Microphase Separation in Block Copolymers. Zeroth Approximation Including Surface Free Energies[1]

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ABSTRACT: The conditions necessary for microphase separation in block copolymers containing an arbitrary number of blocks of two monomers, A and B, are developed as a function of block copolymer composition, molecular weight, number of blocks per molecule, and interaction parameter between the corresponding homopolymers. As the number of blocks increases in block copolymer samples of equal composition and molecular weight, it is predicted that microphase separation becomes more and more difficult, *i.e.*, that it occurs at higher and higher values of the interaction parameter, χ_{AB}. The results of the present treatment are compared with the conditions for phase separations in mixtures of homopolymers.

In a previous work,[2] it was shown that it is possible to make reasonable predictions of microphase separation in block copolymers without any consideration of the surfaces between microphases. Some approximations are made in the present work in order to calculate the free energies of the surfaces between microphases. When these surface free energies are included in the theoretical treatment, it becomes possible to make separate predictions for two-, three-, four-, or multiblock copolymers. As the number of blocks increases in block copolymer samples of equal composition and molecular weight, microphase separation becomes more and more difficult.

Assumptions. The block copolymers considered here are monodisperse samples in which every molecule has the same molecular weight, the same average composition in terms of two monomers A and B, and the same sequence distribution in terms of number of blocks of each type, A and B. When microphase separation occurs, there is no change in molecular disorder within each block *except* directly at the very sharp boundary between microphases. Complete separation between the microphases is assumed, partly for simplicity, partly because of the analogy with ordinary micelles and other intramolecular phase separations, and partly because of experimental evidence such as the electron micrographs of osmium tetroxide treated films of styrene–butadiene copolymers.[3]

Enthalpy. Using these assumptions and the lattice theory of solutions, the enthalpy change on microphase separation is

$$\Delta H = \frac{-kTV}{V_r} v_A{}^c v_B{}^c \chi_{AB} \left(1 - \frac{2}{z}\right) \qquad (1)$$

where V is the total volume of the system, T is the absolute temperature, k is the Boltzmann constant, V_r is the volume of a lattice site, z is the coordination number of the lattice, $v_A{}^c$ and $v_B{}^c$ are the volume fraction of monomer A and B in the copolymer molecules, respectively, and χ_{AB} is the interaction parameter between A units and B units. Equation 1 is the Hildebrand[4]–Scatchard[5a]–Van Laar[5b] heat of mixing that is lost on microphase separation if we consider the fixed composition of each polymer chain in the calculation. For each monomer unit in the chain, only $z - 2$ contacts are random before microphase separation, since two contacts are fixed by the composition of the chain. It is also assumed that the only contacts between A and B after microphase separation are at the surfaces between microphases and consist *only* of A–B junctions within block copolymer molecules.

It is unfortunate that the coordination number of the lattice, z, appears in eq 1, making it necessary to choose a value for this quantity. Values of $z = 6$ or $z = 8$ have been used in this work.

Entropy. The entropy change per copolymer molecule when microphase separation occurs is

$$\frac{\Delta S}{k} = \ln (v_A{}^c)^{v_A{}^c}(v_B{}^c)^{v_B{}^c} - 2(m - 1)\left[\frac{\Delta S_{dis}}{R}\right] + \ln (m - 1) \qquad (2)$$

where m is the number of blocks in the block copolymer molecule. The first term on the right-hand side of eq 2 is concerned with the decrease in available volume for each block in the molecule after microphase separation assuming that there is no volume change on mixing. This term was discussed in a previous paper.[2] The second term on the right-hand side of eq 2 is the additional entropy decrease caused by immobilization at the microphase surface of the A and B units that link the blocks in each copolymer molecule. This total immobilization of just one A unit and one B unit linking two blocks is consistent with the assumption of very sharp interfaces made in the enthalpy derivation. In reality, the block-linking segments may not be entirely immobilized, while the neighboring segments may have lost some of their disorientation entropy; this situation is approximated by saying that the block-linking segments are totally immobilized while all other segments have their full disorientation entropy. The $(\Delta S_{dis}/R)$ in this term of eq 2 stands for the disorientation entropy gain on fusion per segment of a polymer. It remains to decide whether to use a theoretical or an

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(2) S. Krause, *J. Polym. Sci., Part A-2*, 7, 249 (1969).

(3) G. E. Molau and W. M. Wittbrodt, *Macromolecules*, 1, 260 (1968).

(4) J. H. Hildebrand, *J. Amer. Chem. Soc.*, 57, 866 (1935).

(5) (a) G. Scatchard, *Chem. Rev.*, 7, 321 (1931); (b) J. J. Van Laar, *Z. Physik. Chem.*, A137, 421 (1928).

experimental value for this entropy. This will be done after a brief explanation of the third term on the right-hand side of eq 2.

