

Supporting Information: ABA Triblock Brush Polymers: Synthesis, Self-Assembly, Conductivity, and Rheological Properties

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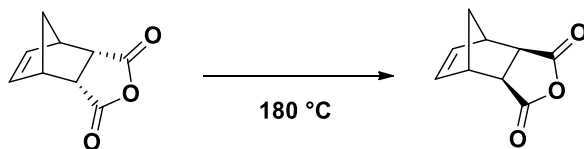
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General:

All reagents were used as received unless otherwise noted. Carbic anhydride was purchased from Acros Organics. Propargylamine, copper(I) bromide, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), methyl α -bromoisobutyrate, N,N,N',N''-pentamethyldiethylenetriamine (PMDETA), sodium azide, triethylamine, 6-aminohexanoic acid, 4-dimethylaminopyridine, poly(ethylene glycol) methyl ether ($M_n=2000$ g/mol), and pyridine were purchased from Sigma Aldrich. Grubbs' second-generation catalyst $[(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh]$ was generously supplied by Materia. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotopes Labs. Toluene, benzene, dichloromethane (DCM), dimethylformamide (DMF), methanol, tetrahydrofuran (THF), pentane, sodium sulfate, and magnesium sulfate were purchased from VWR.

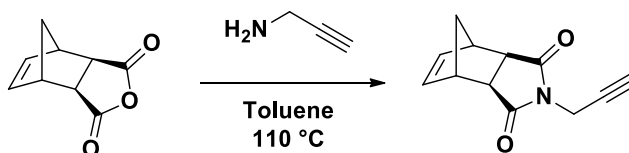
Synthesis of norbornene *exo*-anhydride (1):



Scheme S1: Synthesis of norbornene *exo*-anhydride.

A 500 mL round bottom flask was half filled with commercially available norbornene *endo*-anhydride (carbic anhydride), fitted with a reflux condenser, and heated neat at 180 °C for 16 hours. The resulting molten yellow solid was slowly cooled to 75 °C and benzene was added before the entire volume crystallized to facilitate dissolution. The resulting mixture was heated to reflux and crystallized at room temperature. The recrystallization in benzene was repeated three additional times to yield a white or slightly off-white crystalline solid (ca. 30 g isolated mass). 1H NMR ($CDCl_3$) δ (ppm): 6.31 (2H, t), 3.43 (2H, s), 2.99 (2H, s), 1.65 (1H, m), 1.42 (1H, m).

Synthesis of norbornene propargyl imide (2):

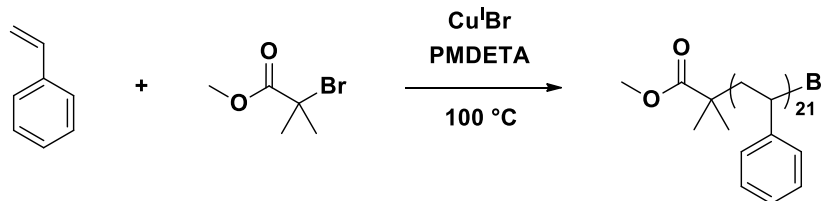


Scheme S2: Synthesis of norbornene propargyl imide.

Norbornene *exo*-anhydride (**1**) (1.0 eq., 62.59 g, 381.2 mmol), propargylamine (1.0 eq., 21.00 g, 381.2 mmol), triethylamine (0.1 eq., 3.86 g, 38.1 mmol) and toluene (300 mL) were mixed in a round bottom flask equipped with a Dean-Stark trap. The mixture was heated to reflux for 15 hours. The resulting orange solution was cooled to room temperature, and the toluene was removed *in vacuo*. The crude solid was recrystallized in ethanol to yield light brown, plate-like crystals (56.25 g). ¹H NMR (CDCl₃) δ (ppm): 6.28 (2H, m), 4.20 (2H, d), 3.30 (2H, m), 2.70 (2H, d), 2.17 (1H, t), 1.50 (1H, d), 1.25 (1H, d).

Synthesis of polystyrene macromonomer:

- 1) Synthesis of polystyrene (**3**) using atom transfer radical polymerization

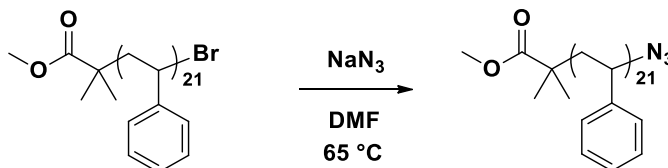


Scheme S3: Atom transfer radical polymerization of styrene.

Styrene monomer (500 mL) was stirred with basic alumina for 30 min and filtered to yield a clear liquid. Styrene (50.0 eq., 350 mL, 3.054 mol) was added to a 500 mL Schlenk flask equipped with a stir bar and septum. The flask was charged with ligand *N,N,N',N',N''*-pentamethyldiethylenetriamine (0.3 eq., 3.83 mL, 0.018 mol) and subsequently freeze-pump-thawed three times to remove oxygen. The flask was frozen in liquid nitrogen, placed under an active flow of argon (while still frozen), and Cu^IBr (0.3 eq., 2.63 g, 0.018 mol) was quickly added upon removal of the septum. The septum was re-attached, the argon flow stopped, and the flask was evacuated. (Caution: argon condenses at liquid nitrogen temperatures and can cause an explosion upon expansion when thawed.) Three additional pump/purge (argon/vacuum) cycles were performed and the flask was left under dynamic vacuum for at least 5 min. The flask was thawed in warm water and placed under argon. Most, but not all, of the copper dissolved to yield a green solution. (A blue color indicates oxygen contamination; a yellow color indicates insufficient copper dissolution – both result in a failed polymerization.) In a separate flask, methyl α -bromoisobutyrate was freeze-pump-thawed three times. Methyl α -bromoisobutyrate (1.0 eq., 7.90 mL, 0.061 mol) was injected into the Schlenk flask containing styrene and the

mixture was heated in an oil bath pre-set to 100 °C. Aliquots were collected every ca. 30 min under a dynamic flow of argon. Conversion was monitored by ¹H NMR. The polymerization was quenched in liquid nitrogen after 2 hr 35 min at approximately 38% conversion. The viscous solution was warmed to room temperature, diluted with tetrahydrofuran (100 mL), filtered through basic alumina to remove copper, and precipitated into methanol at -78 °C. The polymer was redissolved in THF and reprecipitated five more times into methanol at -78 °C and dried *in vacuo* to yield a white powder.

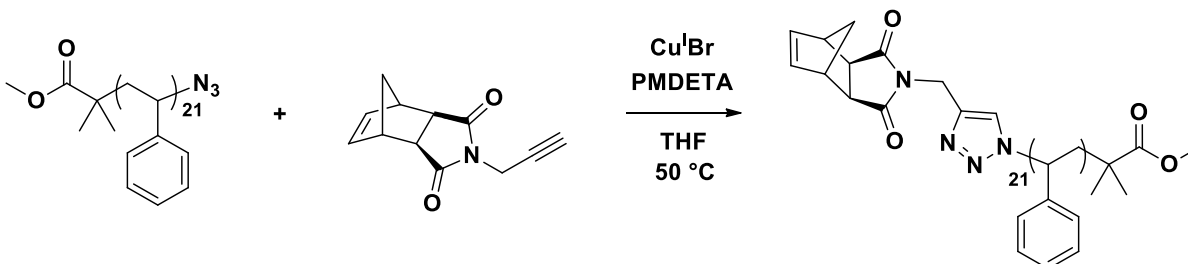
2) Synthesis of polystyrene-azide (**4**)



Scheme S4: Synthesis of polystyrene-azide.

Polystyrene (**3**) (1.0 eq., 73 g, 37.0 mmol), sodium azide (3.0 eq., 7.12 g, 109.5 mmol), and dimethylformamide (350 mL) were mixed in a round bottom flask equipped with a stir bar and reflux condenser. The mixture was heated at 65 °C for 16 hr and then cooled to room temperature. The product was precipitated into methanol at -78 °C, redissolved in THF, and the precipitation procedure was repeated 4 additional times. Quantitative conversion of the end group was observed by ¹H NMR (CDCl₃) δ (ppm): PS-Br 4.6–5.0 ppm, PS-N₃ 3.75–4.25.

3) Synthesis of polystyrene macromonomer (**5**)

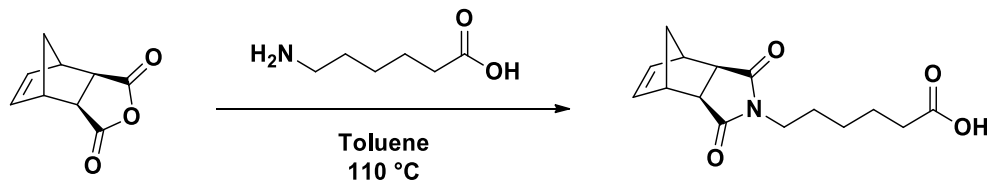


Scheme S5: Synthesis of polystyrene macromonomer.

Polystyrene-azide (**4**) (1.0 eq., 64.30 g, 30.6 mmol), norbornene propargyl imide (**2**) (1.5 eq., 9.24 g, 45.9 mmol), and Cu^IBr (0.4 eq., 1.76 g, 12.3 mmol) were added to a 500 mL three-neck round bottom flask equipped with a stir bar, reflux condenser, and two septa. The flask was pump/purged with argon three times and placed under argon. Dry tetrahydrofuran (180 mL) was added via syringe, followed by N,N,N',N',N''-pentamethyldiethylenetriamine (0.4 eq., 2.56 mL, 12.3 mmol), upon which the solution turned light green and clear. The flask was heated at 50 °C for 16 hr and cooled to room temperature. The solution was diluted with tetrahydrofuran (100 mL), filtered through basic alumina to remove the copper, and precipitated into methanol at -78 °C. The precipitation was repeated 5 additional times to yield a white powder.

