Supporting Information

for

Imidazolium-containing, Hydrophobic-Ionic-Hydrophilic ABC Triblock Copolymers: Synthesis, Ordered Phase-Separation, and Supported Membrane Fabrication

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Materials and General Procedures. 1-Bromohexane, 1-dodecanol, 5-norbornene-2-carboxylic acid, triethylene glycol monomethyl ether, *p*-toluenesulfonyl chloride, potassium carbonate, triethylamine, ethyl vinyl ether, and oxalyl dichloride were all purchased from the Sigma-Aldrich Co., and used as received. Dicyclopentadiene and 1-vinylimidazole were purchased from TCI America, and used as received. Lithium bis(trifluoromethylsulfonyl)amide ($LiTf_2N$) was purchased as Fluorad™ Lithium Trifluoromethane Sulfonimide from the 3M Company. All solvents were purchased from Sigma-Aldrich or Mallinckrodt, Inc., and purified/dehydrated via N_2-pressurized activated alumina columns, and de-gassed. Additionally, the CH_2Cl_2 used as the solvent in ring-opening metathesis polymerization (ROMP) reactions was purified by re-filtering over activated alumina prior to de-gassing. The H_2O used for synthesis was purified and de-ionized, with a resistivity value greater than 12 MΩ cm^{-1}. All chemical syntheses were carried out in a dry argon atmosphere using standard Schlenk line techniques, unless otherwise noted. Silica gel purification was performed using 230–400 mesh, normalphase silica gel purchased from Sorbent Technologies.

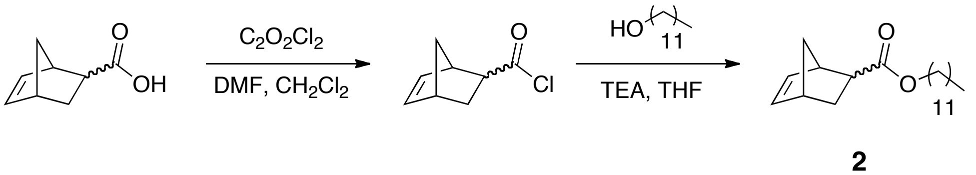
Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker 300 Ultrashield^{TM} (300 MHz for ^{1}H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. Fourier-transform infrared spectroscopy (FT-IR) measurements were performed using a Matteson Satellite series spectrometer (neat, thin film samples on Ge crystals). High-resolution mass spectrometry (HRMS) with electrospray (ES) analysis was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado, Boulder. Small-angle X-ray scattering (SAXS) data were collected using a Rigaku S-Max 3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_α), Confocal Max-Flux Optic, Gabriel multi-wire area detector, and a Linkam thermal stage. For SAXS analysis, the BCP samples were sandwiched between Kapton discs. Exposure times for the samples were typically on the order of 1800–43200 s.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (endo:exo 80:20) (2).[1] Monomer **2** was prepared as previously described in the literature.[1] Spectroscopic and purity analysis data were consistent with those previously reported.[1]

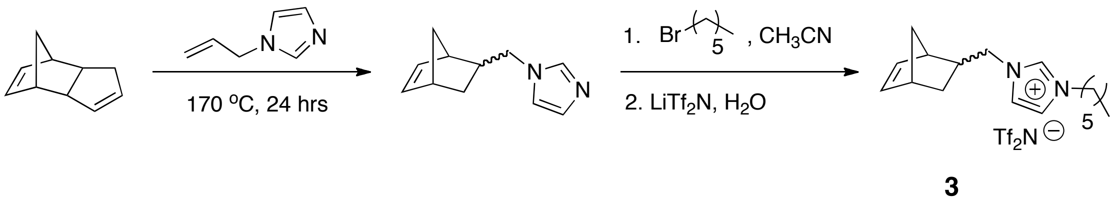
3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3*H*-imidazolium bis(trifluoromethylsulfonyl)amide (endo:exo 80:20) (3).[1] Monomer **3** was prepared as previously described in the literature.[1] Spectroscopic and purity analysis data were consistent with those previously reported.[1]

Triethylene glycol monomethyl ether tosylate (5). In a procedure adapted from the literature,[2] triethylene glycol monomethyl ether (20.5 g, 125 mmol) and dry triethylamine (35.0 mL, 251 mmol) were added under air-free conditions to a 500-mL round-bottom flask containing CH_2Cl_2 (50 mL). Tosyl chloride (41.8 g, 219 mmol) dissolved in THF (50 mL) was added to the solution, and stirred at 0 °C before warming to room temperature overnight. The crude product was extracted with CH_2Cl_2 (3 x 100 mL), washed with 1 M HCl (2 x 250 mL), dried with anhydrous $MgSO_4$, and concentrated to a yellow oil. The product was isolated from excess TsCl via column chromatography (CH_2Cl_2, EtOAc) resulting in a clear, yellow oil matching literature characterization data (29.1 g, 73% yield). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.82-7.80 (d, 2H), 7.37-7.34 (d, 2H), 4.16 (t, 2H), 3.71-3.54 (m, 10H), 3.38 (s, 3H), 2.46 (s, 3H).

