(6) Barkley, M. S.; Zimm, B. H. *J. Chem. Phys.* **1979**, *70*, 2991.
(7) Allison, S. A.; Schurr, J. M. *Chem. Phys.* **1979**, *41*, 35.
(8) Allison, S. A.; Shibata, J. H.; Wilcoxon, J.; Schurr, J. M. *Biopolymers*, **1982**, *21*, 729.
(9) Carpenter, D. K.; Skolnick, J. *Macromolecules* **1981**, *14*, 1284.
(10) Swanson, E.; Teller, D. C.; de Haën, C. *J. Chem. Phys.* **1978**, *68*, 5097.
(11) Teller, D. C.; Swanson, E.; de Haën, C. *Methods Enzymol.* **1979**, *61*, 103.
(12) Bloomfield, V.; Dalton, W. O.; Van Holde, K. E. *Biopolymers* **1967**, *5*, 135.
(13) Oseen, C. W. "Mathematik and ihre Anwenudungen in Monographien and Lehrbüchern"; Hilb, E., Ed.; Akademische Verlagsgresellschaft: Leipzig, 1927; Vol. 1.
(14) Rotne, J.; Prager, S. *J. Chem. Phys.* **1969**, *50*, 4831.
(15) Yamakawa, H. *J. Chem. Phys.* **1970**, *53*, 436.
(16) Garcia de la Torre, J.; Bloomfield, V. *Biopolymers* **1977**, *16*, 1747, 1765.
(17) Garcia de la Torre, J.; Bloomfield, V. *Q. Rev. Biophys.* **1981**, *14*, 81.
(18) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1.
(19) Allison, S. A.; Easterly, R. A.; Teller, D. C. *Biopolymers* **1980**, *19*, 1475.
(20) Happel, J.; Brenner, H. "Low Reynolds Number Hydrodynamics"; Leyden: Noordhoff, 1973.
(21) Jackson, J. D. "Classical Electrodynamics"; Wiley-Interscience: New York, 1975.
(22) Landau, L. D.; Lifschitz, E. M. "Theory of Elasticity"; Pergamon Press: New York, 1959; Vol. 7.
(23) Collie, C. H.; Hasted, J. B.; Riston, D. M. *Proc. Phys. Soc. London* **1948**, *60*, 145.
(24) Berne, B.; Pecora, R. "Dynamic Light Scattering"; Wiley-Interscience: New York, 1976.
(25) Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Am. Chem. Soc.* **1974**, *96*, 6840.
(26) Schurr, J. M. *Biophys. Chem.* **1979**, *9*, 413.

# Generalized View of Molecular Weight Dependence of Microdomain Size of Block Polymers. Appraisal of Hadziioannou–Skoulios' Data on Binary Mixtures of Block Polymers

**Takeji Hashimoto**

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.* *Received January 29, 1982*

ABSTRACT: An appraisal of Hadziioannou–Skoulios' data on binary mixtures of block polymers $\alpha$ and $\beta$ has been carried out to derive a scaling rule relating microdomain size with average molecular weight of the mixture. The mixtures as well as the pure block polymers $\alpha$ and $\beta$ studied in this work have the lamellar microdomain. Hadziioannou–Skoulios' results on the lamellar identity period $D$ of the mixtures are found to be summarized as $D \sim \bar{M}_n^{a}$ and $S/N \sim \bar{M}_n^{1-a}$, where $a = {}^2/_3$ to ${}^4/_5$ for the molecular weight range covered in this study, $\bar{M}_n$ is the number-average molecular weight of the block polymers in the mixture, and $S/N$ is the average interfacial area occupied per chemical junction point of the block polymers. This result is a generalized form obtained for the pure block polymer, for which $\bar{M}_n$ should be replaced by the molecular weight of the block polymer.

## I. Introduction

We discuss here the relationship between the size of the microdomain structure of amorphous block polymers and the molecular weight of the block polymer composed of A and B polymer chains under a strong segregation limit where A and B exert a strong repulsive potential; i.e., $\chi_{AB}Z \gg 2$ ($\chi_{AB}$ being the Flory–Huggins interaction parameter between A and B and $Z$ being the total degree of polymerization for the block chain).[1,2] For pure block polymers having a very narrow molecular weight distribution, this relationship has been extensively studied, and the following scaling rule has been derived for polystyrene–polyisoprene (SI) and polystyrene–polybutadiene (SB) di- and triblock polymers giving rise to the lamellar microdomains[3] over the range of molecular weights $M_t$ from ca. $2 \times 10^4$ to $2 \times 10^5$:

$$D_l = 0.024 M_t^{2/3}\ (\mathrm{nm}) \tag{1}$$

$$(S/N)_l = 0.14 M_t^{1/3}\ (\mathrm{nm}^2) \tag{2}$$

where $D_l$ is the identity period of the lamellar microdomains, $(S/N)_l$ is the average interfacial area occupied by a single chemical junction point of the block polymer, and $M_t$ is the total molecular weight. It should be noted that for ABA triblock polymers, $M_t$ refers to the molecular weight of the diblock polymers A–(1/2)B. It has also been shown[3] that this rule, obtained for a limited range of molecular weight, can be quantitatively explained in terms of equilibrium theories based upon statistical mechanical treatments of random flight chains in confined space.[4-8] However, it should be noted that the theories indicate that the functional form $D \sim M^a$ is not very good over the whole molecular weight range and $a$ is not exactly equal to ${}^2/_3$ even in the high molecular weight limit. Since this point is essential, we will clarify it more rigorously below in the context of Helfand–Wasserman's *narrow interphase approximation.*[7]

