Supporting Information

for

Self-Assembly of Highly Asymmetric, Poly(Ionic Liquid)-rich Diblock Copolymers and the Effects of Simple Structural Modification on Phase Behavior

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1) Determination of the DP and M_n values of the series of PS macro-initiators 3.

Table S1. DP, M_n, and PDI values of the PS macro-initiators **3**. The M_n values are rounded down to nearest hundred g/mol.

BCP	DP	M_n (g/mol)	PDI
3a	15	1,800	1.15
3b	20	2,400	1.10
3c	25	2,900	1.12
3d	30	3,400	1.08
3e	34	3,800	1.12
3f	36	4,000	1.13
3g	37	4,100	1.13
3h	40	4,400	1.11
3i	45	5,000	1.13

The PS macro-initiators **3a–i** were synthesized using the procedures previously reported.[1] The DP and M_n values of the synthesized PS macro-initiators **3a–i** were calculated based on the ^{1}H NMR peak integral of protons (*D*) on the TMS end-group relative to that of the protons (*E*) on the benzene ring for these polymers (Eqs. 1 and 2).[1] See Figure S1 below for example data used to calculate these values for **3h**.

$$\mathrm{DP} = \frac{\mathrm{E}_{^1\mathrm{H\ NMR\ Integration}} \times 9}{\mathrm{D}_{^1\mathrm{H\ NMR\ Integration}} \times 5} \qquad \text{(Eq. 1)}$$

$$M_n = (\mathrm{DP} \times M_{\mathrm{monomer}}) + M_{\mathrm{TMS\text{-}EBMP}} \qquad \text{(Eq. 2)}$$

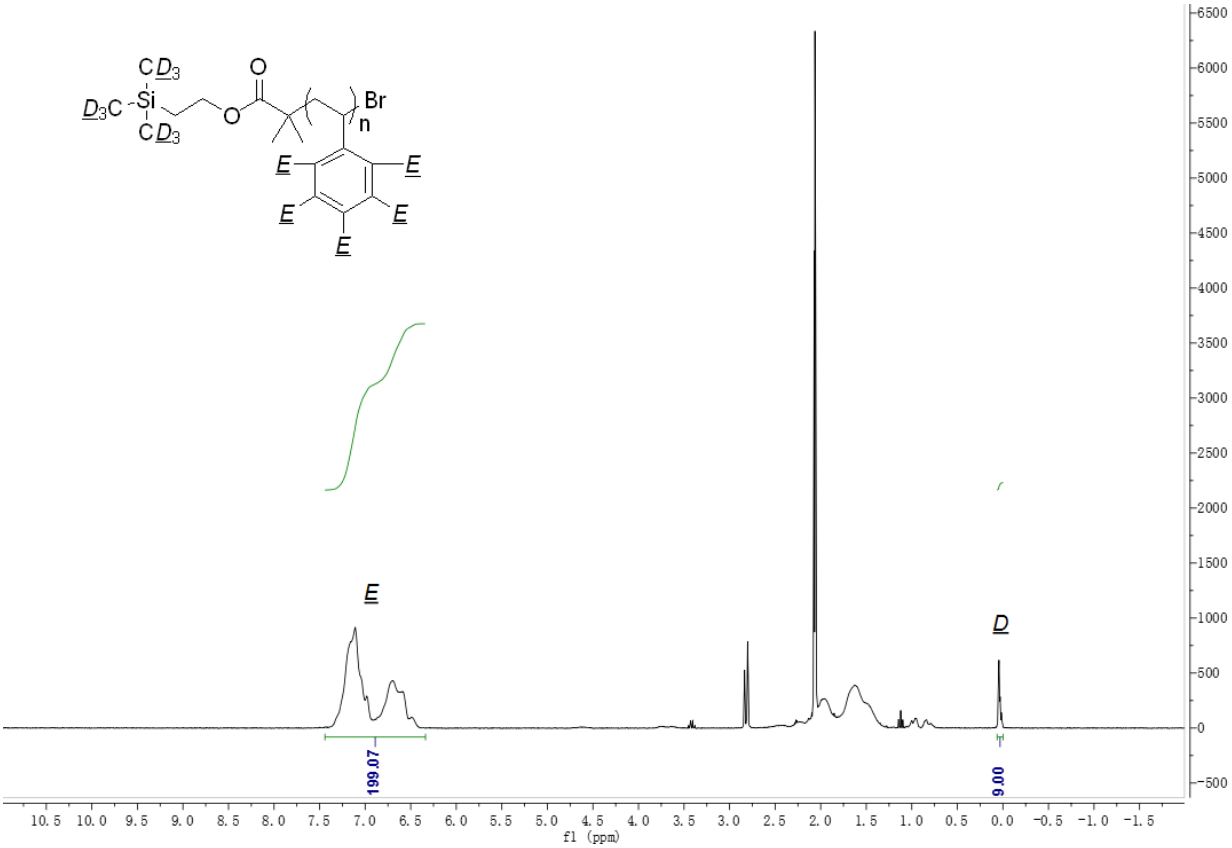

Figure S1. Example ^{1}H NMR spectrum of **3h**, and the ^{1}H NMR peak assignments used for calculating the DP and M_n value. Calculated DP = 39.8 ≅ 40, M_n = 4,433 ≅ 4,400 g/mol.

2) Determination of the block composition ratio and M_n values of the series of PS-PIL BCPs 1.

Table S2. Block composition ratios and M_n values of PS-PIL BCPs **1**. The M_n values are rounded down to nearest hundred g/mol.

BCP	n	m	M_n (g/mol)
1a	15	35	18,600
1b	20	30	16,700
1c	25	25	14,900
1d	30	18	12,000
1e	34	15	11,000
1f	36	14	10,800
1g	37	13	10,400
1h	40	12	10,200
1i	34	10	8,600
1j	40	10	9,200
1k	40	9	8,700
1l	40	8	8,300
1m	45	5	7,400
1n	15	35	20,100
1o	20	30	18,000
1p	25	25	15,900
1q	30	18	12,800
1r	34	14	11,100
1s	40	9	9,100
1t	45	5	7,600
1u	35	15	11,500
1v	40	10	9,500
1w	20	30	18,800
1x	25	25	16,600

The block composition ratios and M_n values of PS-PIL BCPs **1a–t** were determined via ^{1}H NMR analysis.[1] See Figure S2 for an example spectrum and ^{1}H NMR peaks assignments used for these calculations. The PS:PIL ratio can be calculated by Eq. 3. The length of PIL block can be calculated by Eq. 4 and confirmed by end-group analysis (Eq. 5). The M_n of PS-PIL BCPs can be calculated by Eq. 6.

$$\text{PS:PIL ratio} = \frac{[F_{^1\text{H NMR Integration}} - (6 \times B_{^1\text{H NMR Integration}})]}{B_{^1\text{H NMR Integration}} \times 5} \quad \text{(Eq. 3)}$$

$$\text{PS block length m} = \frac{\text{n}}{\text{Styrene:imidazolium–styrene ratio}} \quad \text{(Eq. 4)}$$

$$\text{PIL length m} = \frac{B_{^1\text{H NMR Integration}} \times 9}{D_{^1\text{H NMR Integration}}} \quad \text{(Eq. 5)}$$

$$M_n = (n \times M_{styrene}) + (m \times M_{monomer\ 2}) + M_{TMS\text{-}EBMP} \quad \text{(Eq. 6)}$$

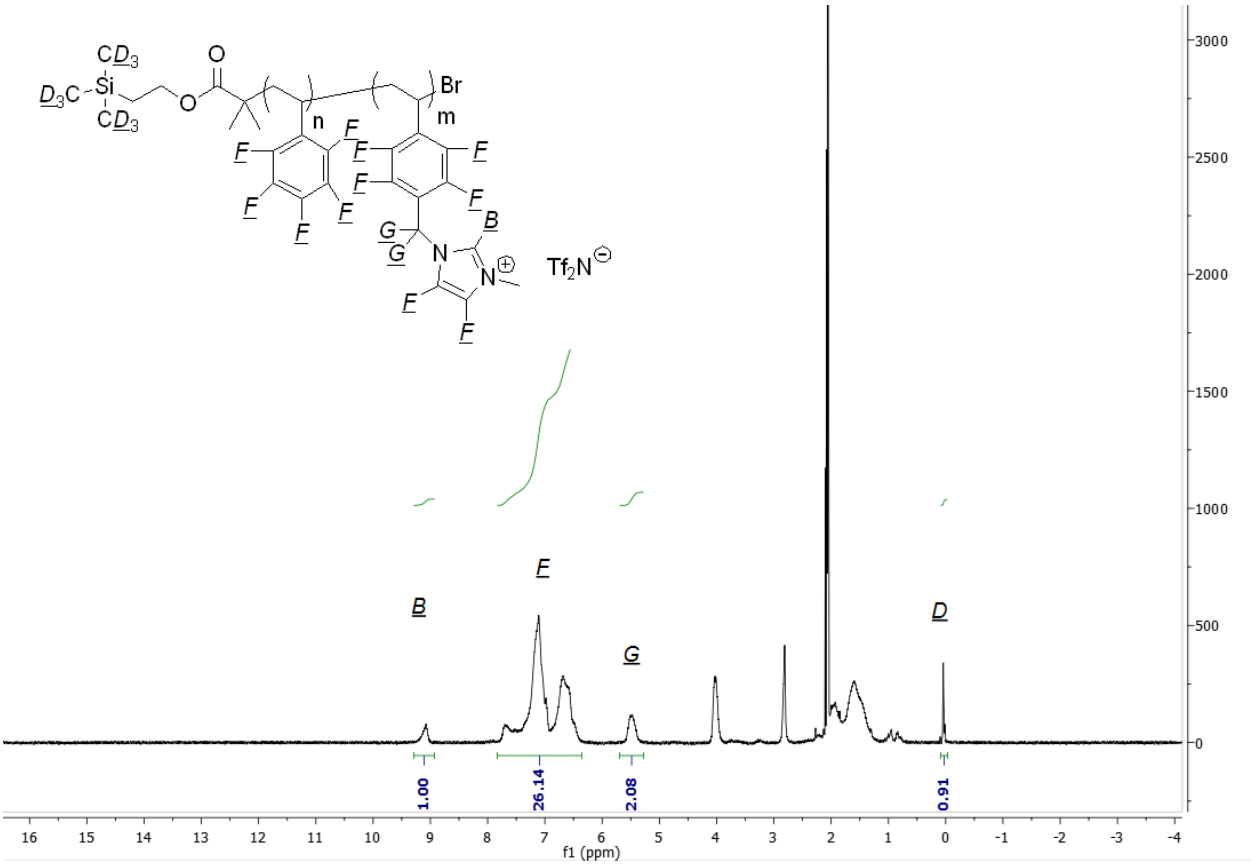

Figure S2. Example ^{1}H NMR spectrum of PS-PIL BCP **1j**, and the ^{1}H NMR peak assignments used for calculating the block composition ratio and M_n value. The calculated PS:PIL is 4.02, m = 9.93 ≅ 10, M_n = 9,227 ≅ 9,200 g/mol.

