Supporting Information for

Structure and Properties of Bicontinuous Microemulsions from Salt-Doped Ternary Polymer Blends

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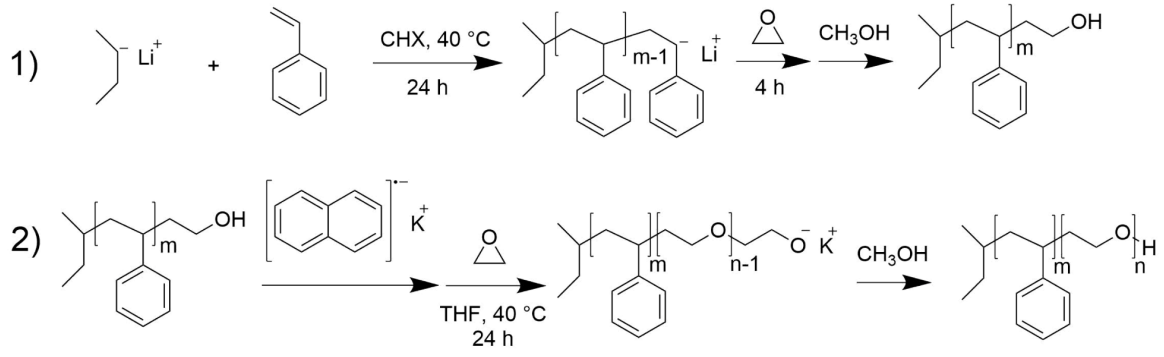


Figure S1: Reaction scheme for the anionic polymerization of PS-*b*-PEO (SO).

MALDI-MS measurements were done on an AB SCIEX 5800 MALDI/TOF mass spectrometer. In the case of PEO, tetrahydrofuran (THF) was used as the solvent and solutions of PEO (10 mg/mL), sodium trifluoroacetate (NaTFA) (10 mg/mL) and 1,8,9-trihydroxyanthracene (dithranol) (10 mg/mL) were mixed at a volume ratio of 10:3:60. In the case of PS and SO, THF was used as the solvent and solutions of PS or SO (10 mg/mL), silver trifluoroacetate (AgTFA) (10 mg/mL), and dithranol (20 mg/mL) were mixed at a volume ratio of 20:10:100. The solutions were then spotted onto the steel targets and allowed to air dry.

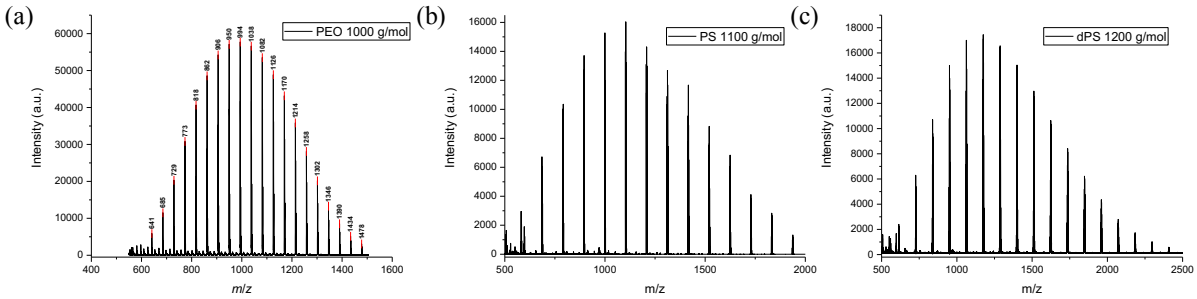


Figure S2: MALDI−TOF spectra and the number-averaged molecular weights of (a) PEO homopolymer, (b) PS homopolymer, and (c) dPS homopolymer.

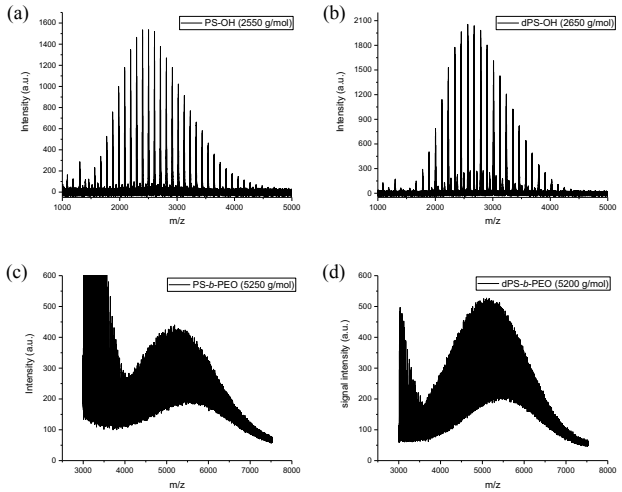


Figure S3: MALDI−TOF spectra and the number-averaged molecular weights of (a) PS-OH precursor, (b) dPS-OH precursor, (c) PS-*b*-PEO (SO) diblock copolymer and (d) dPS-*b*-PEO (dSO) diblock copolymer.

