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Microphase separation of comb copolymers with two different lengths of side chains

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The phase behavior of the monodisperse *AB* comb copolymer melt contained the macromolecules of special architecture is discussed. Each macromolecule is assumed to be composed of two comb blocks which differ in numbers of side chains and numbers of monomer units in these chains. It is shown (by analysis of the structure factor of the melt) that microphase separation at two different length scales in the melt is possible. The large and small length scales correspond to separation between comb blocks and separation between monomer units in repeating fragments of blocks, respectively. The classification diagrams indicated which length scale is favored for a given parameters of chemical structure of macromolecules are constructed.

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I. INTRODUCTION

A distinctive feature of block-copolymer melts is their ability to form spatially periodic mesophases whose period falling within the nanometer range [1]. This unique property of block copolymers opens up possibilities for their application in nanotechnology for the creation of photonic crystals, nanoporous materials, and high-density storage media [2–5]. The periodic structures formed in melts of the simple binary block-copolymer (e.g., diblock copolymer) melts are usually characterized by one spatial length scale. The hierarchical structures which have more than one characteristic length scale have been found both theoretically and experimentally in copolymer melts whose macromolecules consist of more than two types monomer units [6–16]. These hierarchical mesophases constitute the short length scale structure formed within the large scale one. As it was shown recently, two scale structures can be also obtained in the binary block-copolymer melts which contain the macromolecules of specially designed architecture [17–27]. Up to now, the two-scale behavior has been theoretically discovered for several types of architectures of block-copolymer macromolecules comprised only two distinct types of the monomer units. These architectures, depicted in Fig. 1, include (a) linear-comb block copolymer, (b) linear-alternating block copolymer, (c) linear-alternating-linear block copolymer, and (d) linear-alternating-linear-alternating block copolymer.

The possibility of formation of two-scale structures in binary block-copolymer melts was predicted by Nap *et al.* [17] for copolymers of types (a) and (b) presented in Fig. 1. It was found that the inverse structure factor of these copolymer melts can have either one minimum or two minima. The presence of two minima indicates that two different length scales may occur at microphase separation. It is very important that these length scales differ markedly in value. The smaller of these scales is determined by the radius of gyration of repeating fragment of alternating or comb block and the larger one by the radius of gyration of the whole macromolecule. It was shown that depending on the parameters (m,n) of chemical structure of macromolecules presented in Figs. 1(a) and 1(b), the microphase separation can occur at only one or at both length scales. The so-called classification diagram presented in paper [17] indicates which length scale is realized for a given set of parameters (m,n). The existence of bifurcation point in (m,n)-parameter space was established [17]. Below this point, the inverse structure factor has only one minimum whereas above bifurcation point it can have two minima.

The number of theoretical studies has been undertaken to describe the formation of the hierarchical structures with double periodicity in melts of copolymers whose architectures are presented in Fig. 1 [18–29]. The phase diagram of the linear-comb block-copolymer melt [Fig. 1(a)] was constructed in the framework of weak segregation theory (WST) [18,19]. The investigation of the same system by using the self-consistent field theory (SCFT) revealed the possibility of formation of various hierarchical nanostructures [20]. The

