

## Non-intuitive trends in Flory-Huggins interaction parameters in polyether-based polymers

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### 1- Synthesis

#### Materials

Chemicals were purchased from Sigma Aldrich or TCI America and used as received unless otherwise noted. rac-Lactide was recrystallized twice from ethyl acetate prior to use. Tetrahydrofuran (THF) was collected directly from a dry solvent system. Ethylene oxide (EO) was degassed through freeze–pump–thaw cycle and distilled to a flamedried buret immediately before use. Allyl glycidyl ether was dried over CaH<sub>2</sub> and distilled from butyl magnesium chloride prior to use. Styrene was distilled over CaH<sub>2</sub>. Potassium naphthalenide was prepared from potassium metal and naphthalene (recrystallized from diethyl ether) in dry THF and allowed to stir with a glass-coated stir-bar for 24 h at room temperature prior to use. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc.

#### Instrumentation

<sup>1</sup>H and DOSY NMR spectra were recorded using a Varian 400, 500, or 600 MHz spectrometer with the solvent signal as internal reference. Gel permeation chromatography (GPC) was performed on a Waters 2690 separation module equipped with Waters 2414 refractive index and 2996 photodiode array detectors using CHCl<sub>3</sub> containing 0.25% triethylamine as eluent at a flow rate of 1 mL/min. Molecular weight distributions were calculated relative to linear polystyrene standards.

#### Synthesis and characterization of polymers

Procedure for the synthesis of poly(allyl glycidyl ether) (PAGE).

Anionic polymerizations were carried out on a Schlenk line in custom glass reactors under an argon atmosphere. The potassium alkoxide initiator was formed by titration of benzyl alcohol with potassium naphthalenide under argon until a persistent green color was observed in solution indicating the quantitative deprotonation of the benzyl alcohol. The polymerization

of allyl glycidyl ether was carried out in THF solution at 40 °C for 20 h followed by termination with methanol.

A detailed procedure for the synthesis of PAGE (16 kg/mol) is provided. Benzyl alcohol (10.8 mg, 0.1 mmol) was titrated with potassium naphthalenide (0.3 M) followed by the addition of allyl glycidyl ether (1.6 g, 14 mmol). After termination with methanol the polymer was precipitated into hexane, the hexane was decanted, and the polymer was dried under vacuum and obtained in near quantitative yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): d 3.4–3.73 (m, 916H, –CH<sub>2</sub>–CH(CH<sub>2</sub>–O–CH<sub>2</sub>–CH=CH<sub>2</sub>)–O–), 3.98 (d, 352H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>), 4.53 (s, 2H, Ph–CH<sub>2</sub>–O–), 5.14, 5.25 (dt, d, 173H, 170H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>), 5.88 (td, 161H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>) and 7.27–7.35 (m, 5H, Ph–CH<sub>2</sub>–O–) ppm.