The molecular weight distributions of the synthesized PS precursors and SO copolymers were determined to be narrow by size-exclusion chromatography (SEC) performed in THF at 25 °C on an Agilent 1260 Infinity system (see Figure S4). The eluents were monitored by a Wyatt Optilab T-rEX refractive index detector, and the corresponding molecular weights and distributions were determined by using Zimm plots obtained from a Wyatt Dawn Heleos II multiangle light scattering (MALS) detector.

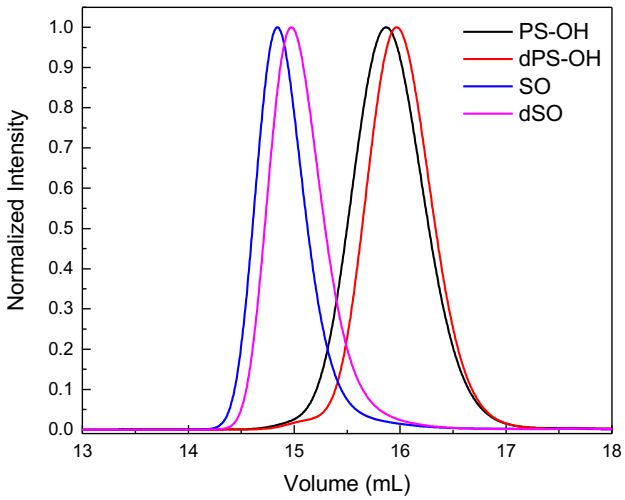


Figure S4: RI traces of PS-OH, dPS-OH, SO, and dSO by SEC.

A Bruker HD-500 instrument was used to determine the ^{1}H NMR spectrum of the SO (Figure S5). The f_{PEO} was determined to be 0.5, which agrees well with the value determined by MALDI-TOF.

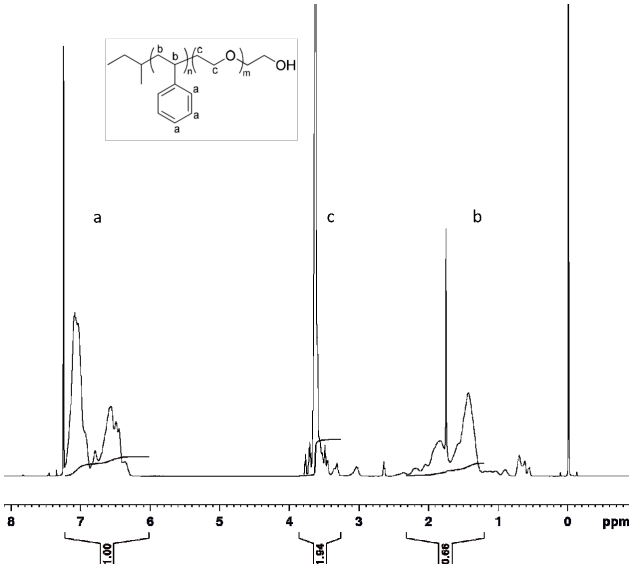


Figure S5: The chemical structure and the ^{1}H NMR spectrum of the SO.

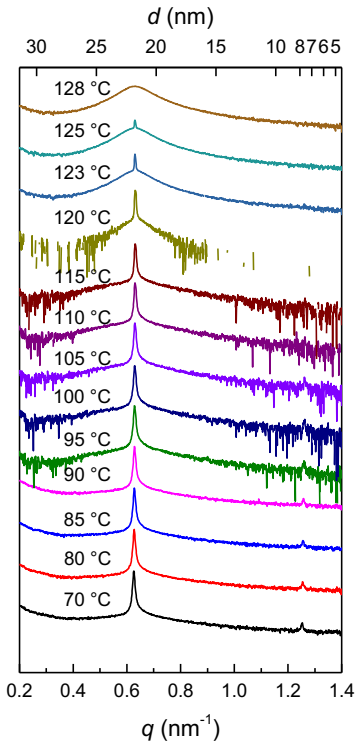


Figure S6: SAXS patterns for LiTFSI-doped PS-*b*-PEO with $r = [Li^+]/[EO] = 0.03$. The scattering patterns have been background subtracted and vertically shifted for clarity.