The third term on the right-hand side of eq 2 arises for copolymers containing three or more blocks because of the larger number of sites available for the block-linking segments on the surfaces between microphases. The number of sites on the surfaces available to the A portions of the A–B block-linking segments is equal to $N_c(m - 1)$, where N_c is the total number of copolymer molecules in the system. The first A segment of the ith molecule to be placed on a surface has $(m - 1)(N_c - i + 1)$ possible placements, while the other A segments of the same molecule that are linked to B segments are fixed on the surface close to the first such A segment. If we consider all possible arrangements of the block-linking segments of all N_c molecules on the surfaces between microphases, we find that these number approximately

$$\Omega = \frac{1}{N_c!}\prod_{i=1}^{N_c}(m - 1)(N_c - i + 1) = (m - 1)^{N} \qquad (3)$$

Per molecule, the entropy calculated from eq 3 is $k \ln (m - 1)$, the third term on the right-hand side of eq 2. This term does not exist when $m = 2$ and is negligible with respect to the other terms for large values of m.

It is now necessary to determine a reasonable value for $(\Delta S_{\mathrm{dis}}/R)$, the entropy lost when one segment of a polymer molecule is immobilized. It seems reasonable to consider the entropy of disorientation per segment as calculated by Flory[6] in his considerations of entropy of fusion of polymers. In his calculation, the disorientation entropy per segment is

$$\frac{\Delta S_{\mathrm{dis}}}{R} = \ln\left[\frac{(z - 1)}{e}\right] \qquad (4)$$

where e is the base of the natural logarithms. As z varies from 4 to 12, values of $(\Delta S_{\mathrm{dis}}/R)$ vary from 0.1 to 1.4. This variation is very large; it is also very difficult to choose an appropriate coordination number for the lattice. Presumably, a reasonable value of z would be greater than 4 and less than 12. If $z = 8$ is picked, $(\Delta S_{\mathrm{dis}}/R)$ has a value close to 1.0, and this value will be used in numerical calculations involving eq 4. This number is reasonable even upon consideration of experimentally determined values of $(\Delta S_{\mathrm{dis}}/R)$. Bondi[7] has tabulated values of $(\Delta S_{\mathrm{dis}}/R)$ for a number of polymers; these values are calculated from experimentally determined entropies of fusion after subtracting the entropy connected with change in volume of the sample. These values of $(\Delta S_{\mathrm{dis}}/R)$ vary from 0.93 for polyethylene to 3.0 for poly-1,4-*cis*-butadiene. Isotactic polypropylene is 1.45, isotactic poly-1-butene 1.25, isotactic polystyrene 1.0, polyoxymethylene 1.5, polyethylene oxide 2.35, and poly-*p*-xylene is 4.3. Poly-1,4-*cis*-isoprene is 0.85, while poly 1,4-*trans*-isoprene is 3.5.

No matter what value is picked for $(\Delta S_{\mathrm{dis}}/R)$, the entropy change on microphase separation calculated from eq 2 becomes more and more negative as the number of blocks in each copolymer molecule increases. In other words, it is already evident that entropy considerations will make microphase separation more difficult as the number of blocks per molecule increases.

Free Energy. The free energy change on microphase separation for the whole system of N_c copolymer molecules occupying volume V is

$$\frac{\Delta G}{kT} = \frac{-V}{V_r} v_A{}^c v_B{}^c \chi_{AB}\left(1 - \frac{2}{z}\right) - N_c \ln (v_A{}^c)^{v_A{}^c}(v_B{}^c)^{v_B{}^c} + 2N_c(m - 1)(\Delta S_{\mathrm{dis}}/R) - N_c \ln (m - 1) \qquad (5)$$

When $\Delta G = 0$, the separated system is in equilibrium with the completely mixed system; solution of this equation allows calculation of critical values of χ_{AB}, $(\chi_{AB})_{cr}$, for various values of $v_A{}^c$ and m. Since

$$V = N_c(V_A n_A{}^c + V_B n_B{}^c) \qquad (6)$$

where V_A and V_B are the volumes of A and B repeat units, respectively, and $n_A{}^c$ and $n_B{}^c$ are the numbers of A and B units in each copolymer molecule, respectively, we get

$$(\chi_{AB})_{cr} = \frac{zV_r}{(z - 2)V_A n_A{}^c v_B{}^c}\left\{-\ln (v_A{}^c)^{v_A{}^c}(v_B{}^c)^{v_B{}^c} + 2(m - 1)\left[\frac{\Delta S_{\mathrm{dis}}}{R}\right] - \ln (m - 1)\right\} \qquad (7)$$

When eq 7 is used to make predictions about the types of block copolymers that will exhibit microphase separation, it is convenient to let $V_r = V_A = V_B$,[8] and to set a convenient value for z, possibly $z = 6$ or 8, and for $(\Delta S_{\mathrm{dis}}/R)$, possibly 1.0.

