CORRECTIONS

J. D. Vavasour and M. D. Whitmore*: Self-Consistent Theory of Block Copolymers with Conformational Asymmetry. Vol. 26, Number 25, December 6, 1993, pp 7070−7075.

This paper included the results of numerical SCF calculations of the microphase diagram of conformationally asymmetric diblock copolymers, considering the lamellar phase, the hexagonal phase which consists of cylinders on a hexagonal lattice, and the cubic phase which consists of spheres on a body-centered cubic lattice. In carrying out these calculations, the unit cells were approximated by cylinders and spheres for the hexagonal and cubic structures, respectively. We reported that conformational asymmetry introduced direct, although small, transition "windows" from the homogeneous (H) phase to the lamellar (L) and cylindrical (C) phases, i.e., H ↔ L and H ↔ C transitions. This was exhibited explicitly in Figure 2 of that paper, which was calculated for the extreme case of very high conformational asymmetry, with parameter $\epsilon \equiv (\rho_{0\mathrm{B}} b_{\mathrm{B}}^2)/(\rho_{0\mathrm{A}} b_{\mathrm{A}}^2) = 0.1$, where $\rho_{0\kappa}$ and b_κ are the pure component monomer density and statistical segment length of block κ, respectively, for $\kappa = \mathrm{A}$ or B.

Subsequently, Matsen and Schick[1] carried out a series of numerical SCF calculations without approximating the unit cells. They did not obtain these transition windows. Instead, their results are consistent with the microphase boundaries merging at a critical point at copolymer A-block volume fraction $f_{\mathrm{A}} = 0.650$ and $\chi Z = 11.92$, where χ is the Flory interaction parameter and Z is the copolymer degree of polymerization, and they speculated that the difference might be due to the different treatments of the unit cells.

These results motivated us to reexamine our earlier work, improve our numerical procedures, and repeat our calculations. This has resulted in a revised phase diagram, which is shown below. It is very similar to our original figure except that, to within our numerical uncertainty, all the phase boundaries merge at a critical point. These results, including the location of the critical point, are consistent with those of Matsen and Schick. We conclude that there is no evidence that the numerical SCF theory predicts direct H ↔ L or H ↔ C transitions, except at a critical point, with or without the approximate unit cells. Of course, finite numerical precision precludes ruling out very narrow windows. On the basis of our estimated uncertainty, we place an upper limit on the widths of these windows to be on the order of $\delta f_{\mathrm{A}} \lesssim 0.002$.

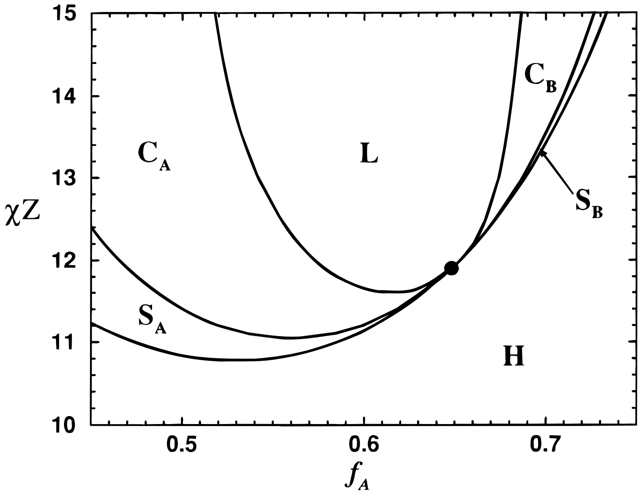

Figure 1. Part of the microphase diagram calculated for highly asymmetric copolymers with $\epsilon \equiv (\rho_{0\mathrm{B}} b_{\mathrm{B}}^2)/(\rho_{0\mathrm{A}} b_{\mathrm{A}}^2) = 0.1$. The labels indicate the regions of stability of the homogeneous phase (H), layers (L), A- and B-centered spheres ($\mathrm{S_A}$ and $\mathrm{S_B}$), and A- and B-centered cylinders ($\mathrm{C_A}$ and $\mathrm{C_B}$). To within numerical uncertainty, the phase boundaries merge at a critical point, indicated by the filled circle.

References and Notes

(1) Matsen, M. W.; Schick, M. *Macromolecules* **1984**, *27*, 4014.

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