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Computer-Aided Comparative Investigation of Architecture Influence on Block Copolymer Phase Diagrams

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ABSTRACT: The microphase separation in melts of asymmetric triblock and trigraft, periodic polyblock and polygraft, and star-shaped copolymers of two types $((A_n)_k(B_m)_k)$ and $(A_nB_m)_k$ is investigated within the framework of the mean field approximation. To enable rapid comparison of the behavior of various types of block copolymer architecture, a special program "Supercrystal" using previously calculated higher correlators of specific systems is elaborated. Surfaces of phase transition between phases with different supercrystal symmetry and a spatially homogeneous state are constructed as a function of molecular architecture and the Flory parameter χ . A behavior similar to a tricritical one is observed in melts of star-shaped copolymers of the kind $(A_n)_k(B_m)_k$ with $k > 5$, k being the number of arms. Phase diagrams obtained for the other systems are like the phase diagram obtained by Leibler for the molten diblock copolymer, but the temperatures of the phase transitions differ considerably for copolymers consisting of the same blocks connected in a different manner. There are limiting phase diagrams for both polyblock and polygraft systems in the limit $k \rightarrow \infty$, k being the number of blocks A_nB_m in a chain.

I. Introduction

In this paper we present the broadest collection to date of phase diagrams of flexible block copolymer systems of various architecture. In addition to phase diagrams of molten diblock¹ and asymmetric triblock copolymers² calculated early within the framework of the mean field approximation¹⁻⁴ of the so-called weak crystallization theory,⁵⁻¹³ we constructed in the same approximation phase diagrams of molten asymmetric trigraft, periodic polyblock and polygraft, and star-shaped copolymers of two types $((A_n)_k(B_m)_k)$ and $(A_nB_m)_k$. To be able to carry out the corresponding very cumbersome calculations, we elaborated a special program enabling construction of the phase diagrams for a very broad class of block copolymer systems apart from those that are presented in the paper. Thus, the aim of the paper is to describe typical phase diagrams as well as to explain how the program works and to what extent the results obtained are valid. To this end our exposition is the following. First, we recall what is the weak crystallization and other main physical concepts of the current understanding of microphase separation phenomena. In section II typical phase diagrams of asymmetric triblock and graft copolymers are presented and compared. In section III typical phase diagrams of star-shaped copolymers of the $(A_n)_k(B_m)_k$ and $(A_nB_m)_k$ kinds are constructed, and a new type of tricritical-like behavior is predicted. In section IV periodic polyblock and polygraft copolymers are considered. Discussion and conclusions are given in section V.

The microphase separation (MPS, domain structure formation, supercrystallization) of solutions and melts of copolymers is one of the most interesting phenomena of polymer science, from both the physical and the technological points of view. Now, after much effort over the past 20 years, the physical nature of domain structure formation is understood sufficiently well. From the point of view of Landau phase transition theory¹⁴ a system under microphase separation undergoes a set of phase transitions that are described conventionally in terms of the vector order parameter

$$\Phi_\alpha(r) = \rho_\alpha(r) - \bar{\rho}_\alpha \quad (1)$$

where $\rho_\alpha(r)$ is the local density of monomers of sort α (i.e.,

the number of monomers per unit volume) and $\bar{\rho}_\alpha = \int \rho_\alpha(r) dr/V$ is the average value of the density over the volume V of the system.

All components of the order parameter are equal to zero throughout the entire volume of the system in the high-temperature homogeneous phase (liquid), but when the temperature decreases, the order parameter can become a spatially periodic function, possessing the symmetry of a Bravais lattice:

$$\Phi_\alpha(r) = \sum_{\{q\}} A(q_i) \exp(iq_i \cdot r) \quad (2)$$

where the sum is carried out over all vectors of the corresponding inverse lattice. A change in temperature or in the chemical structure of the system can lead to either a continuous or a discrete alteration of its equilibrium thermodynamic state, described by the set of amplitudes $A(q_i)$ in the sum (2). An abrupt change (i.e., phase transition) takes place, for example, in the case of altering the type of Bravais lattice. The determination of surfaces (points) of phase transitions as a function of the temperature and the polymer structure is the aim of a theory of the microphase separation of heteropolymer systems.