3) Temperature-dependent SAXS profiles for PS-PIL BCPs 1a–x.

For a complete description of the SAXS analysis procedures, see the Experimental Section in the main publication.

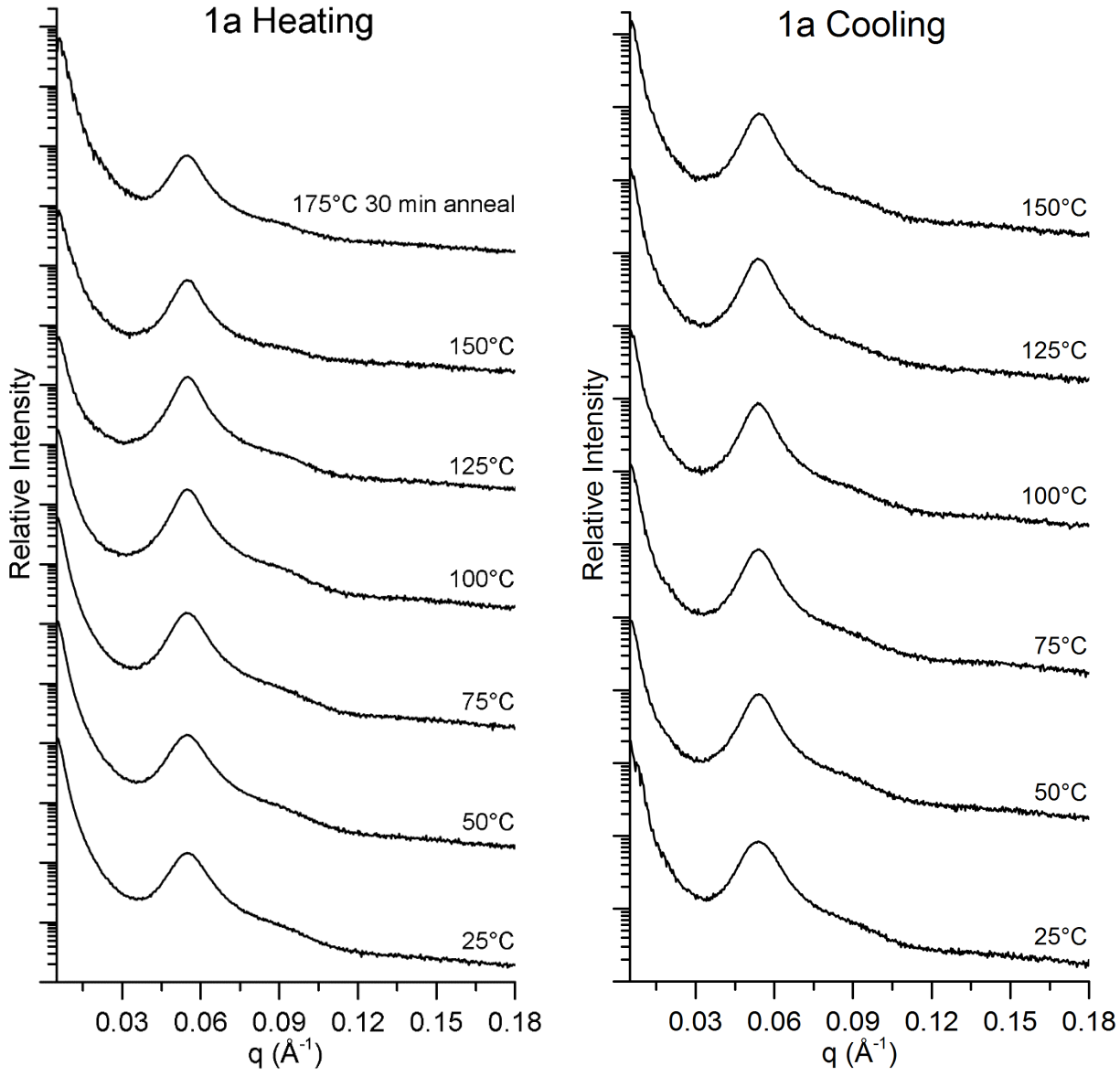

Figure S3.1. Temperature-dependent SAXS profiles for PS-PIL BCP sample **1a**.

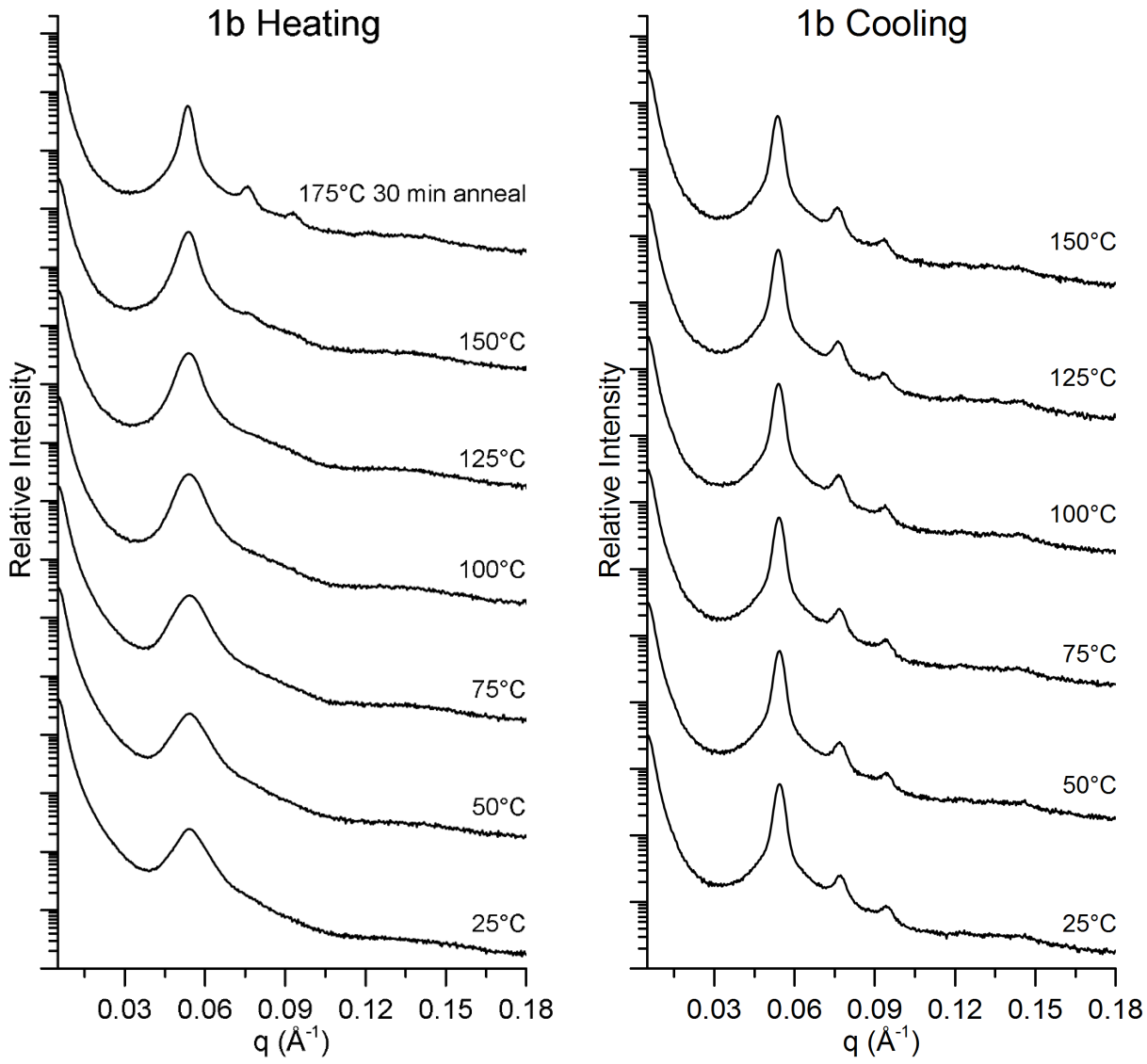

Figure S3.2. Temperature-dependent SAXS profiles for PS-PIL BCP sample **1b**.