The free energy density of the microdomain formation $f$ is given by[7]

$$f(D_l) = c_1(M_t/D_l) + c_2(D_l/M_t^{1/2})^p + c_3 \log D_l \tag{3}$$

where the coefficient $c_i$'s are constants independent of molecular weight $M_l$ and identity period $D_l$ but dependent on Kuhn's statistical segment length, densities, the interaction parameter $\chi$, etc. The first term on the right-hand side of eq 3 arises from surface free energy, the second term from the constraint entropy loss (loss of entropy from confining the chains in their respective domains), and the third term from the placement entropy loss (loss of entropy from confining the chemical junction points in the interfacial regions). The constant $p$ was numerically evaluated to be 2.5.[7] In the high molecular

0024-9297/82/2215-1548$01.25/0

weight limit, the first two terms on the right-hand side of eq 3 are important. Consequently, minimization of $f$ with respect to $D_l$ leads to

$$D_l \sim M_t^a \tag{4a}$$

$$a = (1 + \tfrac{1}{2}p)/(1 + p) \simeq \tfrac{9}{14} = 0.643 \tag{4b}$$

i.e., a value close to $^2/_3$. In the low molecular weight limit, the third term of eq 3 is more important than the second term, leading to

$$D_l \sim M_t \tag{5}$$

Consequently, the theory predicts that $a$ is not really a constant independent of $M_t$ but rather shifts from 1 to the limiting value of $^9/_{14}$ with increasing molecular weight, probably behaving like $^2/_3$ for observations over a limited molecular weight range. One must keep in mind, however, the limitation of the theory coming from the narrow interphase approximation. The approximation is good for the high molecular weight limit but breaks down in the low molecular weight limit. Consequently, the prediction of eq 5 and the prediction of increasing $a$ with decreasing molecular weight may require further investigations and have to be tested with more rigorous theories, possibly in terms of a full theory.[6]

The same scaling rule has been shown to be applicable also to other domain morphologies; e.g., for spherical domains, the radius $R_A$, the interdomain distance $D_s$, and $(S/N)_s$ are given by

$$R_A \sim M_A^{2/3} \tag{6a}$$

$$D_s \sim M_t^{2/3} \tag{6b}$$

$$(S/N)_s \sim M_t^{1/3} \tag{6c}$$

over the molecular weight range $8 \times 10^4$ to $7 \times 10^5$ covered in the experiment,[9] where $M_A$ is the molecular weight of the constituent block polymer forming the spherical domains and $(S/N)_s$ is the average interfacial area per chemical junction point of the block chain for the spherical domain. This relationship also can be described by the equilibrium theory,[8] except for the preexponential factors, which are complicated due to the nonequilibrium effect encountered in solidification processes of the microdomain structure.[9]

In this paper we extend our studies along these lines to the case where there exists a molecular weight distribution. As a special case of the molecular weight distribution, we consider here a special molecular weight distribution produced by mixing two block polymers $\alpha$ and $\beta$ of ABA triblock polymers or AB diblock polymers (A and B being polystyrene or polyisoprene). Here we restrict our considerations to the case hwere both $\alpha$ and $\beta$ form lamellar microdomains in the equilibrium state. The experimental data come from a recent work by Hadziioannou[10] and Hadziioannou and Skoulios.[11] We will show that the scaling rule as given by eq 1 and 2 is valid also for the binary mixture in which $\alpha$ and $\beta$ are molecularly mixed in the lamellar microdomains if $M_t$ is replaced by the number-average molecular weight of the mixture.

## II. Experimental Section

The details of the experimental technique, specimens, and results are described in the original paper by Hadziioannou and Skoulios[11] and in the thesis by Hadziioannou.[10] We shall briefly describe the features related to this report.

We discuss their results on binary mixtures of SI-5 with SI-3, SI-5 with $S_D$I-7, SI-4 with SIS-3, SIS-2 with SI-5, SIS-3 with SI-3, ISI-2 with SI-3, ISI-1 with SI-4, and SIS-2 with ISI-2. All the block polymers were prepared by sequential anionic polymerization and have an alternating lamellar morphology in the equilibrium state (the weight fraction of polystyrene is close to 0.5 for all the block polymers). The identity period of the domains depends on the molecular weight of the block polymer. The binary mixtures were prepared as follows. The two block polymers $\alpha$ and $\beta$ were mixed in dilute benzene solution (concentration less than 2%). After vigorous stirring, the solutions were freeze-dried until the solvent was removed completely. The solid residue was then molded under vacuum and oriented according to their technique. Small-angle X-ray scattering (SAXS) from all of the film specimens of the binary mixtures showed a series of equidistant peaks, indicating that each mixture also contains a lamellar microdomain structure of a single identity period $D$, the value $D$ being between $D_\alpha$ and $D_\beta$, the identity periods of the lamellar domains of the respective pure block polymers $\alpha$ and $\beta$. The evidence strongly supports that the mixing occurs at the molecular level as they concluded. It is also important to note that the identity period of the lamellar microdomains of the mixture is as uniform as those of the corresponding pure block polymers $\alpha$ and $\beta$. The values $D$ (corresponding to the value $d$ according to their notation) are plotted as a function of molar concentration for the various mixtures listed above. In the next section we further advance the analyses to establish a scaling rule on the values $D$ with average molecular weight for the binary mixture.