Up till now the aim was achieved in two approximations. At the beginning of the development of the microphase separation theory the phenomenon was considered in the so-called narrow interphase approximation, which corresponds to a case of almost complete segregation, when every domain consists mainly of monomers of the same sort.¹⁵⁻²⁰ A second approximation was advanced after understanding (first by Leibler¹ and de Gennes²¹ and then independently by Erukhimovich²²) the fact that microphase separation of a heteropolymer is connected with an instability of its homogeneous state with respect to spatial fluctuations of the densities $\{\rho_i(r)\}$ of a finite period. It is the fluctuations that dominate at the initial stage of domain structure formation, with segregation of unlike monomers remaining weak. The situation is considered in the framework of the so-called weak crystallization theory,⁵⁻⁹ taking into account in the sum (2) only those components that correspond to inverse Bravais lattice vectors which have a magnitude q_0 , the radius of the first coordination sphere of the lattice. (In this paper we will

use also the term "supercrystallization", which implies the presence of a large parameter L/a , where L is a period of a crystal lattice and a is the Kuhn length.) It is within the framework of the weak crystallization theory that the detailed theoretical analysis of domain structure formation was carried out by Leibler in his classic paper.¹

It is evident that each of these two theories has, in accordance with their range of application, its own advantages and shortcomings, a detailed comparison of which is beyond the scope of our paper. (A detailed discussion of both approaches is available.^{4,9,10}) The aim of this paper is a more particular one: to draw attention to which is, in our opinion, the most important advantage of the weak crystallization theory, namely, the possibility to give a complete description of the dependence of the initial microphase separation's stages on the chemical structure of heteropolymer systems. A preliminary consideration of this question was undertaken by Erukhimovich.^{22,23}

Among other things, a general analysis of the instability of the homogeneous state of polydisperse flexible heteropolymers with respect to spatial density fluctuations of a finite period L was given in ref 22. In ref 23 spinodals were first obtained both for asymmetric triblock and trigraft copolymers and for periodic polyblock and polygraft copolymers, both A and B blocks being assumed to be flexible. Many of these results were obtained later in ref 24, where polyblock and polygraft copolymers with flexible blocks A and rigid blocks B were considered as well, and in refs 2 and 25 (for symmetric and asymmetric triblock and trigraft flexible copolymers). Besides, the spinodals were obtained for $(A_nB_m)_k$ and $(A_n)_k(B_m)_k$ star flexible copolymers.^{2,25}

However, the corresponding phase diagram in the plane (χ, f) ($\chi = \chi N$, χ is the conventional Flory parameter characterizing A-B interaction, $N = n + m$ is the polymerization index of typical diblock copolymer macromolecules A_nB_m of which a considered compound macromolecule is formed, and $f = n/N$ is its composition) has only been constructed for the cases of a molten diblock copolymer⁶ and of asymmetric triblock copolymers.²

The fact is that the Leibler-like construction of phase diagrams involves very cumbersome calculation of so-called higher correlators of copolymer macromolecules of complicated chemical structure. However, it is polymer systems of complicated chemical structure that are the most interesting from the point of view of technological applications. It is useful, for example, to know in what way the blocks should be connected to make a certain supercrystal lattice at either high or low temperatures. Furthermore, microphase separation takes place, possibly, in polyelectrolyte systems^{4,12,26-28} as well as in gels and heteropolymer networks.²⁹ There are many other questions which are of practical interest but which, unfortunately, cannot be answered without hard calculations.

So, there arises the necessity to solve a new both scientific and technological problem: to provide users with a package of special programs to calculate phase diagrams and other characteristics of particular systems which are of interest to them. These programs must allow for complicated chemical structures of polymer systems (using explicit expressions for higher structural correlators of various polymers), the nontrivial character of volume interaction (by means of choice of phenomenological equation of state of the corresponding system of quasi-monomers), the effects of fluctuations, the presence of micelles, etc.

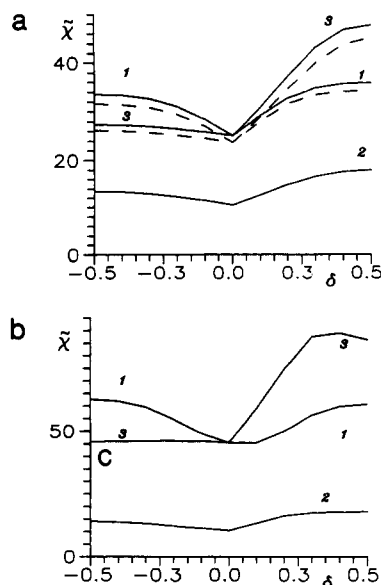


Figure 1. Phase diagrams of asymmetric triblock and graft copolymers $A_nB_mA_l$ on the plane (χ, δ) at fixed values of f . Curves labeled by numbers 1, 2, and 3 correspond to molten diblock copolymer with $f = 0.2, 0.5$, and 0.8 , respectively. (a) Lines of phase transition DIS-bcc (dashed) and bcc- Δ (solid); (b) lines of phase transition Δ -LAM.