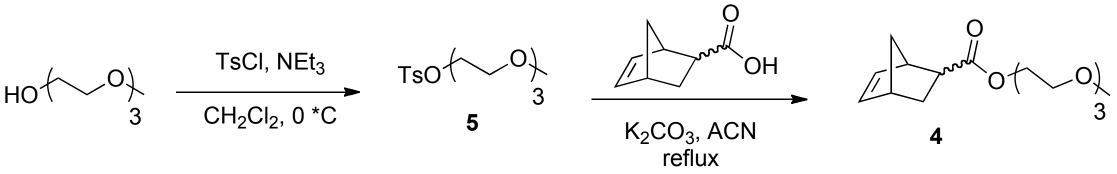
2-(2-(2-Methoxyethoxy)ethoxy) ethyl bicycle[2.2.1]hept-5-ene-2-carboxylate (4). Norbornene-2-carboxylic acid (8.68 g, 62.8 mmol) and K_2CO_3 (17.4 g, 126 mmol) were stirred in CH_3CN (64 mL) before adding tosylate **5** (10.0 g, 31.4 mmol) and heating the mixture to reflux for 48 h. The crude product was then extracted with EtOAc (3 x 100 mL), washed with $NaHCO_3$ (2 x 300 mL) and H_2O (2 x 300 mL), dried with anhydrous $MgSO_4$, and concentrated to a clear, yellow oil (8.93 g, 85% yield). ^{1}H NMR (300MHz, CDCl3): δ 6.20-5.93 (m, 2H), 4.24-4.16 (m, 2H), 3.70-3.54 (m, 10H), 3.39 (s, 3H), 3.23-2.90 (m, 3H), 1.91-1.26 (m, 4H). ^{13}C NMR (75 MHz, CDCl3): δ 176.2, 174.7, 138.0, 137.7, 135.7, 132.4, 71.9, 70.5, 69.2, 63.5, 63.3, 59.1, 49.6, 46.7, 46.3, 45.7, 43.2, 43.0, 42.5, 41.6, 30.4, 29.3. IR (neat): 2944.7, 28.74.2, 1728.8, 1450.8, 1335.5, 1271.1, 1251.8, 1176.2, 1106.5, 1068.7, 1041.6, 942.5 cm^{-1}. HRMS (ES) calcd. for (MH+): 285.1702; observed 285.1702.



Scheme S1. Synthesis scheme for hydrophobic alkyl-functionalized norbonene monomer **2**.



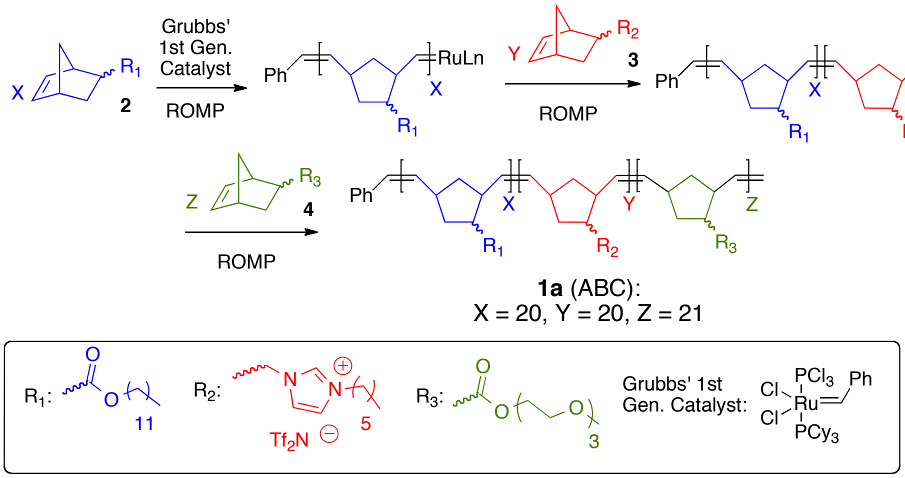
Scheme S2. Synthesis scheme for imidazolium-functionalized norbonene monomer **3**.



Scheme S3. Synthesis scheme for polyethylene glycol-functionalized norbornene monomer (**4**).

General Procedure for ROMP of Monomers 2, 3, and 4 to Form Triblock Copolymers.[1] A flame-dried Schlenk flask was charged with the desired amount of Grubbs 1st-generation catalyst and a stirbar under argon. The appropriate amount of CH_2Cl_2 was then added to the Schlenk flask to form a catalyst solution with the desired concentration. The appropriate amount of the first monomer was then added to the catalyst solution from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe under argon atmosphere. Upon consumption of all of the monomer (as verified by ^{1}H NMR analysis) to form the first copolymer block, the second monomer was added from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe. Upon complete consumption of the second monomer (as verified by ^{1}H NMR analysis) to form the second copolymer block, the third monomer was added from a dry, degassed stock solution

(CH_2Cl_2 solvent) via syringe. Upon completion of the third and final monomer, the ROMP triblock copolymerization mixture was quenched with excess of ethyl vinyl ether. The resulting triblock copolymer was then isolated by removal of the solvent in vacuo. ^{1}H NMR analysis of triblock copolymers **1a–c** confirmed the absence of any residual monomer.



Scheme S4. Sequential ROMP of monomers **2**, **3**, and **4** to yield triblock copolymer **1a**.

Sample Procedure for Sequential ROMP of Monomers 2, 3, and 4 to Form Triblock Copolymer 1a. Under argon atmosphere, Grubbs' 1st-generation catalyst (39.3 mg, 0.0478 mmol) was dissolved in dry, degassed CH_2Cl_2 (2.3 mL). Monomer **2** (7.72 g, 25.2 mmol) was diluted to a total volume of 25 mL with dry, degassed CH_2Cl_2. From this monomer solution, 0.95 mL (0.956 mmol) was added to the catalyst solution, and the reaction mixture was stirred at room temperature until the polymerization of **2** was complete (4 h). Monomer **3** (13.5 g, 25.0 mmol) was then diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2. From this monomer solution, 0.96 mL (0.96 mmol) was then added to the living ROMP polymerization mixture containing polymerized **2**, and the reaction was stirred at room temperature for 17 h. Monomer **4** (9.58 g, 33.7 mmol) was diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2. From this monomer solution, 0.71 mL (0.96 mmol) was added as the final sequential addition to the living ROMP triblock copolymerization, and the reaction was stirred at room temperature for 7 h. The ROMP copolymerization mixture was then quenched by addition of excess ethyl vinyl ether (3 mL). The resulting triblock copolymer **1a** was isolated by removal of the solvent and other volatile compounds in vacuo at ambient temperature for 24 h (1.10 g, 98% yield).