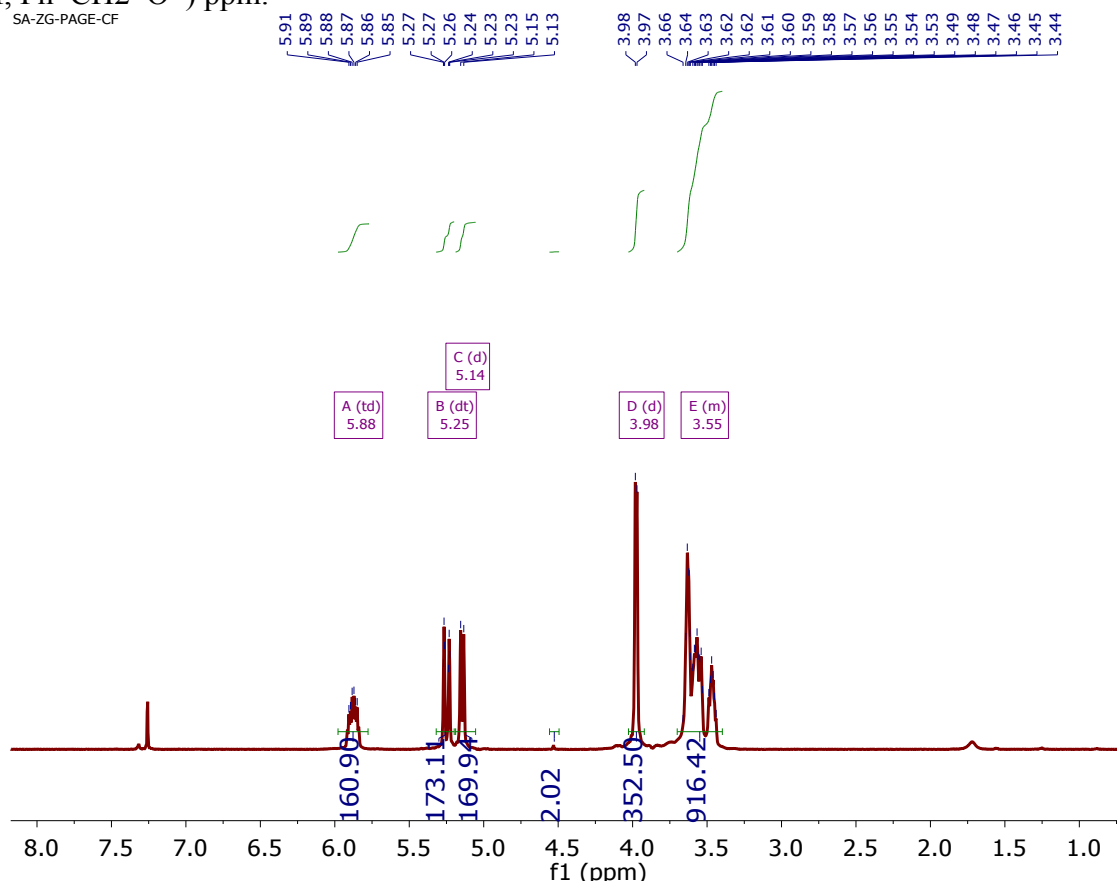


Figure S 1. <sup>1</sup>H NMR of PAGE

Procedure for the synthesis of poly(allyl glycidyl ether)-b-poly(lactide) (PAGE-b-PLA). PAGE macroinitiator was weighed into an oven-dried, 100 mL round bottom flask equipped with a stir bar and septum and cryo-dried overnight with minimal amount of toluene under vacuum (0.1 Torr). The flask was charged with lactide and 0.5 mol% Triazabicyclodecene (TBD) in DCM. After stirring for short period of time, benzoic acid was added to quench the reaction. The reaction solution was precipitated into 20 mL of hexane, the hexane was decanted, and the polymer was dried under vacuum. Monomer conversion was followed using <sup>1</sup>H NMR spectroscopy.

A detailed procedure for the synthesis of PAGE-PLA is provided. PAGE (0.48 g, 0.03 mmol) was cryo-dried overnight after dissolved in 4 ml of toluene. The flask was charged with lactide (0.85 g, 5.9 mmol) dissolved in 5 ml of DCM and TBD (1.4 mg, 10 μmol) was finally added in. A monomer conversion of 95% was calculated from the crude <sup>1</sup>H NMR spectrum after which The reaction solution was precipitated into 20 mL of hexane, the hexane was decanted, and the polymer was dried under vacuum to obtain a viscous solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): d 1.58 (dt, 1458H,  $-\text{C}(\text{O})-\text{CH}-(\text{CH}_3)-\text{O}-$ ), 3.38–3.71 (m, 703H,  $-\text{CH}_2-\text{CH}(\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2)-\text{O}-$ ), 3.98 (d, 266H,  $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 4.53 (s, 2H,  $\text{Ph}-\text{CH}_2-\text{O}-$ ), 5.11–5.31 (m, 632H,  $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$  and  $-\text{C}(\text{O})-\text{CH}-(\text{CH}_3)-\text{O}-$ ), 5.88 (ddd, 120H,  $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$ ), and 7.27–7.35 (m, 5H,  $\text{Ph}-\text{CH}_2-\text{O}-$ ) ppm.

