses of ~80 µm.

Small angle neutron scattering (SANS) experiments:

Small angle neutron scattering (SANS) experiments were carried out at the Center for Neutron Research at the National Institute of Standards and Technology (NCNR) using the 30 meter NIST-NG7 instrument on thin film samples spin coated on 1 inch diameter silicon wafers with the neutron beam incident along the surface normal. The wavelength, ?, was 8 Å with a wavelength spread, ? ?/?, of 0.22. Sample to detector distances of 1.5 m and 11.75 m were used which gave a q range of 0.0028 - 0.3 Å-1. Four or more samples were stacked to increase the scattering volume. To provide neutron contrast between the pores and the PMSSQ matrix, a deuterated alkyl chain was introduced in the porogen (G4-PEO10K/d_7). Figure S-x shows SANS profiles of MSSQ containing 40wt% porogen at 40°C and after thermal treatment 450°C. The thermal treatment removes organic porogen thus generate porous structures. A strong peak from inter-particle correlation was observed for the mixture of MSSQ and porogen already at 40°C, which suggests two-phase structure of the mixture.



Dynamic mechanical analysis

Thin films of these block copolymers show microphase separated morphologies, as evidenced by two Tg’s in the DMA spectra for the 3rd- 6th generation copolymers (Figure S-2).

Preparation of thin films. Thin films were prepared from freshly mixed hybrid solution of Organosilicate at 20 wt. % solids and **1-a** . The **1-a** surfactant was dissolved in Propylene Glycol -n- Propylether (PnP) to yield a 20 wt. % solution. A scintillation vial was charged with 2.00g **1-a** solution and 3.00g of the Organosilicate solution. The resulting solution was allowed to mix on a mechanical shaker for 5 min. to yield a homogenous solution. Thin films were obtained by spin casting the solution through a 0.2 μn syringe filter on to clean wafers. The wafers were spun at 3000 rpm for 30 seconds. The films were cured on a hotplate from 50 °C to 450 °C with a ramp rate of 5 °C/min. followed by a soak cure at 450 °C for 2 hours under a nitrogen environment.