Note: The synthetic procedure for triblock copolymers ***1b*** *and* ***1c*** *used the same quantities of Grubbs' catalyst and monomers from the above listed monomer stock solutions, as well as block polymerization reaction times with the only procedural difference being the sequence of monomer addition. For* ***1b****, the monomer addition/block polymerization sequence order was* ***4****,* ***2****, and then* ***3****. For* ***1c****, the monomer addition/block polymerization sequence order was* ***2****,* ***4****, and then* ***3****.*

Triblock copolymers **1a–c**, albeit with varying alkyl hydrophobic:ionic:non-charged hydrophilic block sequences, have the same chemical shifts in ^{1}H and ^{13}C NMR within ±0.05 ppm due to being based on the same repeat units, so only one set of ^{1}H and ^{13}C NMR chemical shifts is presented for the sake of being non-repetitive. Copolymer block composition, block lengths, and extrapolated copolymer M_n values were determined via the combined use of ^{1}H NMR integration analysis, experimental confirmation of living ROMP character, and several control/comparison experiments against homopolymer physical blends, as detailed in our initial publication on the synthesis and basic characterization of these alkyl-imidazolium BCPs.[1] See the following sections for summaries of the spectroscopic, compositional, and M_n values of the triblock copolymer samples **1a–c** prepared in this paper and analyzed by these prior procedures, as well as examples of the determination methods.

(1a) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (br s, imidazolium C2), 7.28 (br s, imidazolium C4 and C5), 5.42-5.34 (b, -C(*H*)=C(*H*)-), 4.22-4.00 (b, -COO-C*H*$_2$-, -C(*H*)$_2$-N-CH-N-C(*H*)$_2$-(CH_2)$_4$$CH_3$), 3.66-3.38 (b, -O-(C*H*$_2$)$_2$-O-, -O-C*H*$_3$), 3.25-2.40 (br m, -imidazolium-(CH_2)$_5$-C*H*$_3$), 2.00-1.50 (b, -COO-(CH_2)$_{11}$-C*H*$_3$), 1.45-0.95 (br m, -COO-CH_2-(C*H*$_2$)$_{10}$-CH_3), 0.90-0.86 (br m, -imidazolium-CH_2-(C*H*$_2$)$_4$-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 162.8, 103.8, 71.9, 70.5, 69.2, 63.2, 59.1, 31.9, 30.8, 29.7, 29.4, 28.7, 22.7, 22.2, 14.1, 13.8. Block repeat unit molar ratio = 1:0.98:1.07 (alkyl hydrophobic:imidazolium ionic:non-charged hydrophilic); block length composition = 20-*b*-19.6-*b*-21.4; estimated M_n = 22,800 g mol^{-1}.

(1b) Block repeat unit molar ratio = 1:0.86:0.91 (non-charged hydrophilic:alkyl hydrophobic:imidazolium ionic); block length composition = 20-*b*-17.2-*b*-18.2; estimated M_n = 20,800 g mol^{-1}.

(1c) Block repeat unit molar ratio = 1:1.14:0.94 (alkyl hydrophobic:non-charged hydrophilic:imidazolium ionic); block length composition = 20-*b*-22.8-*b*-18.9; estimated M_n = 22,800 g mol^{-1}.

Determination of BCP Composition and Molecular Weights. As discussed in our previous paper,[1] conventional methods used to directly determine polymer molecular weights (e.g., GPC, NMR endgroup analysis, matric-assisted laser desorption ionization time-of-flight mass spectrometry, and light scattering) of our imidazolium-containing BCPs yielded inconclusive results. These difficulties are likely associated with the very different physical properties of these BCPs due to their highly ionic nature, compared to conventional non-charged polymers.[3] Consequently, the block composition ratios, block lengths, and estimated M_n values for triblock copolymers **1a–c** were determined via a combination of ^{1}H NMR repeat unit/block length composition analysis and confirmation of living polymerization behavior with observed molecular weight control for each monomer.

(a) Sample Calculation for Determining Hydrophobic:Imidazolium:Non-charged Hydrophilic Block Composition Ratios (for 1a). Block composition ratios were determined via ^{1}H NMR in order to compare the hydrophobic (alkyl), ionic (imidazolium), and non-charged hydrophilic blocks for each triblock copolymer. The signals for the unstrained alkene polymer backbone protons for all three blocks overlap between 5.34–5.42 ppm to create a broad peak (signal B in Figures S1–S3). The signals for the methylene protons adjacent to the ester linkers in the hydrophobic and non-charged hydrophilic blocks and the methylene protons adjacent to the imidazolium unit in the ionic block overlap to create a broad signal between 4.00–4.22 ppm (signal C in Figures S1–S3). The signals for the methylene protons in the ether chain in the non-charged hydrophilic block overlap to create a broad signal between 3.66–3.38 ppm (signal D in Figures S1–S3). There are 2 unstrained protons per repeat unit for the hydrophobic block (x), 2 unstrained protons per repeat unit for the imidazolium block (y), and 2 unstrained protons per repeat unit for the non-charged hydrophilic block (z) (see Equation S1). There are 2 methylene protons per repeat unit for the hydrophobic block (x), 2 methylene protons per repeat unit for the non-charged hydrophilic block (z), and 4 methylene protons per repeat unit for the imidazolium block (y) (see Equation S2). There are 13 methylene protons in the ether chain per repeat unit for the non-charged hydrophilic block (z) (see Equation S3).

$$2x + 2y + 2z = B_{1H\ NMR\ Integration} \qquad \text{(Eq. S1)}$$

$$2x + 4y + 2z = C_{1H\ NMR\ Integration} \qquad \text{(Eq. S2)}$$

$$13z = D_{1H\ NMR\ Integration} \qquad \text{(Eq. S3)}$$

Using the three equations to solve for the three unknowns, x, y, and z, the hydrophobic:imidazolium:non-charged hydrophilic block compositions (x, y, z) can be quantified for each triblock copolymer sample **1a**, **1b**, and **1c**, as shown below:

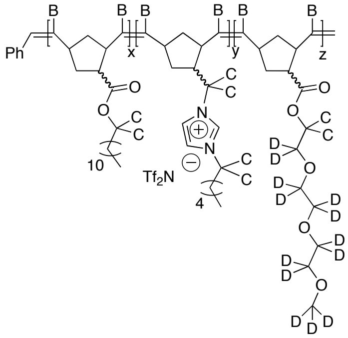
i. Block Composition Ratio for triblock copolymer 1a (Figure S1):

$$2x + 2y + 2z = 6.04$$

$$2x + 4y + 2z = 7.97$$

$$13z = 13.83$$

$$\mathbf{x = 1.0, y = 0.98, z = 1.07}$$



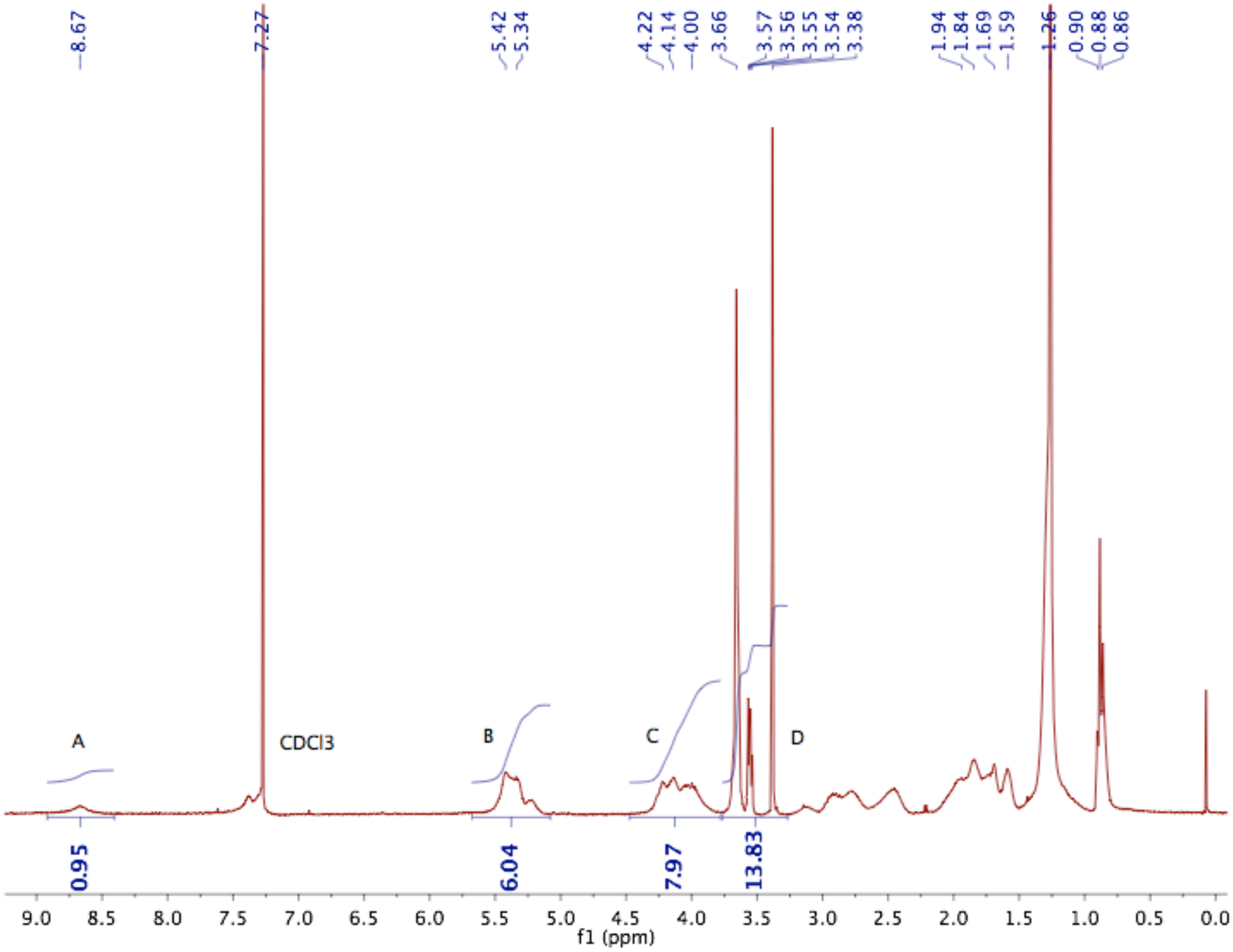


Figure S1. An example ^{1}H NMR spectrum of triblock copolymer **1a**, and the ^{1}H NMR peak assignments used to calculate the hydrophobic:ionic:non-charged hydrophilic block composition (i.e., repeat unit) ratio in **1a**.

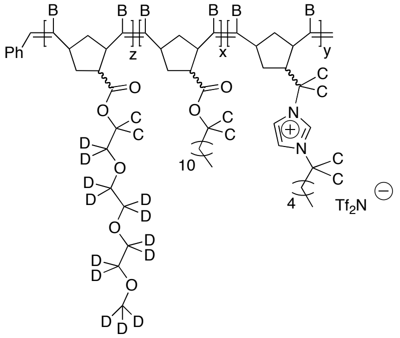
ii. Block Composition Ratio for triblock copolymer 1b (Figure S2):