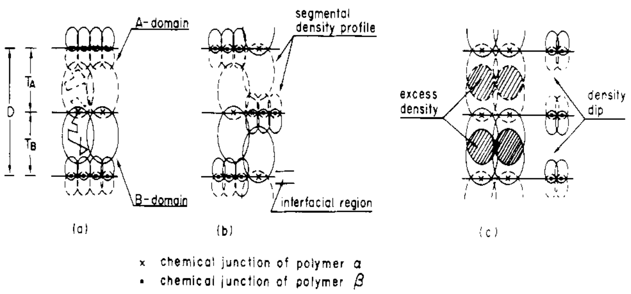

**Figure 1.** Schematic diagrams showing the segmental density profile of A-block chain (broken lines) and B-block chain (solid lines) and the spatial distribution of the chemical junction points of the block polymers $\alpha$ having larger molecular weight (marked by ×) and $\beta$ having smaller molecular weight (marked by solid squares).

## III. Model and Analyses

Since polymeric solids are highly *incompressible*, in the equilibrium state, A-block chains must be packed uniformly in the A microdomains in such a way that the segmental density of the A microdomains is identical with that of the bulk A polymer. The requirement should be satisfied also for binary mixtures of the block polymers $\alpha$ and $\beta$. The requirement invokes a constraint in the spatial distribution of chemical junction points of the block polymers having larger molecular weight ($\alpha$) and smaller molecular weight ($\beta$) such that it satisfies the demand of the *uniform volume filling* of the space.

Figure 1 is a schematic diagram for the segmental density profile of A-block chain (broken lines) and B-block chain (solid lines) and the spatial distribution of the chemical junction points for the $\alpha$ polymers (marked by ×) and $\beta$ polymers (marked by solid squares). Due to the repulsive potential between A and B, the A and B chains are stretched, with their end-to-end vectors preferentially oriented normal to the interfaces between the A and B domains. The segments of a given polymer A are supposed to heavily overlap and interpenetrate those of neighboring polymers A, both laterally and longitudinally, to result in uniform filling of the space.[3] The figure underestimates overlaps of molecules for simplicity in drawing. For example, for block polymers having $M_t = 1.0 \times 10^5$, we estimated that the average nearest-neighbor distance between two chemical junction points is nearly equal to 2.6 nm and is much smaller than $\langle r^2 \rangle^{1/2} = [\langle R_x^2 \rangle + \langle R_y^2 \rangle]^{1/2} = 2^{1/2}\langle R_x^2 \rangle^{1/2} \simeq 13.6$ nm, the root-mean-square end-to-end distance of the chain molecules in the domain space projected parallel to the interface,[3] indicating a heavy interpenetration of neighboring molecules in the lateral direction, i.e., in directions parallel to the interface. The uniform filling of the space with segments invokes also a heavy interpenetration of molecules normal to the interface.

Parts a and b of Figure 1 show examples of a special type of spatial distribution of the chemical junction points which satisfy the demand of uniform space filling, while Figure 1c shows one which does not satisfy the demand. In Figure 1a, the chemical junction points of the $\alpha$- and $\beta$-block polymers are arranged in series along the lamellar normal and in parallel along the direction parallel to the interface, while in Figure 1b they are arranged alternately in both directions. The spatial arrangement of Figure 1c will create regions of excess density and density deficiency and be energetically unfavorable. The real system may be a random mixture of the two types of packing in Figure 1a,b, i.e., the high and low molecular weight blocks being easily interdispersed on the interface, with the probability of many small-block chains (or many large-block chains) opposing each other on opposite interfaces being small.

On the basis of the model shown in Figure 1, we may assume that the volume $V$ of the microdomain system composed of a mixture of polymers $\alpha$ and $\beta$ is equal to the sum of the volumes $V_\alpha$ and $V_\beta$ for the microdomain systems composed only of polymers $\alpha$ and $\beta$, respectively.

$$V = V_\alpha + V_\beta \tag{7}$$

Since $V_\alpha \sim S_\alpha D_\alpha$, $V_\beta \sim S_\beta D_\beta$ and $V \sim SD$, where $D_\alpha$ and $D_\beta$ are the domain identity periods of the systems composed only of polymers $\alpha$ and $\beta$, respectively, $D$ is the period for the molecular mixture of polymers $\alpha$ and $\beta$, $S_\alpha$ and $S_\beta$ are the interfacial areas of the systems composed only of polymers $\alpha$ and $\beta$, respectively, and $S$ is the interfacial area for the mixed system. Thus it follows that

$$SD = S_\alpha D_\alpha + S_\beta D_\beta \tag{8}$$

Dividing both sides of eq 8 by the total number of molecules $\alpha$ and $\beta$, $N = N_\alpha + N_\beta$, $N_\mathrm{K}$ being the number of K polymers (K = $\alpha$ or $\beta$),

$$\frac{S}{N}D = x_\alpha \frac{S_\alpha}{N_\alpha}D_\alpha + x_\beta \frac{S_\beta}{N_\beta}D_\beta \tag{9}$$

where $x_\mathrm{K}$ is the number fraction of K polymers (K = $\alpha$ or $\beta$).