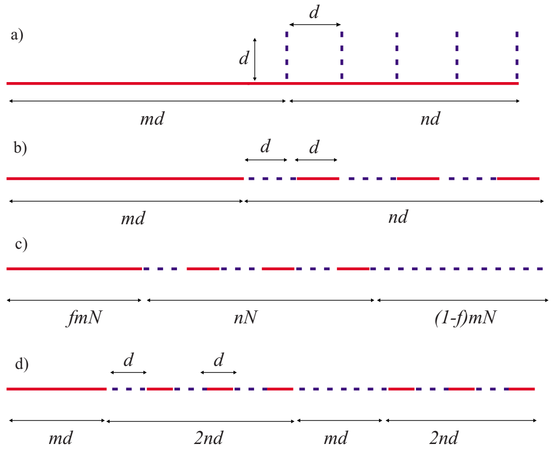

FIG. 1. (Color online) Models of macromolecules whose architecture involves two length scales. Solid and dotted lines correspond to the blocks of *A*-type and *B*-type monomers, respectively. Macromolecule consist of (a) *A* homopolymer block attached to the *AB*-comb copolymer block, (b) *A* homopolymer block linked to the *AB* multiblock copolymer, (c) *A* homopolymer and *B* homopolymer blocks attached from both sides of *AB*-multiblock copolymer, and (d) *A* homopolymer block, *AB* multiblock, *B* homopolymer blocks, and *AB*-multiblock copolymer attached successively. Parameters *m*, *n*, *f*, and *N* determine the chemical structure of macromolecule.

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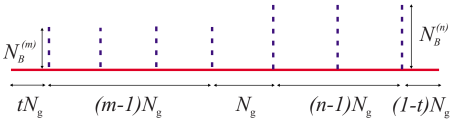

FIG. 2. (Color online) Model of macromolecule considered in this paper. The figure corresponds to macromolecule with $m=4$ and $n=3$ side chains comprised $N_B^{(m)}$ and $N_B^{(n)}$ monomers, respectively.

phase behavior of the monodisperse melt of linear-alternating block copolymer [Fig. 1(b)] was investigated within SCFT [21,22]. The formation of hierarchical lamellae-in-lamella phases with two length scales was demonstrated. The microphase separation in melt of the linear-alternating-linear block copolymer [Fig. 1(c)] has been studied both within WST [23–25] and SCFT [26]. The classification diagram [24] and phase diagrams [25–27] have been found. The general diagrammatic algorithm for finding coefficients of the Landau free-energy expansion for the description of thermodynamical behavior of multiblock copolymers whose macromolecules contain blocks of two types substantially differing in length has been put forward in paper [28]. Later, this algorithm has been used in paper [29] to describe within WST the phase behavior of copolymer melt whose macromolecules comprise periodically repeating segments of type (d) (Fig. 1). The possibility of two-scale behavior in melts of double-grafted block copolymers has been discussed in paper [30]. The hierarchical lamellae-in-lamella structures were observed experimentally for copolymer whose macromolecules comprised two long polystyrene blocks attached to the both ends of middle multiblock consisting of alternating short polystyrene and polyisoprene blocks [31].

In this paper we discuss the possibility of formation of two scale structures in the comb copolymer melt whose macromolecule contains side chains of two different lengths. This architecture depicted in Fig. 2 differs from those investigated previously (Fig. 1). The objective of this study is to analyze within WST the dependence of the structure factor of this melt on the parameters of chemical structure of macromolecules. We intend to demonstrate that such comb copolymer melt is to exhibit microphase separation characterized by two length scales which differ in value noticeably.

The paper is organized as follows. The model of comb copolymer and its parameterization is discussed in the next section. The expression for the structure factor of the system is given in the Sec. III. Section IV contains the results of modeling and discussion.

II. MODEL

We consider the incompressible melt of monodisperse AB comblike macromolecules. Each macromolecule consists of homopolymer A backbone with homopolymer B side chains attached to it. The total number of side chains is n_s. We suppose that each of m side chains located successively from one end of macromolecule consists of $N_B^{(m)}$ monomer units, whereas each of the rest of n side chains contains $N_B^{(n)}$ monomers ($n_s=m+n$) (Fig. 2). The number of monomer units between successive grafting points of backbone is N_g. The number of monomer units before the first side chain and after the last one is equal to tN_g and $(1-t)N_g$ respectively, where t is so-called asymmetry parameter [32]. Thus, number of monomer units of backbone is $N_A=n_sN_g$. The total number of the monomer units in macromolecule is equal to $N=N_A+mN_B^{(m)}+nN_B^{(n)}$. Both A and B monomer units are assumed to be of an equal size a. Such macromolecule can be considered as composed of two comb copolymer blocks, (m) block and (n) block, whose backbones attached to each other. The number of monomer units of repeating fragment of (m) block and (n) block is $N_g+N_B^{(m)}$ and $N_g+N_B^{(n)}$, respectively. Here, repeating fragment includes a part of backbone between two successive grafting points: one of grafting points and side chain attached to it.