Quantitative conversion of the end group was observed by ^1H NMR (CDCl_3) δ (ppm): PS- N_3 3.75–4.25, PS-norbornene 4.89–5.05.

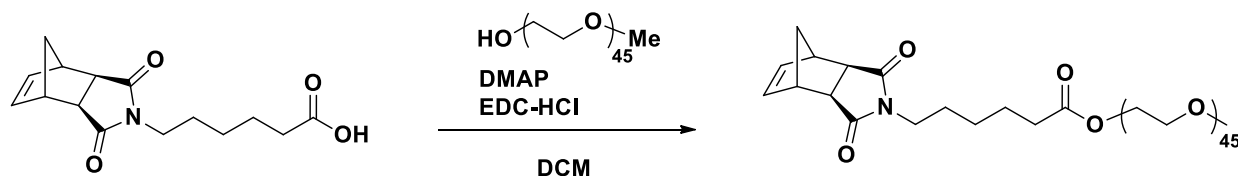
Synthesis of norbornene carboxylic acid imide (6):



Scheme S6: Synthesis of norbornene carboxylic acid imide.

Norbornene *exo*-anhydride (**1**) (1.0 eq., 8 g, 48.7 mmol), 6-aminohexanoic acid (1.0 eq., 6.39 g, 48.7 mmol), triethylamine (0.1 eq., 0.679 mL, 4.87 mmol), and toluene (51 mL) were added to a round bottom flask equipped with a stir bar and reflux condenser. The mixture was heated at $110\text{ }^\circ\text{C}$ for 19 hr, cooled to room temperature, and the solvent was removed *in vacuo*. The remaining solid was redissolved in dichloromethane, washed with water (x3), washed with brine (x3), and dried with magnesium sulfate. The solvent was removed *in vacuo* to yield a white or slightly off white solid. ^1H NMR (CDCl_3) δ (ppm): 6.28 (2H, m), 3.46 (2H, t), 3.27 (2H, m), 2.35 (2H, t), 1.72–1.18 (10H, m).

Synthesis of PEO macromonomer (7):



Scheme S7: Synthesis of PEO macromonomer.

Norbornene carboxylic acid imide (**6**) (1.2 eq., 19.742 g, 71.2 mmol), poly(ethylene glycol) methyl ether ($M_n=2000\text{ g/mol}$, 1.0 eq., 118.641 g, 59.3 mmol), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.6 eq., 18.244 g, 117.5 mmol), 4-dimethylaminopyridine (0.1 eq., 0.725 g, 5.9 mmol), and dichloromethane (790 mL) were mixed in a 1 L round bottom flask equipped with a stir bar. The reaction was stirred for 24 hr and about half of the dichloromethane was removed *in vacuo*. The mixture was washed with 1 M HCl (x3), brine (x1), and dried with sodium sulfate. Most of the solvent was removed *in vacuo* and the remaining solution was precipitated into diethyl ether at $-78\text{ }^\circ\text{C}$. The off-white solid was filtered and dried *in vacuo* to yield 123.3 g (93%) of isolated material.

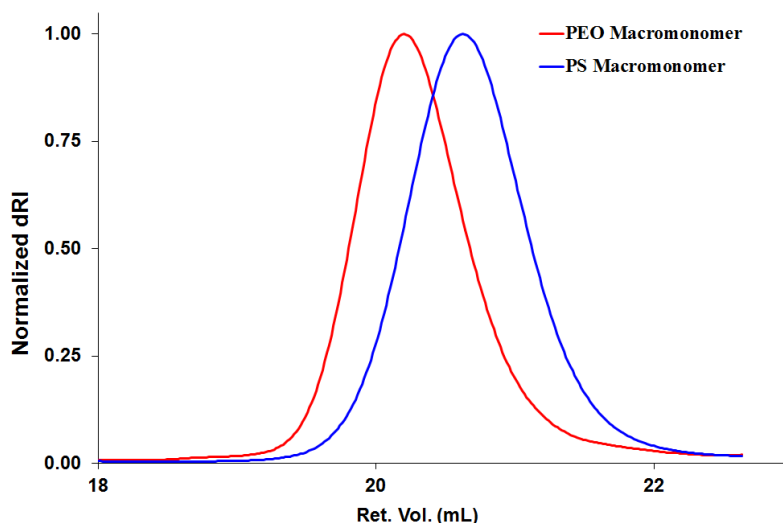


Figure S1: Size exclusion chromatograms of polystyrene and poly(ethylene oxide) macromonomers. Mobile phase: THF with 1 vol% triethylamine.

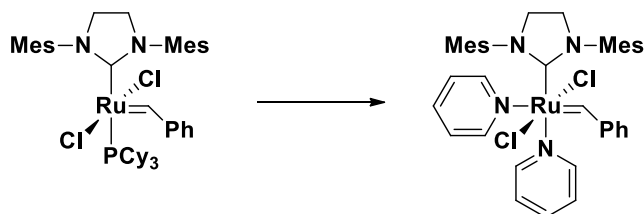
Table S1: Macromonomer molecular weight information.

Macromonomer	Molecular Weight (kDa)				\bar{D}	N
	M_n (NMR)	M_n (SEC)	M_w (SEC)	M_w (SEC)		
PS	2.54	2.43	2.50	2.50	1.03	21 [#]
PEO	2.46	2.58	2.68	2.68	1.04	45 [*]

[#]Determined by ¹H NMR, excludes endgroups

^{*}As reported by supplier

Synthesis of ruthenium catalyst [(H₂IMes)(pyr)₂(Cl)₂Ru=CHPh] (8)

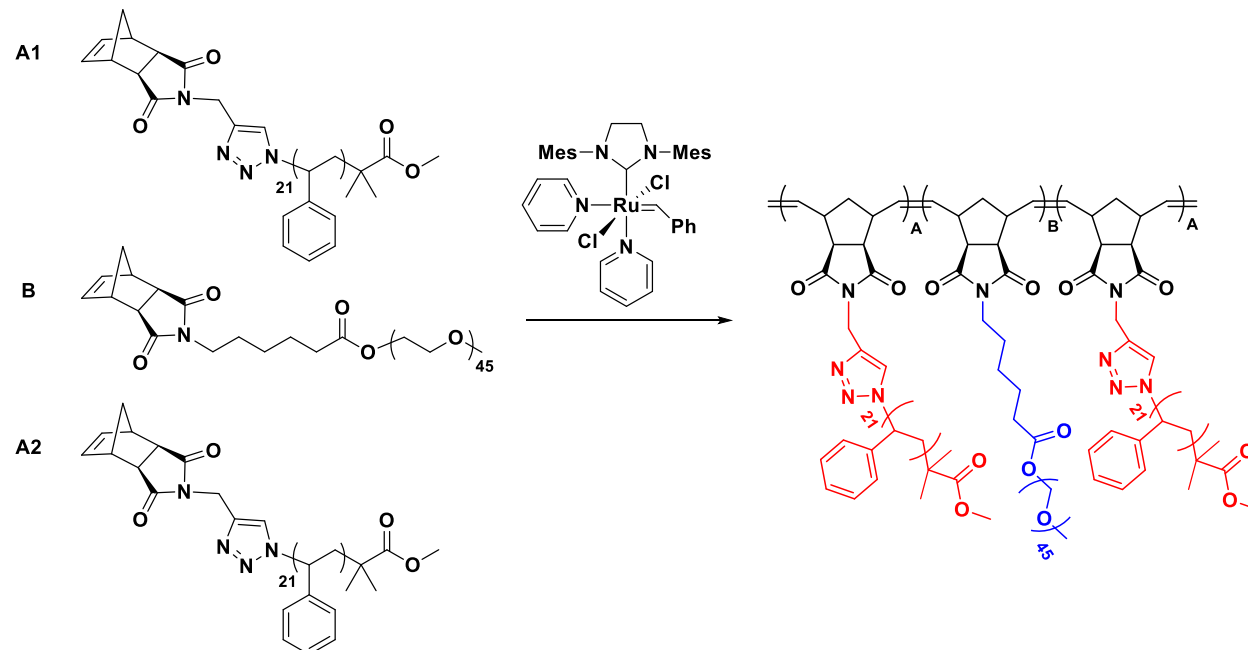


Scheme S8: Synthesis of bispyridine ruthenium catalyst.

Grubbs' second-generation catalyst [(H₂IMes)(PCy₃)(Cl)₂Ru=CHPh] (1.0 eq., 1.0 g, 1.4 mmol) and pyridine (30.0 eq., 3.3 mL, 41.4 mmol) were mixed in a 30 mL glass jar. The mixture was stirred in air at room temperature for 5 minutes. A color change from dark purple-red to dark green was immediately observed. After 5 minutes, room-temperature pentane (15 mL) was layered onto the green mixture. The jar was capped under air and cooled in a freezer for 24 hr. After 24 hr, the catalyst was isolated by vacuum filtration, washed with 30 mL pentane (x3), and dried *in vacuo* to afford 0.87 g (87%) of isolated

material. ^1H NMR (C_6D_6) δ (ppm): 19.63 (1H, s), 8.63 (2H, s), 8.33 (2H, s), 8.02 (2H, d), 7.19 (1H, t), 6.87–6.11 (9H, m), 3.41 (4H, d), 2.83 (6H, s), 2.42 (6H, s), 2.12 (6H, s).

Synthesis of poly[(norbornene-*graft*-styrene)-*block*-(norbornene-*graft*-ethylene oxide)-*block*-(norbornene-*graft*-styrene)] (gPS-*g*PEO-*g*PS) (9):



Scheme S9: Synthesis of ABA triblock brush polymers.