As a first step along the line we elaborate the program "Supercrystal", enabling us to calculate the higher correlators and then to construct phase diagrams of melts of flexible two-component copolymers of any complicated chemical structure in the mean field approximation corresponding to the theory of weak crystallization. The theoretical background of the program is essentially identical to approach of Leibler¹ with some technical improvements and will not be given in the paper. So, we present here phase diagrams of some new block copolymer systems obtained using the program.

II. Phase Diagrams of Asymmetric Triblock and Graft Copolymers $A_nB_mA_l$

To describe the structure of the copolymers let us introduce their composition $f = m/N$, $N = m + n + l$ being the polymerization index of a macromolecule $A_nB_mA_l$, and symmetry parameter δ defined in ref 23 as follows: $|\delta| = n/(n + l)$, the parameter δ taking negative values for trigraft copolymers and positive values for triblock ones. (In refs 2 and 25 the symmetry parameter is denoted τ .)

Results of our calculations can be presented in the form of sections of phase transition surfaces between the homogeneous (liquid) state of the melt and the supercrystal phases constructed in the space (f, δ, χ_{tr}) .

The sections at various values of f determine $\chi_{tr}(\delta)$ as functions of the symmetry parameter δ and are shown in Figure 1. One can see that, as a rule, in both systems the parameter χ_{tr} increases if the macromolecule asymmetry decreases. However, the phase transition Δ -LAM in molten triblock copolymers seems to be an exception to the rule. For example, in the case of $f = 0.8$, the function $\chi_{\Delta-LAM}(\delta)$ (upper curve of Figure 1b) has a maximum.

Instead of analyzing sections of surfaces $\chi(f, \delta)$ at a given f , we could consider ones at a given δ . Two examples of such sections for symmetric triblock copolymer with $\delta = 0.25$ and $\delta = 0.5$ can be found in ref 2. As another example, we present here in Figure 2a similar phase diagrams for symmetric trigraft copolymers ($\delta = -0.5$). Here and in other figures the regions of the existence of liquid (disordered) and supercrystal body-centered cubic, triangular, and lamellar phases are denoted DIS, bcc, Δ , and

