Macromolecules 1993, *26,* 396-397

Notes

Dependence of the Interphase Thickness on Chain Length in Block Copolymers: Revisited

Richard J. Spontak*

Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45239

John M. Zielinski

Performance Chemicals Technology, Air Products and Chemicals Inc., Allentown, Pennsylvania 18195

Received June 29, 1992
Revised Manuscript Received September 11, 1992

Diblock copolymers undergo microphase separation into ordered morphologies when the magnitude of repulsive interactions between the blocks exceeds a critical value of χN (χ is the Flory–Huggins interaction parameter and N is the degree of polymerization) at the order–disorder transition (ODT). Investigators have continually sought to advance thermodynamic theories which would correlate molecular parameters of the copolymers with observed morphologies. Early approaches[1–4] focused on microphase-separated block copolymers in the strong-segregation limit (SSL) and predicted microstructural dimensions in reasonably good agreement with experimental data. Shortly after the first SSL models were introduced, Leibler[5] proposed a mean-field formalism which identified the weak-segregation limit (WSL) and the conditions responsible for the ODT. A variety of additional theoretical treatments have since appeared in the literature, focusing on either the WSL[6,7] or the SSL.[8,9]

Melenkevitz and Muthukumar[10] and Shull[11] have recently proposed mean-field formalisms which predict microstructural dimensions in both segregation regimes, as well as the conditions corresponding to the ODT (in the absence of critical fluctuations[6]). Predictions obtained from both approaches reveal novel relationships in the crossover from WSL to SSL. One such relationship of particular interest arises in the self-consistent-field (SCF) calculations provided by Shull[11] and reflects the dependence of the interphase thickness (λ') on the copolymer chain length. Those predictions are shown in Figure 1 and reveal that, at low χN, λ' exceeds its asymptotic value (λ_∞), obtained from

$$\lambda_\infty = 2b/(6\chi)^{1/2} \tag{1}$$

where b is the statistical segment (monomer) length used to calculate the unperturbed radius of gyration of the copolymer molecule (R_g) from $b(N/6)^{1/2}$. Equation 1 is the narrow-interphase approximation (NIA), first introduced by Helfand and Wassermann[4] for copolymers in the limit of infinitely incompatible blocks. Initially believed to be applicable when $\chi N \geq 20$, the NIA has proven extremely valuable as a means of estimating λ' in the SSL.

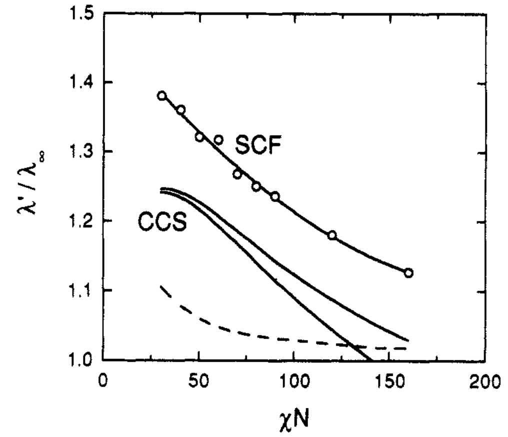

Figure 1. Predicted $\lambda'/\lambda_\infty(\chi N)$ obtained from the SCF approach taken by Shull[11] (○) and the CCS formalism presented here for perfectly symmetric diblock copolymers. The two CCS curves correspond to R_g values of 10 (upper) and 100 nm (lower). Predictions from the theory proposed by Broseta et al.[13] for incompatible homopolymer blends are also provided (dashed line) for comparison.

Many SSL approaches[4,8,9] which require a uniform microdomain density explicitly implement eq 1 or a suitable variation thereof to facilitate free-energy minimization. In these formalisms, $\lambda' = \lambda_\infty$ for all N. Theoretical treatments based on confined-chain statistics (CCS) rely on assumptions regarding uniform core density but, in return, predict λ' as a function of N, instead of assuming eq 1 a priori.[2,3] The objective of this note is to compare quantitatively predictions for $\lambda'(\chi N)$ obtained from the SCF calculations reported by Shull[11] with those acquired from a CCS formalism for a symmetric AB diblock copolymer.