In order to simplify the further consideration, let us assume that

$$N_g=d, \quad N_B^{(m)}=\alpha d, \quad N_B^{(n)}=d, \quad (0\leq\alpha\leq 1), \tag{1}$$

so total number of the monomer units is

$$N=Kd, \quad K=(1+\alpha)m+2n. \tag{2}$$

The fractions of monomer units of each type in macromolecule, (m) block, and (n) block are given by the following expressions, respectively:

$$X_A=(m+n)/K, \quad X_B=1-X_A,$$

$$X_A^{(m)}=m/K, \quad X_A^{(n)}=X_A-X_A^{(m)},$$

$$X_B^{(m)}=m\alpha/K, \quad X_B^{(n)}=X_B-X_B^{(m)}. \tag{3}$$

It should be noted that value $\alpha=1$ corresponds to the model of the conventional AB comb copolymer [32–34], whereas for $\alpha=0$, the model proposed by Nap *et al.* [17] is recovered.

III. THEORY

To analyze the microphase separation in melt, we resort to the WST [35,36]. The WST is built upon the representation of the Landau free energy $\mathcal{F}\{[\tilde{\psi}_\alpha]\}$ of a copolymer melt in a form of the Taylor functional series in powers of the Fourier transforms $\tilde{\psi}_A(\mathbf{q}),\tilde{\psi}_B(\mathbf{q})$ of the order parameters $\psi_A(\mathbf{r}),\psi_B(\mathbf{r})$. Each αth of them represents a deviation of local density $\rho_\alpha(\mathbf{r})$ of monomer units of αth type at point $\mathbf{r}$ from its volume average value ($\alpha=A,B$). Due to the incompressibility of melt, the condition $\tilde{\psi}_A(\mathbf{q})=-\tilde{\psi}_B(\mathbf{q})=\tilde{\psi}(\mathbf{q})$ holds and the expression for the free energy assumes the form

$$\mathcal{F}\{[\tilde{\psi}]\}=\sum_{k=2}^{\infty}\frac{1}{k!}\sum_{\{\mathbf{q}_i\}}\tilde{\Gamma}_k(\mathbf{q}_1,\ldots,\mathbf{q}_k)\prod_{i=1}^{k}\tilde{\psi}(\mathbf{q}_i)$$
$$\times\,\delta_K(\mathbf{q}_1+\cdots+\mathbf{q}_k). \tag{4}$$

The functional (4) is completely characterized by the kth order vertex functions $\tilde{\Gamma}_k(\mathbf{q}_1,\ldots,\mathbf{q}_k)$ which are determined by architecture and composition of copolymer and interactions between monomer units. The calculation of these functions at least up to the fourth order is required to investigate within WST the possible types of equilibrium morphologies of the microphase separated structures.

Because the further discussion will be restricted to examination of boundary of the thermodynamical stability of the spatially homogeneous state of copolymer melt, it is sufficient to consider only vertex function of the second order. This function determines the structure factor $S(q)$ of the melt

$$\tilde{\Gamma}_2(\mathbf{q}_1,\mathbf{q}_2)\delta_K(\mathbf{q}_1+\mathbf{q}_2) \equiv \tilde{\Gamma}_2(q) = S^{-1}(q),$$

$$|\mathbf{q}_1| = |\mathbf{q}_2| = q. \tag{5}$$

It can be written in the following form [33,35]:

$$\tilde{\Gamma}_2(q) = \tilde{\Gamma}_2^{(0)}(q) - 2\chi,$$

$$\tilde{\Gamma}_2^{(0)}(q) = \frac{X_{AA}(q) + 2X_{AB}(q) + X_{BB}(q)}{X_{AA}(q)X_{BB}(q) - [X_{AB}(q)]^2}, \tag{6}$$

