# Notes

## Molecular-Weight Dependence of Cylindrical Microdomains

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When two incompatible monomers A and B form a copolymer molecule, the copolymer melt undergoes a spatial segregation at low temperature due to the chemical interactions at a junction point. These regular structures can be spherical, cylindrical or lamellar depending on the weight fraction of one of the blocks. This process of self-assembly is driven by total free energy minimization, with enthalpic and entropic contributions.

Equilibrium free energy of the ordered structures in the strong-segregation limit (SSL) is rather well established by several authors.[1−3] In the case of lamellar morphology, they give

$$d \sim N^{2/3} \tag{1}$$

This two/thirds power law is supported by experimental results.[4−6] However, in the case of the weak-segregation limit (WSL), the spatial period $d$ is simply proportional to the radius of gyration, $R_G$, of a copolymer molecule and is given by[7]

$$d \sim R_G \sim N^{1/2} \tag{2}$$

In contrast, much less work has been done on the molecular-weight dependence of cylindrical morphology. A number of investigators[8,9] reported that the two/third power law does not appear to be satisfactory for explaining the experimental data for cylindrical morphology. In this note, we investigate the molecular-weight dependence of cylindrical microdomains and derive a relationship on the basis of a phenomenological free energy model for cylindrical morphology.

The free energy per chain of cylindrical diblock copolymers can be written as

$$F = F_i + F_{c1} + F_{c2} \tag{3}$$

where $F_i$ is the interfacial energy per chain at the A block-B block interface and $F_{c1}$ and $F_{c2}$ are the conformational energies per chain for the inner and the outer block, respectively. They are approximated by the following expressions[10,11]:

$$F_{cj} = \frac{3}{2}k_B T\left[\left(\frac{R_j}{R_{j0}}\right)^2 + \left(\frac{R_{j0}}{R_j}\right)^2 - 2\right] \tag{4}$$

where $j$ is the index for the inner or the outer block, $R_j$ is the end-to-end distance of block $j$ in the microphase-separated morphology. In the Alexander-de Gennes[12,13] formalism this end-to-end distance is taken as the thickness of the layer in the structure corresponding to the block $j$. The ideal Gaussian chain end-to-end distance of the block $j$ is denoted by $R_{j0}$, which is the reference state for the chain conformational energy that is given by $a_j N_j^{1/2}$, where $N_j$ is the degree of polymerization of block $j$ and $a_j$ is the statistical segment length of the polymer in block $j$. The Wigner−Seitz unit cell for two-dimensional cylindrical lattice is a hexagon. With $d$ defined as the distance between the centers of two cylinders, $R_1$ and $R_2$ can be parametrized with a single variable, $d$, as follows:[1]

$$R_1 = (3^{1/2}/2\pi)^{1/2}\phi^{1/2}d \tag{5}$$

$$R_2 = (3^{1/2}/2\pi)^{1/2}(1 - \phi^{1/2})d \tag{6}$$

Here, $\phi$ is the volume fraction of polymer A. The above formalism allows one to forego the usual complicated numerical work resulting from the hexagonal boundary condition. As a result, eq 3 for the free energy per chain becomes

$$F = F_i + F_{c1} + F_{c2} = \gamma_i 2\pi R_1 \frac{\phi}{\pi {R_1}^2}\frac{V}{p} + \frac{3}{2}k_B T\left[\left(\frac{R_1}{R_{10}}\right)^2 + \left(\frac{R_{10}}{R_1}\right)^2 + \left(\frac{R_2}{R_{20}}\right)^2 + \left(\frac{R_{20}}{R_2}\right)^2 - 4\right] = 3.81\frac{N}{\rho d}\phi^{1/2}\gamma_i + \frac{3}{2}k_B T\left[Ad^2 + \frac{B}{d^2} - 4\right] \tag{7}$$

where $\rho = pN/V$, $V$ is the domain volume, $N$ is the degree of polymerization, and $p$ is the number of copolymer chain in the system, and $A$ and $B$ are functions of $R_{10}$, $R_{20}$, and volume fraction, given by

$$A = \frac{\sqrt{3}/2\pi}{{R_{10}}^2}\phi + \frac{\sqrt{3}/2\pi}{{R_{20}}^2}(1 - \phi^{1/2})^2 \tag{8}$$

$$B = \frac{{R_{10}}^2}{\sqrt{3}/2\pi}\frac{1}{\phi} + \frac{{R_{20}}^2}{\sqrt{3}/2\pi}\frac{1}{(1 - \phi^{1/2})^2} \tag{9}$$