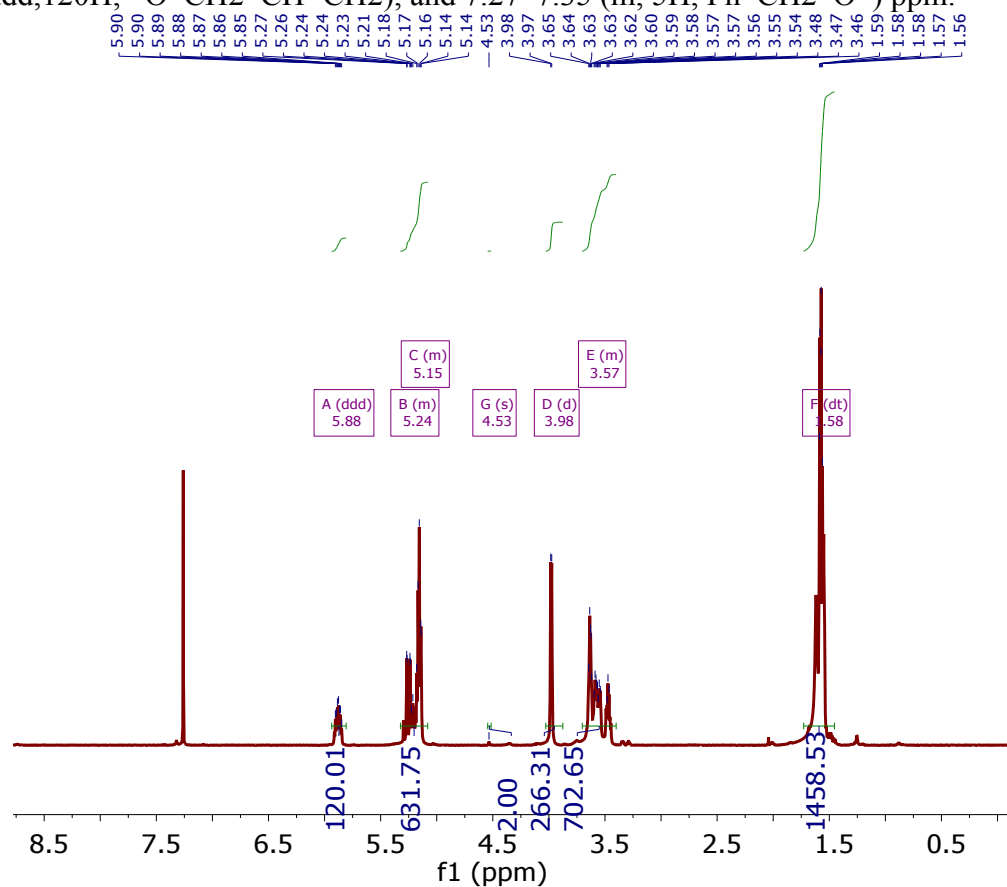


Figure S 2.  $^1\text{H}$  NMR of PAGE-PLA

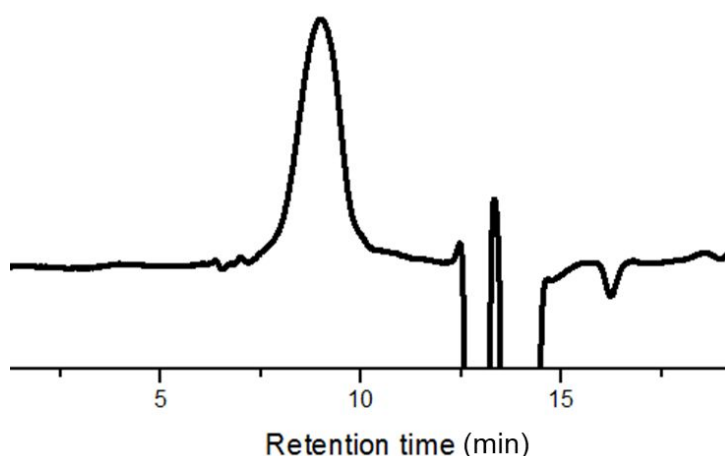


Figure S 3. GPC trace of PAGE-PLA in chloroform versus poly(styrene) standards.

Procedure for the synthesis of poly(allyl glycidyl ether)-b-poly(lactide) (PAGE-b-PEO). PAGE macroinitiator was weighed into custom thick-walled glass reactors fitted with ACE threads under an inert argon atmosphere. The reactors were fitted with a buret containing a premeasured quantity of THF, a flexible connector to a buret containing ethylene oxide on ice

at 0 °C, a glass arm containing a port for a 6 mm puresep septum, and connectors to the Schlenk line. The reactors were equipped with a stir bar and cryo-dried overnight with minimal amount of toluene under vacuum (0.1 Torr). THF drawn from a solvent purification system was introduced by opening the threaded stopcock on the attached buret. Potassium naphthalenide (0.3 M in THF) was added dropwise by cannula until a light green color persisted in solution, indicating complete deprotonation of the macroinitiator. Ethylene oxide was added by lifting the cold buret and allowing the ethylene oxide to drain into THF solution. After 20 hours at 40 C, reaction was quenched with acidic methanol and subsequently precipitated in hexane. Purified polymers were dried under vacuum for characterization of NMR and GPC.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d 3.35–3.82 (m, 2030H, –CH<sub>2</sub>–CH(CH<sub>2</sub>–O–CH<sub>2</sub>–CH=CH<sub>2</sub>)–O– and –CH<sub>2</sub>–CH<sub>2</sub>–O–), 3.97 (d, 299H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>), 4.53 (d, 2H, Ph–CH<sub>2</sub>–O–), 5.14, 5.24 (d, d, 293H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>), 5.80–6.01 (m, 141H, –O–CH<sub>2</sub>–CH=CH<sub>2</sub>) and 7.3–7.35 (m, 5H, Ph–CH<sub>2</sub>–O–) ppm.