$$2x + 2y + 2z = 6.30$$

$$2x + 4y + 2z = 8.37$$

$$13z = 14.85$$

$$\mathbf{z = 1.00, x = 0.86, y = 0.91}$$



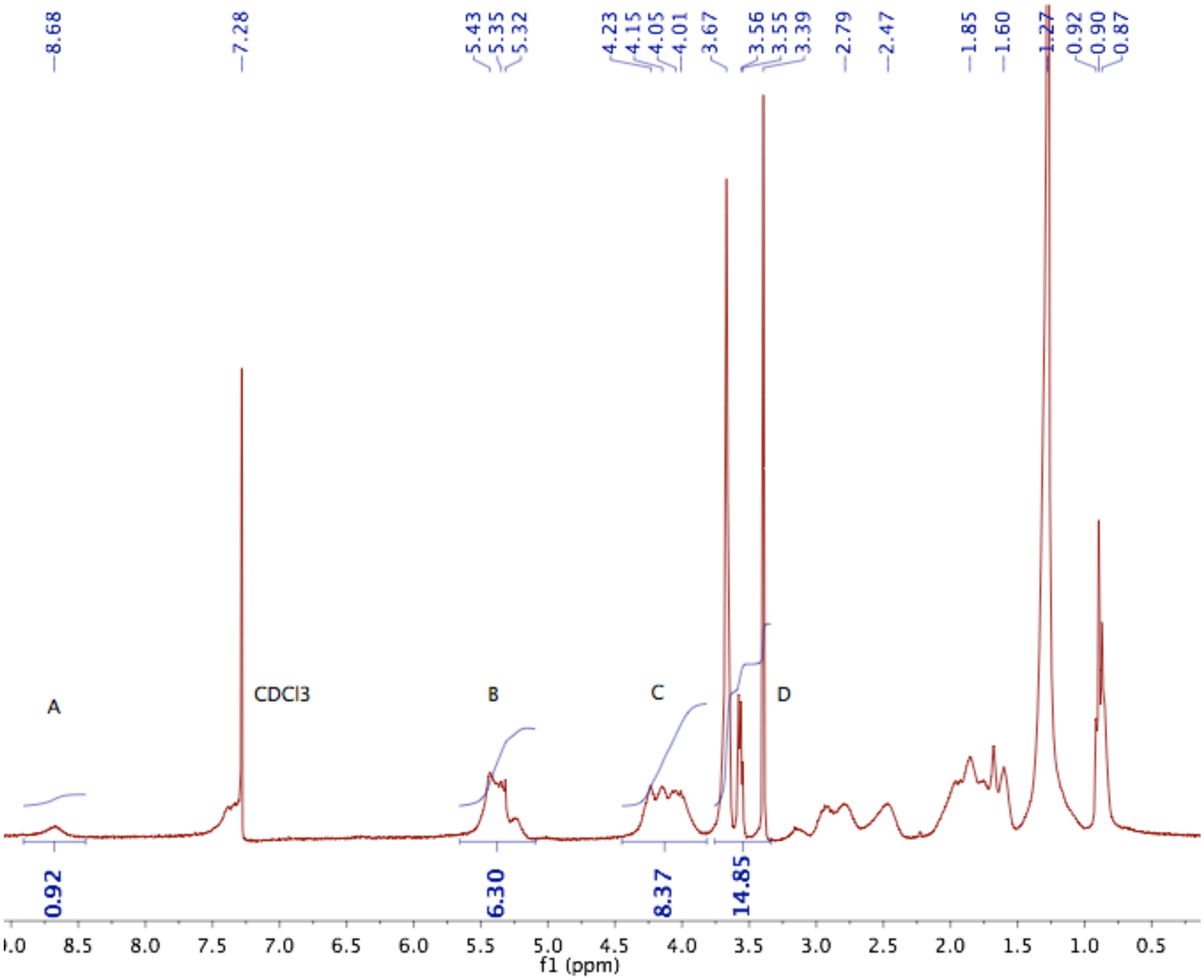


Figure S2. An example ^{1}H NMR spectrum of triblock copolymer **1b**, and the ^{1}H NMR peak assignments used to calculate the non-charged hydrophilic:hydrophobic:ionic block composition (i.e., repeat unit) ratio in **1b**.

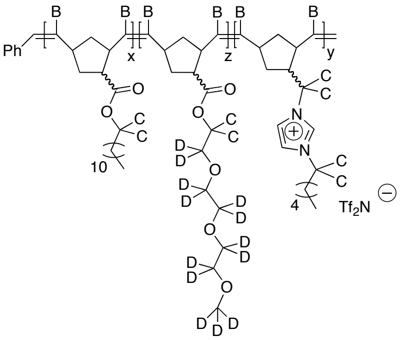
iii. Block Composition Ratio for triblock copolymer 1c (Figure S3):

$$2x + 2y + 2z = 7.51$$

$$2x + 4y + 2z = 9.80$$

$$13z = 18.08$$

$$\mathbf{x = 1.0, z = 1.14, y = 0.94}$$



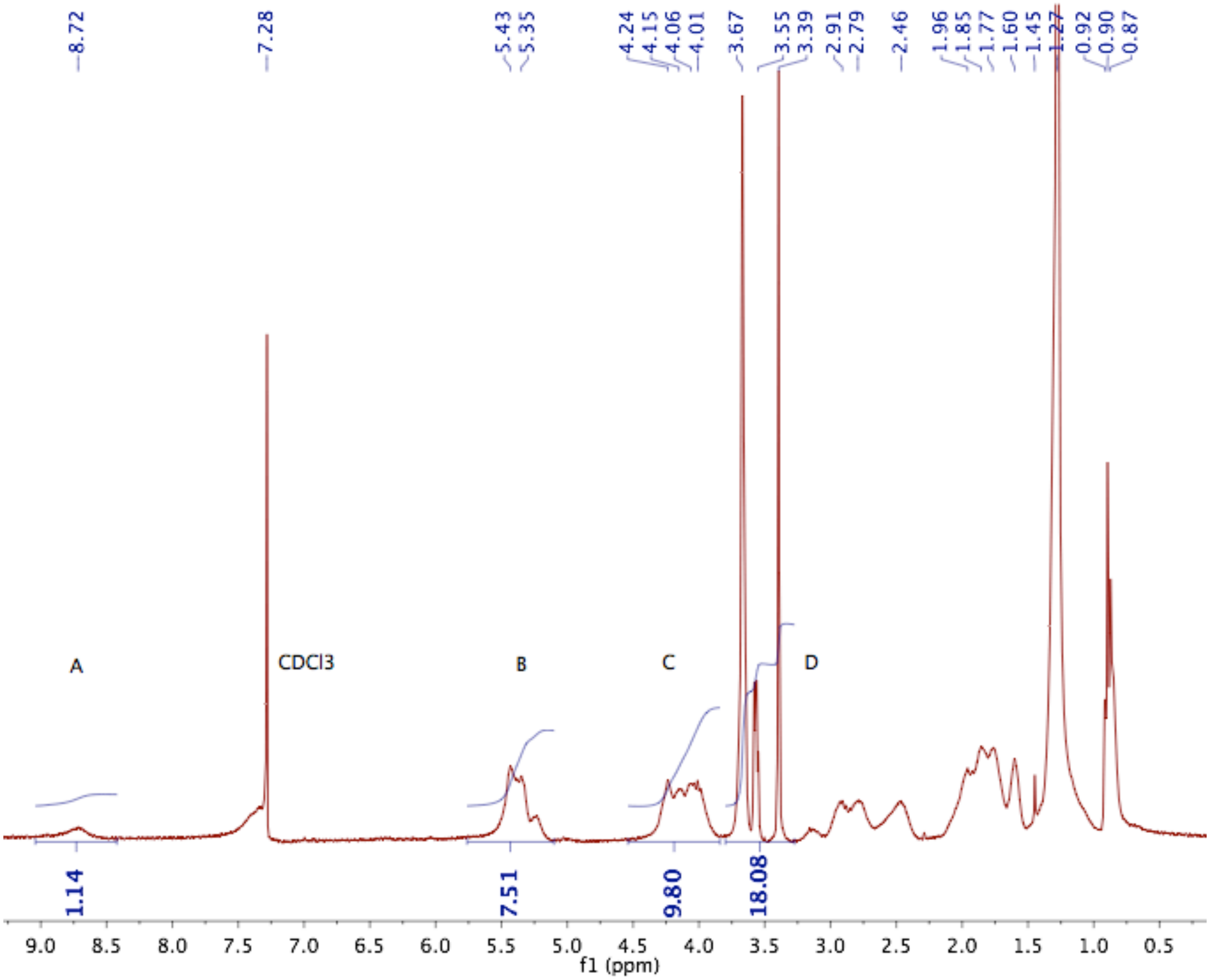
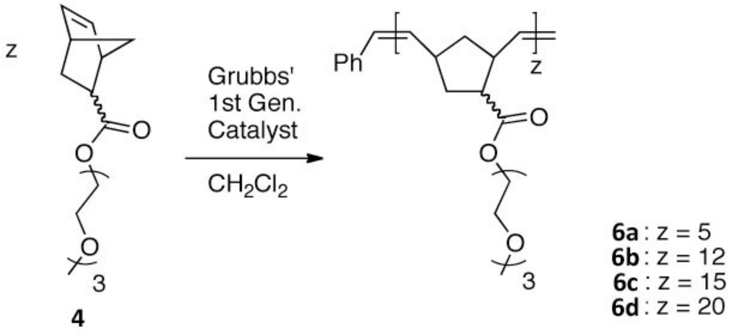