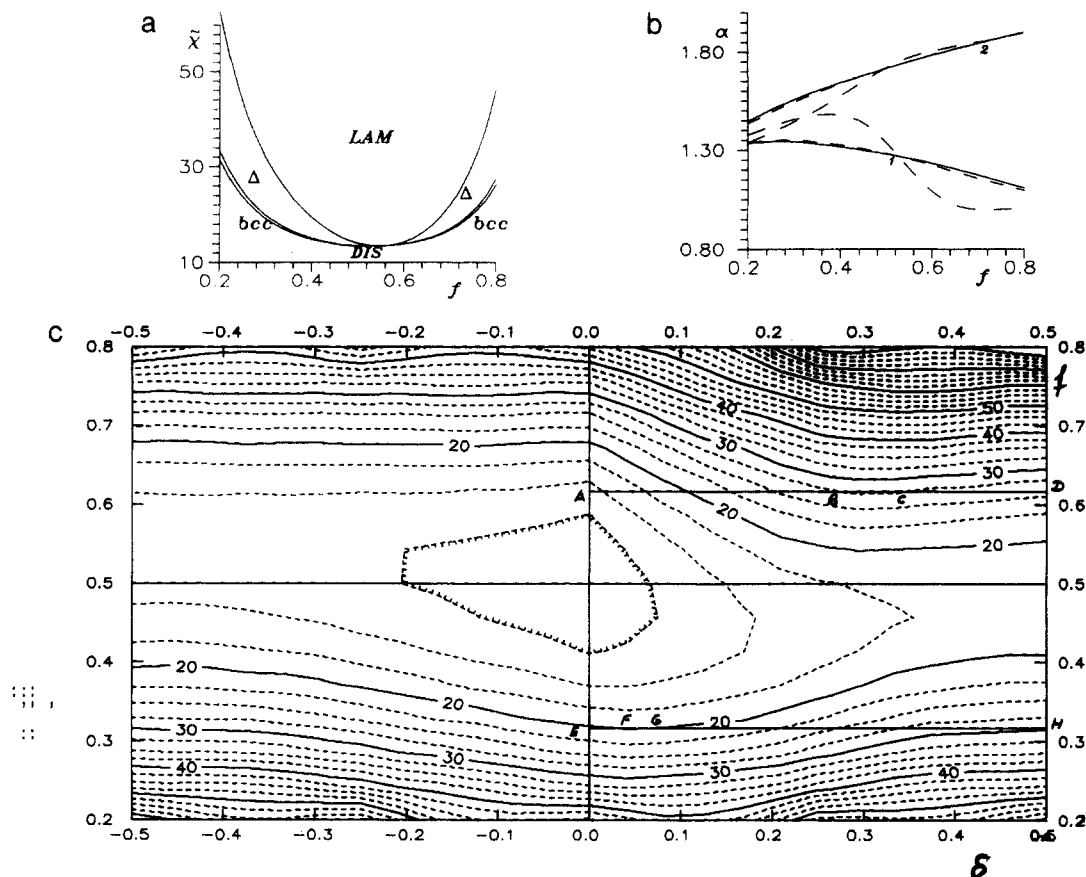


Figure 2. (a) Typical succession DIS-bcc-Δ-LAM of phase transitions for symmetric trigraft copolymer ($\delta = -0.5$) on the plane $(\tilde{\chi}, f)$. (b) Phase diagrams of asymmetric triblock and graft copolymers at fixed values of δ rebuilt in terms of the reduced quantity $\alpha_s(f) = \chi(f, \delta)/\chi(f, 0)$. The curves $\alpha_s(f)$ labeled by numbers 1 and 2 correspond to symmetric triblock ($\delta = 0.5$) and graft ($\delta = -0.5$) copolymers, respectively. In pairs of almost merging lines solid lines correspond to phase transition DIS-bcc and dashed lines to bcc-Δ; other lines correspond to Δ-LAM. (c) Projection of the lines of phase transition Δ-LAM on the plane (f, δ) .

LAM, respectively. All the diagrams demonstrate the same succession of phase transitions DIS-bcc-Δ-LAM as the case of molten diblock copolymer.

To analyze the influence of chemical structure on these phase diagrams, it is more convenient to consider the reduced quantity $\alpha_s(f) = \chi(f, \delta)/\chi(f, 0)$ (recall, that $\chi(f, 0)$ corresponds to the molten diblock copolymer). One can see that the parameter χ increases (and, respectively, the corresponding transition temperature decreases) compared with the diblock copolymer case (with the fraction f of monomers pertaining to the central block B_m increased) for phase transitions in the symmetric triblock ($\delta = 0.5$) copolymer. The behavior of a symmetric graft ($\delta = -0.5$) copolymer is more complicated. Here for the phase transitions DIS-bcc and bcc-Δ the parameter χ decreases (correspondingly, the temperature of these transitions increases) compared with the diblock copolymer ones (with the fraction f of monomers pertaining to the central block B_m increased), whereas the reduced quantities characterizing the phase transition Δ-LAM are nonmonotonous functions of f . It should be stressed, however, that according to the results of our calculation presented in Figure 2b the value $\alpha(f)$ stays greater than unity over the entire range of f . This means that the homogeneous state of a molten diblock copolymer is less stable to transition into supercrystal phases than any triblock copolymer of the same composition.

It is instructive also to present the projections of the sections of the surface $S(f, \delta, \tilde{\chi}_{\Delta-LAM}) = 0$, corresponding to the first-order phase transition between the triangular and lamellar phases, by planes $\tilde{\chi} = \text{constant}$ (I.E. is grateful to Prof. Monnerie for suggesting this kind of data presentation). These sections are drawn in Figure 2c with