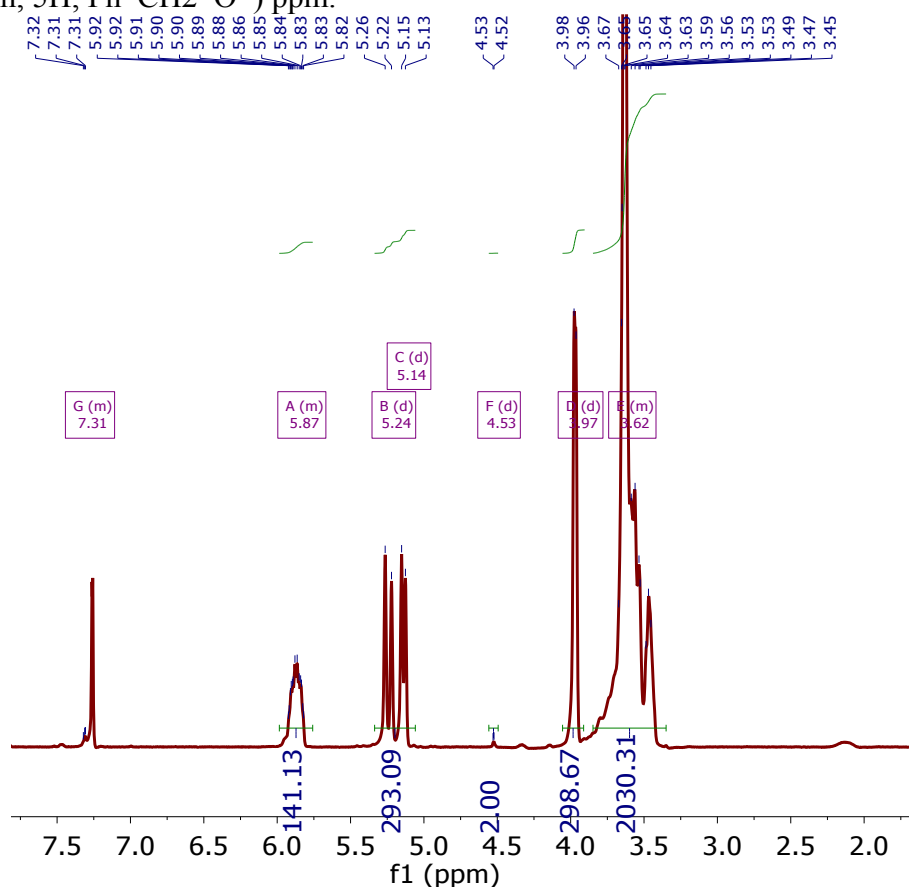


Figure S 4. <sup>1</sup>H NMR of PAGE-PEO



Figure S 5. GPC trace of PAGE-PEO in chloroform versus poly(styrene) standards.

Procedure for the synthesis of poly(styrene)-b-poly(allyl glycidyl ether) (PS-b-PAGE). Distilled styrene was transferred into a dry buret. PS macroinitiator was synthesized in an anionic polymerization manner following standard procedure and terminated with EO with similar experimental set up with EO polymerization. After precipitation in methanol and drying under vacuum for 24 hours at 40 °C, the macroinitiator was further cryo-dried under vacuum overnight. THF drawn from a solvent purification system was introduced and potassium naphthalenide (0.3 M in THF) was added dropwise by cannula until a light green color persisted in solution, indicating complete deprotonation of the macroinitiator. AGE was then added. After 20 hours at 40 °C, reaction was quenched with acidic methanol and subsequently precipitated in methanol. Purified polymers were dried under vacuum for characterization of NMR and GPC.

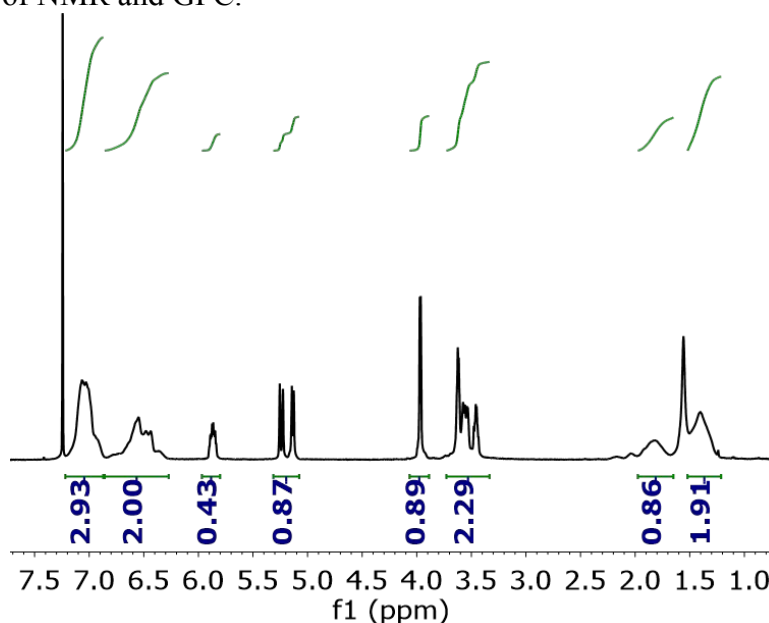


Figure S 6.  $^1\text{H}$  NMR of PS-PAGE

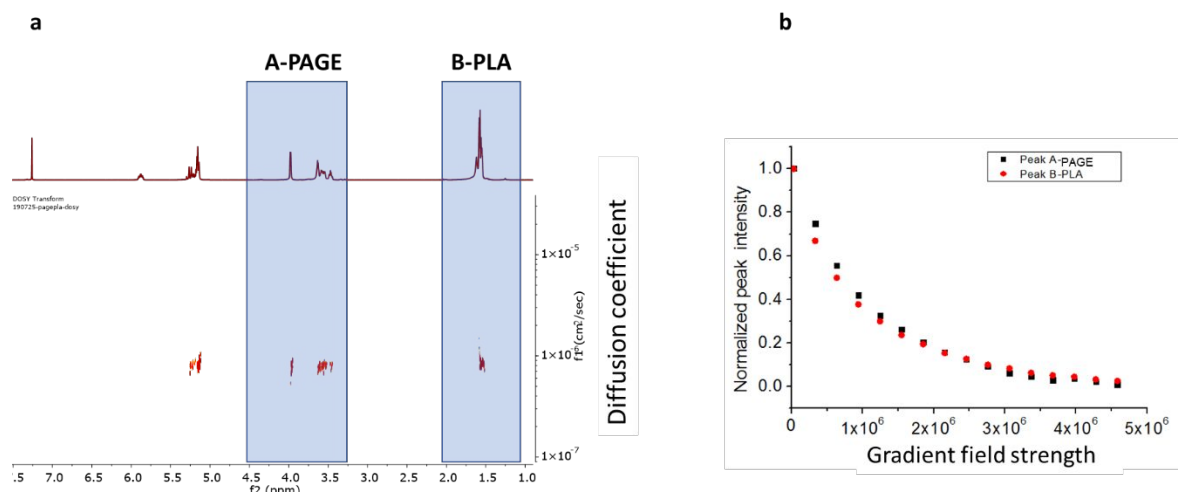


Figure S 7. <sup>1</sup>H DOSY NMR of block copolymer PAGE-PLA(a), and identical attenuation rate of peak intensity of both blocks versus gradient field strength(b).