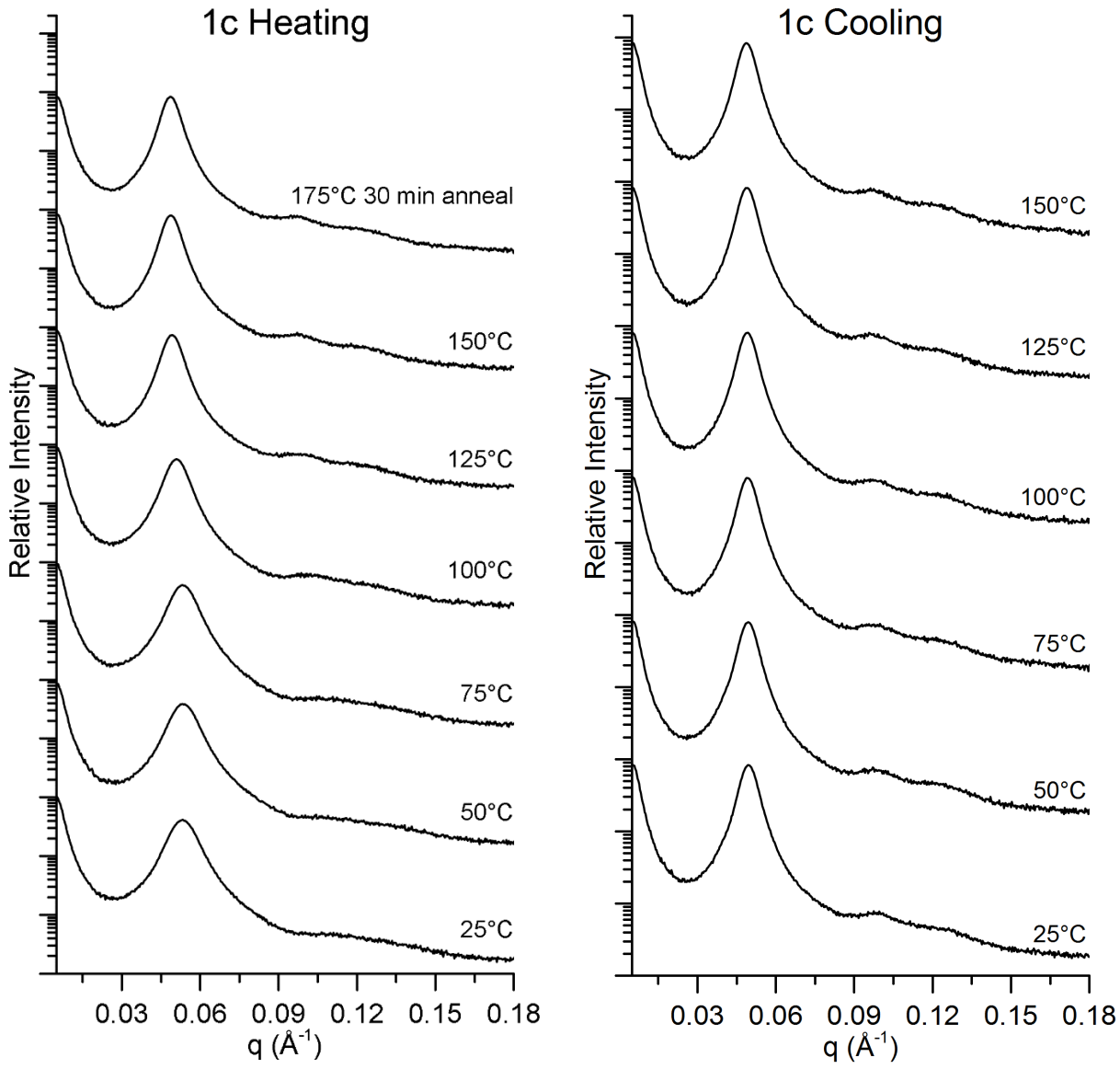

Figure S3.3. Temperature-dependent SAXS profiles for PS-PIL BCP sample **1c**.

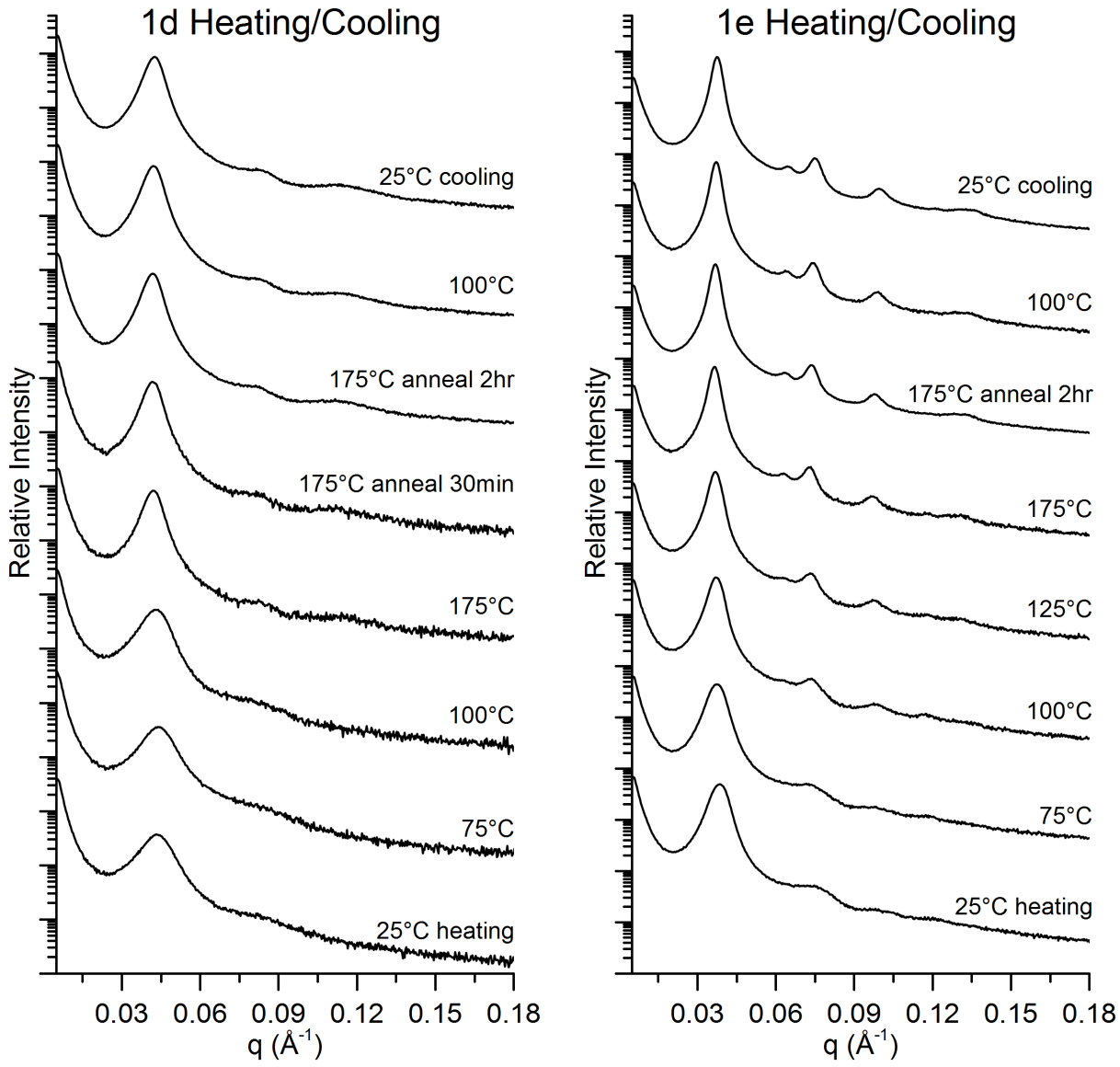

Figure S3.4 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1d and 1e**.

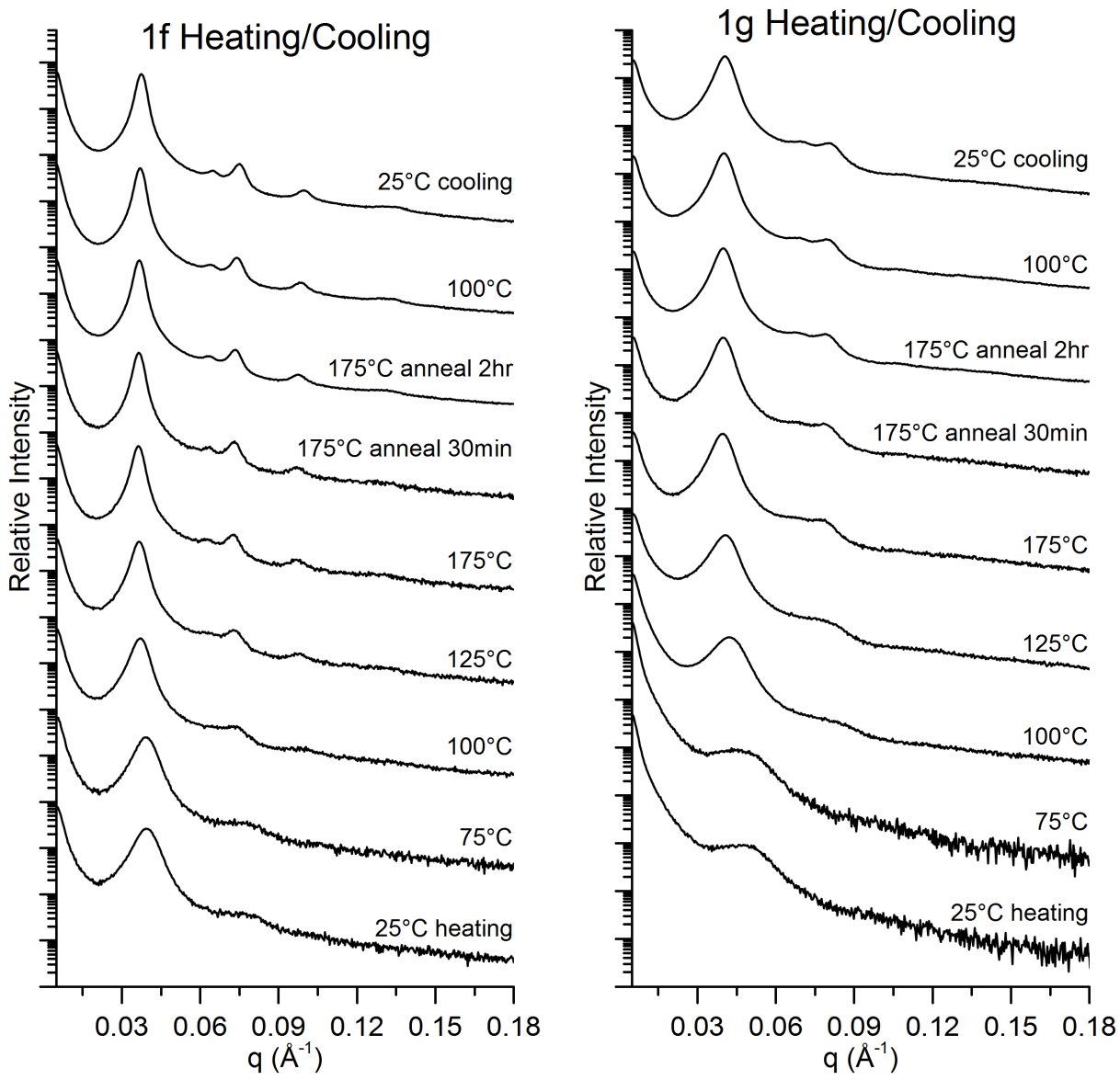

Figure S3.5 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1f and 1g**.