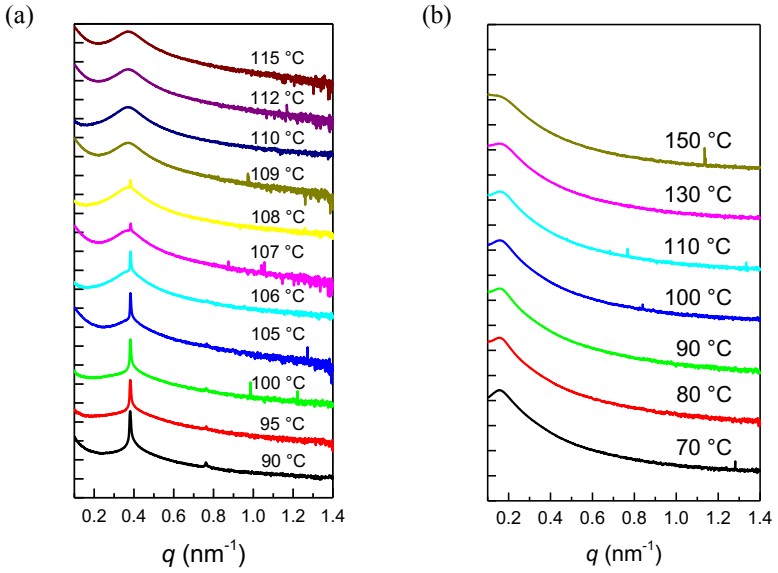
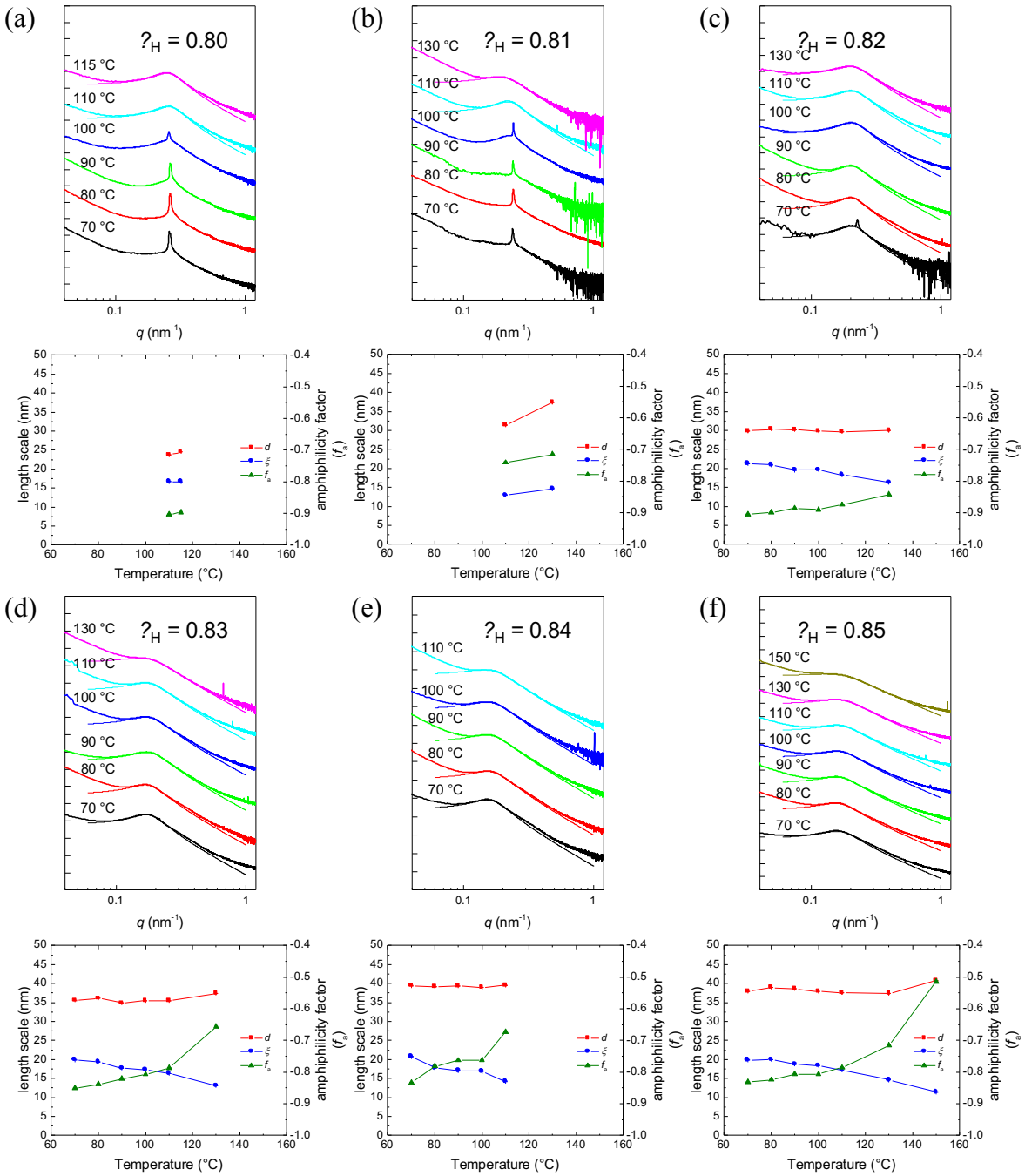