Figure S3. An example ^{1}H NMR spectrum of triblock copolymer **1c**, and the ^{1}H NMR peak assignments used to calculate the hydrophobic:non-charged hydrophilic:ionic block composition (i.e., repeat unit) ratio in **1c**.

(b) Monomer 4 verification of living polymerization character with molecular weight control. Living character and molecular weight control for ROMP homopolymerizations of monomers **2** and **3** are thoroughly discussed in our previous paper.[1] The same systematic ROMP homopolymerizations to verify linear molecular weight control, living character, and low-PDI nature of monomer **4** were performed and described here.

ROMP experiments with monomer **4** showed that increasing the monomer-to-catalyst ratio increases the (absolute) molecular weight while maintaining low PDI of poly(**4**) samples in a linear fashion by GPC analysis, indicative of a living polymerization with predictable molecular weight control. Four samples of poly(**4**) oligomers (i.e., **6a–d**) were synthesized by polymerizing monomer **4** with varying mole ratios of Grubbs' 1st-generation catalyst (Scheme S5). The number-average molecular weight (M_n) and PDI values of these model homopolymers were determined using GPC with polystyrene (PS) molecular weight standards in THF (Figure S4). The GPC M_n values were then compared to the absolute M_n values determined via ^{1}H NMR endgroup analysis. The GPC M_n values (vs. PS standards) for each homopolymer were found to be slightly different than the absolute M_n values determined by NMR endgroup analysis because poly(**4**) has a different chemical structure and thus a different hydrodynamic volume than PS in the same solvent. The measured PDI values ranged from 1.14–1.26, and a linear relationship was observed between monomer-to-catalyst molar ratio used in the ROMP reactions and the M_n values of the poly(**4**) samples formed (Figure S4).



Scheme S5. Non-charged hydrophilic oligomers (i.e., **6a–d**) used for M_n determination via GPC analysis (and substantiated by NMR endgroup analysis) in order to confirm living polymerization behavior.

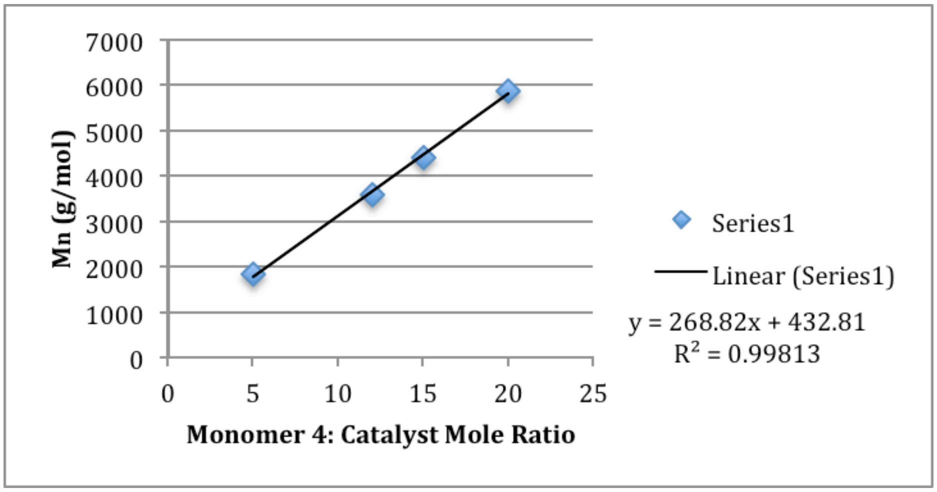


Figure S4. Linear relationship between monomer-to-catalyst molar ratio used and M_n from GPC analysis for various poly(**4**) oligomers. PDI values were consistent and ranged from 1.14-1.26, indicative of living polymerization with molecular weight control.