## 2- Small-Angle X-ray Scattering (SAXS)

Samples were prepared by using a spatula at room temperature to fill a 1 mm thick aluminum washer with the block copolymer. One side of the sample washer was glued to a Kapton window with high temperature stable silicone adhesive (Dow Corning), and the entire sample cell was annealed in a vacuum oven ( $10^{-9}$  Torr) at 150 °C for 24 h. After annealing, a second Kapton window was glued to the washer to completely seal the polymer sample.

X-ray scattering measurements were performed as a function of temperature at the National Synchrotron Light Source II (NSLS-II, beamline 11-BM, Brookhaven National Laboratory), with an X-ray energy of 13.5 keV, and at the Advanced Light Source (ALS, beamline 7.3.3, Lawrence Berkeley National Laboratory), with an X-ray energy of 10 keV, and at the Stanford Synchrotron Radiation Lightsource (SSRL, beamline 1-4). The calibration was performed using silver behenate standards.

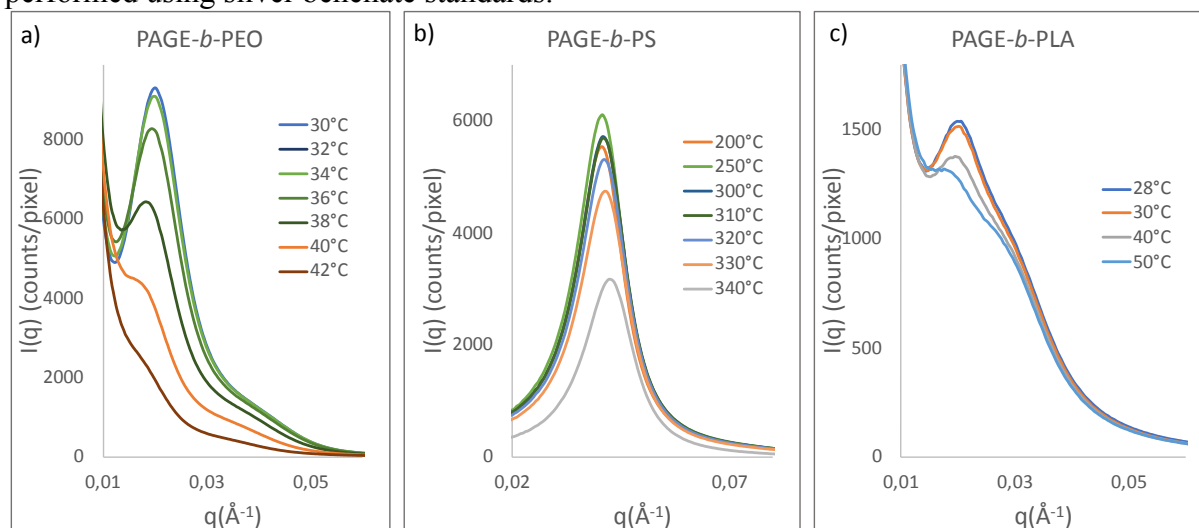


Figure S 8. SAXS profiles at different temperature of PAGE-b-PEO (a), PAGE-b-PS (b), PAGE-b-PLA (c). The decrease of the intensity of the curves indicate the ODT transition.

To calculate the  $\chi$  parameter, the following expression for intensity as a function of  $q$  was used:

$$I(q) = \left( \frac{b_1}{v_1} - \frac{b_2}{v_2} \right)^2 S(q) = C S(q) = C \left( \frac{F(f,q,Rg)}{N} - 2\chi \right)^{-1}$$

Where:

$$F(f,q,Rg) = \frac{g(1,q,Rg)}{g(f,q,Rg)g(1-f,q,Rg) - \frac{1}{4}[g(1,q,Rg) - g(f,q,Rg) - g(1-f,q,Rg)]^2}$$

$g(f,q,Rg)$  is the Debye function:

$$g(f,q,Rg) = \frac{2[f(q^2 Rg^2) + e^{-f(q^2 Rg^2)}]}{(q^2 Rg^2)^2}$$

and the scattering lengths ( $b_i$ ) and volumes ( $v_i$ ) are represented by a constant scalar  $C$  in order to account for the arbitrary units of scattering

The above structure factor  $S(q)$  was defined in Mathematica as a model (modelMaterial) for each material as a function of volume fraction,  $q$ ,  $Rg$ ,  $N$ , and  $C$ . This model was called in a nonlinear fit with 95% confidence intervals to fit disordered scattering peaks:

fitMaterialTemp=

NonlinearModelFit[

dataMaterialTemp[[start;;stop]], {1,2}], {modelMaterial, 500 > Rg > 1, 1 >  $\chi$  > 0, C > 0}, {Rg,  $\chi$ , C}, q, ConfidenceLevel -> 0.95];

where dataMaterialTemp is a 4-column text file with  $q$ , Intensity,  $q$  error, and Intensity error, and start and stop are integers referring to data points bounding the disordered peak.