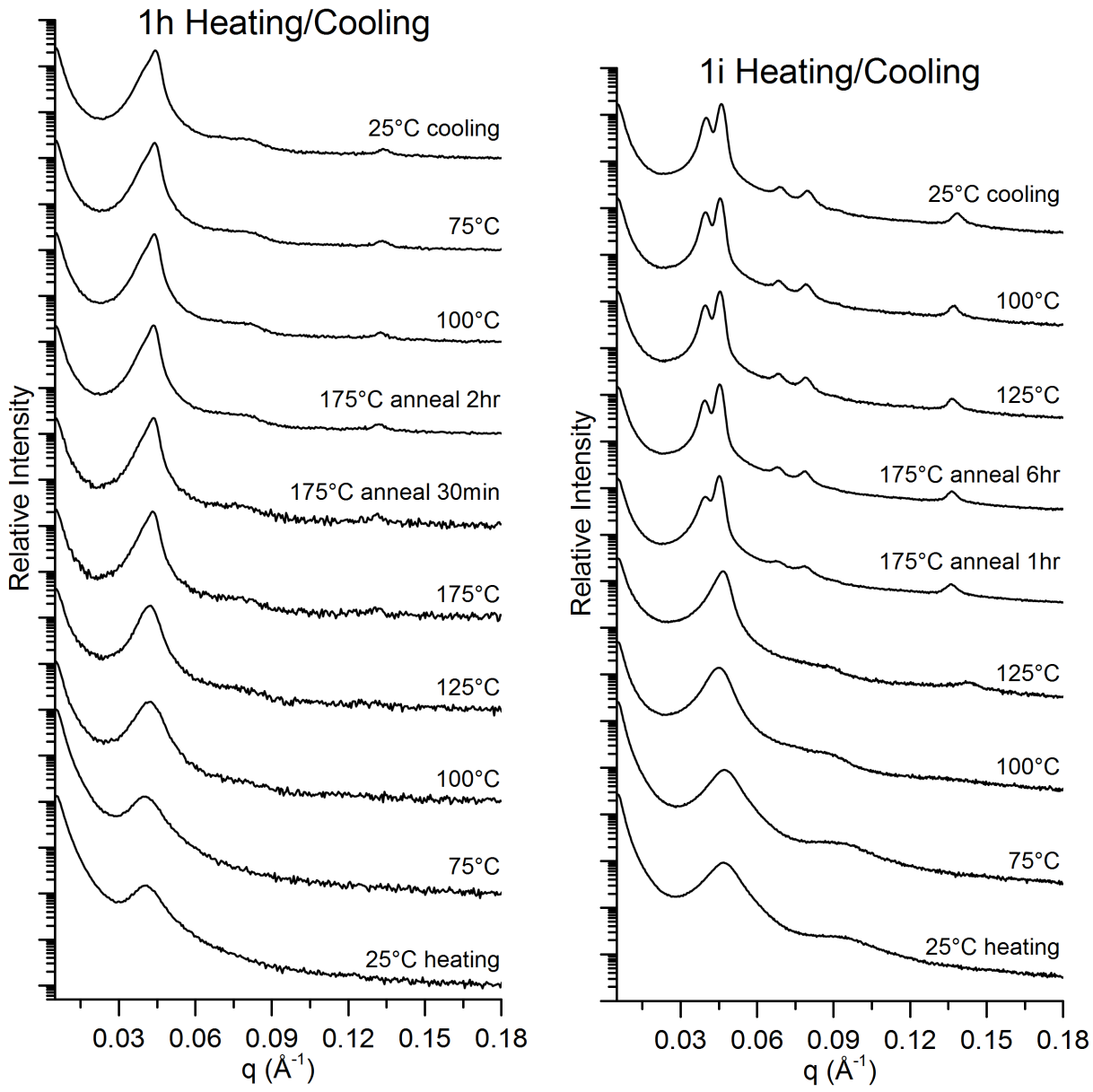

Figure S3.6 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1h and 1i**.

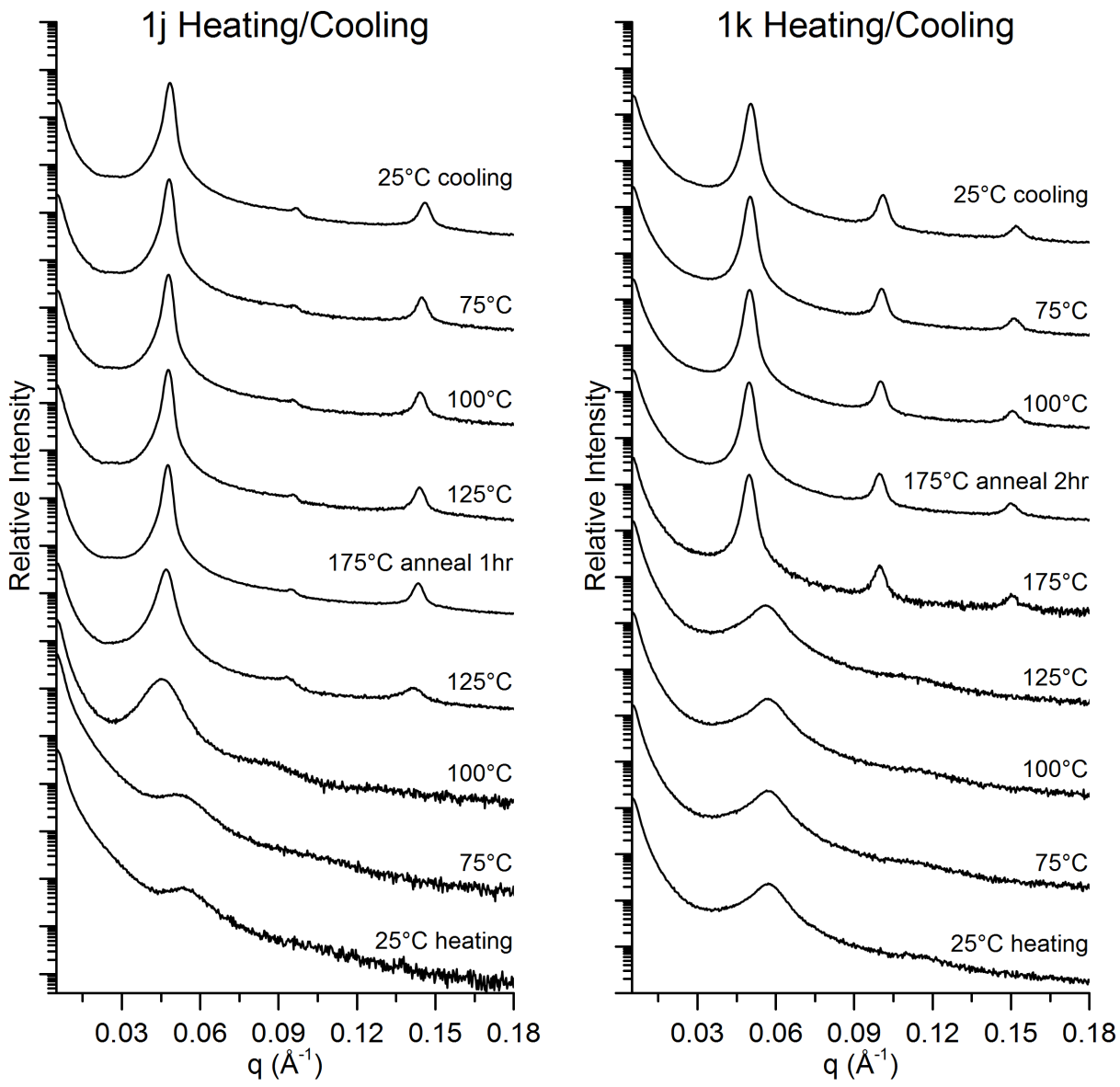

Figure S3.7 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1j and 1k**.