the contour interval 2.5, each fourth being marked by the corresponding values of $\tilde{\chi}_{\Delta-LAM}(\delta)$. (The unlabeled curves are drawn as dashed ones to make the picture more transparent.) The center of Figure 2c corresponds to the symmetric diblock copolymer with the value of $\tilde{\chi}_{\Delta-LAM}(\delta) = 10.5$. As shown in Figure 2c for $\tilde{\chi}_{\Delta-LAM}(\delta) = 12.5$, near the center these sections are closed circles, the lamellar phase being of thermodynamic advantage inside the circles. (Recall that their left half corresponds to trigraft copolymers and their right half to triblock copolymers.) One can see that the lines $f(\delta)$ are generally nonmonotonous so that the equation $\partial f(\delta, \tilde{\chi})/\partial \delta = 0$, $f(\delta, \tilde{\chi})$ being the function defined implicitly by the equation $S(f, \delta, \tilde{\chi}) = 0$, has a root $\delta(\tilde{\chi})$. This means that there exists a region on the plane $(f, \tilde{\chi})$ such that the phase state of a triblock copolymer with certain values of f and $\tilde{\chi}$ situated in the region will change nonmonotonously when increasing the value of δ . This point is exemplified by straight lines ABCD and EFGH, corresponding to values of $f = 0.617$ and $f = 0.317$, respectively. One can see that these lines cross twice the projections of the sections of the surface $S(f, \delta, \tilde{\chi}_{\Delta-LAM}) = 0$ by planes $\tilde{\chi} = 27.5$ (for $f = 0.617$) and $\tilde{\chi} = 20$ (for $f = 0.317$). Otherwise, if the change of δ due to some chemical processes proceeds at the fixed values $\tilde{\chi} = 27.5$, $f = 0.617$ and $\tilde{\chi} = 20$, $f = 0.317$, the systems under investigation will be in the triangular state inside intervals BC and FG, respectively, and in the lamellar state outside these intervals. One can see that for triblocks with a large central block the Δ-phase can be observed when both side blocks are of the same order, while for triblocks with a small central block the Δ-phase exists only when one of side blocks is much smaller than the other.

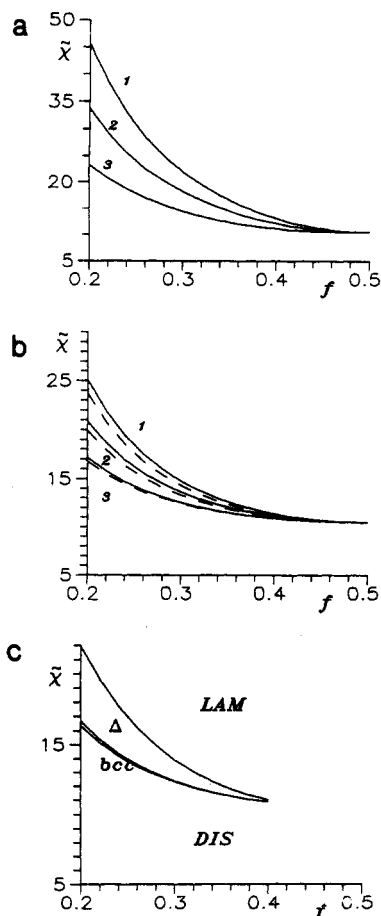


Figure 3. (a,b) Phase diagrams of $(A_n)_k(B_m)_k$ stars with $k = 1, 2$, and 5 are presented, which are marked by numbers $1, 2$, and 3 , respectively. (a) Lines of phase transition Δ -LAM; (b) analogous lines of phase transitions DIS-bcc (dashed) and bcc- Δ (solid); (c) phase diagram of star $(A_n)_6(B_m)_6$.

III. Phase Diagrams of Star Copolymers $(A_n)_k(B_m)_k$ and $(A_nB_m)_k$

In this section we shall refer to stars with a general structural formula $(A_n)_k(B_m)_k$ as stars of kind A and stars with a general structural formula $(A_nB_m)_k$ as stars of kind B. The structure of the copolymers is described by its composition $f = m/N$, $N = m + n$ being the polymerization index of block A_nB_m , and by the number k of arms. Results of our calculations can be presented in the form of sections of phase transition surfaces between the homogeneous (liquid) state of melt and supercrystal ones constructed in the space (f, δ, χ) with $\chi = \chi N$.