The thermodynamic theory employed here is similar to those originally proposed by Meier[2] and Williams and coworkers.[3] While many of the details are purposefully omitted here, suffice it to say that the model presumes that, upon microphase separation, the free energy is minimized with respect to each of the characteristic microstructural dimensions present within a postulated morphology. Predictions are restricted here to the lamellar morphology, which consists of the regions to which the A and B blocks are confined (T_A and T_B, respectively) and the interphase (λ'). Conservation of junction sites dictates[2] that T_A and T_B are coupled, resulting in a two-parameter free-energy (Δg) minimization:

$$\left(\frac{\partial \Delta g}{\partial \beta}\right) = \left(\frac{\partial \Delta g}{\partial \Gamma}\right) = 0 \tag{2}$$

For an idealized symmetric diblock copolymer ($N_A = N_B = N/2$), Δg is expressed as

$$\frac{\Delta g}{RT} = -\chi N\left\{\phi_A(1-\phi_A) - \frac{\beta}{1-\beta}\left[\epsilon_1(q) + \frac{\epsilon_2(q)}{3\beta^2\Gamma N}\right]\right\} - \ln\left(\frac{\beta}{1-\beta}\right) - 2\left[\ln\left(\frac{4}{\pi}\sin\frac{\pi\beta}{2}\right) - \frac{\pi^2}{12} - \frac{3}{2}\left(\frac{\Gamma}{2} - 1 - \ln\frac{\Gamma}{2}\right)\right] \tag{3}$$

where R is the gas constant, T is absolute temperature, and ϕ_A is the volume fraction of block A. The two

---

* To whom correspondence should be addressed at the Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7907.

0024-9297/93/2226-0396$04.00/0

dimensionless parameters used in the minimization are defined as $\Gamma \equiv 2T_A{}^2/b^2N$ and $\beta \equiv \lambda' q/2T_A$, where q determines the sharpness[3] of the interphase composition profile (ϕ_A'), given by

$$\phi_A' = 0.5\{1 - \tanh\,[q(x^* - 0.5)]\} \qquad (4)$$

Here, x^* is the spatial position within the interphase normalized with respect to $\lambda' q/2$. In all subsequent predictions, q is set equal to 4 to emulate a realistic profile in the SSL. The interphase thickness (λ') employed here is defined[4,8,9,11] as

$$\lambda' \equiv \left(\frac{\mathrm{d}\phi_A'}{\mathrm{d}x^*}\right)^{-1}_{x^*=0.5} \qquad (5)$$

One may show[3,12] that $\epsilon_1(q)$ and $\epsilon_2(q)$ in eq 3 can be written as $\tanh\,(q/2)/(2q)$ and $(q/2)[\tanh\,(q/2) - \tanh^3\,(q/2)/3]$, respectively. For $q = 4$, $\epsilon_1 = 0.12$ and $\epsilon_2 = 1.33$. Equation 2 is solved by numerical methods, with the corresponding values of β and Γ used to calculate microstructural dimensions, such as λ', at equilibrium. The ratio λ'/λ_∞ is explicitly determined from

$$\frac{\lambda'}{\lambda_\infty} = \frac{\beta(3\Gamma)^{1/2}}{4}(\chi N)^{1/2} \qquad (6)$$

Predicted λ'/λ_∞ as a function of χN within the context of the present treatment are displayed in Figure 1. These predictions indicate that λ' exceeds λ_∞ by as much as 25% at low χN. Thus, both the SCF[11] and CCS treatments clearly predict substantial interphase broadening at low χN. As seen in Figure 1, λ'/λ_∞ from the SCF[11] calculations are consistently larger than those from the CCS approach adopted here. For additional comparison, predictions obtained by Broseta et al.[13] for homopolymer blends of finite incompatibility are also provided in Figure 1. By relaxing the NIA (eq 1) and solving the mean-field equations, they have demonstrated that

$$\frac{\lambda'}{\lambda_\infty} = \left[1 - \frac{8 \ln 2}{\chi N}\right]^{-1/2} \qquad (7)$$

for perfectly symmetric homopolymers ($N_A = N_B = N/2$). Predicted λ'/λ_∞ from both the SCF[11] and CCS treatments deviate more markedly from unity than do those obtained from eq 7. At $\chi N \approx 30$, for instance, λ' is predicted to exceed λ_∞ by about 11% for homopolymer blends, 38% for block copolymers (SCF), and 24% for block copolymers (CCS).