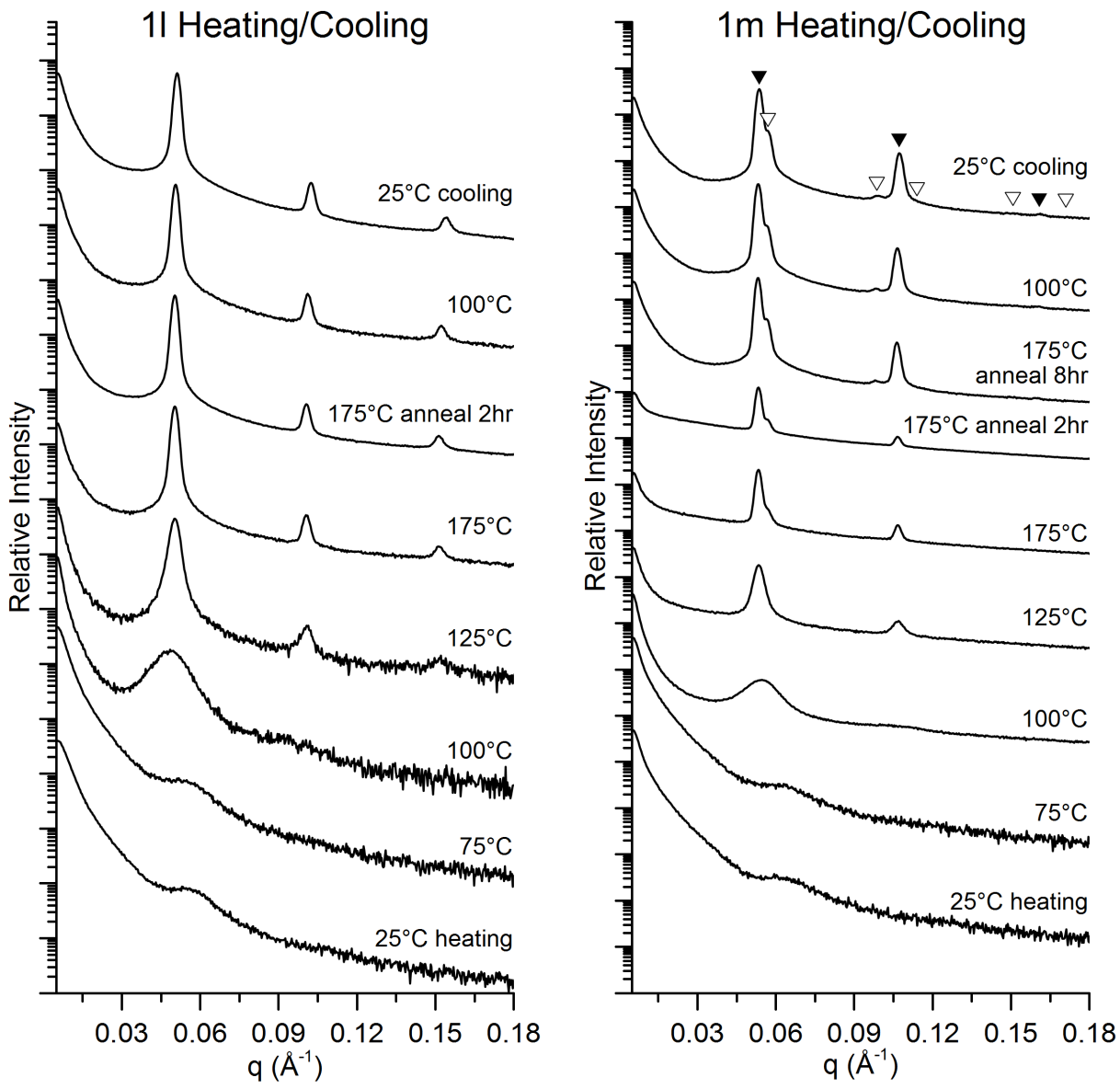

Figure S3.8 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1l and 1m**.

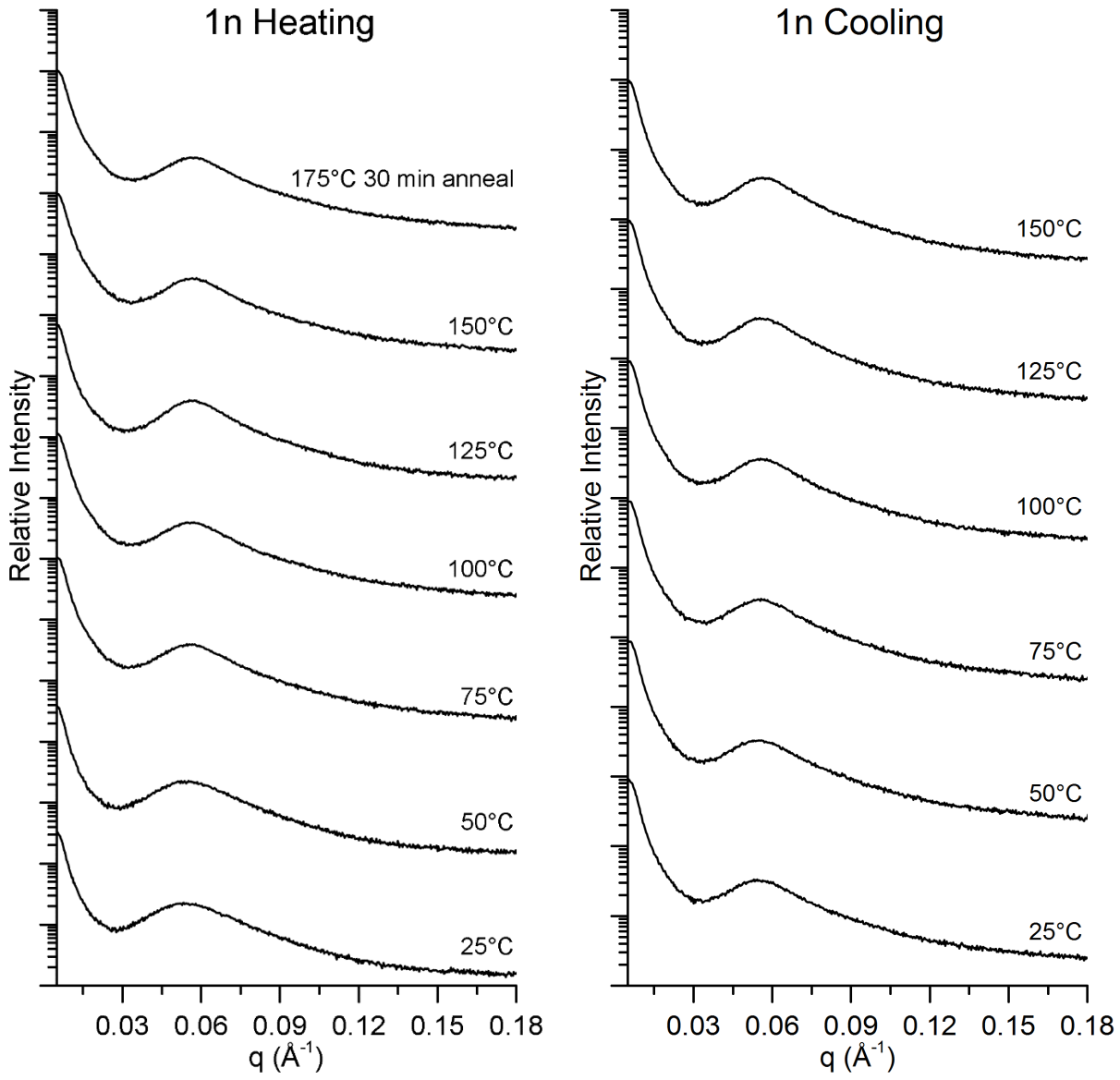

Figure S3.9 Temperature-dependent SAXS profiles for PS-PIL BCP sample **1n**.

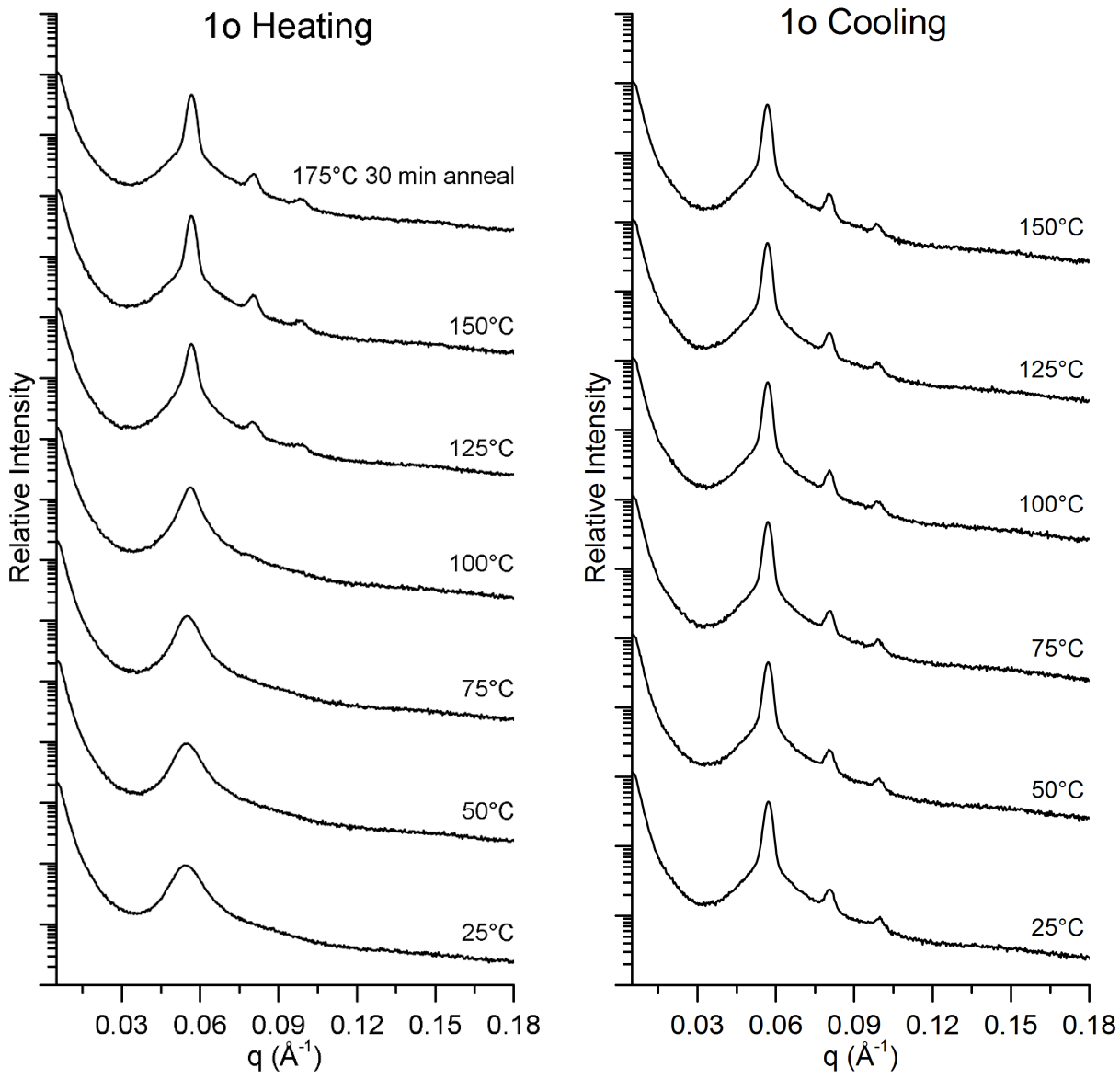

Figure S3.10 Temperature-dependent SAXS profiles for PS-PIL BCP sample **1o**.