In Figure 3a,b phase diagrams are presented for stars of kind A with values $k = 1, 2$, and 5 . One can see that the value of $\chi_k(f)$ at the phase transition decreases when k increases. The minimal value of $\chi_k(f)$ occurs at the same value of $f = 0.5$ for each of these values of k . Analogous lines of phase transitions DIS-bcc (dashed) and bcc- Δ (solid) at these values of k are shown in Figure 3b. The combination of the results presented to Figure 3a and Figure 3b gives the customary succession of phase transitions DIS-bcc- Δ -LAM. A quite different behavior is observed in melts of stars of kind A with $k > 5$, in which case there exists an interval (f_1, f_2) outside of which the ordinary sequence DIS-bcc- Δ -LAM of phase transitions takes place as well. For example, for stars of this kind with $k = 6$, it is $(0.429, 0.571)$; the corresponding phase diagram is shown in Figure 3c. However, inside the interval our program does not work because of a divergence of our free energy minimization procedure. To explain the

situation in the region let us discuss the calculational procedure used in our program in more detail.

To obtain the phase diagram of systems under supercrystallization it is conventional to minimize the Landau expansion of its free energy in powers of the order parameter $\Phi(r)$ with respect to values of the amplitudes $A_i = A(q_i)$ occurring in expression 2:

$$F = F_0 + \min \Delta F$$

$$\Delta F/VT = \sum_{\{q_i\}} \gamma^{(2)}(q_i) |A_i|^2/2 + \sum_{q_i+q_j+q_k=0} \gamma^{(3)}(q_i, q_j, q_k) A_i A_j A_k/3! + \sum_{q_i+q_j+q_k+q_l=0} \gamma^{(4)}(q_i, q_j, q_k, q_l) A_i A_j A_k A_l/4! \quad (3)$$

where F_0 is the free energy of the spatially homogeneous (disordered, liquid) state. The coefficients $\gamma^{(i)}$ are expressed explicitly in terms of the structural characteristics of macromolecules.^{1-4,22-24} It can be verified that all moduli of the equilibrium amplitudes A_i are equal to the same value A , resulting in the following expression for ΔF :

$$\Delta F = \tau A^2/2 + \alpha_n A^3/6 + \beta_n A^4/24 \quad (4)$$

where α_n, β_n , and τ are certain functions introduced first for molten diblock copolymer.¹ In our case they depend on both the composition f and the number of arms k (τ depends on χ as well). They are different for different supercrystal lattices (marked by subscript n) and are calculated explicitly using our program. Thus, any free energy minimization procedure will converge to a fixed point only if the condition $\beta_n > 0$, prescribing the stability of the solution with respect to fluctuations of amplitudes A_i , is fulfilled. Meanwhile immediate calculations show that in the interval (f_1, f_2) the value β_1 , corresponding to a lamellar structure, is negative, while values β_n , corresponding to other supercrystal structures, are positive. This unusual behavior of the lamellar phase is caused by the fact that the coefficient $\gamma^{(4)}(q_1 \dots q_4) = \gamma^{(4)}(h_1, h_2)$ is a function of the angles between vectors of the inverse lattice. Were there no angle dependence of the coefficient $\gamma^{(4)}$, the contribution of the fourth order in expansions 3 and 4 would have the same sign for lattices of any symmetry and all supercrystal states would be unstable simultaneously.

From the point of view of the conventional phase transition theory,¹⁴ the presence of the above divergence just implies that our assumption about the irrelevance in expansion 4 of higher order terms is incorrect. Indeed, in the vicinity of the point at which all functions α_n, β_n , and τ are equal to zero (recall that the point is called a tricritical one), one should allow for members of the fifth and sixth powers of the order parameter in expansion 4 of the free energy. Thus, one should go beyond the scope of Leibler's theory to calculate phase diagrams of stars of the kind A inside the interval (f_1, f_2) and consider here their behavior as tricritical. We hope to return to the problem in future publications.

Now consider the melt of stars of kind B. In Figure 4a corresponding lines of the phase transition Δ -LAM are presented, the lines for $k = 1, 2, 5$, and 10 being marked by these numbers, respectively. One can see that curves $\chi_k(f)$ drop (the corresponding transition temperatures rise) when the number of arms k increases, the minima of the lines moving toward larger values of f . One can see that the general behavior of these curves is like that of the