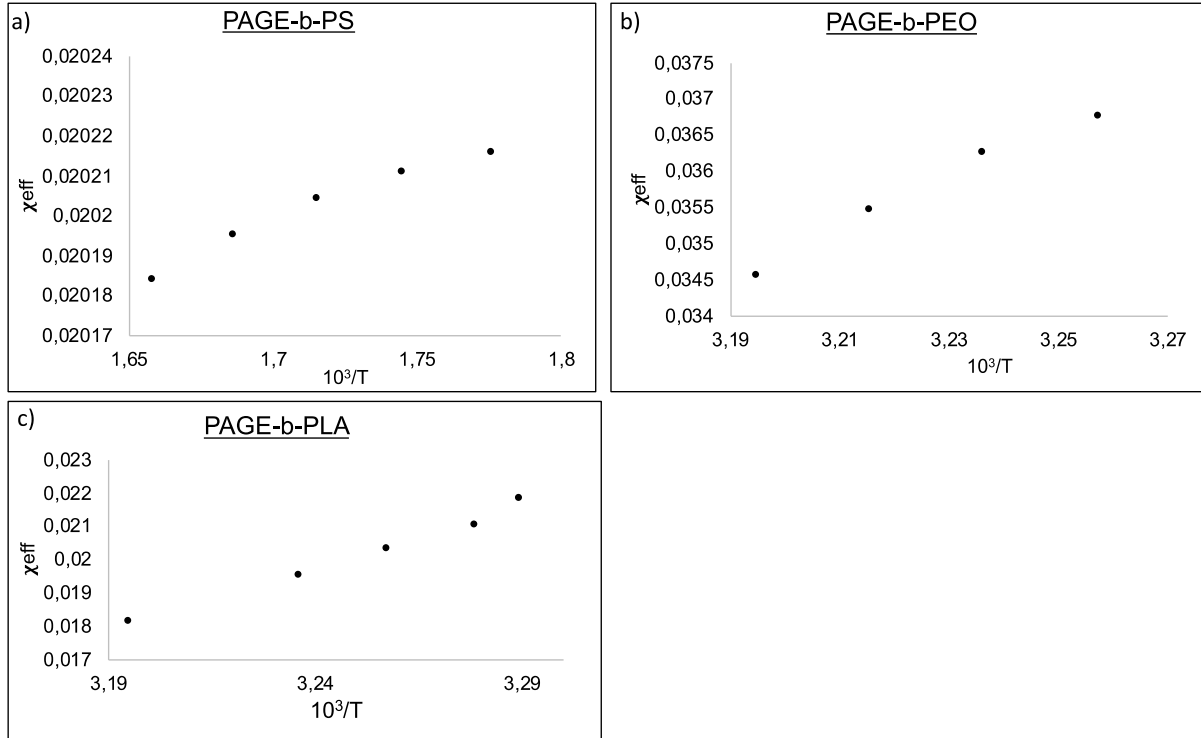


Figure S 9. Temperature dependence of  $\chi$  calculated by fitting the SAXS profiles based on the random phase approximation (RPA) at different temperatures for a series of BCPs

The full width at half maximum (FWHM) on the primary peak of the SAXS pattern was calculated from the equation of the Gaussian used to fit the curves

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

and calculated with the equation:  $FWHM = 2\sqrt{2\ln\sigma}$

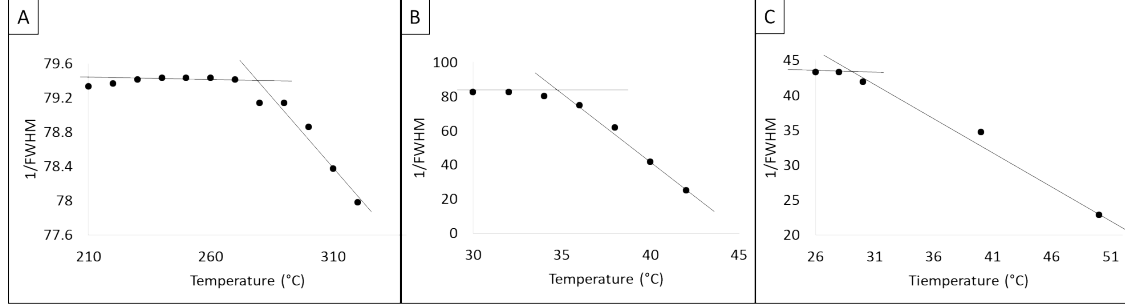


Figure S 10. Temperature dependence of full width at half maximum (FWHM) on the primary peak of (A) PS-b-PAGE, (B) PEO-b-PAGE, and (C) PLA-b-PAGE.

### 3- Simulation Details

Fully atomistic molecular dynamics simulations of neat and blended PAGE and PEO homopolymers (10mers) were performed using the Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS) package.<sup>1</sup> Interaction potentials between atoms were modeled as a sum of bonded ( $b$ ) and non-bonded ( $nb$ ) interactions:

$$U = U_b + U_{nb} \quad (1)$$

The bonded potentials ( $U_b$ ) account for the bond, angle, dihedral, and improper dihedral interactions, while the non-bonded ( $U_{nb}$ ) potentials account for the Lennard-Jones (LJ) and Coulombic interactions. The total interatomic potential is thus defined as:

$$U = \sum_{Bonds} k_b(b - b_o)^2 + \sum_{Angles} k_\theta(\theta - \theta_o)^2 + \sum_{Dihed} \sum_{m=1}^4 \frac{k_m}{2} [1 + (-1)^{m+1} \cos m\phi] \\ + \sum_{Imp} k_\psi(1 - \cos(2\psi)) + \sum_{i,j} f_{ij} \left\{ \frac{e^2 z_i z_j}{4\pi\epsilon_o r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} \quad (2)$$