Now for the system composed only of polymer $\alpha$

$$S_\alpha D_\alpha = 2N_\alpha \bar{v}_\alpha \tag{10}$$

where $\bar{v}_\alpha$ is the molecular volume of polymer $\alpha$, which is given by

$$\bar{v}_\alpha = M_\alpha N_\mathrm{A}/\rho_\alpha \tag{11}$$

where $M_\alpha$ is the molecular weight of polymer $\alpha$, $N_\mathrm{A}$ is Avogadro's number, and $\rho_\alpha$ is the mass density. From eq 10 and 11, it follows that

$$\frac{S_\alpha}{N_\alpha}D_\alpha = 2N_\mathrm{A}M_\alpha/\rho_\alpha \tag{12}$$

A similar equation is obtained for polymer $\beta$. Now we assume that the microdomain formed by the mixture $\alpha$ and $\beta$ at the molecular level is identical with that formed by the polymer having an average molecular weight $\bar{M}_\mathrm{x}$, the type of average being determined below. Then

$$\frac{S}{N}D = 2N_\mathrm{A}\bar{M}_\mathrm{x}/\rho \tag{13}$$

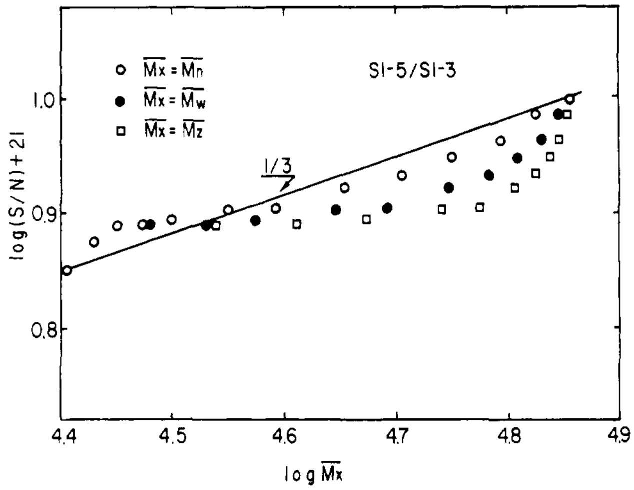

**Figure 2.** Functional fit of $S/N$ vs. $\bar{M}_\mathrm{x}^{\alpha}$, where $\bar{M}_\mathrm{x}$ is the number-, weight-, or $z$-average molecular weight.

where $\rho$ is the mass density of the mixed system. Noting that one may assume with a good accuracy

$$\rho = \rho_\alpha = \rho_\beta \tag{14}$$

one finally obtains from eq 9 and 12–14

$$M_\mathrm{x} = x_\alpha M_\alpha + x_\beta M_\beta = \bar{M}_\mathrm{n} \tag{15}$$

Consequently, the assumption of no volume change on mixing (eq 7) directly results in a prediction that the microdomain formed by the mixture of the block polymers $\alpha$ and $\beta$ at the molecular level is identical with that formed by the block polymer having a number-average molecular weight of the polymers $\alpha$ and $\beta$ (eq 15). From eq 13, it follows that

$$D = \frac{N}{S}\langle \bar{v} \rangle_\mathrm{n} \sim \frac{N}{S}\bar{M}_\mathrm{n} \tag{16}$$

$$\sim \bar{M}_\mathrm{n}^{2/3} \tag{17}$$

From eq 16 and 17, $N/S$ scales as

$$N/S \sim \bar{M}_\mathrm{n}^{-1/3} \tag{18}$$

Figure 2 shows the functional fit of $N/S$ with various types of average molecular weights $\bar{M}_\mathrm{x}$ ($\bar{M}_\mathrm{n}$, $\bar{M}_\mathrm{w}$, and $\bar{M}_z$). In fact $\bar{M}_\mathrm{n}$ gives the best functional fit as shown in the figure. These are generalized forms of eq 1 and 2. In the next section we check whether we can interpret the data obtained by Hadziioannou and Skoulios in terms of eq 17, derived from eq 7 and 14.

## IV. Results and Discussion

Hadziioannou and Skoulios plotted the spacing $D$ of binary mixtures as a function of molar fraction [C]. We replot here their results on $D$ as a function of number-average molecular weight $\bar{M}_\mathrm{n}$. Figure 2 shows the logarithm of $S/N$ plotted as a function of the logarithm of various average molecular weights $\bar{M}_\mathrm{x}$ ($\bar{M}_\mathrm{n}$, $\bar{M}_\mathrm{w}$, and $\bar{M}_z$) for the binary mixture SI-5/SI-3. The straight line shows a slope of $^1/_3$. It is shown that the number-average molecular weight gives the best functional fit of the type $N/S \sim \bar{M}_\mathrm{x}^{\beta}$ ($\beta \simeq -^1/_3$ if $\bar{M}_\mathrm{x} = \bar{M}_\mathrm{n}$). Typical plots of $D$ and $S/N$ vs. $\bar{M}_\mathrm{n}$ for the binary mixture SI-5/SI-3 are shown in Figure 3, in which the straight lines for log $D$ vs. log $\bar{M}_\mathrm{n}$ and log ($S/N$) vs. log $\bar{M}_\mathrm{n}$ have slopes of $^2/_3$ and $^1/_3$, respectively. The good fits of the data points with the straight lines verify the scaling rules of eq 17 and 18.