In a glove box, three separate vials were prepared containing solutions of macromonomers in dry dichloromethane. Vial A1: PS macromonomer (10.0 eq., 0.635 g), DCM (4.27 mL); Vial B: PEO macromonomer (80.0 eq., 4.554 g), DCM (40 mL); Vial A2: PS macromonomer (10.0 eq., 0.635 g), DCM (5 mL). A fourth vial was prepared with the ruthenium catalyst (31.1 mg, 0.025 mmol) in 1.244 mL DCM. The polymerization was initiated by injecting 0.726 mL of the catalyst solution into vial A1. After 40 minutes, a small aliquot was extracted, quenched with ethyl vinyl ether, and vial B was quickly added in full to vial A1. After 100 min, a small aliquot was extracted, quenched with ethyl vinyl ether, and vial A2 was added in full to vial A1. After 120 min, vial A1 was removed from the glove box, rapidly stirred, and quenched with 5 mL of ethyl vinyl ether. The ABA triblock brush polymer was precipitated into diethyl ether (600 mL) at $-78\text{ }^\circ\text{C}$, filtered, and dried *in vacuo* to yield an off white powder.

Size Exclusion Chromatography (SEC):

SEC data were collected using two MZ-Gel SDplus 300x8.0 mm columns with $10\text{ }\mu\text{m}$ beads, an Agilent 1100 series autosampler and pump, and a Wyatt ViscoStar viscometer, Optilab rEX differential refractive index detector, and three-angle miniDAWN TREOS light scattering detector. On-line determination of dn/dc assumed 100% mass elution under the peak of interest. The mobile phase was THF with 1 vol%

triethylamine, which eliminated artificial dragging effects in pure THF (presumably arising from PEO/column interactions).

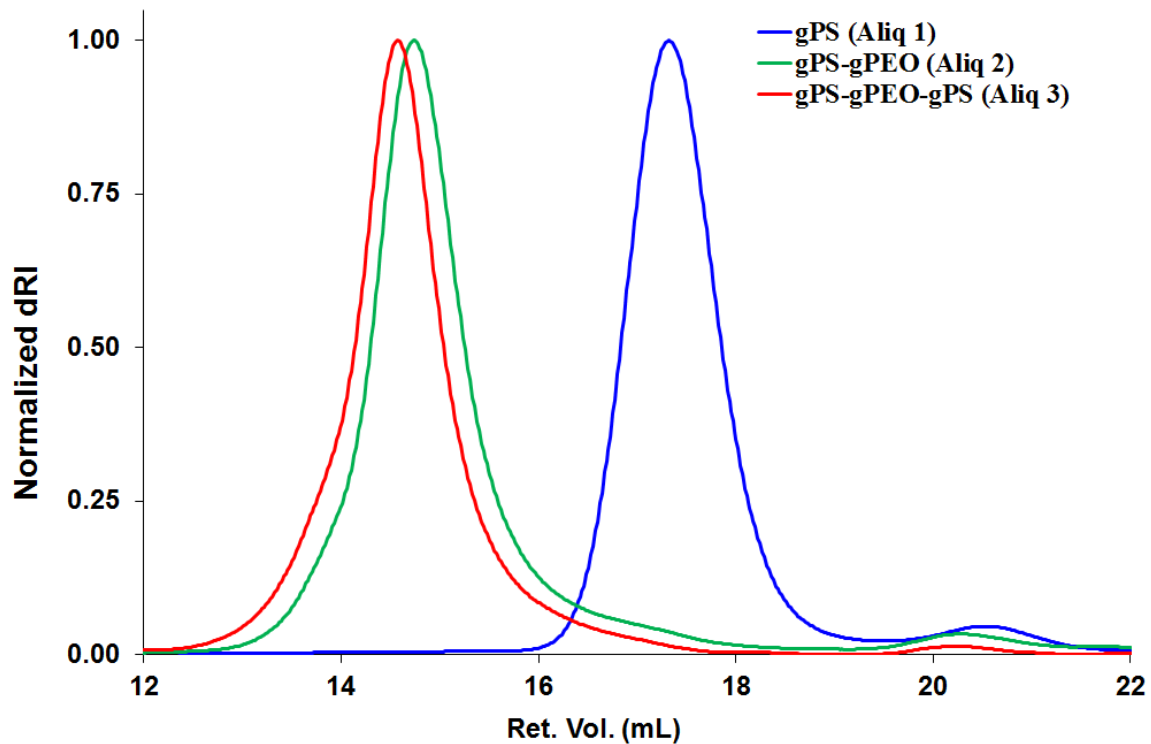


Figure S2: Size exclusion chromatograms of gPS_{11} - $gPEO_{78}$ - gPS_{11} triblock brush polymer. Mobile phase: THF with 1 vol% triethylamine.

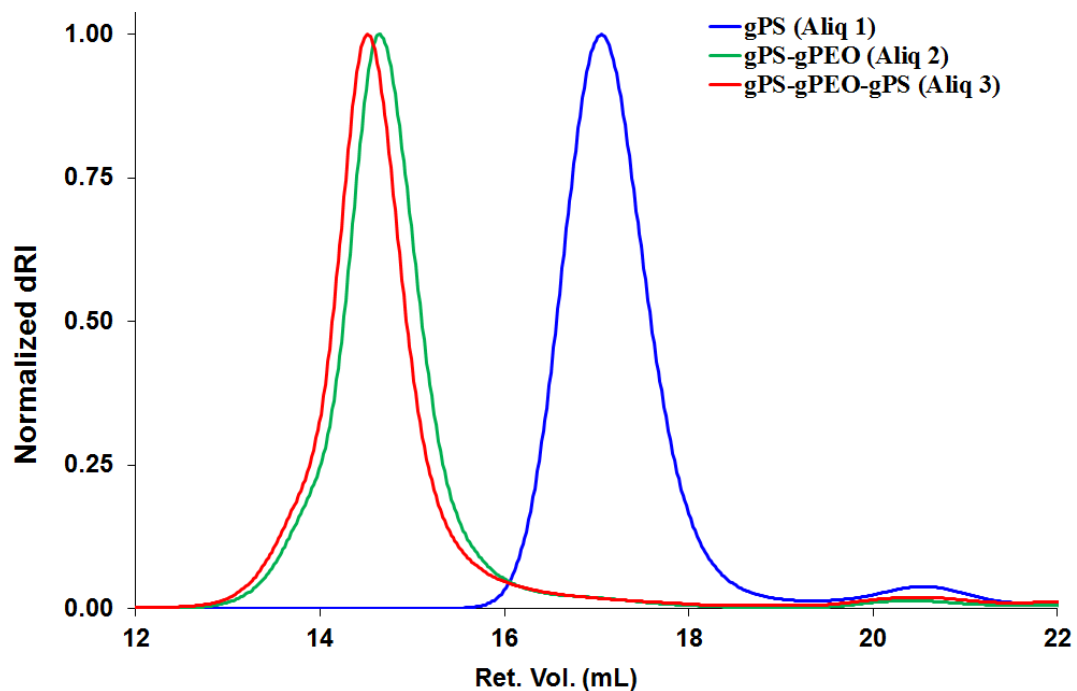


Figure S3: Size exclusion chromatograms of gPS_{15} - $gPEO_{119}$ - gPS_{15} triblock brush polymer. Mobile phase: THF with 1 vol% triethylamine.

Table S2: Summary of gPS_{11} - $gPEO_{78}$ - gPS_{11} triblock brush polymer size exclusion chromatography molecular weight data. The dn/dc value of the diblock and triblock copolymers was arbitrarily set to 0.050.

Sample	N_{target}	N_{calc}	M_n (kDa)	SEC		\bar{D}	dn/dc (mL/g)
				M_w (kDa)	\bar{D}		
gPS_{11}	10	11 [^]	28.8	29.3	1.02	0.165 [*]	
gPS_{11} - $gPEO_{78}$	10-80	11 [^] -78 [#]	459.7	518.3	1.13	0.050	
gPS_{11} - $gPEO_{78}$ - gPS_{11}	10-80-10	11 [^] -78 [#] -11 [#]	656.5	764.8	1.17	0.050	

[#]Calculated by ¹H NMR

[^]Calculated by SEC

^{*}Measured by SEC

Table S3: Summary of gPS_{15} - $gPEO_{119}$ - gPS_{15} triblock brush polymer size exclusion chromatography molecular weight data. The dn/dc value of the diblock and triblock copolymers was arbitrarily set to 0.050.

Sample	N_{target}	N_{calc}	M_n (kDa)	SEC		\bar{D}	dn/dc (mL/g)
				M_w (kDa)	\bar{D}		
gPS_{15}	15	15 [^]	38.41	38.55	1.00	0.165*	
gPS_{15} - $gPEO_{119}$	15-120	15 [^] -119 [#]	562.6	604.2	1.07	0.050	
gPS_{15} - $gPEO_{119}$ - gPS_{15}	15-120-15	15 [^] -119 [#] -15 [#]	710.0	769.3	1.08	0.050	

[#]Calculated by 1H NMR

[^]Calculated by SEC

*Measured by SEC

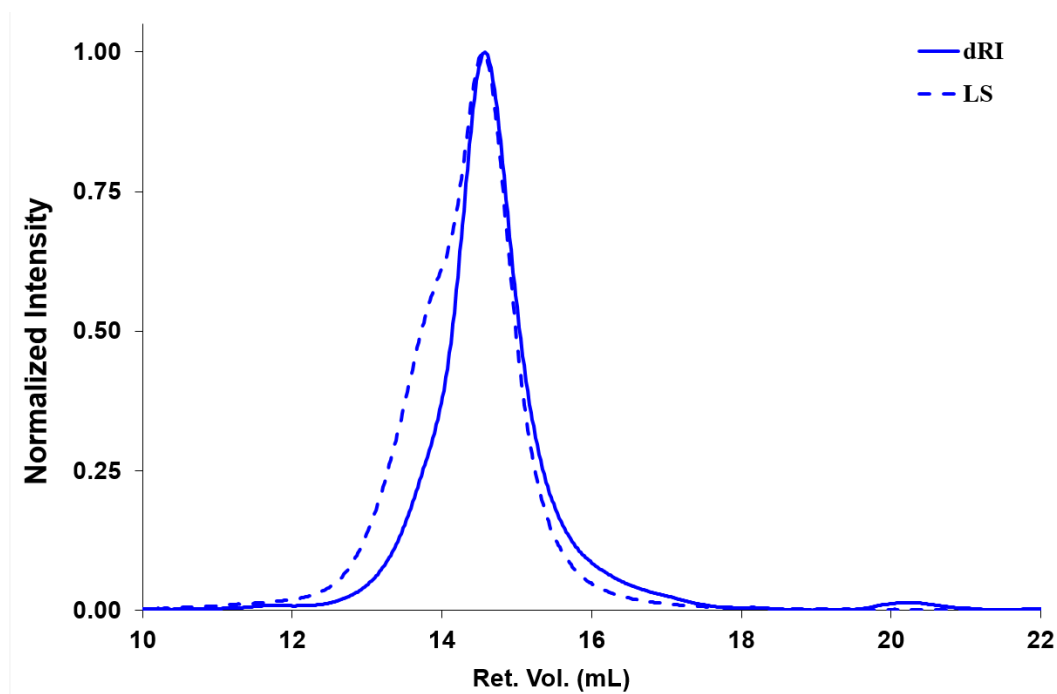


Figure S4: Comparison of gPS_{11} - $gPEO_{78}$ - gPS_{11} differential refractive index (dRI) and light scattering (LS) SEC traces.

