

Appendix

The following equations from Matsen and Bates⁴⁶ were used to estimate the domain spacing and domain size of theoretical block copolymers in the strong segregation regime with identical properties to the gradient copolymers synthesized in our experiments. The Kuhn length of PS is 0.68 nm and the Kuhn length of PMMA 0.74 nm. The Flory-Huggins parameter was estimated at 220 °C (oven temperature) to be 0.036.

R – Equilibrium domain size

D* - Domain spacing

a – Statistical segment length (Kuhn length)

χ – Flory-Huggins parameter

N – Degree of polymerization

f – Minority component fraction (i.e. $f < .50$)

T – Temperature [Kelvin]

$$R = a \left(\frac{\beta}{2(\alpha^A + \alpha^B)} \right)^{\frac{1}{3}} \chi^{\frac{1}{6}} N^{\frac{2}{3}}$$
$$\chi = 0.028 + \frac{3.9}{T}$$

For cylinders:

$$\alpha^A = \frac{\pi^2}{16}$$

$$\alpha^B = \frac{\pi^2 (1 - f^2)^3 (3 + f^2)}{16(1 - f)^2}$$

$$\beta = \frac{2f^{\frac{1}{2}}}{6^{\frac{1}{2}}}$$

$$D^* = \left(\frac{3\pi^4}{4} \right)^{\frac{1}{6}} R$$

For lamellar:

$$\alpha^A = \frac{\pi^2 f}{8}$$

$$\alpha^B = \frac{\pi^2 (1 - f)}{8}$$

$$\beta = \frac{1}{6^{\frac{1}{2}}}$$

$$D^* = 2R$$