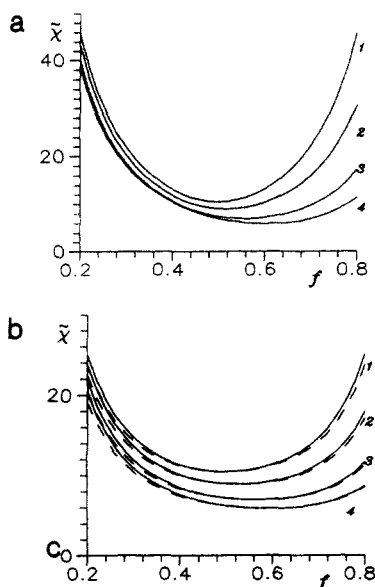


Figure 4. Phase diagrams of $(A_n B_m)_k$ stars with $k = 1, 2, 5$, and 10 are presented, which are marked by numbers 1, 2, 3, and 4, respectively. (a) Lines of phase transition Δ -LAM; (b) analogous lines of phase transitions DIS-bcc (dashed) and bcc- Δ (solid).

spinodals of these systems which are shown in Figure 4 of ref 2. Analogous lines of phase transitions DIS-bcc (dashed) and bcc- Δ (solid) for the same value of k are shown in Figure 4b. Combining the results presented in Figure 4a and Figure 4b gives an ordinary succession of phase transitions DIS-bcc- Δ -LAM. Note that the phase with bitetrahedral symmetry is absent in the succession, although it is observed in experiments.³⁰ The structures of the first coordination spheres of the bitetrahedral and bcc lattices are the same, so it follows that in our approximation the free energies of the lattices are the same, too. Therefore, within the framework of the conventional version of the weak crystallization theory, which takes account only of vectors of the first coordination sphere in the sum (2), one cannot distinguish between these two phases. We intend to give a more thorough discussion of the problem in future publications.

IV. Phase Diagram of Polyblock and Polygraft Copolymers $(A_n B_m)_k$

To describe the structure of these copolymers let us use the number of blocks k of each type and their composition $f = n/N$, $N = n + m$ being a polymerization index of a "period" $A_n B_m$. Besides, it is supposed that in polygraft copolymers B blocks are grafted periodically across n monomers to a main chain consisting of monomers of the sort A.

In Figure 5a lines of phase transitions DIS-bcc (solid) and bcc- Δ (dashed) are presented for the case of molten polyblock copolymers with $k = 1, 2, 4$, and 10. All the lines are symmetric about the line $f = 0.5$, since properties of incompressible polyblock copolymer are invariant as to the rearrangement of blocks A and B. Thus, they take their minimal values at $f = 0.5$. In Figure 5b analogous lines of phase transitions are shown for the case of molten polygraft copolymers with $k = 1, 4$, and 10. One can see that minima of $\chi_k(f) = N\chi_k(f)$ move toward smaller f if k increases.

In the limit $k \rightarrow \infty$ there are limiting phase diagrams in both polyblock and polygraft copolymer systems. The same behavior of the spinodals of these systems was discovered early in refs 23 and 24. It follows from calculations that the limiting lines almost merge with the

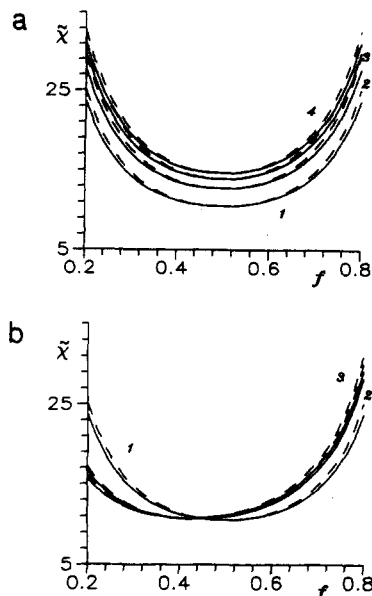


Figure 5. Phase diagrams of polyblock (a) and polygraft (b) copolymers $(A_n B_m)_k$, k being the number of "quasimonomers" $A_n B_m$. To simplify the figures lines of phase transitions DIS-bcc (solid) and bcc- Δ (dashed) are presented only; lines of transition Δ -LAM are shown in Figure 6. (a) Numbers 1, 2, 3, and 4 denote lines corresponding to $k = 1, 2, 4$, and 10, respectively; (b) numbers 1, 2, and 3 denote lines corresponding to $k = 1, 4$, and 10, respectively.

corresponding lines of phase transitions for the systems with $k = 10$, so we do not represent them in the figures. The phenomenon can be explained easily by using the concept of quasimonomers, the role of quasimonomers being played by the "separated blocks" A_n and B_m .²³ Indeed, the total density-density correlation function of the systems can be divided into a sum of correlation functions describing the intrablock correlations of monomers and the correlations of monomers pertaining to different blocks (inter-quasimonomers correlations). When the number of periods k increases, the correlation function ceases to depend on k and is determined only by the full density of quasimonomers just as the Debye function of an N -mer does in the region $(qa)^2 N \gg 1$.