Figure S7: SAXS patterns for blends with $r = 0.03$, $\phi_{PEO+LiTFSI}/\phi_{PS} = 1$, (a) $\phi_H = 0.70$ and (b) $\phi_H = 0.85$. The scattering patterns have been background subtracted and vertically shifted for clarity.


(a)
?H = 0.80
115 °C
110 °C
100 °C
90 °C
80 °C
70 °C
(b)
?H = 0.81
130 °C
110 °C
100 °C
90 °C
80 °C
70 °C
(c)
?H = 0.82
130 °C
110 °C
100 °C
90 °C
80 °C
70 °C
(d)
?H = 0.83
130 °C
110 °C
100 °C
90 °C
80 °C
70 °C
(e)
?H = 0.84
110 °C
100 °C
90 °C
80 °C
70 °C
(f)
?H = 0.85
150 °C
130 °C
110 °C
100 °C
90 °C
80 °C
70 °C
q (nm-1)
length scale (nm)
amphiphilicity factor (fa)
Temperature (°C)
d
ξ
fa

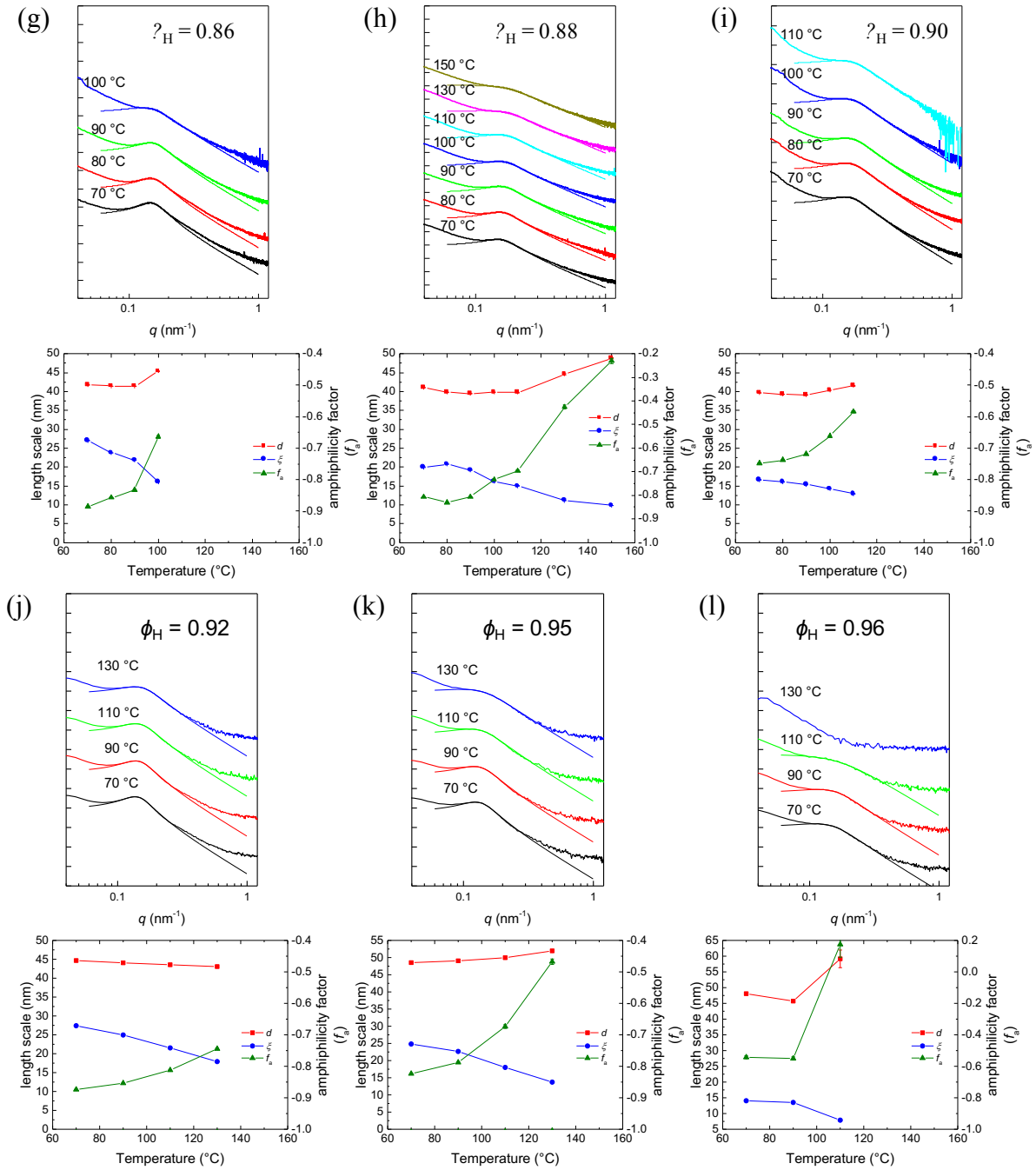


