X. Supporting Information – SAXS scattering data analysis details.

Here we summarize the scattering function $I(q)$ from the disordered melt of an A-B diblock copolymer with a polydispersity in molecular weight and an asymmetry in segmental volume. The details are given in Leibler, L. *Macromolecules* **1980**, *13*, 1602-1617 and in Sakurai, S *et al. Macromolecules* **1992,** 25, (10), 2679-2691.

$$I(q) = \mathrm{K}[S(q)/W(q) - 2\chi]^{-1} \tag{A1}$$

where K is a proportionality constant which is not important in the present work and χ is defined in the text.

$$S(q) = \langle S_{\mathrm{S,S}}(q)\rangle_{\mathrm{v}} + 2\langle S_{\mathrm{S,MMA}}(q)\rangle_{\mathrm{v}} + \langle S_{\mathrm{MMA,MMA}}(q)\rangle_{\mathrm{v}} \tag{A2}$$

$$W(q) = \langle S_{\mathrm{S,S}}(q)\rangle_{\mathrm{v}} \langle S_{\mathrm{MMA,MMA}}(q)\rangle_{\mathrm{v}} + \langle S_{\mathrm{S,MMA}}(q)\rangle_{\mathrm{v}}^{2} \tag{A3}$$

where

$$\langle S_{\mathrm{X,X}}(q)\rangle_{\mathrm{v}} = r_{c,n} f_{X,n}^{2} g_{X,n}^{(2)}(q) \tag{A4}$$

$$\langle S_{\mathrm{S,MMA}}(q)\rangle_{\mathrm{v}} = r_{c,n} f_{S}\, f_{MMA}\, g_{S,n}^{(1)}(q) g_{MMA,n}^{(1)}(q) \tag{A5}$$

$$r_{c,n} = (v_{\mathrm{S}}N_{\mathrm{S,n}} + v_{\mathrm{MMA}}N_{\mathrm{MMA,n}}) / (v_{\mathrm{S}} + v_{\mathrm{MMA}})^{1/2} \tag{A6}$$

$$g_{X,n}^{(1)}(q) = \frac{1}{x_{X,n}}\{1 - [x_{X,n}(\lambda_X - 1) + 1]^{-(\lambda_X - 1)^{-1}}\} \tag{A7}$$

$$g_{X,n}^{(2)}(q) = \frac{2}{x_{X,n}^{\;2}}\{-1 + x_{X,n} + [x_{X,n}(\lambda_X - 1) + 1]^{-(\lambda_X - 1)^{-1}}\} \tag{A8}$$

$$x_{X,n} \equiv (N_{X,n} b_X^{\;2} / 6) q^2 \tag{A9}$$

$$\lambda_{X,n} = N_{X,w} / N_{X,n} \tag{A10}$$

Where X = S or MMA, v_{X} is the molecular volume of X, with $v_{\mathrm{S}} \sim 100$ cm^3/mol and $v_{\mathrm{MMA}} \sim 84.7$

cm^3/mol. f_X is the volume fraction of X. $N_{X,n}$ and $N_{X,w}$ is the number-average and weight-average degree of polymerization of X block chain, respectively. b_X is the segment length of X, where $b_S \sim 0.68$ nm, and $b_{MMA} \sim 0.74$ nm. Here we assume $\lambda_S = \lambda_{MMA} \equiv \lambda$, which can be estimated from M_w/M_n for the block copolymer chains as a whole,

$$\lambda = (M_w / M_n - 1)/(w_S{}^2 + w_{MMA}{}^2) + 1 \tag{A11}$$

Where $w_S = 1 - w_{MMA}$ is the weight fraction of S block chain in the PS-*b*-PMMA block copolymers. All parameters used are summarized in Table 1. χ was determined as a value which gives rise to a best fit between the experimental and theoretical relative intensity distributions, and summarized in Table 2.

Table 1. Characteristic Parameters Used to Evaluate χ values.

Sample	w_s	f_S	N_S	N_{MMA}	λ	$r_{c,n}$
1	0.53	0.56	143	131	1.1	276
2	0.5	0.53	123	129	1.1	252

Table 2. Temperature dependence of χ values.

T, °C	χ for sample 1	χ for sample 2
230	0.0373	
220	0.0374	0.0373
210	0.0375	0.0375
200		0.0377
190		0.0379
180		0.0381
170		0.0382
160		0.0383
150		0.0384
140		0.0385
130		0.03854
120		0.03856