To investigate the influence of the "degree of macropolymerization" k on the value of χ , it is useful to use the following reduced value of the latter: $\alpha(f) = \chi(f, k)/\chi(f, 1)$. Graphics of this kind are presented in Figure 6. One can see that in the region of small values of f phase transition parameters alter more for polygraft copolymer than for polyblock copolymers.

V. Discussion

The collection of phase diagrams presented in this paper answers the question of how the parameters of the phase transitions between liquid and different supercrystal phases of a heteropolymer are influenced by its block architecture, i.e., the way the blocks in the macromolecules are connected. As shown above, variation in block copolymer architecture can cause both considerable quantitative (up to a double drop of transition temperatures) and qualitative change of its phase diagram. This fact is of great importance for technological applications of heteropolymer systems.

However, doubts about the validity of both the weak crystallization theory and its mean field approximation, which were involved in our calculations, have been expressed.^{4,9,10} Indeed, because of the presence of some sources of inaccuracies, there are reasons for such doubts.

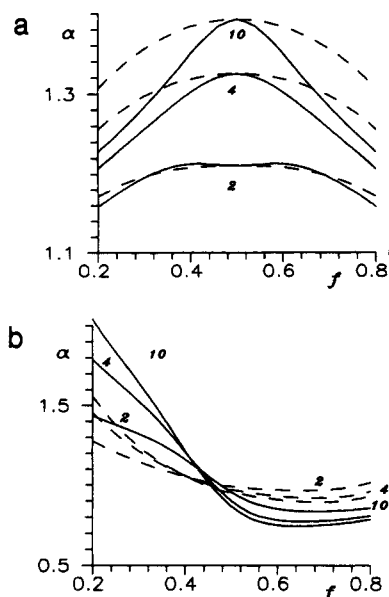


Figure 6. Reduced (as to diblock copolymer) phase diagrams of polyblock (a) and polygraft (b) copolymers in variables α - f . For solid lines $\alpha = \chi(k, f)/\chi(l, f)$ for phase transition Δ -LAM; for dashed lines α is the same quantity for transition bcc- Δ . Lines are marked by values of their number of blocks.

The first source of inaccuracy is connected with the enhancement of concentration fluctuations near the boundary of the region of absolute instability with respect to these fluctuations, which is not taken into account in the Leibler-like consideration above. Thorough computer-aided investigation of the question undertaken by us by a generalization of the Brazovskii-Fredrickson-Helfand approach^{12,13,31} (see also ref 11) enables us to maintain that the results presented in this paper have a rather broad region of applicability. A more serious inaccuracy is connected with omitting in expression 2 all members with vectors q that do not belong to the first coordination sphere.^{32,33} Indeed, just these omitted members give the main contribution to $\Phi_\alpha(r)$ in the region of the narrow interface theory and are to be compared with those calculated in the weak crystallization theory to obtain the condition of its validity. However, before evaluating the members, one should take into account all weakly fluctuating quantities having, generally speaking, the same order of magnitude.

In addition, we would like to draw attention to an even more important point of this paper—the possibility of combining recent advances in exact polymer theory and the facilities of a computer technique to consider various types of block copolymer architecture simultaneously. The time which is needed to compute and construct any of above phase diagrams using our program and a 16-bit microcomputer equipped with an 80286 processor, 80287 math coprocessor, and 640 KB of memory did not exceed 10 min. We believe that computer-aided methods to describe and predict properties of block copolymer systems

of complicated chemical structure can become a powerful new tool of new polymer materials design.

Acknowledgment. We thank a referee for mentioning refs 2 and 11. I.E. is grateful to Profs. L. Monnerie and L. Leibler for useful discussion and to T. Duke for reading the manuscript. We acknowledge financial assistance from PRF as well.

Supplementary Material Available: A list of correlators of the second, third, and fourth order for asymmetric triblock and trigraft and periodic polyblock and polygraft copolymers as well as star-shaped ones of the $(A_n)_k(B_m)_k$ and $(A_nB_m)_k$ kind (24 pages). Ordering information is given on any current masthead page.

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