Figure S8: SAXS patterns (top) and domain spacing (d), correlation length (ξ), and amphiphilicity factor (f_a) (bottom) as a function of temperature associated with the best fits of the T-S model for blends in the BμE channel with $r = 0.03$. (a) – (l) $\phi_H = 0.80$, 0.81, 0.82, 0.83, 0.84, 0.85, 0.86, 0.88, 0.90, 0.92, 0.95, 0.96, respectively.

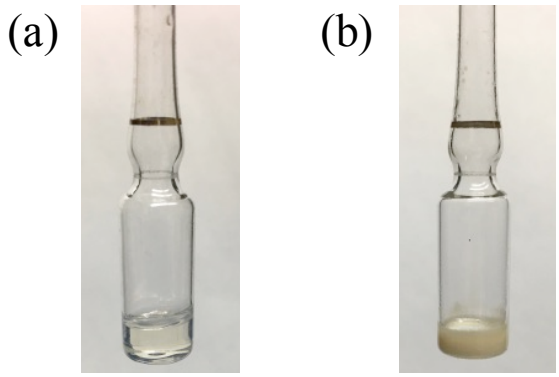


Figure S9: Photographs of LiTFSI-doped S/O/SO with r = 0.03, (a) ϕ_H = 0.86 and (b) ϕ_H = 0.88 at 120 °C.

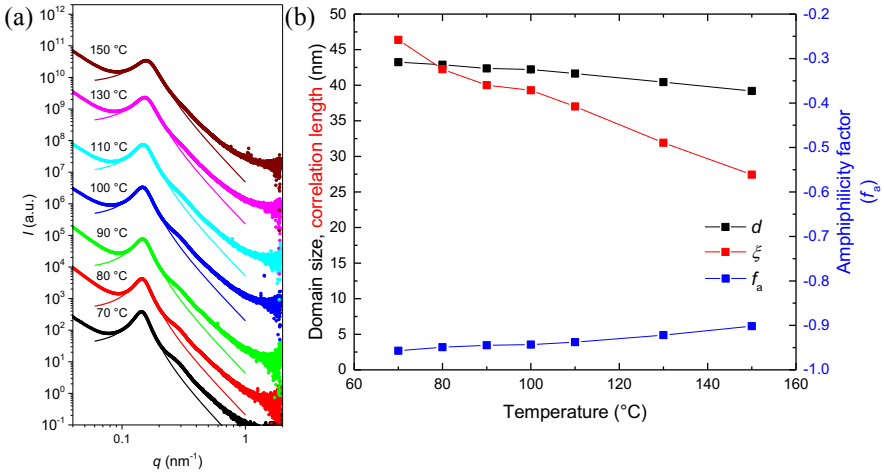


Figure S10: (a) SAXS patterns and (b) fitting results from the T-S model of a S/O/SO blend with ϕ_H = 0.88 and r = 0.06 as a function of temperature.