where interactions between monomer units are taken into account via Flory-Huggins parameter χ [37] and $X_{\alpha\beta}(q)$ $(\alpha,\beta=A,B)$ are the Fourier transforms of the second-order correlation functions of densities of monomer units [38,39]. These correlation functions can be written as $X_{\alpha\beta}(q) = (d^2/N)G_{\alpha\beta}(q)$, where

$$G_{AA} = (m+n)^2 g_D[(m+n)y],$$

$$G_{AB} = \alpha H(\alpha y)\frac{1}{y}\{2m - f(m;y)[e^{-ty} + e^{(t-1-n)y}]\}$$
$$+ H(y)\frac{1}{y}\{2n - f(n;y)[e^{-(t+m)y} + e^{(t-1)y}]\},$$

$$G_{BB} = m\alpha^2 g_D(\alpha y) + n g_D(y) + 2[\alpha H(\alpha y)]^2\frac{e^{-y}}{(1-e^{-y})^2}[m(1 - e^{-y}) - 1 + e^{-my}] + 2\alpha H(\alpha y)H(y)e^{-y}f(m;y)f(n;y) + 2[H(y)]^2\frac{e^{-y}}{(1-e^{-y})^2}[n(1-e^{-y}) - 1 + e^{-ny}]. \tag{7}$$

Here, $y=d(a^2q^2/6)$ and the following designations have been used:

$$g_D(x) = \frac{2}{x^2}(x - 1 + e^{-x}),$$

$$H(x) = \frac{1}{x}(1 - e^{-x}),$$

$$f(k;x) = \frac{1 - e^{-kx}}{1 - e^{-x}}. \tag{8}$$

It is easy to verify that for value $\alpha=0$ expressions (7) coincide with ones derived earlier for linear-comb block copolymer [17].

The function $\tilde{\Gamma}_2(q)$ (6) determines the spinodal in the phase space (χ,α,m,n). At spinodal, the spatially homogeneous state of melt becomes unstable against microphase separation, i.e., formation of periodic structure. For the fixed parameters of chemical structure (α,m,n), the spinodal condition assumes the form [35]

$$\left.\frac{\partial\tilde{\Gamma}_2(q)}{\partial q}\right|_{q^*} = 0, \quad \left.\frac{\partial^2\tilde{\Gamma}_2(q)}{\partial q}\right|_{q^*} > 0, \quad \tilde{\Gamma}_2(q^*) = 0. \tag{9}$$

According to the expressions (6) and (9), the spinodal value of Flory-Huggins parameter is