Figure 4 shows the molecular weight dependence of $D$ and $S/N$ for the binary mixtures SI-5/S$_\mathrm{D}$I-7, SI-4/SIS-3, SIS-2/SI-5, and SIS-3/SI-3. The molecular weights of the

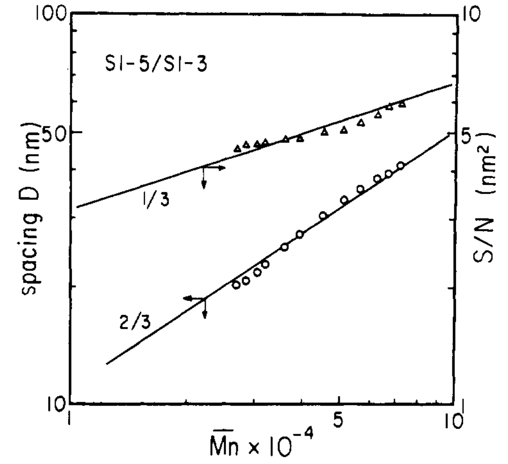

**Figure 3.** Variations of the lamellar spacing $D$ and interfacial area occupied by a single block chain $S/N$ with number-average molecular weight $\bar{M}_n$ for the binary mixture SI-5/SI-3.

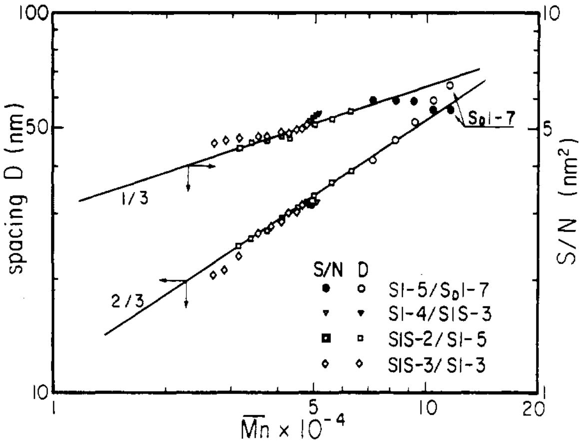

**Figure 4.** Variations of $D$ and $S/N$ with $\bar{M}_n$ for the binary mixtures SI-5/S$_D$I-7, SI-4/SIS-3, SIS-2/SI-5, and SIS-3/SI-3. The molecular weights of the SIS triblock polymers are converted to those of the corresponding diblock polymers S–(1/2)I.

SIS triblock polymers are converted to those of the corresponding diblock polymers S–(1/2)I in Figure 4. Again the data points fit straight lines reasonably well, verifying the scaling rules of eq 17 and 18. Figure 5 shows linear plots of $D$ and $S/N$ vs. $\bar{M}_n$ or [C] for the mixture SI-5/SI-3. The solid and open circles are data points for $S/N$ and $D$, respectively, which fit reasonably well the curves given by

$$S/N = 0.14\bar{M}_n^{1/3}\ (\mathrm{nm}^2) \tag{19}$$

$$D = 0.024\bar{M}_n^{2/3}\ (\mathrm{nm}) \tag{20}$$

Figure 6 shows plots of $D$ vs. $\bar{M}_n$ for the binary mixtures ISI-1/SI-4, ISI-2/SI-3, and SIS-2/ISI-2. Again the molecular weights of ISI and SIS triblock polymers are converted to those of the corresponding diblock polymers I–(1/2)S and S–(1/2)I, respectively. The data for which ISI block polymers are involved deviate from the relationships given by eq 17 and 18, which obviously requires further investigations and clarifications. The straight line with the slope $^2/_3$ was drawn by connecting the data points for pure SI-3, SIS-2, and SI-4. Furthermore, in Figure 4, the data points obtained for the mixture rich in S$_D$I-7 in SI-5/S$_D$I-7 (where S$_D$ refers to the deuterated polystyrene block sequence) start to deviate from the straight lines, which again requires further investigations.