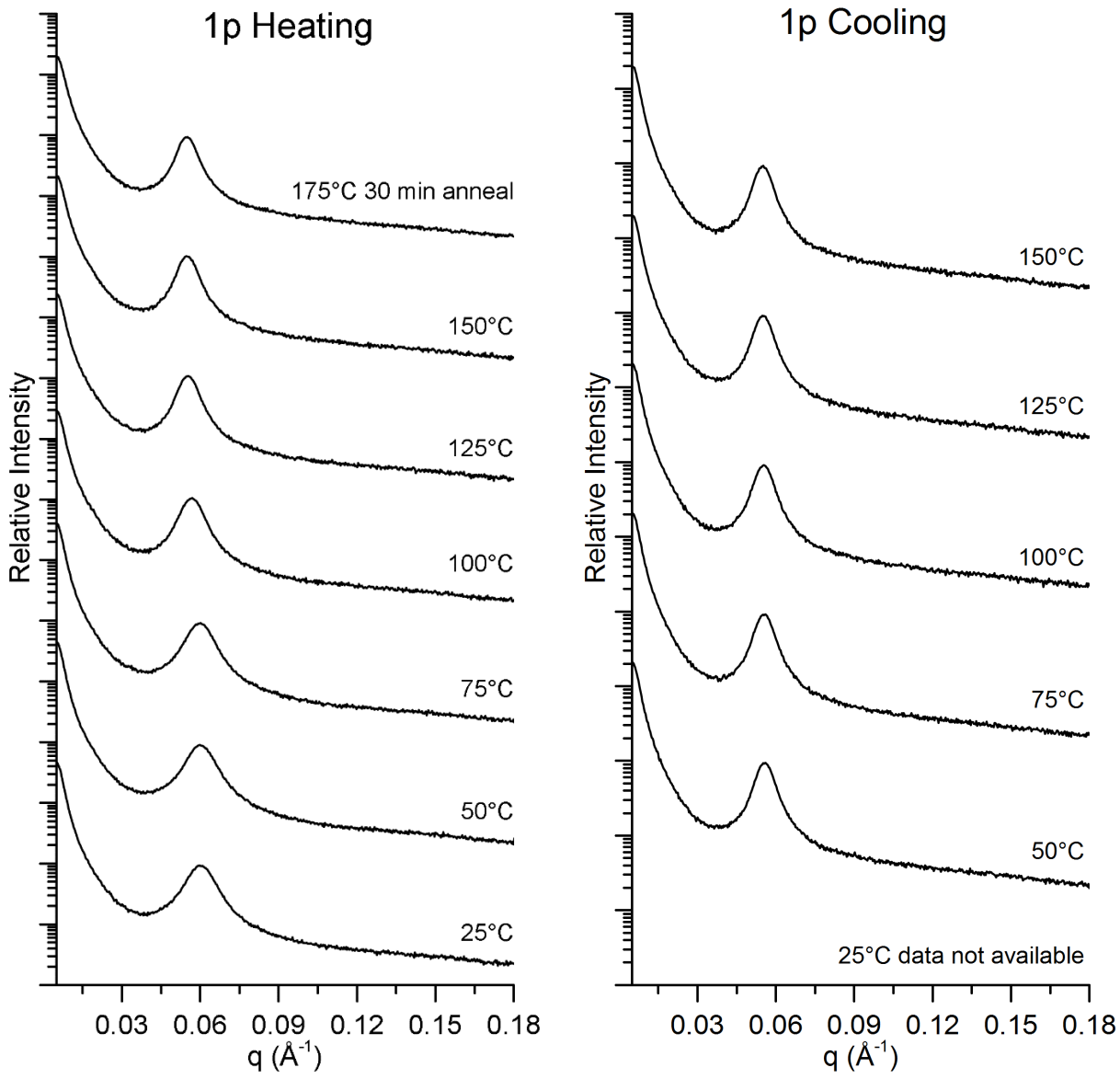

Figure S3.11 Temperature-dependent SAXS profiles for PS-PIL BCP sample **1p**.

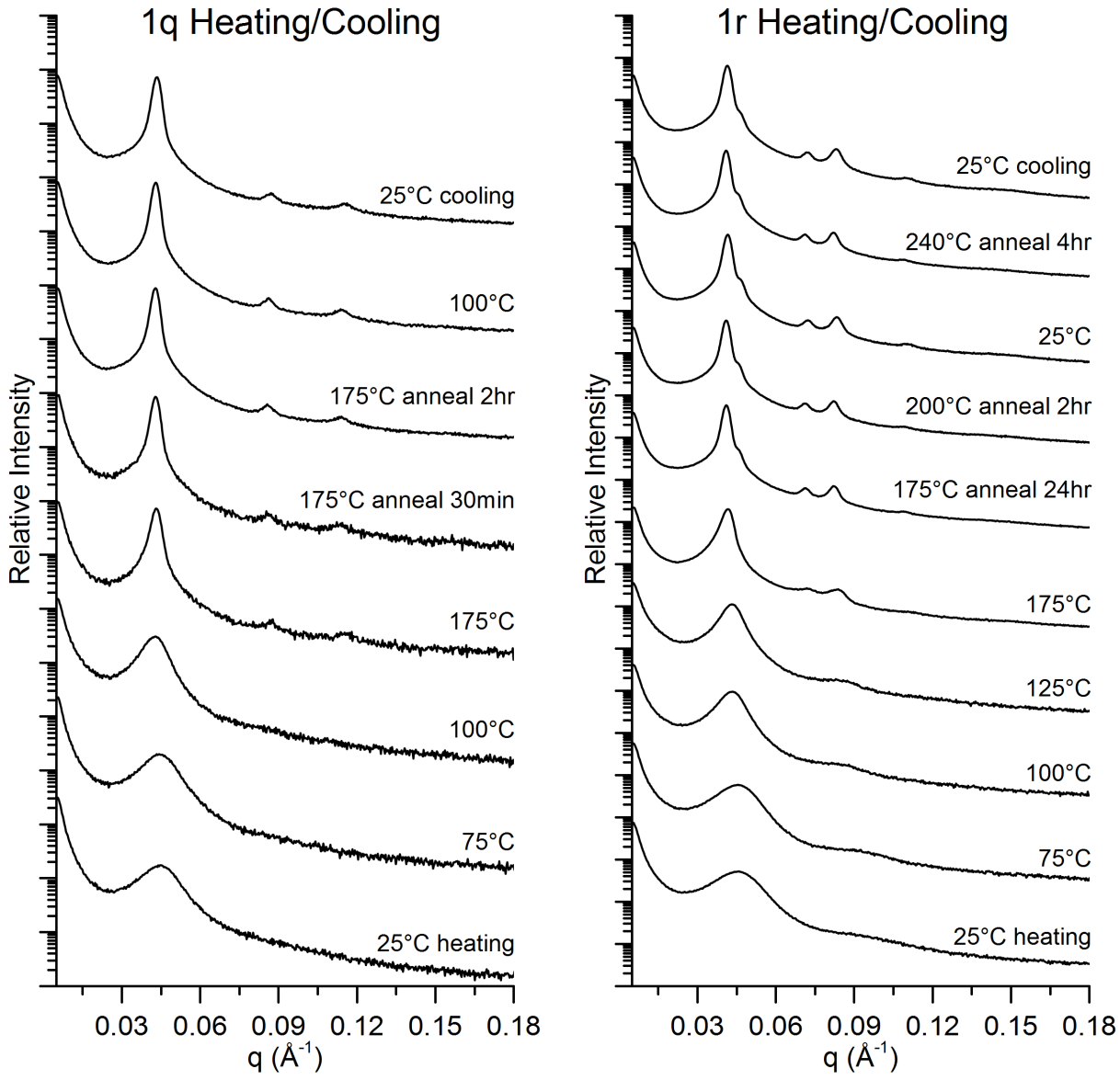

Figure S3.12 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1q and 1r**.