Here, we are interested in the molecular-weight dependence of the lattice period $d$. For this purpose, we put

$$N_1 = \alpha N, \quad N_2 = (1 - \alpha)N \tag{10}$$

Substitution of eq 10 into eq 7 and minimization with respect to $d$ gives

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$$d^3 = \frac{C}{A} + \frac{B}{A}\frac{1}{d} \tag{11}$$

where

$$C \equiv \frac{1.27\phi^{1/2}\gamma_i N}{k_B T\rho} \tag{12}$$

In eq 11, $C/A$ and $B/A$ are functions of the degree of polymerization index $N$. To see the molecular weight dependence, eq 11 is rearranged to

$$d^3 = f_1 N^2 + f_2 N^2 \frac{1}{d} \tag{13}$$

where $f_1$ is a function of volume fraction, $a$, interfacial tension, $\rho$, and temperature and $f_2$ is a function of volume fraction and $a$, defined by

$$f_1 \equiv \frac{1.27\phi^{1/2}\gamma_i}{k_B T\rho}\left[\frac{\sqrt{3}/2\pi}{a_1^2\alpha}\phi + \frac{\sqrt{3}/2\pi}{a_2^2(1-\alpha)}(1-\phi^{1/2})^2\right]^{-1} \tag{14}$$

$$f_2 \equiv \left[\frac{a_1^2\alpha}{\sqrt{3}/2\pi}\frac{1}{\phi} + \frac{a_2^2(1-\alpha)}{\sqrt{3}/2\pi}\frac{1}{(1-\phi^{1/2})^2}\right]\left[\frac{\sqrt{3}/2\pi}{a_1^2\alpha}\phi + \frac{\sqrt{3}/2\pi}{a_2^2(1-\alpha)}(1-\phi^{1/2})^2\right]^{-1} \tag{15}$$

It is interesting to examine two limiting cases in eq 13. If $d$ goes to infinity, eq 13 simply reduces to

$$d = f_1^{1/3} N^{2/3} \tag{16}$$

This result gives the power law index $^2/_3$ that coincides with the value for the lamellar morphology. On the other hand, if $d$ goes to zero, eq 13 leads to

$$d = f_2^{1/2} N^{1/2} \tag{17}$$

which again coincides with the value predicted for the lamellar morphology in the WSL. The relationship given by eq 13 is shown in Figure 1. It is seen from the figure that the power index, $n$, increases gradually with increasing degree of polymerization (molecular weight), the minimum being $^1/_2$ and the maximum being $^2/_3$.

The two extreme cases also result when the relative magnitude of $f_1$ with respect to $f_2/d$ is large or small. When $f_1$ is relatively much larger than $f_2/d$, the power index becomes $^2/_3$, and it is $^1/_2$ in the opposite case. Take the effect of interfacial tension first. A higher $\gamma_i$ increases the lattice period $d$ to decrease the surface-to-volume ratio, resulting in an increase in the power law index. In the limiting regime of SSL, $f_1 \gg f_2/d$ and the index becomes $^2/_3$; in the other limiting regime of WSL, $f_1 \ll f_2/d$ and the index approaches $^1/_2$. These results coincide with the scaling of the lattice period for the two extreme cases of WSL ($\chi N \ll 1$) and SSL ($\chi N \gg 10$) in terms of the interaction parameter $\chi$ or $\chi N$.

According to eq 13, the power law index becomes smaller as the temperature increases. As the temperature increases, the system goes to the order−disorder transition region and the power law index reaches $^1/_2$, which was predicted for the weak-segregation limit.[7]

From the above analysis, we know that a larger (smaller) surface tension and a lower (higher) temperature gives a higher (lower) power law index. The two

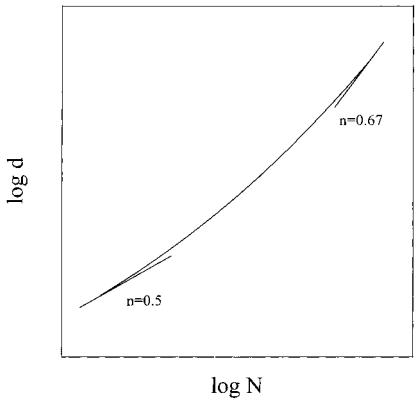


**Figure 1.** Log−log plot of the lattice period, $d$, with the degree of polymerization index, $N$. In the lower molecular-weight region, the power law index approaches $^1/_2$, and in the higher molecular-weight region, power law index approaches $^2/_3$.