The interfacial area per unit volume can be calculated using Porod's law:

$$\lim_{q\to\infty} I(q)q^4 = 2\pi\left(\Delta\rho\right)^2 S_{\mathrm{I}} \tag{1}$$

where $\Delta\rho$ is the difference in scattering length density of pure dPS and PEO, and S_{I} is the microemulsion interfacial area per unit volume. Note that penetration of dPS homopolymer into the dPS block will not change $\Delta\rho$, and $I(q)$ in the high q range can be approximated by the T-S fit shown in Figure 3a. These allow us to calculate S_{I} and derive the detailed structure of the copolymer monolayer. Figure S11 shows that S_{I} is also a weak function of temperature, similar to the result from the polyethylethylene (PEE)/polydimethylsiloxane (PDMS)/PEE-PDMS system. The surface area can then be converted to the area per block copolymer, A_{c}, by $A_{\mathrm{c}} = S_{\mathrm{I}} v_{\mathrm{c}} / (1-\phi_{\mathrm{H}})$, where v_{c} is the volume per copolymer molecule. In the temperature range studied, A_{c} lies between 1.3 – 1.7 nm^2. The modest increase in S_{I} with temperature agrees with the decrease in ξ, which combined with the fact that d does not change significantly, indicates that the domain size is more polydisperse, according to Chen, et al.[1]

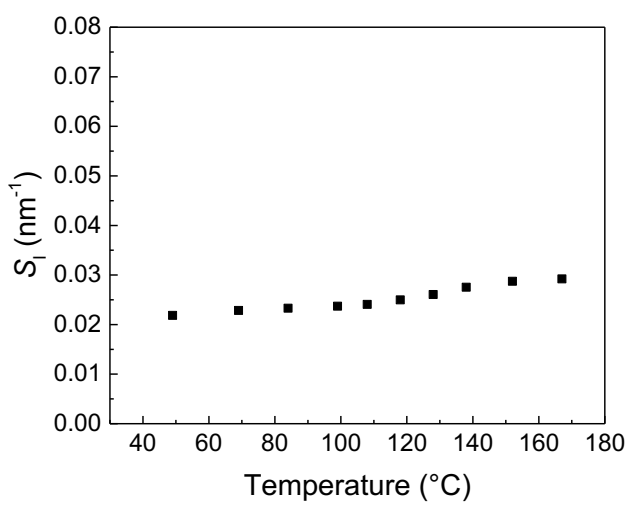


Figure S11: Surface area per unit volume as a function of temperature for dS/O/dSO blends with with r = 0.03 and ϕ_{H} = 0.86.