(c) Calculating Block Length Compositions. Based on the observed living characteristics for the ROMP of monomers **2**, **3**, and **4** by the Grubbs' 1st-generation catalyst, the block length compositions for triblock copolymers **1a–c** were calculated using the monomer-to-catalyst loading ratios (with complete monomer consumption), and the observed block composition (i.e., repeat unit) ratios for each triblock copolymer via

^{1}H NMR analysis (see Equations S4–S6). The blocky architecture and connectivity of **1a-c** are discussed and substantiated by the data presented in the main manuscript.

i. Block Length Composition for triblock copolymer **1a**:

[(Mon:Cat)($x_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($y_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($z_{\text{block ratio}}$)] (Eq. S4)

[(20)(1.0)]-*b*-[(20)(0.98)]-*b*-[(20)(1.07)] = 20-*b*-19.6-*b*-21.4

ii. Block Length Composition for triblock copolymer **1b**:

[(Mon:Cat)($z_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($x_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($y_{\text{block ratio}}$)] (Eq. S5)

[(20)(1.0)]-*b*-[(20)(0.86)]-*b*-[(20)(0.91)] = 20-*b*-17.2-*b*-18.2

iii. Block Length Composition for triblock copolymer **1c**:

[(Mon:Cat)($x_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($z_{\text{block ratio}}$)]-*b*-[(Mon:Cat)($y_{\text{block ratio}}$)] (Eq. S6)

[(20)(1.0)]-*b*-[(20)(1.14)]-*b*-[(20)(0.94)] = 20-*b*-22.8-*b*-18.9

(c) Calculating Triblock copolymer Molecular Weight. As mentioned previously, conventional methods used to directly determine the molecular weights of triblock copolymers **1a–c** (e.g., GPC, end group analysis) were attempted, but all yielded inconclusive results. The M_n value for each triblock copolymer **1a–c** was estimated by multiplying the calculated lengths of each block with the molecular weight value of the appropriate repeat unit:

i. Triblock copolymer **1a**:

$$20(307\ g/mol) + 19.6(540\ g/mol) + 21.4(285\ g/mol) \cong 22{,}800\ g/mol$$

ii. Triblock copolymer **1b**:

$$20(285\ g/mol) + 17.2(307\ g/mol) + 18.2(540\ g/mol) \cong 20{,}800\ g/mol$$

iii. Triblock copolymer **1c**:

$$20(307\ g/mol) + 22.8(285\ g/mol) + 18.9(540\ g/mol) \cong 22{,}800\ g/mol$$

Solubility Analysis. Triblock copolymers **1a–c** have unique solubility characteristics compared to an analogous physical blend (PB) mixture of poly(**2**) + poly(**3**) + poly(**4**). When mixed with MeOH at 10 wt %, triblock copolymers **1a–c** form lightly colored solutions, whereas PB analogues show clearly different behavior by forming heterogeneous mixtures (Figure S5).

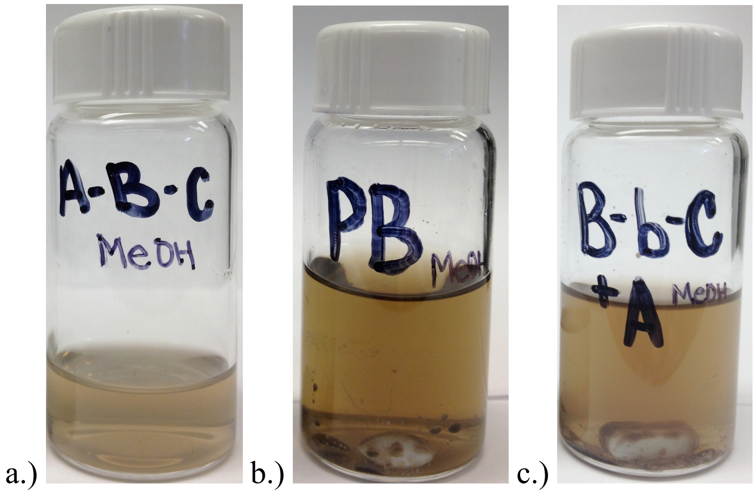


Figure S5. Photographs showing the difference in solubility behavior at 10 wt% loading in MeOH between: (a) triblock copolymer **1a**; (b) a (poly(**A**) + poly(**B**) + poly(**C**)) homopolymer physical blend; and (c) a (B-*b*-C diblock CP + poly(**2**)) physical blend.

NMR DOSY Studies. NMR DOSY experiments were performed using a Varian Inova-400 NMR spectrometer at 400.157 MHz for ^{1}H observation in DMSO-d_6 at 10 mg/mL sample concentration. Specific parameters were chosen as optimum to achieve nearly complete decay. Diffusion coefficients are listed below. As expected, the triblock copolymers **1a–c** each exhibit only one diffusion coefficient, indicative of only one species in solution, whereas the various PB control samples exhibit more than one diffusion coefficient, indicative of multiple polymer species present.

i. Triblock copolymer **1a**: 0.06×10^{-10} m^2/s

ii. Triblock copolymer **1b**: 0.07×10^{-10} m^2/s

iii. Triblock copolymer **1c**: 0.06×10^{-10} m^2/s

iv. PB of (poly(**2**) + poly(**3**) + poly(**4**)): 0.24×10^{-10}; 0.33×10^{-10}; 0.39×10^{-10} m^2/s

v. PB of (B-*b*-C diblock copolymer + poly(**2**)): 0.19×10^{-10}; 0.44×10^{-10} m^2/s

SAXS Analysis. In order to understand the phase separation between each interface (e.g., hydrophobic:ionic, hydrophobic:non-charged hydrophilic, ionic:non-charged hydrophilic), SAXS data was collected for 3 synthesized diblock copolymers with 25-*b*-25 block length compositions: AC (hydrophobic-*b*-non-charged hydrophilic), BC (ionic-*b*-non-charged hydrophilic), AB (hydrophobic-*b*-ionic). Representative SAXS data (100 °C) are shown in Figure S6 for each of the diblock copolymers synthesized. For AC and AB, prominent principal diffraction peaks in addition to multiple higher order reflections are consistent with melt-state lamellar (L) phase morphologies. For BC, neither a prominent principal diffraction peak nor any higher order reflections are observed. Therefore, no specific morphology can be assigned to BC. Notably, the d spacings ($d = 2\pi/q$) for the BCP species AC and AB are similar (AC: 22.9 nm and AB: 27.9 nm).