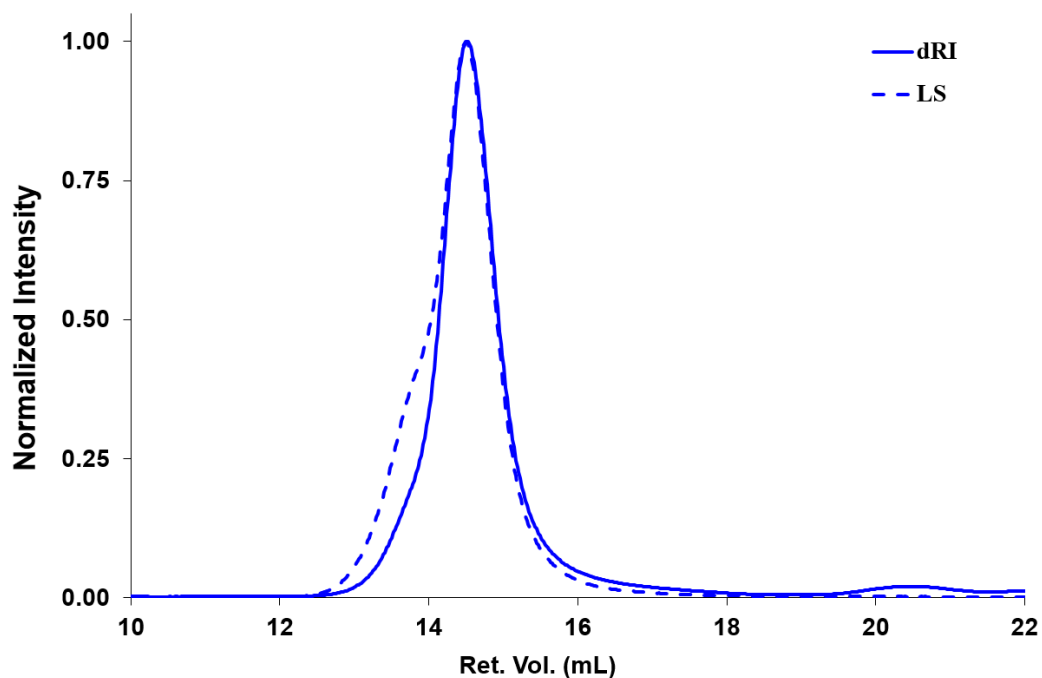


Figure S5: Comparison of gPS_{15} - $gPEO_{119}$ - gPS_{15} differential refractive index (dRI) and light scattering (LS) SEC traces.

The high molecular weight shoulder in the light scattering SEC signal (**Figure S4-S5**) is exacerbated at high PEO N_B values (data not shown). We have evidence that this shoulder is related to an impurity in the commercially available (Sigma Aldrich) mono-functional 2000 g/mol PEO. Since the LS signal $\sim M \cdot c$ (where M is molecular weight and c is polymer concentration) while the dRI signal $\sim c$, the concentration of species giving rise to the shoulder for gPS_{11} - $gPEO_{78}$ - gPS_{11} and gPS_{15} - $gPEO_{119}$ - gPS_{15} is relatively small at this N . The orders of magnitude price difference between small quantities of extensively purified PEO (e.g. from Jenkem) and large quantities of readily available PEO may warrant using the latter if a process is capable of tolerating the behavior observed in **Figures S4-S5**.

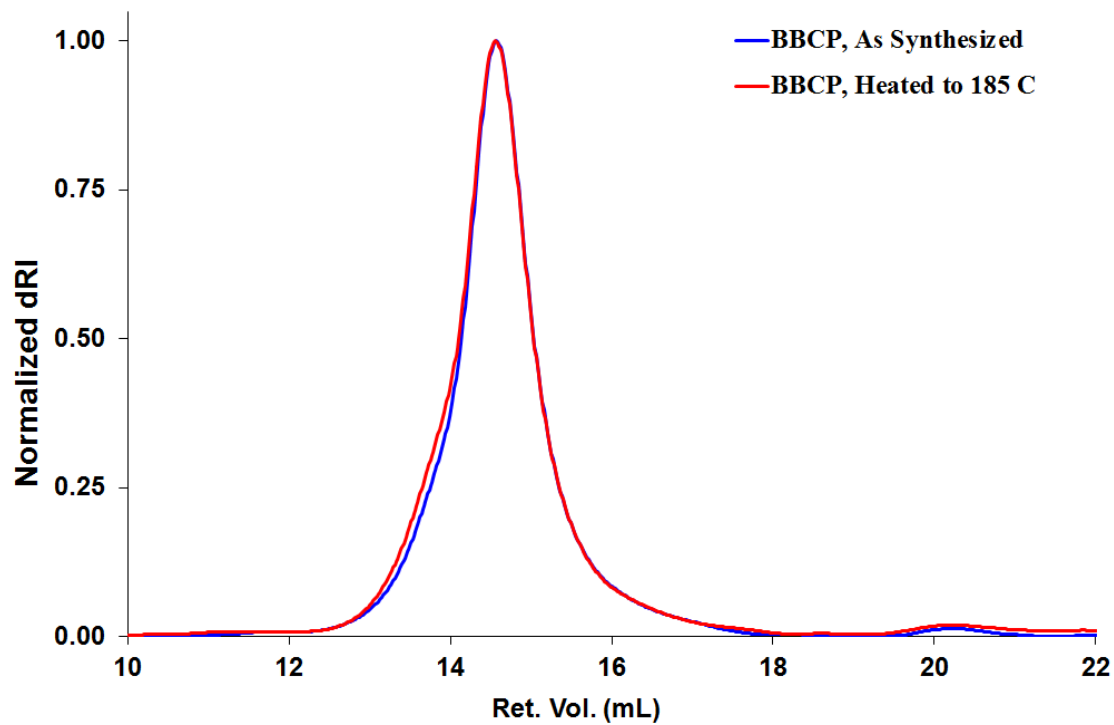


Figure S6: Thermal stability of gPS_{11} - $gPEO_{78}$ - gPS_{11} as measured by SEC. **Blue curve:** as synthesized. **Red curve:** sample characterized by rheology (maximum heating temperature 185 °C, under N_2).

Table S4: SEC molecular weight characterization corresponding to **Figure S6**.

Sample	M_n (kDa)	M_w (kDa)	\mathcal{D}
As Synthesized	656.5	764.8	1.17
Heated to 185 °C	730.4	882.8	1.21

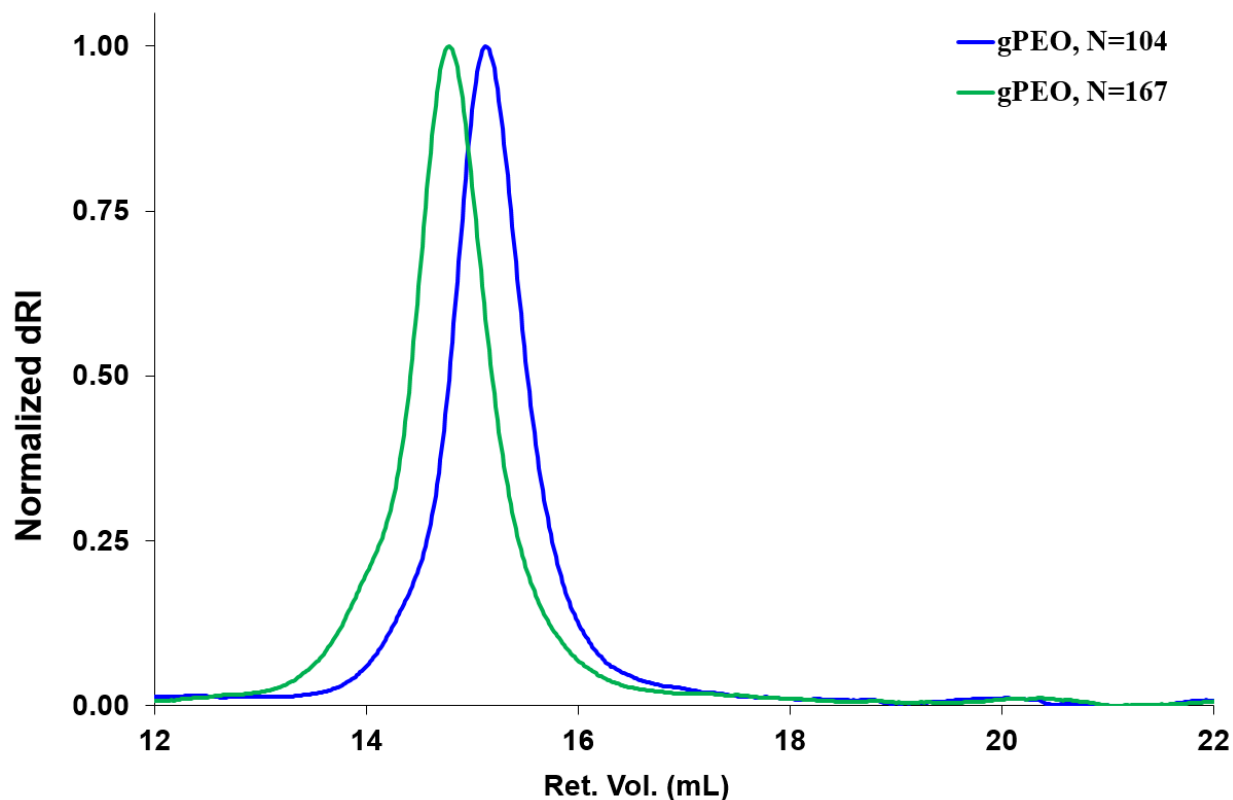


Figure S7: *g*PEO brush homopolymer ($N=104$ and 167) SEC traces.