We briefly discuss below a possible mechanism that gives rise to mixing of the two block polymers $\alpha$ and $\beta$ at the molecular level. Since polymers $\alpha$ and $\beta$ have about the same fraction of A- and B-block chains, the two polymers will not undergo liquid–liquid phase separation at temperatures above the *critical temperatures* ($T_c$'s) for the microphase separations of the $\alpha$- and $\beta$-block polymers or at concentrations below the *critical concentrations* ($C_c$'s) for the microphase separations of $\alpha$ and $\beta$. Rather they will mix at the molecular level. This is simply because the effective Flory–Huggins interaction parameter $\chi_{\alpha\beta}$ between polymers $\alpha$ and $\beta$, which is given by[12]

$$\chi_{\alpha\beta} = \chi_{AB}(f_{A\alpha} - f_{A\beta})^2 = \chi_{AB}(f_{B\alpha} - f_{B\beta})^2 \rightarrow 0 \tag{21}$$

is close to zero since $f_{A\alpha} = f_{A\beta}$ and $f_{B\alpha} = f_{B\beta}$, where $f_{A\alpha}$ and $f_{B\alpha}$ are the volume fractions of A- and B-block chains in the block polymer $\alpha$, respectively, and $\chi_{AB}$ is the interaction parameter between polymers A and B. Consequently, phase separation of polymers $\alpha$ and $\beta$, if it exists, occurs merely as a consequence of microphase separation of one of the block polymers, similarly to the phase separation of the binary mixtures (which are miscible in the liquid state) as a consequence of crystallization.

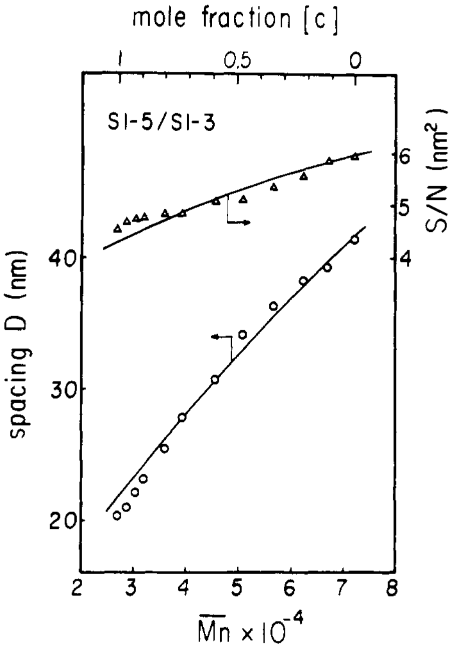

**Figure 5.** Plots of $D$ and $S/N$ vs. $\bar{M}_n$ or [C] for the mixture SI-5/SI-3. The data points (the solid and open circles) fit with the curves given by eq 19 and 20.

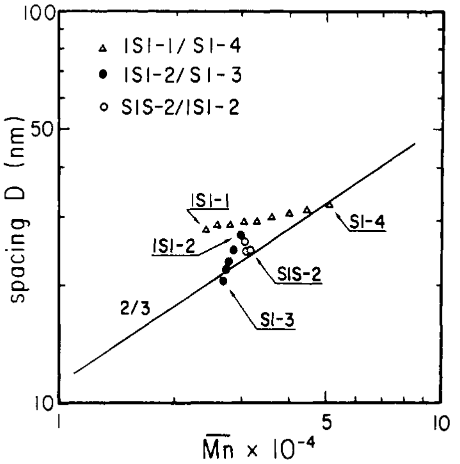

**Figure 6.** Variation of $D$ with $\bar{M}_n$ for the binary mixtures ISI-1/SI-4, ISI-2/SI-3, and SIS-2/ISI-2. The molecular weights of the ISI and SIS triblock polymers are converted to those of the corresponding diblock polymers I–(1/2)S and S–(1/2)I, respectively.

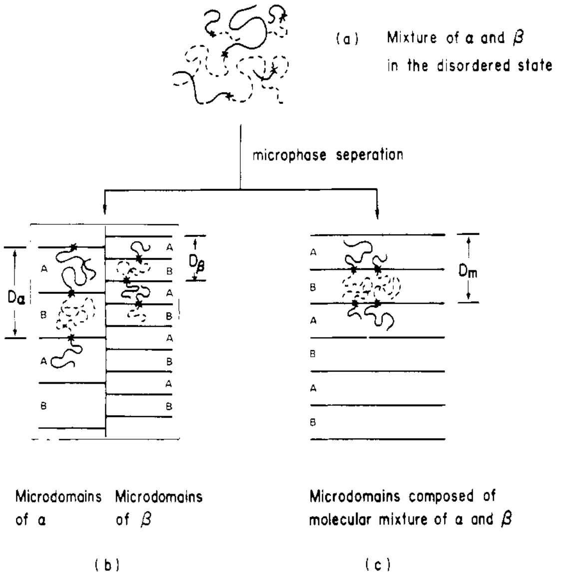

**Figure 7.** Schematic diagrams showing two types of microdomain structures (b) and (c) formed by microphase separation of molecular mixtures of two block polymers $\alpha$ and $\beta$ in the disordered state (a).