Two additional differences in the $\lambda'/\lambda_\infty(\chi N)$ relationships predicted by the SCF and CCS formalisms are apparent from Figure 1. The first is that the λ'/λ_∞ curves generated in the present work are weakly dependent on R_g. When R_g is held constant, and b, N, and χ are all appropriately rescaled to yield a single arbitrary value of χN, the ratio of λ'/λ_∞ is found to be invariant, indicating internal consistency. When $R_g > 20$ nm, a universal $\lambda'/\lambda_\infty(\chi N)$ relationship independent of R_g is produced, as seen by the lower CCS curve in Figure 1. If $R_g < 20$ nm, however, predicted λ'/λ_∞ shift upward as R_g decreases, as exemplified by the upper CCS curve in Figure 1. The second difference is that these predicted curves do not approach unity as an asymptotic limit, a recognized characteristic of the CCS approach.

The dependence of the interphase thickness on copolymer chain length has been an issue of debate in the literature for some time. Numerous studies employing small-angle scattering[14,15] and reflectivity[16,17] have attempted to establish whether or not the interphase thickness depends on N. While Anastasiadis et al.[18] reported that the interfacial tension in blends of immiscible homopolymers is a function of chain length, morphological data from microphase-separated diblock copolymers have, within experimental error, suggested that λ' is independent of N. The CCS approach employed here, unlike many of its uniform-density counterparts, predicts a functional dependence between λ' and N at constant χ. It is of considerable interest that the SCF treatment by Shull[11] predicts a qualitatively similar relationship, while Melenkevitz and Muthukumar[10] reported that, according to their expanded density functional formalism, λ' is only weakly dependent on N in the crossover regime between the strong- and weak-segregation limits. It is hoped that these new theoretical results will rekindle an interest in this issue and lead to further experimental investigation of block copolymer interphases.

Acknowledgment. We thank Dr. K. R. Shull for providing the discrete predictions from his model (shown in Figure 1) and one of the reviewers for helpful comments.

References and Notes

(1) Krause, S. *J. Polym. Sci., Part A-2* **1969**, *7*, 249; *Macromolecules* **1970**, *3*, 85.

(2) Meier, D. J. In *Block and Graft Copolymers*; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: New York, 1973; Chapter 6; *J. Polym. Sci., Part C* **1969**, *26*, 81; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15*, 171; In *Thermoplastic Elastomers: A Comprehensive Review*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser Publishers: New York, 1987; Chapter 12.

(3) Leary, D. F.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 345; **1974**, *12*, 265. Henderson, C. P.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1001.

(4) Helfand, E.; Wassermann, Z. R. *Macromolecules* **1976**, *9*, 879; **1978**, *11*, 960; **1980**, *13*, 994; In *Recent Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum Press: New York, 1974; *Macromolecules* **1975**, *8*, 552; In *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science: London, 1982; Vol. I.

(5) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(6) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.

(7) McMullen, W. E.; Freed, K. F. *J. Chem. Phys.* **1991**, *93*, 9130.

(8) Semenov, A. V. *Sov. Phys.—JETP (Engl. Transl.)* **1985**, *61*, 733.

(9) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

(10) Melenkevitz, J.; Muthukumar, M. *Macromolecules* **1991**, *24*, 4199.

(11) Shull, K. R. *Macromolecules* **1992**, *25*, 2122.

(12) Spontak, R. J.; Williams, M. C.; Agard, D. A. *Macromolecules* **1988**, *21*, 1377.

(13) Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. *Macromolecules* **1990**, *23*, 132.

(14) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.

(15) Richards, R. W.; Thomason, J. L. *Polymer* **1983**, *24*, 1089.

(16) Satija, S. K.; Majkrzak, C. F.; Anastasiadis, S. H.; Russell, T. P. *Mater. Res. Soc. Symp. Proc.* **1990**, *166*, 139.

(17) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.

(18) Anastasiadis, S. H.; Gancar, I.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2980.