Table S5: *g*PEO SEC molecular weight characterization corresponding to **Figure S7**.

Sample	N_{calc}	M_n (kDa)	M_w (kDa)	\bar{D}	dn/dc (mL/g)
<i>g</i> PEO ₁₀₄	104	237.2	253.2	1.07	0.0566
<i>g</i> PEO ₁₆₇	167	381.2	418.4	1.10	0.0566

Differential Scanning Calorimetry (DSC):

Differential scanning calorimetry (DSC) data were collected on a TA Instruments Q2000 under a dry N_2 atmosphere. The samples were heated and cooled between -80 and 120 °C at 20 °C, 10 °C, and 5 °C/min. The reported DSC data were collected on the third heating (and/or cooling) cycle at 5 °C/min. Samples were prepared from the same blend precursor solutions used to cast films for conductivity testing. All sample preparation was performed in a dry room (<-45 °C dew point) to prevent moisture contamination; DSC pans were hermetically sealed in Tzero pans. *g*PEO₁₆₇ homopolymer/ Li^+ blend DSCs (not shown) are nearly identical to the *g*PEO₁₀₄ data in **Figures S10-S11** and **Table S8**.

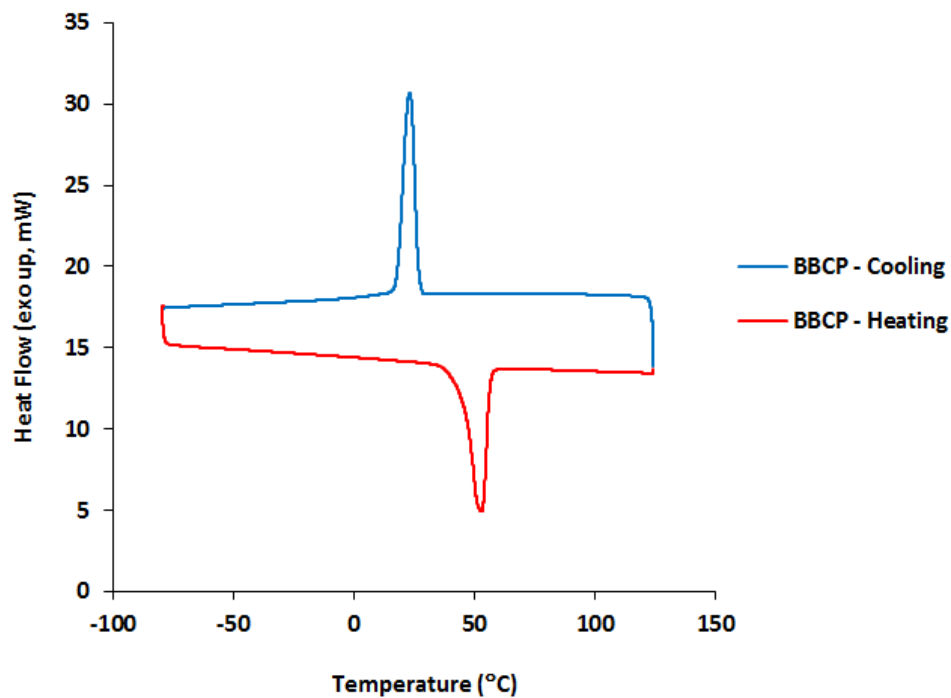


Figure S8: gPS_{11} - $gPEO_{78}$ - gPS_{11} DSC data.

Table S6: Summary of gPS_{11} - $gPEO_{78}$ - gPS_{11} DSC data (see main text, **Figure 2A**).

[EO]:[Li ⁺]	T_g (°C)	T_c (°C)	T_m (°C)	T_m (°C) [#]
BBCP	-	24	51	55
20:1	-56	-19	35	32, 46
15:1	-52	-	34 [*]	51
10:1	-45	-	-	-
5:1	-35	-	-	-
2:1	-19	-	-	-

^{*}Barely observable at 5 °C/min, not observable at 10 and 20 °C/min (see main text).

[#]After \approx 2 months at 23 °C.

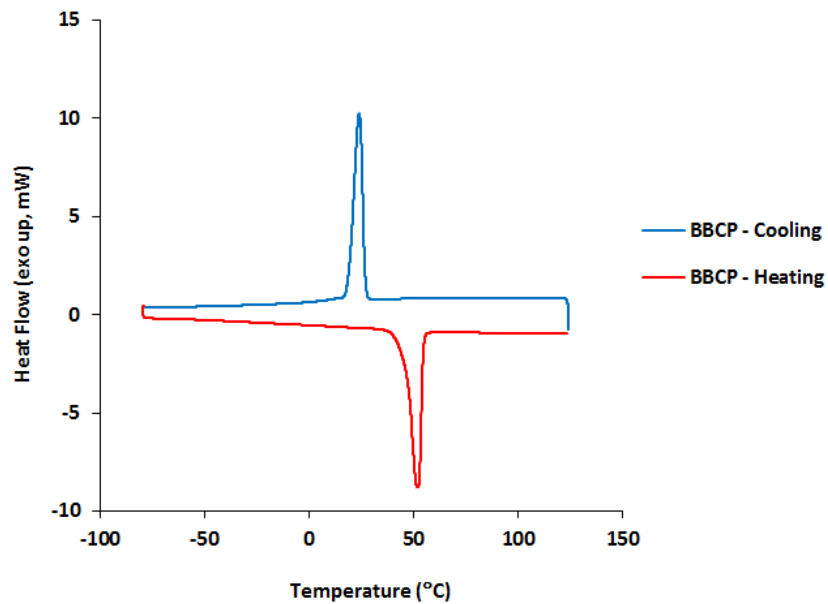


Figure S9: gPS_{15} - $gPEO_{119}$ - gPS_{15} DSC data.

Table S7: Summary of gPS_{15} - $gPEO_{119}$ - gPS_{15} DSC data (see main text, **Figure 2B**).

[EO]:[Li ⁺]	T_g (°C)	T_c (°C)	T_m (°C)	T_m (°C) [#]
BBCP	-	25	51	55
20:1	-56	-36	42	36, 45
15:1	-54	-23	38	37, 46
10:1	-49	-	-	50
5:1	-34	-	-	-
2:1	-14	-	-	-

[#]After \approx 2 months at 23 °C.

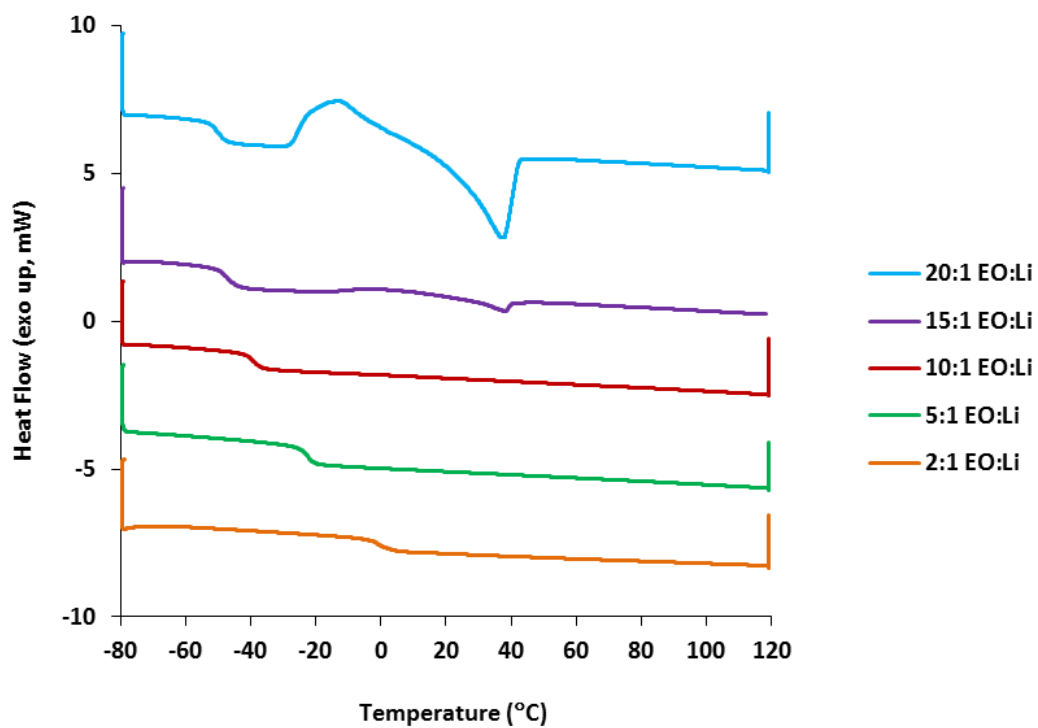


Figure S10: $\text{Li}^+/\text{gPEO}_{104}$ brush homopolymer DSC data.