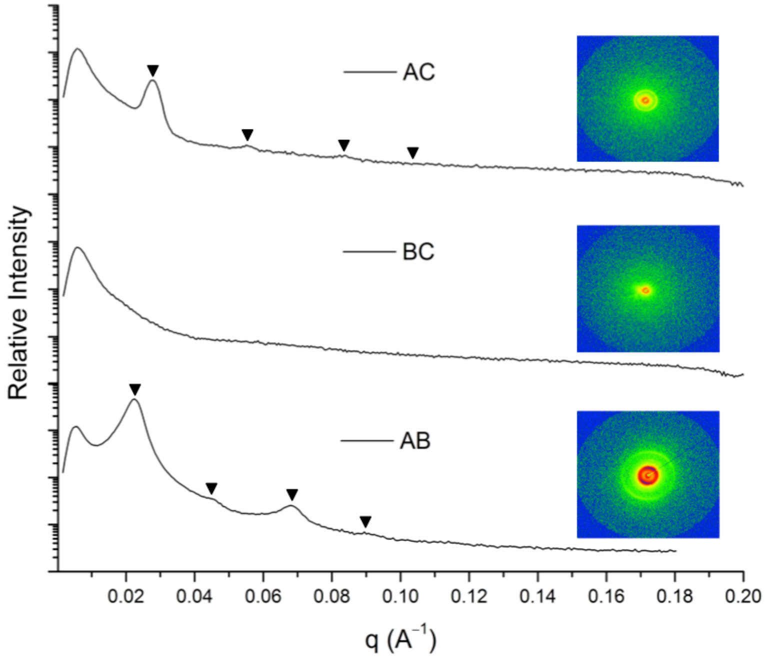
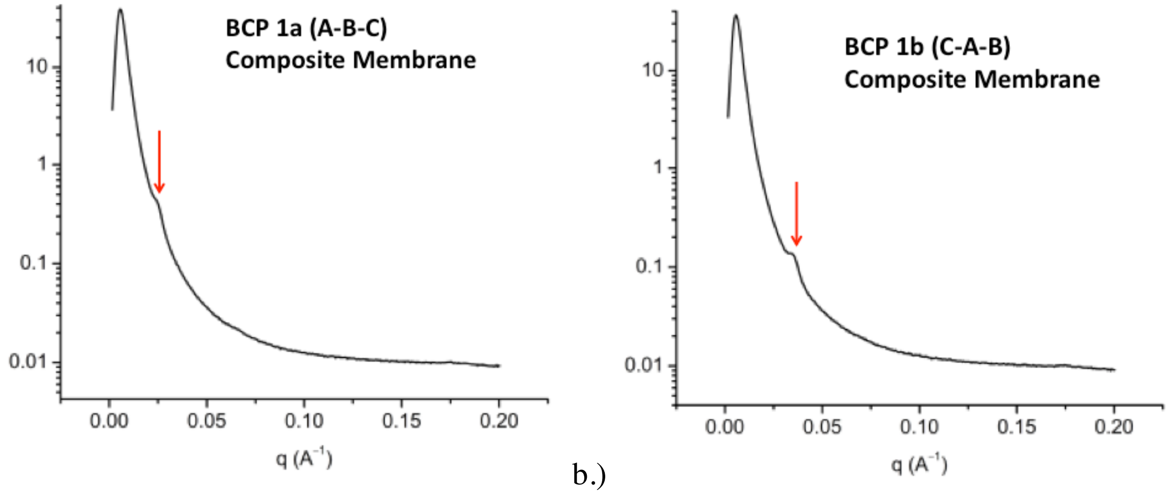


Figure S6. Comparison of SAXS data (collected at 100 °C from heating). Inverted filled triangles represent the location of the allowed reflections for the lamellar morphology, calculated based on the position of the primary scattering wave vector $\mathbf{q}_{100}$: (L) $\mathbf{q}/\mathbf{q}^*$ at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. Inset pictures are the 2D scattering patterns.

SAXS data were collected for the fabricated triblock CP composite membranes **1a** and **1b** (Figure S7). The appearance of the primary scattering peak confirms an ordered, phase-separated structure; however, further identification of an assigned morphology could not be assigned due to the absence of higher-order SAXS peaks. We believe this absence is due to the thin layer of the triblock CP (5–20 μm thick) on top of the much thicker membrane support (which is roughly 150 μm thick).



a.) b.)

Figure S7. SAXS data (collected at 100 °C from heating) of triblock CP composite membranes samples show phase separation evident by the observed primary scattering reflections of (a) triblock CP composite membrane **1a** and (b) triblock CP composite membrane **1b**.

Supported membrane Fabrication. Supported triblock copolymer membranes were fabricated with a 10 wt % triblock copolymer in THF solution, coated on top of a PAN support (supplied by Membrane Technology and Research). The solution quickly spread on the support by tilting the membrane, and the THF evaporated slowly at room temperature before drying under vacuum overnight.

Scanning Electron Microscope (SEM) Imaging. SEM imaging was performed using a JEOL JSM-6480LV, with the acceleration voltage set to 10–15 kV and a spot size of 50 nm. Samples were fractured in liquid nitrogen, dried under vacuum over night, and then coated with gold. At least two samples of each membrane were prepared and the thicknesses were measured at 3 different spots and averaged.

Gas Transport Properties Measurements via the Time-Lag Method. Single-gas permeability values for the supported triblock copolymer membranes were measured by a time-lag apparatus as previously reported.[4] Each experiment began under vacuum conditions and was performed at room temperature (20 °C). Pure gas was applied at feed pressure around 1 bar, measured by an Omega pressure transducer (0–7 bar). The permeate pressure increased with time and was recorded by an Omega pressure transducer (0–1 bar). Permeability measurements of every gas were carried out three times for each membrane, and the experimental error was found to be less than 1.5%. The ideal permeability selectivity (α) is defined as the ratio of the permeability of the more permeable species to the permeability of the less permeable species.

References for Supporting Information:

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