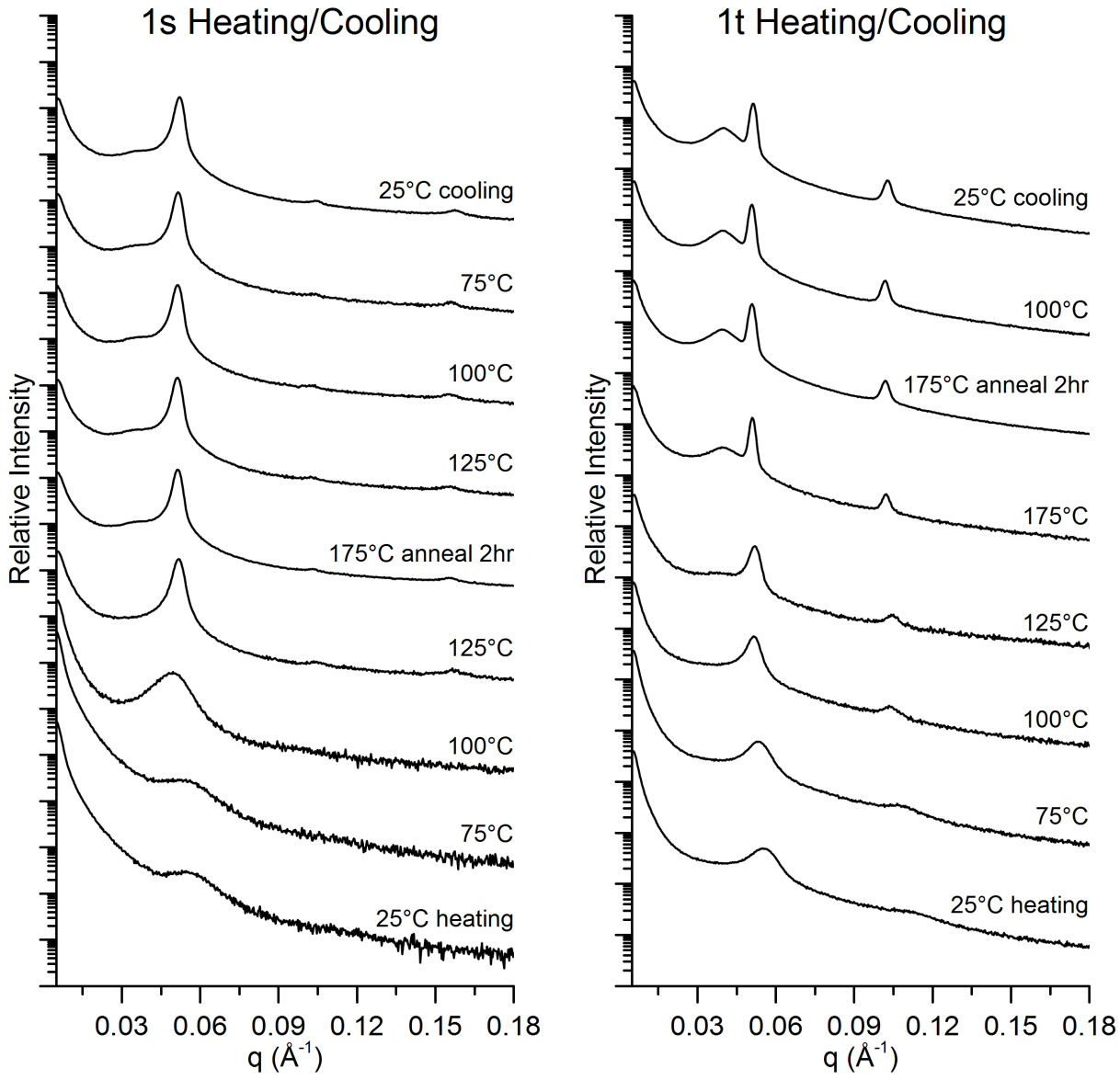

Figure S3.13 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1s and 1t**.

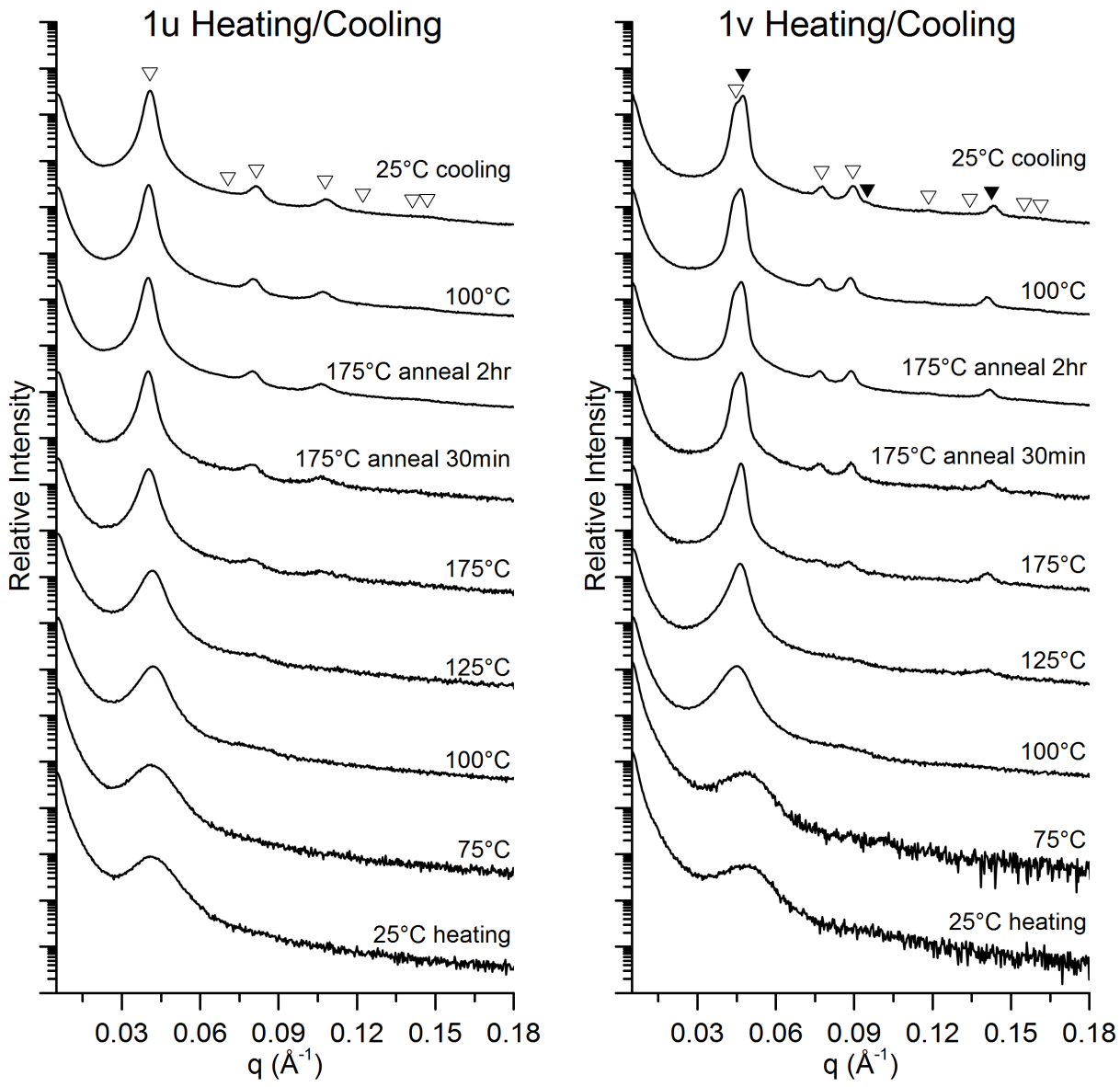

Figure S3.14 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1u and 1v**.

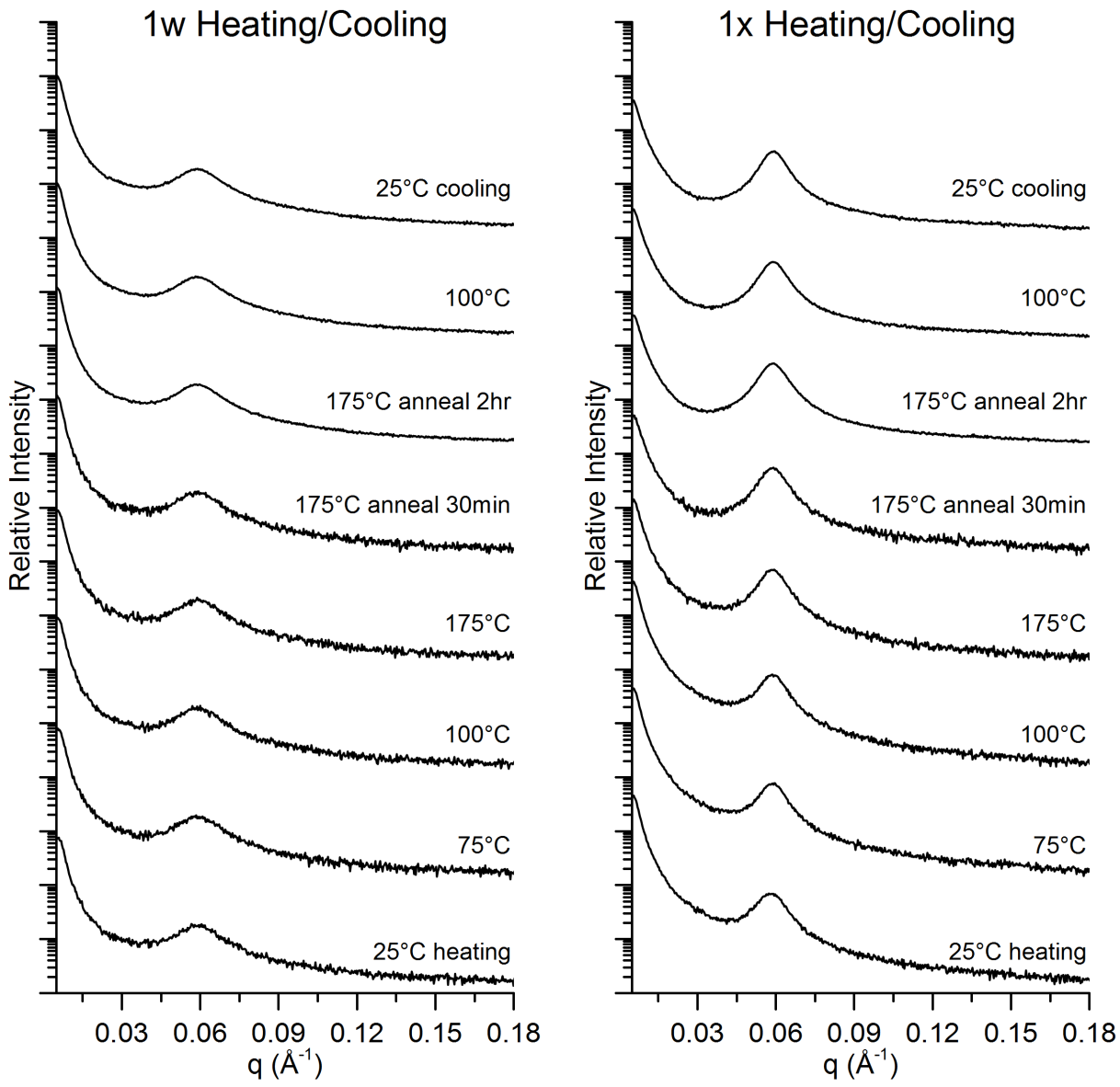

Figure S3.15 Temperature-dependent SAXS profiles for PS-PIL BCP samples **1w and 1x**.

4) Thermal Gravimetric Analysis (TGA)

TGA was run on three PS-PIL BCPs, **1j**, **1r**, and **1t**. All measurements were performed under nitrogen atmosphere with a temperature ramp rate of 10 °C/min from room temperature to 400 °C. No degradation of any sample was observed until 180 °C or higher, with onset degradation temperatures (at 10% weight loss) around 360 °C for all three samples.

Figure S4.1. TGA curve for sample **1j**.