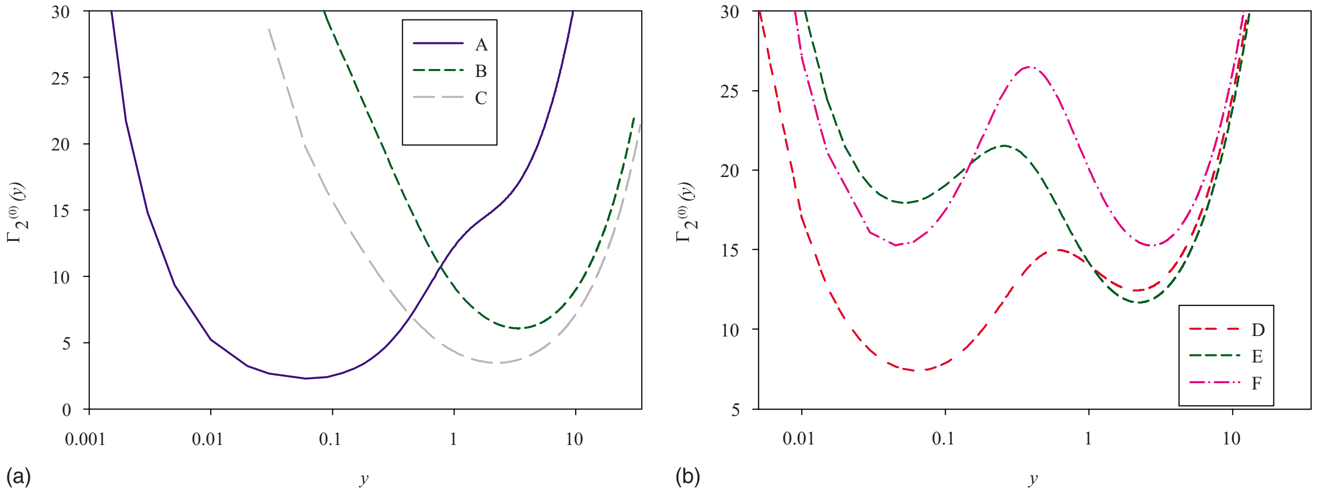

FIG. 3. (Color online) Plot of the inverse structure factor curves as function of y $[y=d(aq)^2/6]$ for various values of parameters (α,m,n). (Left panel) A: (0.2,40,20), B: (0.5,70,3), and C: (0.5,5,50). The single minimum is attained at (A) $q=q_L^*$, (B) $q=q_S^*\approx q_S^{*(m)}$, and (C) $q=q_S^*\approx q_S^{*(n)}$. (Right panel) D: (0.4,20,40), F: (0.6,74,19), and E: (0.45,15,90). The two minima are attained at [(D) and (E)] $q=q_L^*$ and (F) $q=q_S^*\approx q_S^{*(n)}$, $q=q_L^*$, and $q=q_S^*\approx q_S^{*(n)}$. The minimum located at q_L^* (q_S^*) is absolute one in D (E) case. The absolute difference of the minimum values is smaller than 0.0074 in (F) case.

$$\chi_s = \tilde{\Gamma}_2^{(0)}(q^*)/2, \tag{10}$$

where q^* is the location of absolute minimum of function $\tilde{\Gamma}_2(q)$. The value of q^* determines the characteristic length scale $D \sim 1/q^*$ of the microphase-separated structure.

Depending on the values of parameters (α, m, n), the inverse structure factor $\tilde{\Gamma}_2(q)$ for the copolymer melt under consideration has either one minimum or it has two minima. The single minimum can be located at $q = q_L^*$ or $q = q_S^*$ whereas two minima can be attained at $q = q_L^*$ and $q = q_S^*$. In the latter case, one of minima can be absolute or the depths of the both minima can be equal. It is very essential that the inequality $q_L^* \ll q_S^*$ holds so that the corresponding length scales differ noticeably in value. The larger length scale $D_L \sim 1/q_L^*$ corresponds to microphase separation between (m) and (n) blocks of macromolecule and is of magnitude of gyration radius of a whole macromolecule. The smaller length scale $D_S \sim 1/q_S^*$ corresponds to microphase separation between monomers of distinct types in repeating fragments of the blocks of macromolecule and is of magnitude of gyration radius of repeating fragment of (m) or (n) block. For a given value of parameter α $(\alpha > 0)$, the location of q_S^* can vary in range $q_S^{*(n)} \le q_S^* \le q_S^{*(m)}$. Here, the values $q_S^{*(n)}$ and $q_S^{*(m)}$ correspond to the limiting cases $m = 0$, $n \gg 1$ and $n = 0$, $m \gg 1$, respectively. The minimum of inverse structure factor is attained at $q = q_S^* \approx q_S^{*(n)}$ for $n \gg m$, $m > 0$ and at $q = q_S^* \approx q_S^{*(m)}$ for $n \ll m$, $n > 0$. The inverse structure factor curves