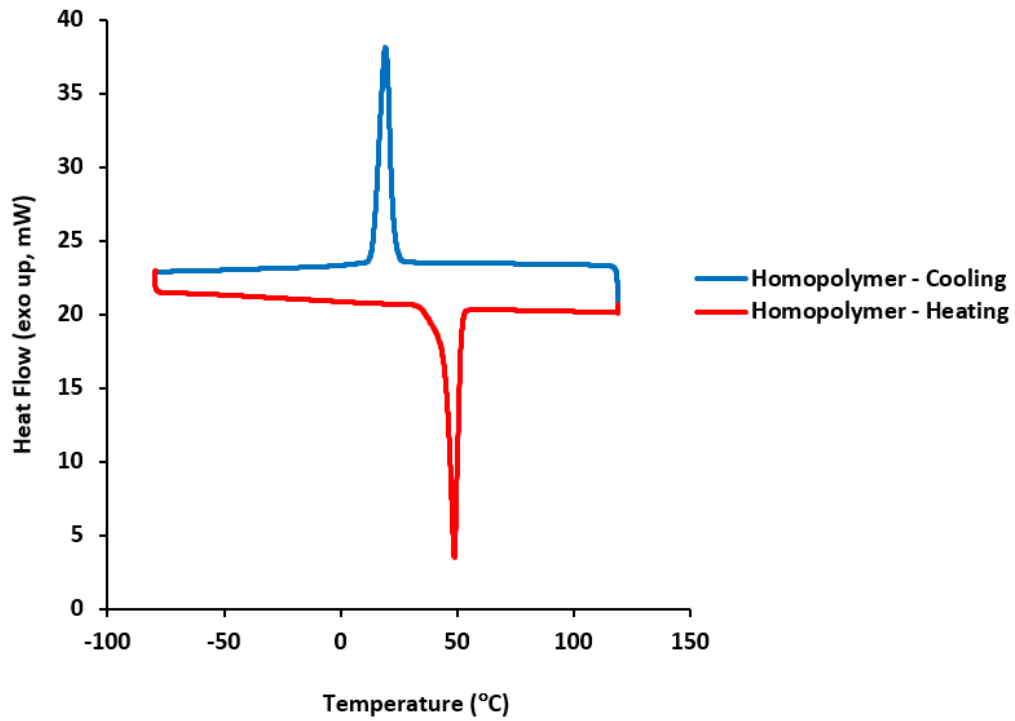


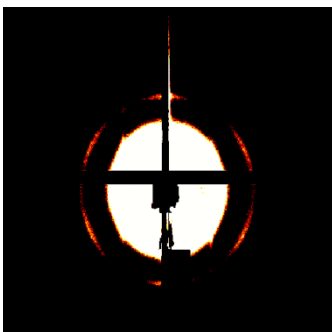
Figure S11: gPEO_{104} brush homopolymer DSC.

Table S8: Summary of $g\text{PEO}_{104}$ brush homopolymer DSC data.

[EO]:[Li ⁺]	T_g (°C)	T_c (°C)	T_m (°C)
<i>g</i> PEO	-	19	49
20:1	-50	-13	38
15:1	-47	-	38
10:1	-38	-	-
5:1	-22	-	-
2:1	-2	-	-

SAXS Data:

SAXS data were collected at Argonne National Laboratory APS Beamline 12-ID-B on the same blend samples that were subjected to DSC analysis (i.e., all samples were prepared in a dry room and hermetically sealed to avoid moisture contamination). The neat BBCP samples were fabricated as follows: 1) BBCP powder (ca. 20 mg) was placed between two sheets of Kapton film, 2) the Kapton film was sandwiched between thick glass slides, 3) the glass slides were compressed with medium-sized binder clips, 4) the films were annealed under vacuum at 120 °C for 2 hrs and subsequently slowly cooled to room temperature under vacuum. The neat BBCP samples clearly flowed during annealing and produced a transparent and slightly light brown film. The Kapton film was cut with scissors to yield approximate dimensions 2x15x0.07 mm (height x width x thickness). SAXS data were collected parallel to the Kapton film plane through the sample dimension approximately 2 mm thick.

**Figure S12:** 2-dimensional SAXS pattern of $g\text{PS}_{15}$ - $g\text{PEO}_{119}$ - $g\text{PS}_{15}$ annealed under compression at 120 °C for 2 hours between Kapton.**Table S9:** Summary of $g\text{PS}_{11}$ - $g\text{PEO}_{78}$ - $g\text{PS}_{11}$ SAXS data.

Sample	q^* (1/Å)	D^* (nm)	2nd peak	2nd Peak/ q^*	3rd Peak	3rd Peak/ q^*
BBCP	0.023997	26.2	0.041995	1.75	0.062993	2.63
20:1	0.017998	34.9	0.031496	1.75	≈0.035496	1.97
15:1	0.017998	34.9	0.030996	1.72	0.035996	2.00
10:1	0.017998	34.9	0.031496	1.75	0.036496	2.03
5:1	0.020998	29.9	-	-	-	-
2:1	0.018998	33.1	-	-	-	-

Table S10: Summary of gPS_{15} - $gPEO_{119}$ - gPS_{15} SAXS data.

Sample	q^* (1/Å)	D^* (nm)	2nd peak	2nd Peak/ q^*	3rd Peak	3rd Peak/ q^*
BBCP	0.021997	28.6	0.037496	1.70	0.057993	2.64
20:1	0.017498	35.9	0.029997	1.71	0.035496	2.03
15:1	0.016998	37.0	0.028997	1.71	0.034996	2.03
10:1	0.016998	37.0	0.029497	1.74	0.034996	2.06
5:1	0.015498	40.5	0.026997	1.74	0.031996	2.06
2:1	0.017998	34.9	-	-	-	-

Conductivity Measurements:**General Information:**

All sample preparation was performed in a dry room (dew point <-45 °C) to prevent water contamination. The linear PEO homopolymer (300 kDa) utilized in normalized conductivity experiments was purchased from Sigma Aldrich and dried *in vacuo* at 100 °C before use. $gPEO$ homopolymer was dried *in vacuo* at room temperature before use. The following coin cell parts were purchased from Pred Materials (part# CR2032): coin cell kit (Al-clad case, cap, and gasket), coin cell wave spring (15.0 mm diameter, 1.4 mm height), and coin cell spacer disk (16.0 mm diameter, 1.0 mm thickness). A Princeton Applied Research/Ametek VersaSTAT MC was used for AC impedance measurements. Potentiostatic AC impedance spectra were obtained between 1 MHz and 100 mHz using a 10 mV RMS AC signal. Bulk ionic conductivity (σ) was calculated according to the equation $\sigma=L/(AR)$, where R is the impedance value corresponding to the high frequency plateau of the Bode Re(Z) plot, L is the thickness of the sample and A is the surface area of the polymer electrolyte (taken as the surface area of the disk upon which it was cast, or as 71.48 mm² for $gPEO$ homopolymers). Variable temperature experiments were performed using a Tenney TUJR thermal test chamber, allowing at least 30 minutes for sample equilibration at each temperature before measurement.

Polymer Thin Film Preparation:

Polymer and LiTFSI were dissolved in cyclopentanone (4:1 wt ratio solvent:polymer), stirred for ca. 1.5 hr, and drop cast onto 1 mm thick circular stainless steel discs (area=1.86 cm²). Most of the cyclopentanone was slowly evaporated in a fume hood over the course of 18 hr, which yielded relatively smooth and mostly homogenous films. The samples were placed in a vacuum oven, heated at 120 °C for 21 hr, and slowly cooled to room temperature under vacuum. Separate ¹H NMR experiments (data not shown) confirmed this sample preparation is sufficient to remove all traces of cyclopentanone within the resolution limits of the analytical technique. The *g*PEO samples were surrounded by a Teflon shell (inner punched diameter: 3/8", outer diameter: 5/8", thickness 0.15 mm) to prevent cell shorting during annealing. A second stainless steel spacer was placed on top of the polymer film and the sandwich was pressed into a coin cell using a coin cell wave spring to ensure good electrical contact. The coin cells were annealed under vacuum at 120 °C for 2 hours, cooled to room temperature under vacuum, and then studied by AC impedance spectroscopy. Film thicknesses used in the conductivity calculations were determined after conductivity experiments by removing the spacer+polymer+spacer sandwich from the coin cell, measuring the stack thickness using calipers, and calculating the polymer thickness by difference (typical polymer thickness values were 50-150 μm). Most BBCP polymer films were within 10-20% of their initial (pre-conductivity experiment) thickness. The thickness of the PEO homopolymer films shrank significantly due to their rubbery physical state ($T \gg T_g$). The final thickness of the *g*PEO samples was 0.15 mm as expected from the Teflon shell thickness.

Reproducibility:

Conductivity measurement reproducibility was probed with *g*PS₁₁-*g*PEO₇₈-*g*PS₁₁ in two ways: one sample (10:1) was subjected to repeated heating and cooling cycles to verify internal consistency, and the remaining samples (2:1, 5:1, 15:1, 20:1) were refabricated to measure coin cell batch-to-batch uniformity. The data are plotted in **Figure S13**. In addition, two *g*PEO homopolymer samples with different norbornene backbone degrees of polymerization ($N=104$ and 167) were synthesized to probe synthetic batch-to-batch conductivity reproducibility (**Figure S14**).