Predictions. In a previous paper,[2] in which the surfaces between microphases were disregarded, the expression for $(\chi_{AB})_{cr}$ resembled eq 7, but without the factor $z/(z - 2)$ and with the second and third terms on the right-hand side deleted. When that expression was used to calculate $(\chi_{AB})_{cr}$ for a block copolymer whose composition by volume is 25% A and 75% B, with a total degree of polymerization 400, and assuming $V_A = V_r$, $(\chi_{AB})_{cr} = 0.0075$. That is, it was predicted that microphase separation would occur in any such block copolymer if χ_{AB} were greater than 0.0075. Using eq 7 from the present paper, also with $V_r = V_A$, with $(\Delta S_{\mathrm{dis}}/R) = 1.0$, and with $z = 6$ and $z = 8$, predictions can be made for a similar block copolymer with degree of polymerization 400, $v_A{}^c = 0.25$ and $v_B{}^c = 0.75$. and with various number of blocks in the molecules. Results of such calculations are shown in Table I. All the calculated values of $(\chi_{AB})_{cr}$ for $v_A{}^c = 0.25$ are greater than the value 0.0075 calculated without regard for surface effects and without the factor $(z - 2)/z$ in ΔH. Use of this factor would have increased the value from 0.0075 to 0.010 with $z = 8$ and to 0.011 with $z = 6$. At any rate, the surface free energies make microphase separation more difficult than one might otherwise expect and this effect becomes

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(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., Chapter XII, 1953.

(7) A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses," John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter 6.

(8) If this is not true, it can be arranged; one chooses a value of V_r compatible with the χ_{AB} used, and then one calculates $n_A{}^c$ and $n_B{}^c$ of the copolymer with respect to this V_r. See ref 2.

TABLE I
$(\chi_{AB})_{cr}$ FROM EQ 7 FOR TOTAL DEGREE OF POLYMERIZATION 400

z	m	$(\chi_{AB})_{cr}$ if $v_A^c = 0.25$	$(\chi_{AB})_{cr}$ if $v_A^c = 0.50$
6	2	0.052	0.040
	3	0.080	0.060
	4	0.112	0.084
	6	0.181	0.137
	10	0.328	0.246
8	2	0.047	0.036
	3	0.071	0.053
	4	0.100	0.075
	6	0.161	0.121
	10	0.292	0.218

more important as the number of blocks in the copolymer increases. The effect would have been less if a value smaller than 1.0 had been chosen for $(\Delta S_{dis}/R)$.

Table I also shows values of $(\chi_{AB})_{cr}$ calculated from eq 7 for a block copolymer with degree of polymerization 400 but with equal volume fraction of A and B. It is easier to obtain microphase separation in such a polymer than in the one that has 25% A and 75% B by volume. Calculations made for copolymers of different molecular weights give the expected result that microphase separation occurs more easily, *i.e.*, at lower values of χ_{AB}, for higher molecular weight polymers with the same compositions and number of blocks per molecule.

If we wish to compare the results of eq 7 with the behavior expected from a mixture of homopolymers of A and B, we have several choices. We choose to compare the diblock copolymer with $n_A^c = 100$ and $n_B^c = 300$ with a mixture of homopolymer of A and B, where homopolymer A has degree of polymerization 100 and homopolymer B has degree of polymerization 300. The critical value of χ_{AB} at which such a homopolymer mixture just begins to separate into two phases can be calculated using the Flory–Huggins[6] free energy of mixing of such a system (exact equations are given in ref 2). Such a calculation gives $(\chi_{AB})_{cr} = 0.012$ for the homopolymer mixture, a number much smaller than the ~0.05 calculated for the block copolymer. This implies that it is more difficult to achieve microphase separation in a block copolymer than it is to get ordinary phase separation in a mixture of the homopolymers obtained by cutting the connections between blocks in the block copolymer. This is the opposite of predictions made in my earlier paper[2] and agrees with that made by Meier[9] using a different theoretical treatment. However, the critical χ_{AB} of 0.012 calculated here for the homopolymer mixture is for a critical volume fraction of 0.634 for homopolymer A. It is more illuminating to calculate the value of χ_{AB} at which a mixture of these two homopolymers would just separate into two phases when the volume fraction of homopolymer A is 0.25, as it is in the block copolymer. For simplicity of calculation, this value of χ_{AB}, = 0.022 was calculated at the absolute limit of stability of the single phase (the spinodal) instead of the equilibrium limit of stability (the binodal). (The equation for the spinodal of this system is eq 5a of ref 2.) This number is still smaller than $(\chi_{AB})_{cr}$ ~0.05 calculated for the binary copolymer using $(\Delta S_{dis}/R) = 1$. However, a value of $(\chi_{AB})_{cr} = 0.021$ can be calculated for the binary block copolymer using $(\Delta S_{dis})/R) = 0.3$ and $z = 8$, values that are not completely unreasonable. In that case, the calculations show that the homopolymer mixture separates into two phases about as easily as microphase separation occurs when the two homopolymers are bonded together into a diblock copolymer.

It may turn out that different values of $(\Delta S_{dis}/R)$ must be used for different polymer repeat units. In that case, there may exist real systems in which the homopolymer mixture phase separates more easily than the corresponding block copolymer, there may exist other real systems in which the homopolymer mixture phase separates exactly like the corresponding block copolymer, and there may even exist other real systems in which the homopolymer mixture phase separates with greater difficulty (at higher values of molecular weight) than the corresponding diblock copolymer.

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(9) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969).