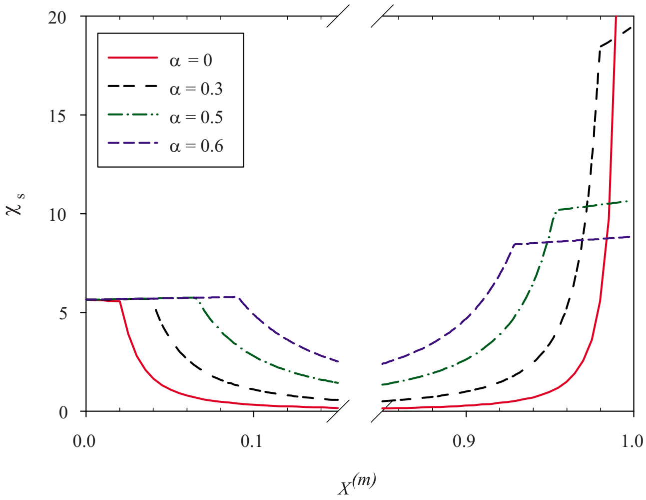

FIG. 4. (Color online) Plot of χ_s vs $X^{(m)}$ for various values of α.

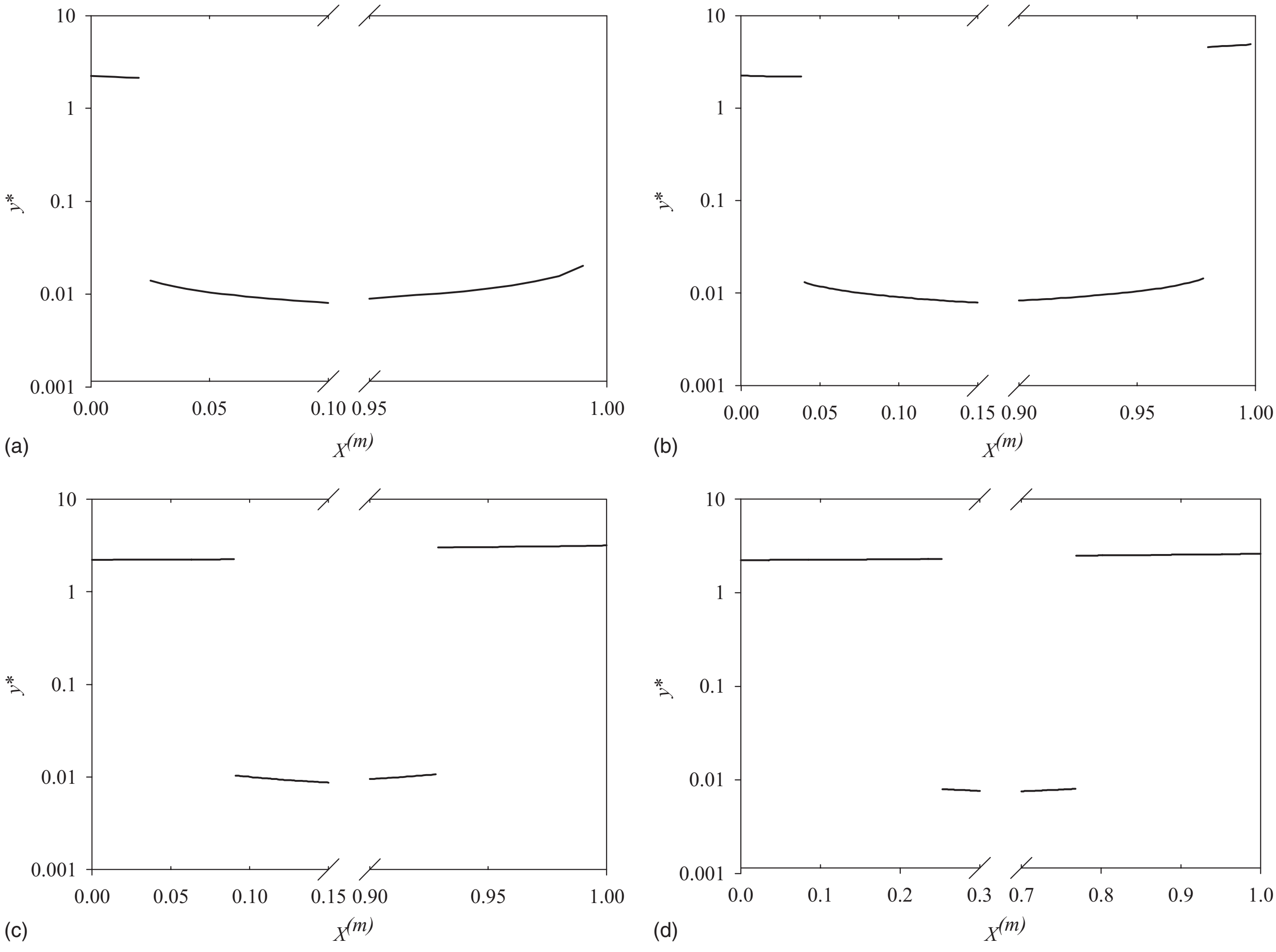

FIG. 5. The plot of location of absolute minimum y^* $[y^* = d(aq^*)^2/6]$ of the inverse structure factor vs $X^{(m)}$ for (a) $\alpha = 0$, (b) $\alpha = 0.3$, (c) $\alpha = 0.6$, and (d) $\alpha = 0.8$.

which exhibit one minimum and two minima are presented in Fig. 3.

IV. RESULTS AND DISCUSSION

The spinodal curve is a plot of parameter χ_s (10) versus copolymer composition. For instance, for the binary multiblock copolymer [34] or comb copolymer [32,34], these curves are plotted in variables (χ_s, X_A), where X_A is the volume fraction of the A-type monomer units. For the copolymer melt under consideration, it is more convenient to plot χ_s versus $X^{(m)}$ where $X^{(m)}=X_A^{(m)}+X_B^{(m)}=m(1+\alpha)/K$ (3) is the fraction of monomer units in (m) block of the macromolecule. With fixing value K (2) which determines the total number of monomer units in macromolecule and parameter α, the $X^{(m)}$ fraction can be made dependent only on parameters m and n. All results discussed below correspond to the value $t=1/2$ and $K=1000$.

Figure 4 shows a plot of spinodal curves $(\chi_s, X^{(m)})$ for the various values of α. The spatially homogeneous (disordered) state of melt is stable in region located below each of these curves whereas microphase separated structures are stable in region located above. As can be seen in Fig. 4, for $\alpha>0$, each curve has generally three parts, corresponding to three possible variants of separation: left and right parts correspond to the separation on small length scale governed by size of repeating fragment of (n) block and (m) block, respectively, and middle part corresponds