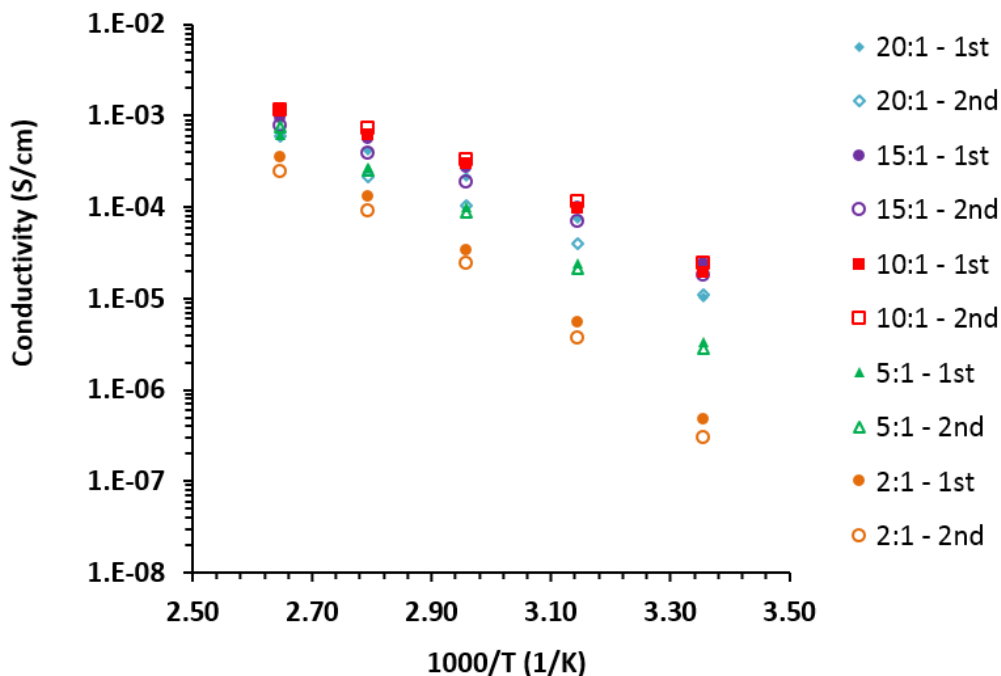


Figure S13: Reproducibility of gPS_{11} - $gPEO_{78}$ - gPS_{11} conductivity measurements. The 20:1, 15:1, 5:1, and 2:1 datasets correspond to two physically different coin cells, while the 10:1 data represent the same coin cell measured on two separate heating cycles.

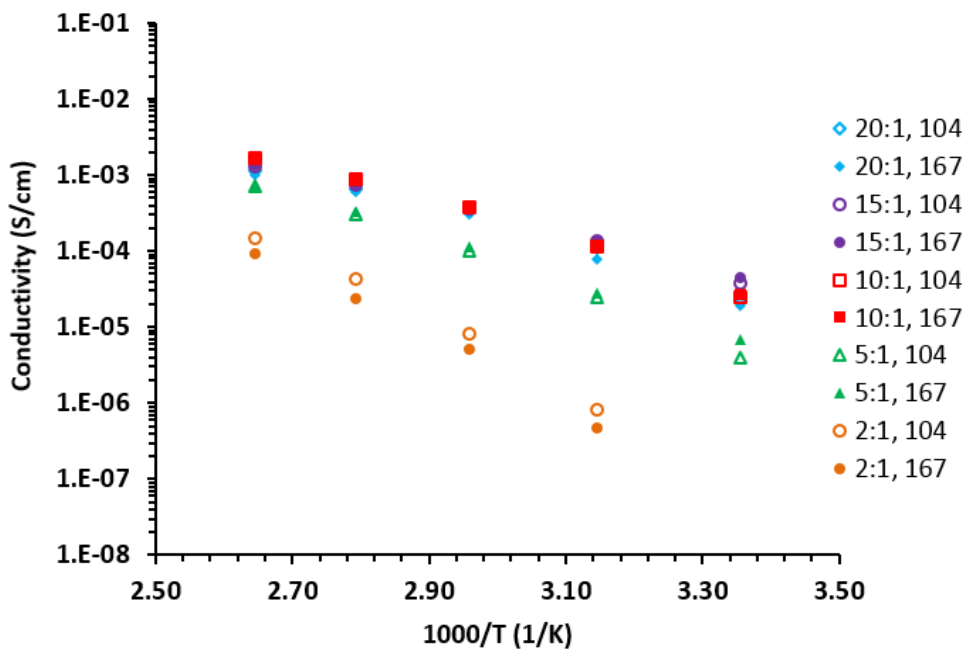


Figure S14: Comparison of $gPEO$ brush homopolymer conductivity data, $N=104$ and 167 .

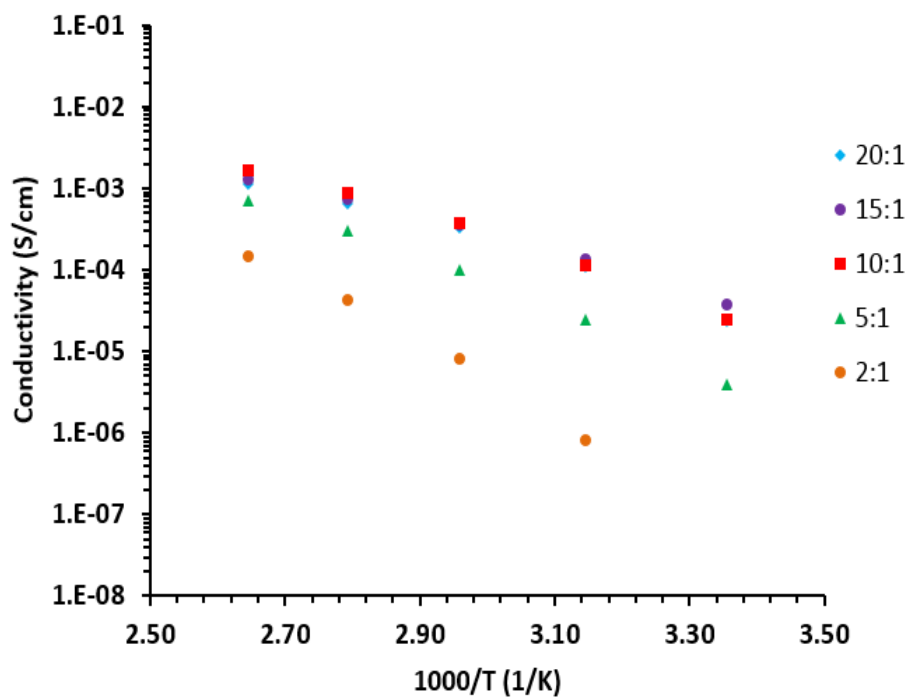


Figure S15: Measured gPEO brush homopolymer conductivity data, $N=104$.

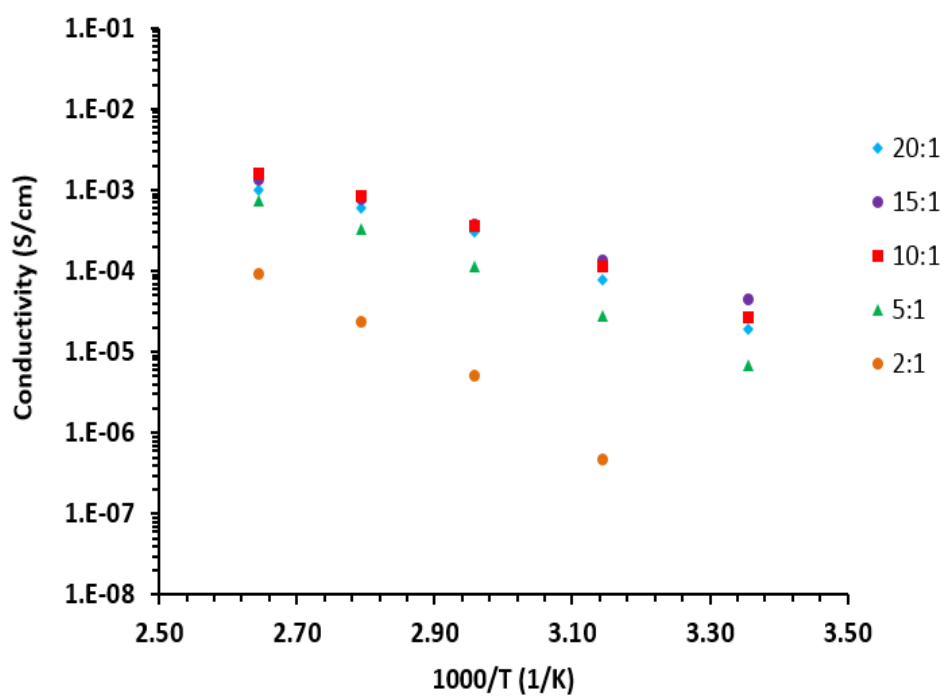


Figure S16: Measured gPEO brush homopolymer conductivity data, $N=167$.

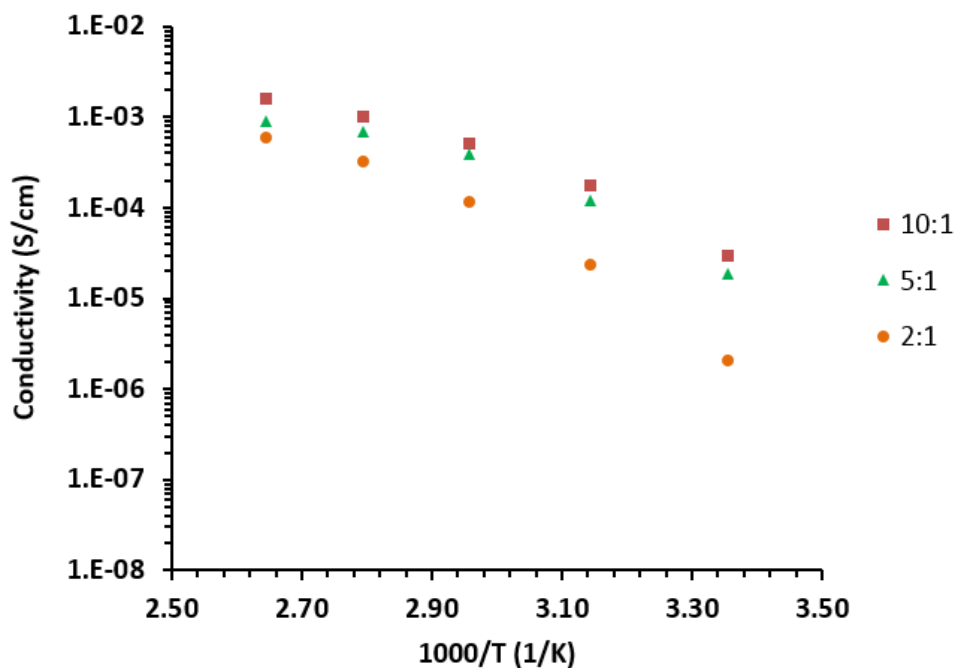


Figure S17: Measured linear 300 kDa PEO homopolymer conductivity data.