In (2),  $k_i$  are force constants,  $b_o$  and  $\theta_o$  are the equilibrium bond length and angle,  $\phi$  is the 1,4-dihedral angle,  $\psi$  is the improper dihedral angle,  $f_{ij}$  is a scaling parameter,  $e$  is the elementary charge,  $z_i$  is the charge valence,  $\epsilon_o$  is the permittivity of free space, and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the LJ parameters. For dihedral interactions (atoms separated by three bonds), the scaling parameter  $f_{ij}$  was set to 0.5. The scaling parameter was assigned to zero for interactions separated by less than three bonds and unity in all other instances. Coulombic interactions are computed in real space up to a 12 Å cutoff, while the long-range Coulombic interactions are handled in k-space via the particle-particle-particle mesh (PPPM) Ewald method with a tolerance of  $10^{-5}$ . LJ parameters  $\epsilon_{ij}$  and  $\sigma_{ij}$  were computed by geometrically mixing the native LJ parameters, such that  $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}}$  and  $\sigma_{ij} = (\sigma_i \sigma_j)^{\frac{1}{2}}$ . OPLS-AA force field parameters were implemented in all simulations and were obtained from previous studies of PAGE and PEO homopolymers.<sup>2,3</sup>

#### 4- System Initialization, Equilibration, and Data Production

Simulation box initialization for neat PAGE, neat PEO, and PAGE/PEO blends all followed the same general procedure outlined below. A single linear chain (PAGE 10mer or PEO 10mer) was constructed in Avogadro,<sup>4,5</sup> packed into a simulation box, and relaxed via successive steepest descent and conjugate gradient minimization with a tolerance criterion of  $10^{-5}$ . The chain was then heated in vacuum to 500 K using a Langevin thermostat and subsequently equilibrated in the NPT ensemble using a Nosé-Hoover thermostat and barostat for 1 ns.

Relaxed chains from the aforementioned 1 ns equilibration runs were then packed into a simulation box using Packmol.<sup>6</sup> Neat homopolymer simulation boxes were packed with 250 chains, while blend simulations contained 125 PAGE and 125 PEO chains. Simulation boxes were relaxed using steepest descent and conjugate gradient minimization with a tolerance of  $10^{-5}$  and then subsequently heated to 400 K in the NVE ensemble using a Langevin thermostat. Once the target temperature was reached, an equilibration run was performed for 30 ns in the NPT ensemble followed by a 50 ns production run. All bonds containing hydrogen were constrained via the SHAKE algorithm,<sup>7</sup> allowing for a 2.0 fs timestep.

#### 5- Pair Correlation Functions

Both the inter- and intrachain pair correlation functions were computed from the atom trajectories of the 400 K neat and blend homopolymer simulations using equations (3) and (4), respectively.

$$g_{ij}(r) = \frac{V}{4\pi r^2 N_i N_j} \left\langle \sum_i^{N_i} \sum_j^{N_j} \delta(r - r_{ij}) \right\rangle \quad (3)$$

$$\omega_{ij}(r) = \frac{1}{N_i N_j} \left\langle \sum_i^{N_i} \sum_j^{N_j} \delta(r - r_{ij}) \right\rangle \quad (4)$$

In (3), the summation is restricted to include only interchain pairs, while in (4) the summation is restricted to intrachain pairs. Equation 3 represents the local density of backbone ether oxygens relative to the bulk density of backbone ether oxygens, while (4) represents the normalized probability density of intrachain distances between backbone ether oxygens.

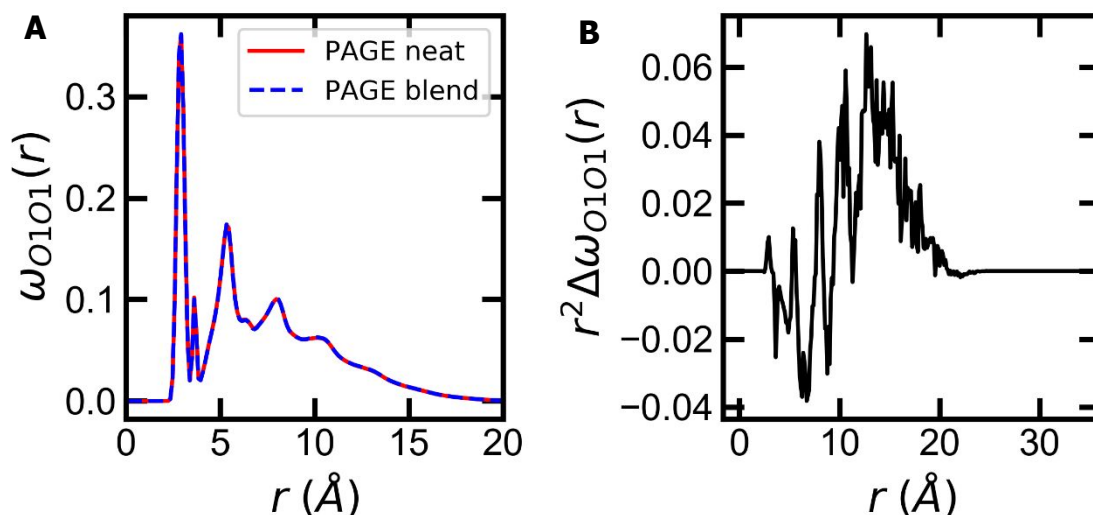


Figure S11. (A) Intrachain O1O1 (backbone oxygen) pair correlation functions and (B) change in the intrachain O1O1 pair correlation functions upon blending for PAGE chains. Positive deviations are seen at large and negative deviations at small distances. This indicates a small increase and decrease in the population of O1O1 pairs separated by large and small distances, respectively. Similar methods have been previously used to study changes in intrachain structure upon blending.<sup>8</sup>