Generally, polymer $\alpha$ (having a high molecular weight) has a higher $T_c$ and a lower $C_c$ than polymer $\beta$ (having a low molecular weight). Consequently, polymer $\alpha$ starts to undergo microphase separation, prior to polymer $\beta$, during a solidification process involving solvent evaporation or lowering of the temperature. When polymer $\alpha$ undergoes microphase separation, polymer $\beta$ acts as a diluent, decreasing $T_c$ or increasing $C_c$ of polymer $\alpha$. One should consider an equilibrium structure resulted from this microphase separation. The equilibrium domain structure may be a mixture of the lamellar microdomain with identity period $D_\alpha$ inherent to polymer $\alpha$ and that with identity period $D_\beta$ inherent to polymer $\beta$ as depicted in Figure 7b or the lamellar microdomain with identity period $D_m$, $D_\beta < D_m < D_\alpha$, as in Figure 7c. In the latter domain polymers $\alpha$ and $\beta$ are mixed at the molecular level. We think that the domain structure in Figure 7b is the most stable one and the structure in Figure 7c is in a metastable state. In the structure in Figure 7c, the low molecular weight block chains advantageously use the high molecular weight blocks to fill the domain center with some chain perturbations. The chain perturbations may generally involve a loss of conformational entropy and hence an increase of free energy. The larger the molecular weight difference of the two polymers, the larger the chain perturbations and hence the larger the free energy of the structure formation. In fact we have reported evidence[13] that the films cast from a dilute solution of a binary mixture of two block polymers $\alpha$ and $\beta$ having widely different molecular weights (e.g., $7.7 \times 10^5$ and $8.1 \times 10^4$) (each having a lamellar microdomain by itself) exhibit the phase-separated domain structure in Figure 7b. However, if the molecular weights of the two polymers are very close to each other (e.g., $1.0 \times 10^5$ and $1.4 \times 10^5$), the solvent-cast films exhibit the lamellar microdomain structure in Figure 7c,[13] corresponding to case where the molecular weights of the two polymers are so close that mixing of the two polymers in the same domains does not involve a significant chain perturbation.

Now let us consider the kinetic effect on the domain structure developed by the microphase separation from a binary mixture of block polymers $\alpha$ and $\beta$ having widely different molecular weights, for which the equilibrium structure will be the one in Figure 7b, as already discussed above. If the rate of the microphase separation is much slower than the rate of the translational diffusion of polymers $\alpha$ and $\beta$, microphase separation of polymer $\alpha$ directly results in phase separation between polymers $\alpha$ and $\beta$. That is, the mesophase of polymer $\alpha$ (i.e., the microdomain structure of polymer $\alpha$) is formed in the disordered phase of polymer $\beta$, which subsequently undergoes microphase separation to result in the microdomain structure of polymer $\beta$ upon subsequent decrease of temperature or increase of concentration, resulting in the equilibrium structure in Figure 7b.

On the other hand, if the rate of the microphase separation is much faster than the rate of the translational diffusion of polymers $\alpha$ and $\beta$, polymer $\beta$ does not have sufficient time to diffuse from the mesophase of polymer $\alpha$ to the disordered phase of polymer $\beta$. Consequently, polymer $\beta$ tends to remain solubilized in the mesophase of polymer $\alpha$, resulting in the metastable structure in Figure 7c.[14]

In the freeze-dried solid residue from the very dilute benzene solution of the mixture in the experiment of Hadziioannou and Skoulios, the polymers $\alpha$ and $\beta$ are probably molecularly mixed and are in the disordered state as in Figure 7a. A subsequent increase of temperature above $T_g$ of polystyrene in the molding and orienting processes leads to microphase separation of polymer $\alpha$, with polymer $\beta$ remaining solubilized in the mesophase of polymer $\alpha$ by either one of the mechanisms discussed above; i.e., the final structure may be (i) a kinetically controlled metastable structure or (ii) an equilibrium structure if polymers $\alpha$ and $\beta$ do not have widely different molecular weights.

Finally we make a brief comment on the exponent $a$ in eq 4. Although our experimental results fit with $a = {}^2/_3$,[3,9] the data reported by Hadziioannou and Skoulios[10,11] and therefore those presented in Figures 3–5 in this paper may fit also with $a = 0.79$ as proposed by Hadziioannou and Skoulios.[10,11] In fact, the values $a = {}^4/_5$ ($\simeq 0.79$) and ${}^2/_3$ correspond to the upper and lower limits of $a$ for the present data, respectively. Consequently, we obtain for the range of the molecular weights covered in this study

$$D_l \sim \bar{M}_n{}^a \qquad (22a)$$

$$S/N \sim \bar{M}_n{}^{1-a} \qquad (22b)$$

with $a = {}^2/_3$ to ${}^4/_5$. Further studies will be required for justification of curve fitting of the type given by eq 17 and for accurate determination of the exponent $a$ by taking into account equilibrium and nonequilibrium aspects of the lamellar domains.[15,16]

**Acknowledgment.** The author is grateful to Dr. Hadziioannou and Professor Skoulios for providing the manuscript of ref 11 prior to publication and for valuable comments. He is also deeply indebted to Dr. E. Helfand for critical review of this paper and many enlightening comments. He also wishes to acknowledge Professor Kawai for encouragement of this work.

## References and Notes

(1) Flory, P. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; Chapter 13.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(3) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(4) Meier, D. J. *J. Polym. Sci., Part C* **1969**, *No. 26*, 81.
(5) Meier, D. J. *Prepr. Polym. Colloq., Soc. Polym. Sci., Jpn.* **1977**, 83.
(6) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(7) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879.