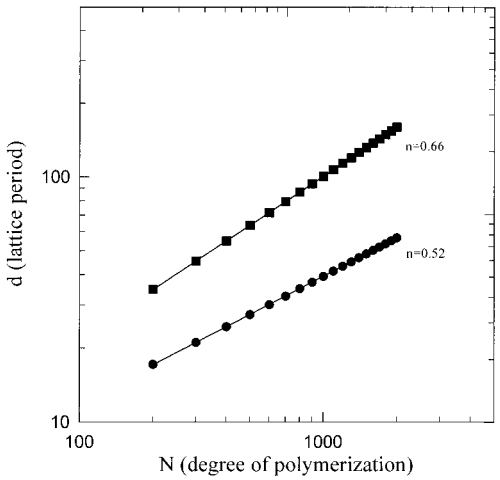


**Figure 2.** Effect of surface tension and temperature on the power law index for two limiting cases. Typical parameters are used in the plot. They are $a_1 = a_2 = 0.6$ nm, and $\phi = \alpha = 0.3$. For the upper line ($n = 0.66$), $f_1 = 10$, and for the lower line ($n = 0.52$), $f_1 = 0.01$.

limiting cases are shown in Figure 2. Typical parameters used in the plot are: $a_1 = a_2 = 0.6$ nm, and $\phi = \alpha = 0.3$. As shown in the figure, the power law index converges to $^2/_3$ when $f_1$ is sufficiently large and to $^1/_2$ when $f_1$ is sufficiently small.

Comparison of the results with the experimental data of diblock copolymers in the literature is limited in that not much data are available. In principle, if we want to know only the molecular-weight dependence, other parameters such as volume fraction, density and temperature should be fixed. But that is not the case for most experimental data. A few sets of experimental data, however, can be used for comparison, and the results are given in Figure 3. The statistical segment lengths for polystyrene (PS), polybutadiene (PB), and polyisoprene (PI) are 0.68, 0.63 and 0.59 nm, respectively,[1] and it is assumed that the volume fraction ($\phi$) and number fraction ($a$) are the same. This assumption may be made in that these parameters have little effect on the overall result. With these values and the assumption, the value of $f_1$ is adjusted so as to fit the data. The values thus determined are given in Figure 3 for the two sets of data. It is seen from Figure 3 that the upper portion of the data from ref 9 approaches a slope of $^2/_3$ in the region where the degree of polymerization or the molecular weight is high. It can also be

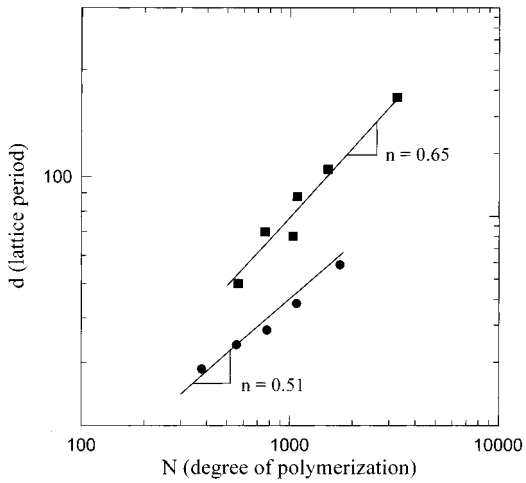


**Figure 3.** Comparison with experimental data with $f_1$ as the fitting parameter. Circles are from ref 8 (PS−PB, $f_1 = 0.01$), and squares are from ref 9 (PS−PI, $f_1 = 0.5$).

seen that the lower portion of the data from ref 8 approaches a slope of $^1/_2$ in the low molecular weight region. Our calculation shows that $f_1$ and $f_2/d$ calculated with the parameters given in ref 8 and ref 9 are 0.03 and ~0.3 and 0.4 and ~0.08, respectively. The values of $f_1$ compare with the fitted value of 0.01 in ref 8 and 0.5 in ref 9, which are within the same order of magnitude. The result also confirms that the system in ref 8 is in the weak segregation limit.

Summarizing, it is shown that the molecular-weight dependence of the cylindrical microdomains of diblock copolymers is such that the power law index ranges from $^1/_2$ to $^2/_3$ depending on the material properties and process conditions. Our simple phenomenological model (eq 13) has been found adequate in predicting the domain size $d$ of the cylindrical domain. Although our model is restricted to the cylindrical morphology, the same approach could be extended to the spherical morphology.

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