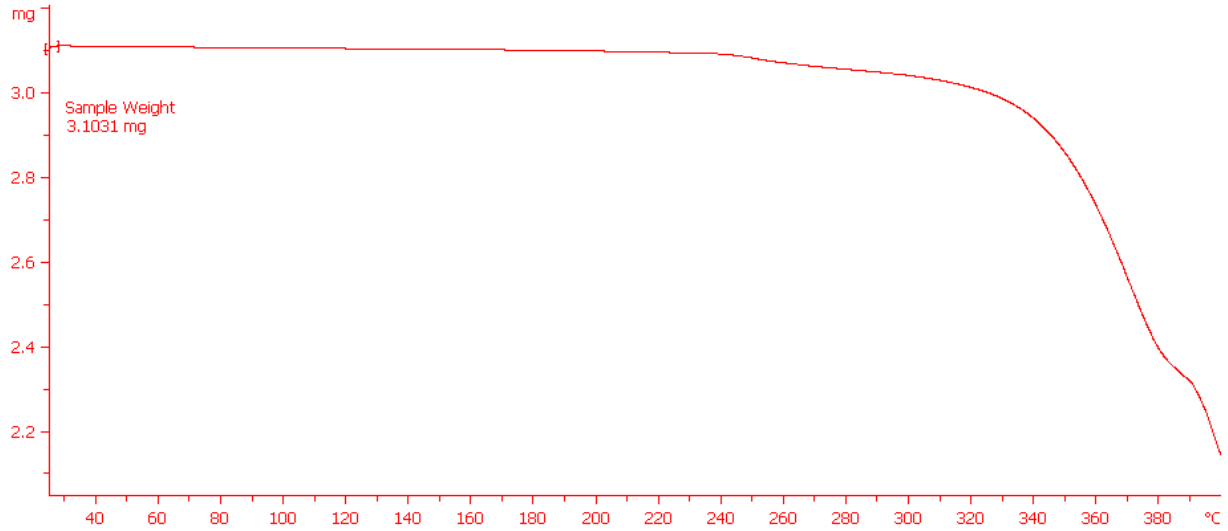

Figure S4.2. TGA curve for sample **1r**.

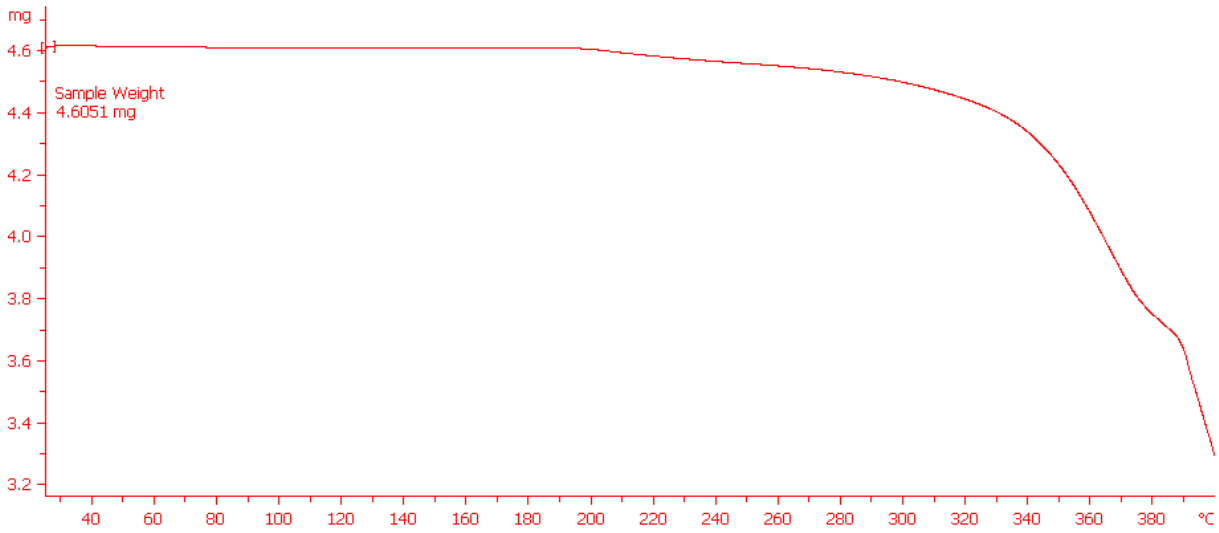

Figure S4.3. TGA curve for sample **1t**.

5) Differential Scanning Calorimetry (DSC)

DSC was run on three PS-PIL BCPs, **1d**, **1g**, and **1k**, using a heat-cool-heat-cool method at 10 °C min^{-1} from -40 °C to 180 °C. Weak transitions around 32 °C and 80 °C were observed for these three BCP samples. The transition at approximately 80 °C is likely the T_g of the PS block, and any transitions at lower temperatures can be attributed to the MePIL block, which is more liquid-like in character due to the IL moiety. It is also possible that no transition is observed for the MePIL block of sample **1k** due the low degree of polymerization of the MePIL block.

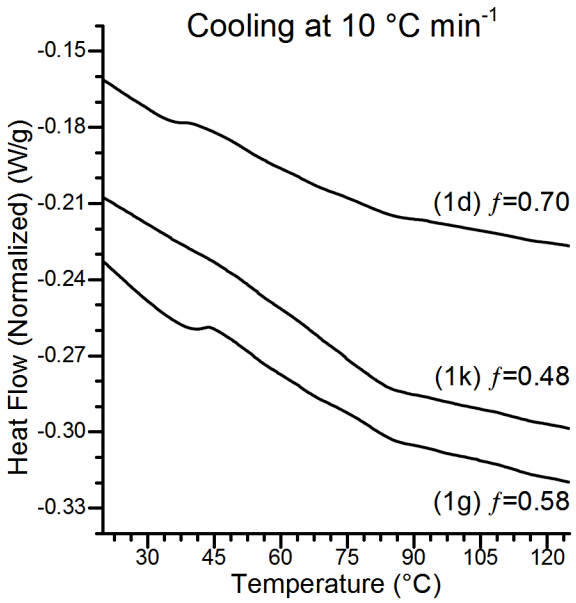

Figure S5. Differential scanning calorimetry data for samples **1d**, **1g**, and **1k.**

6) Gel Permeation Chromatography (GPC)

The following samples were run on a Viscotek GPC-Max chromatography system fitted with three 7.5 x 300 mm PolyPore (Agilent) columns in series, an Alltech external column oven set to 40 °C, and a Viscotek differential refractive index (RI) detector. 10mM $LiTf_2N$ in THF was used as the eluent,[2] and flow rate was 1.0 ml min^{-1}. PS-MePIL samples **1g, 1d,** and **1i** are plotted below, as compared to an ~8700 Da PS sample with a Đ < 1.10. Sample 1i has a molecular weight comparable to that of the PS sample. The PS-MePIL samples all show significant peak widths (all greater than 6 minutes) and variable peak shape. Additionally, sample **1d** is 3400 Da larger than sample **1i**, and should elute earlier than the smaller **1i**, which suggests that column interactions are complicating the elution of these polymers. Based on this evidence, we believe that definitive analysis of these materials with the GPC methodology from ref. 2 is unfeasable.

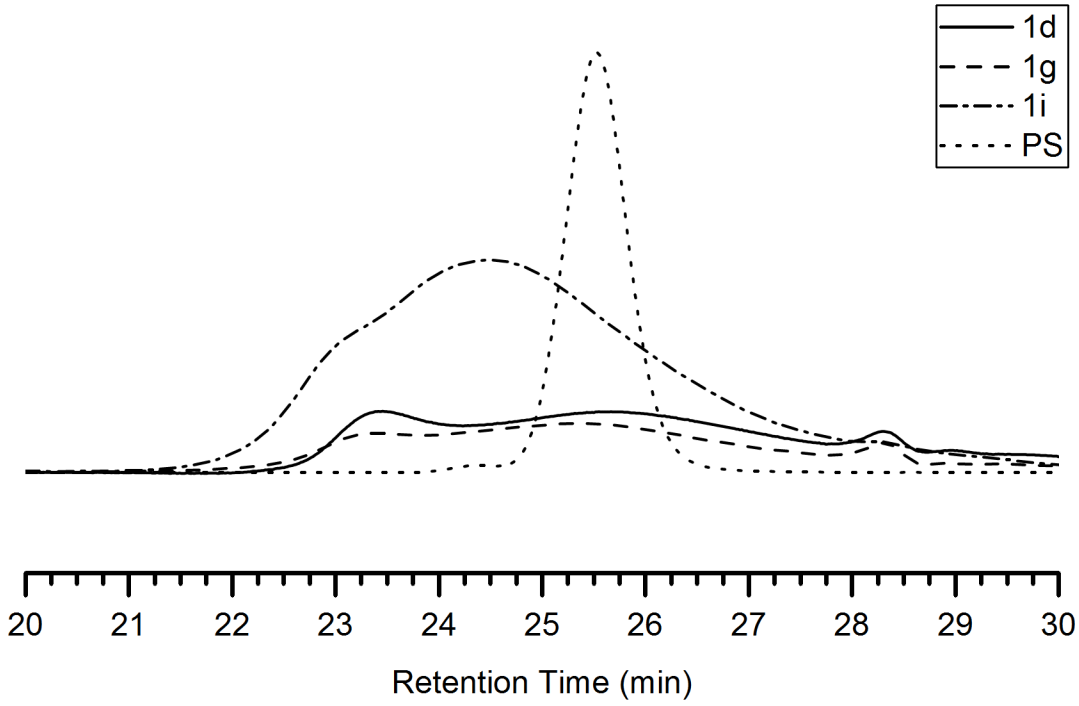

Figure S6. Gel permeation chromatography (GPC) results for selected PS-MePIL BCPs, **1g, 1d,** and **1i**, compared to an uncharged PS homopolymer with low dispersity and a comparable molecular weight.

7) References for the Supporting Information

1 Z. Shi, B. S. Newell, T. S. Bailey and D. L. Gin, *Polymer*, 2014, **55**, 6664–6671.

2 H. He, M. Zhong, B. Adzima, D. Luebke, H. Nulwala and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2013, **135**, 4227–4230.