(8) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978**, *11*, 960.
(9) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(10) Hadziioannou, G. Ph.D. Thesis, presented at Universite Louis Pasteur de Strasbourg, 1980.
(11) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 267.
(12) Roe, R.-J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.
(13) Hasegawa, H.; Shibayama, M.; Hashimoto, T.; Kawai, H. *Polym. Prepr. Jpn.* **1981**, *30* (9), 2110.
(14) At temperatures or concentrations where both polymers $\alpha$ and $\beta$ are able to undergo microphase separation, the final structure may be determined again by a competition of the rate of the microphase separation and the rate of the translational diffusion.
(15) Hashimoto, T.; Shibayama, M.; Kawai, H. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23* (1), 21.
(16) Shibayama, M.; Hashimoto, T.; Kawai, H., submitted to *Macromolecules*.

# Zero-Shear Viscosity Exponent and Polydispersity Effects

**Douglas Alan Bernard and Jaan Noolandi***

*Xerox Research Centre of Canada, 2480 Dunwin Drive,*
*Mississauga, Ontario, Canada L5L 1J9.* *Received December 9, 1981*

ABSTRACT: The zero-shear viscosity of linear chain high polymer melts in the entanglement region is related to the molecular weight by the empirical relation $\eta \propto M^a$, with the widely quoted viscosity exponent $a = 3.4$. The molecular origin of this power law dependence, in particular the value of $a$, is a topic of considerable interest since it appears to be a basic property of these viscoelastic systems. The reptation model of de Gennes predicts an exponent $a = 3$, and although intriguing theoretical explanations of the discrepancy with experiment have been proposed by other workers, none is completely satisfactory. A resolution of this problem is important because it seriously questions the correctness of the fundamental reptation model. A new explanation recently put forth in an attempt to resolve this issue in favor of reptation theory is that polydispersity effects can account for the deviation when $M$ is replaced by $M^* \equiv (M_w M_z M_{z+1})^{1/3}$. In this paper we have examined this claim for a variety of polydisperse systems and have found it to be completely unjustified. General considerations show that in systems for which the *rate of change* of polydispersity with molecular weight is sufficiently high, substantial changes in the viscosity–molecular weight relation must occur when reexpressed in terms of different average molecular weights, and only one kind of average molecular weight can provide a viscosity exponent which is constant. Existing data show that $\log \eta$ is linear against $\log M_w$, but certainly not against $\log M_v$, $\log M_n$, $\log M_z$, or $\log M^*$. This result is complemented by our analysis of studies of anionically polymerized systems, for which extensive data support an exponent $a = 3.4$. Due to the very small rate of variation of polydispersity in these systems, there are no significant corrections to the viscosity exponent as a result of adjusting it to any preferred type of average molecular weight such as $M^*$. Thus the discrepancy in the value of the viscosity exponent remains. Although it may have other causes, it cannot be explained by polydispersity effects through modification of the choice of average molecular weight.

## 1. Introduction

Molecular theories developed recently for the rheology of linear chain high polymer melts give different microscopic interpretations of the empirical relation[1]

$$\eta \propto M^a \qquad (1.1)$$

between the zero-shear viscosity $\eta$ and the molecular weight $M$, with the widely quoted value $a = 3.4$ for the entanglement regime. The reptation model,[2] while very appealing, predicts $a = 3$. Several explanations have been advanced to explain this discrepancy. For example, Doi[3] considers the effect of length fluctuations on chain diffusion and obtains a correction to this value. However, he finds that the power law form of eq 1.1 is not strictly obeyed and that the local zero-shear viscosity exponent

$$a(M) \equiv \partial \ln \eta / \partial \ln M \qquad (1.2)$$

is not a constant but depends on $M$, which disagrees with experiment. From a different vantage point Curtiss and Bird[4] find that their phase–space kinetic theory allows $a = 3 + \beta$ with $\beta > 0$. An exponent differing from 3 can also be obtained within the context of reptation theory by considering a model of hindered reptational diffusion.[5] Unfortunately, these two approaches do not give actual values for the exponent. A different explanation has been proposed[8,9] which suggests that polydispersity effects can account for the deviation between the empirical exponent and the value predicted by reptation theory, but this claim has not been analyzed in detail. Thus the nature of the discrepancy in the viscosity exponent between empirical data and the reptation model remains an open question.

In this paper we address the effects of polydispersity on the molecular weight dependence of the zero-shear viscosity. In fact, there are no data for truly monodisperse samples and most systems must be characterized by some type of average molecular weight $\bar{M}$. One can then attempt to fit a power law of the form in eq 1.1 with $M$ replaced by $\bar{M}$:

$$\eta \propto \bar{M}^a \qquad (1.3)$$

However, one must recognize that the value of the zero-shear viscosity exponent $a$ and, more generally, the form of the viscosity–molecular weight relation itself, will usually depend on the type of average molecular weight with which the viscosity is correlated.

In an analysis of polydisperse reptating melt systems Daoud and de Gennes[6] have stated that the viscosity should be proportional to the weight average of the relaxation time provided by reptation theory for monodisperse systems. This relaxation time varies as the cube of the molecular weight. Computing this average, one finds[7]

$$\eta \propto (M^*)^3 \qquad (1.4)$$

where the average molecular weight to be used is

$$M^* \equiv (M_w M_z M_{z+1})^{1/3} \qquad (1.5)$$

It was recently suggested[8,9] that observed values of the zero-shear viscosity exponent differ from the value $a = 3$

0024-9297/82/2215-1553$01.25/0