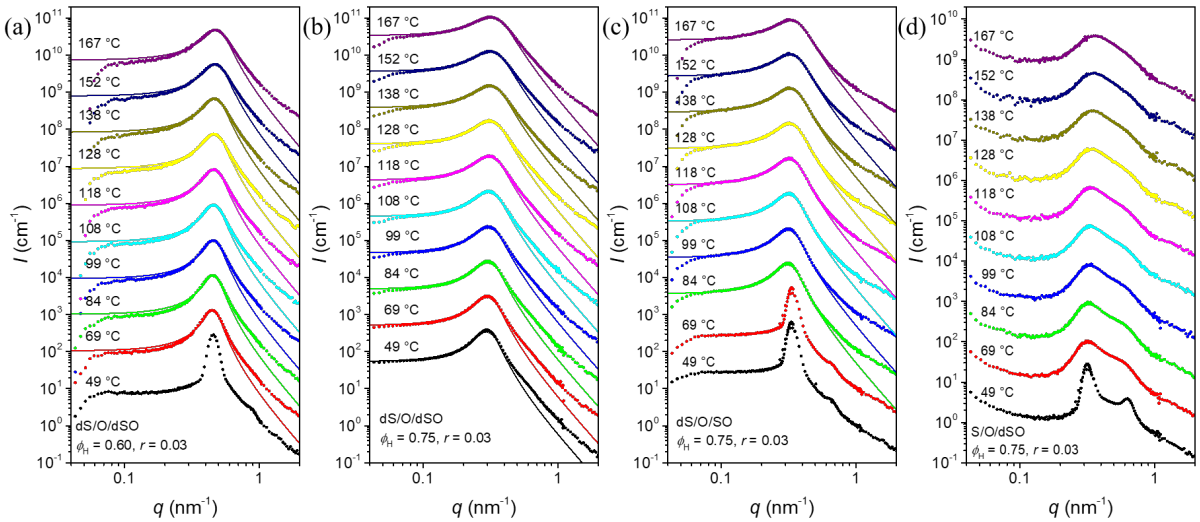


Figure S12: SANS data in absolute units acquired as a function of temperature for (a) dS/O/dSO, $\phi_H = 0.60$, (b) dS/O/dSO, $\phi_H = 0.75$ (c) dS/O/SO, $\phi_H = 0.75$ and (d) S/O/dSO, $\phi_H = 0.75$ with $r = 0.03$. The solids curves are the optimized T-S fits, which are indications of good BμE structures. At low temperature, scattering profiles shown in (a), (c), and (d) demonstrate the LAM morphology. All the scattering patterns have been vertically shifted successively by factors of 10.

Table S1. VFT Fitting Parameters Used for Fitting the DIS and BμE State Conductivity Data in Figure 7.

Sample	E_a (J mol^{-1})	σ_0 (mS cm^{-1})	T_0 (°C)
$\phi_H = 0$	7611	18.3	− 105 ± 39
$\phi_H = 0.18$	3469	6.13	− 33 ± 18
$\phi_H = 0.4$	2587	3.79	− 17 ± 33
$\phi_H = 0.5$	2470	3.10	− 18 ± 13
$\phi_H = 0.6$	3259	4.88	− 44 ± 20
$\phi_H = 0.7$	3694	5.19	− 43 ± 21
$\phi_H = 0.8$	1747	2.90	− 10 ± 4
$\phi_H = 0.86$	2446	5.68	− 33 ± 5
PEO ($r = 0.027$)	4465	43.7	− 78 ± 5

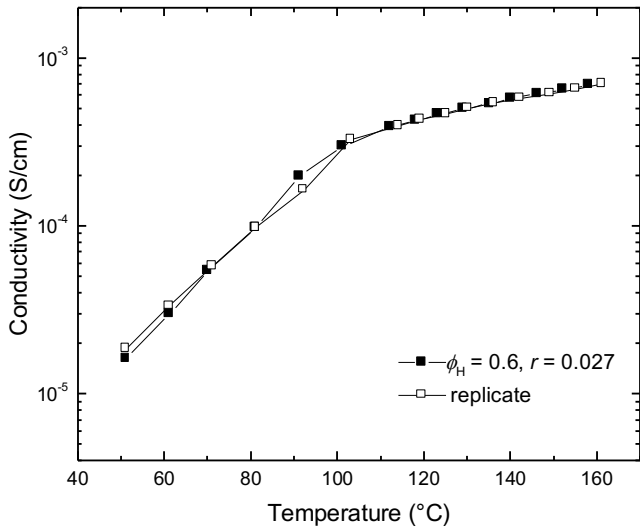


Figure S13: Conductivity profiles of a S/O/SO ternary blend with $\phi_H = 0.6$ and $r = 0.027$.

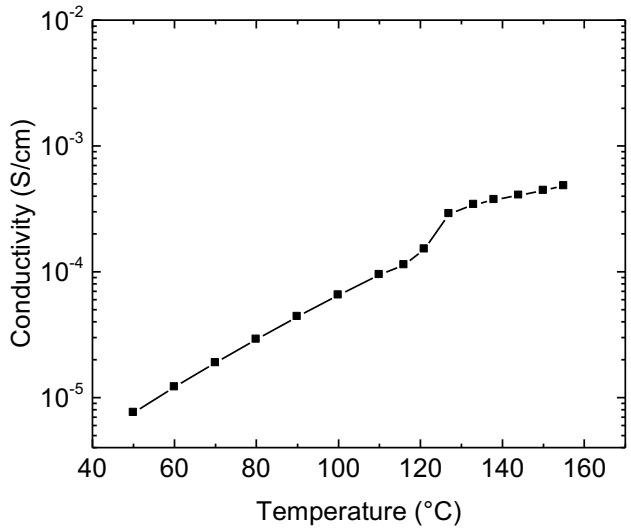


Figure S14: The conductivity profile of SO copolymer with $r = 0.03$. Lines are drawn to guide the eye