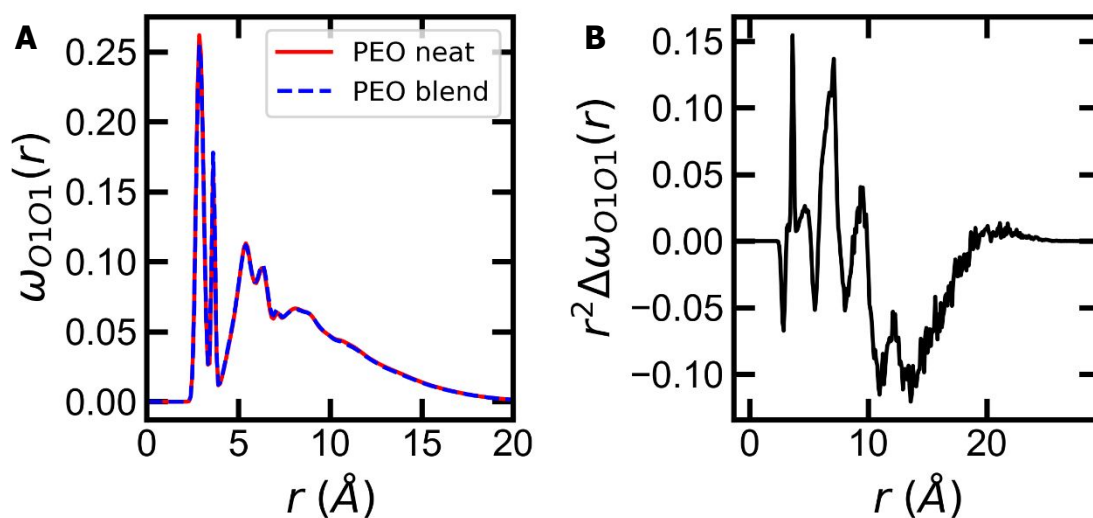


Figure S12. (A) Intrachain O1O1 (backbone oxygen) pair correlation functions and (B) change in the intrachain O1O1 pair correlation functions upon blending for PEO chains. Negative deviations are seen at large and positive deviations at small distances. This indicates a small decrease and increase in the population of O1O1 pairs separated by large and small distances, respectively. Similar methods have been previously used to study changes in intrachain structure upon blending.<sup>8</sup>

## 6- Radii of Gyration, End-to-End Distance, and Conformational Symmetry Parameter

The ensemble average radii of gyration and end-to-end distance were computed via equation (5) and (6), respectively.

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^N \langle (\mathbf{R}_i - \mathbf{R}_{cm})^2 \rangle \quad (5)$$

$$\langle R^2 \rangle = \langle \mathbf{R}_N \cdot \mathbf{R}_N \rangle \quad (6)$$

In (5) and (6),  $\mathbf{R}_i$  is the position of a monomer,  $\mathbf{R}_{cm}$  is the position of the center of mass of a chain, and  $\mathbf{R}_N$  is the displacement between chain ends. The distribution of end-to-end vectors are displayed in Figure S13.

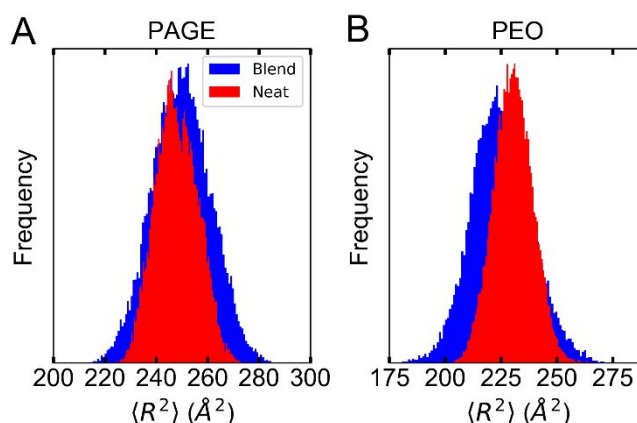


Figure S13. Distribution of end-to-end vectors for (A) PAGE and (B) PEO homopolymers in the neat (red) and blend (blue) melt.

The conformational symmetry parameter ( $\beta_i^2$ ), which describes how far in space a random walk extends per unit volume of chain, was computed using equation (7). The volume of a chain was approximated as  $V_{box}/N_{chain}$ , where  $V_{box}$  is the volume of the homopolymer melt simulation box and  $N_{chain}$  is the number of chains within the box. The  $\langle R_g^2 \rangle$  used were also obtained from the homopolymer melt simulations.

$$\beta_i^2 = \frac{\langle R_g^2 \rangle}{V_i} \quad (7)$$

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