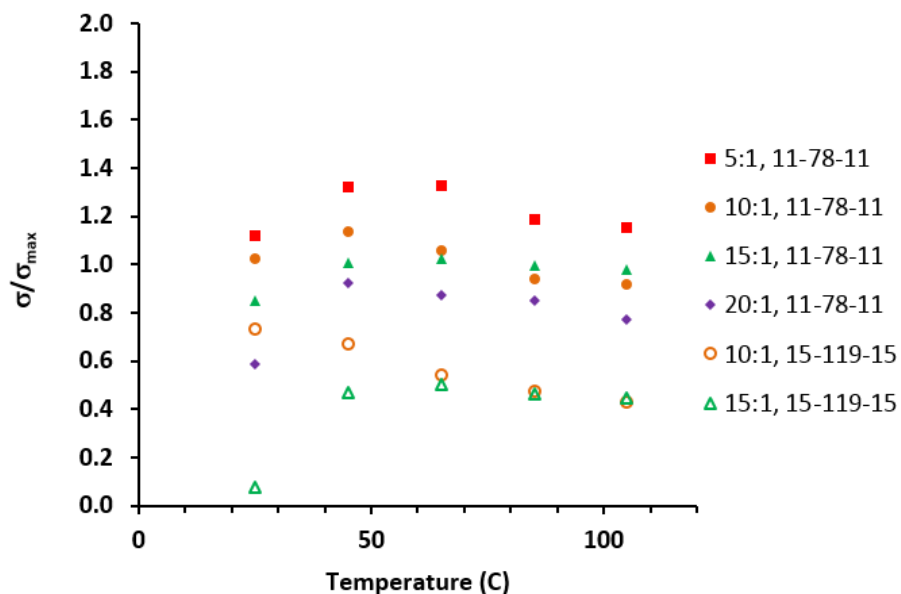


Figure S18: Normalized conductivities of select BCCP samples relative to *g*PEO ($N=104$).

The normalized conductivities reported in **Figure S18** follow the general trends described in the manuscript: moderate blend ratios exhibit large normalized conductivities relative to linear PS-PEO containing 2 kDa PEO chains and *g*PS₁₁-*g*PEO₇₈-*g*PS₁₁ generally yields higher conductivities than *g*PS₁₅-*g*PEO₁₁₉-*g*PS₁₅ at a given blend ratio. The normalized conductivities are fairly sensitive to small differences between the *g*PEO homopolymer and BCCP conductivities at a given temperature.

Consequently, the σ/σ_{\max} values >1 probably reflect experimental uncertainty, and the non-monotonic behavior likely derives from statistical noise due to small fluctuations in the σ_{BBCP} and σ_{gPEO} conductivities at a given temperature around the mean average conductivity, an effect qualitatively dampened when viewing log-scale plots. Similar normalized conductivity trends (magnitudes and statistical variability) were observed with both sets of $g\text{PS}_{11}\text{-}g\text{PEO}_{78}\text{-}g\text{PS}_{11}$ BBCPs normalized to $g\text{PEO}$ with either $N=104$ or $N=167$.

Rheology:

Rheology data were collected on a Rheometric Scientific ARES-M using 25 mm diameter parallel plates under constant flow of nitrogen gas. Bulk BBCP was heated under compression in a 1 mm thick circular mold (25 mm diameter) under vacuum for ca. 16 hr. The sample was loaded into the rheometer, heated to 125 °C, and the gap was reduced to ca. 0.75 mm. The sample was equilibrated for 1 hr and subsequently cooled to 50 °C under a dynamic N_2 purge to visually ensure uniform coverage between the plates. Any polymer overflowing from the edges was removed and the sample was again heated to 125 °C. Each temperature was equilibrated for at least 1.5 hr before data collection began. Strain sweeps were performed at each temperature after equilibration to ensure linear viscoelastic response (G' and G'' independent of applied strain). Frequency sweep data for temperatures 45–125 °C were collected on cooling; temperatures 145–185 °C were collected on heating. Frequency was scanned in the range 0.01–100 rad/sec at each temperature.

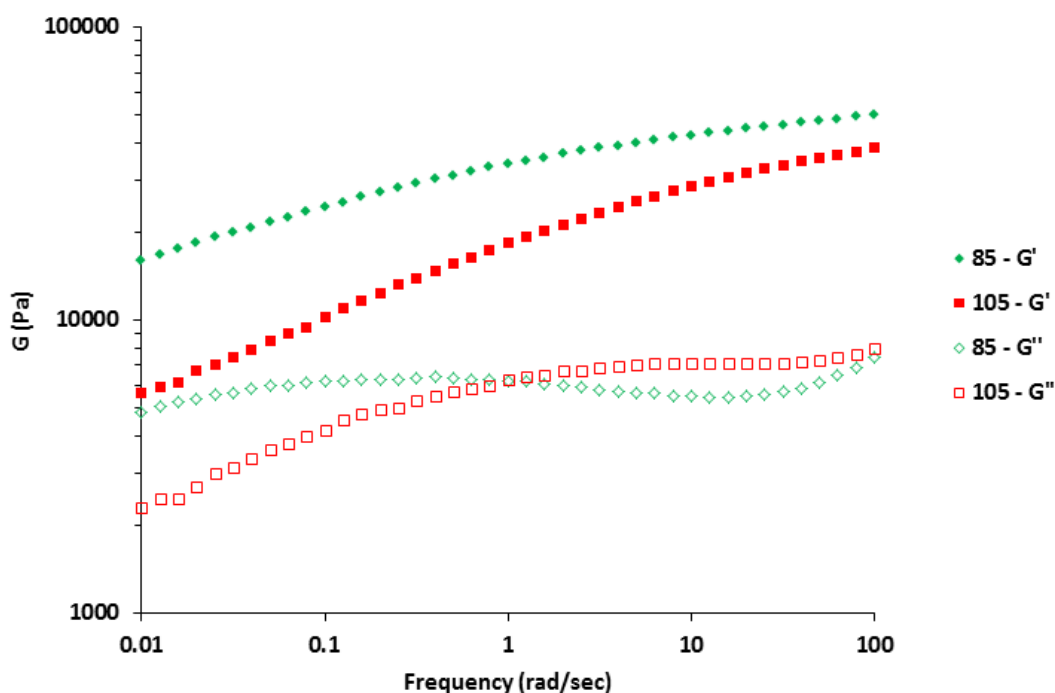


Figure S19: Storage and loss moduli of $g\text{PS}_{15}\text{-}g\text{PEO}_{119}\text{-}g\text{PS}_{15}$ as a function of temperature and frequency.

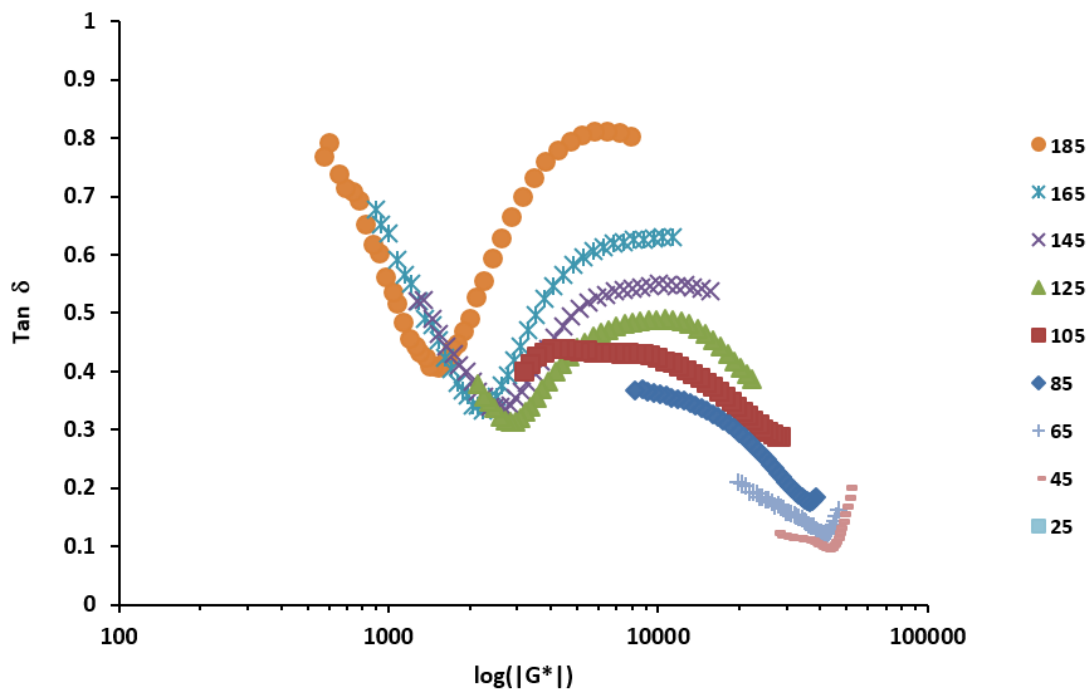


Figure S20: van Gorp-Palmen plot of $\tan \delta$ versus the magnitude of the complex modulus $|G^*| = [(G')^2 + (G'')^2]^{1/2}$ for gPS_{11} - $gPEO_{78}$ - gPS_{11} .