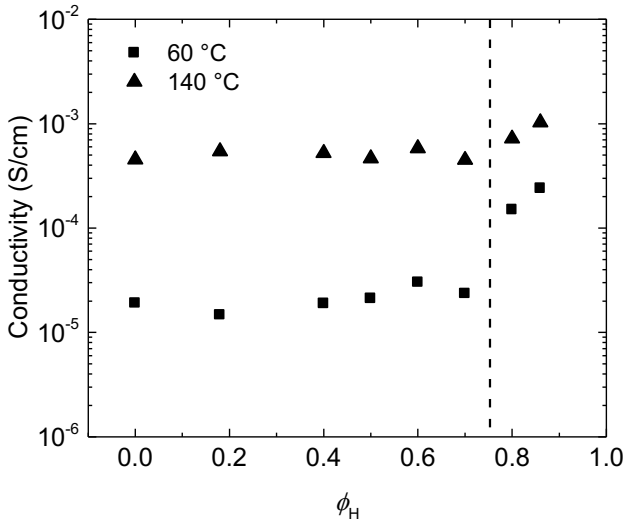


Figure S15: Conductivity profiles of S/O/SO ternary blends with $r = 0.027$ with various ϕ_H at 60 °C (squares) and 140 °C (triangles). The dashed line indicates the crossover of LAM into BμE.

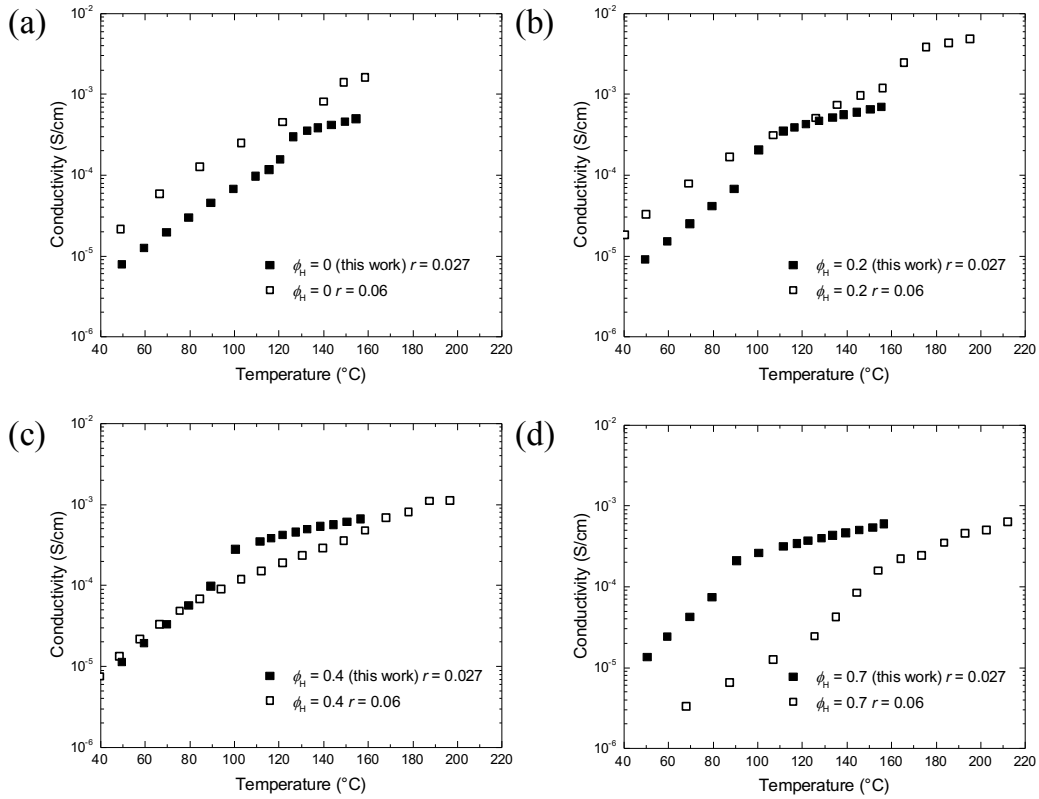


Figure S16: Comparison of the conductivity profiles of S/O/SO ternary blends with $r = 0.027$ (this work) and $r = 0.06$ (ref 2) with various ϕ_H.

(1) Chen, S. H.; Chang, S. L.; Strey, R. On the interpretation of scattering peaks from bicontinuous microemulsions. *Trends in Colloid and Interface Science IV* **1990,** *81*, 30-35.

(2) Irwin, M. T.; Hickey, R. J.; Xie, S.; So, S.; Bates, F. S.; Lodge, T. P. Structure–conductivity relationships in ordered and disordered salt-doped diblock copolymer/homopolymer blends. *Macromolecules* **2016,** *49*, 6928-6939.