to the separation on large scale. When the fraction of monomer units in (m) block is small $(m \ll n)$, the length scale of microphase separation is determined by the repeating fragment of (n) block and the inverse structure factor has single minimum located at $q \approx q_S^{*(n)}$. As $X^{(m)}$ increases, the second minimum located at $q=q_L^*$ appears. Upon further increasing of $X^{(m)}$, the minimum located at $q=q_L^*$ becomes absolute one and the separation on the large length scale takes place (middle parts of curves). If $\alpha>0$ and the value of $X^{(m)}$ has increased sufficiently, the location of local minimum shifts from $q \approx q_S^{*(n)}$ to $q \approx q_S^{*(m)}$. Further growth of $X^{(m)}$ value makes minimum located at $q \approx q_S^{*(m)}$ absolute one. Thus, as fraction of (m)-block monomer units becomes high enough, the length scale of microphase separation is dictated by the radius of gyration of repeating fragment of (m) block. If parameter α equals zero, the right part of curve is absent and the spinodal curve has appearance obtained previously [17] (Fig. 4) $(\alpha=0)$. As parameter α grows, the value χ_s increases for the middle parts of curves presented in Fig. 4. This implies that it requires a lower temperature to obtain a phase separation on a large length scale as number of units in the side chains of (m) block increases. The substantial change in location of the absolute minimum of inverse structure factor at varying of $X^{(m)}$ value is shown in Figs. 5(a)–5(d). "Switching" between upper and lower curves presented in Figs. 5(a)–5(d) corresponds to the drastic change of the length scale of microphase separation. The growth of side chains in (m) block (i.e., increasing of α) narrows the window for separation on large length scale.

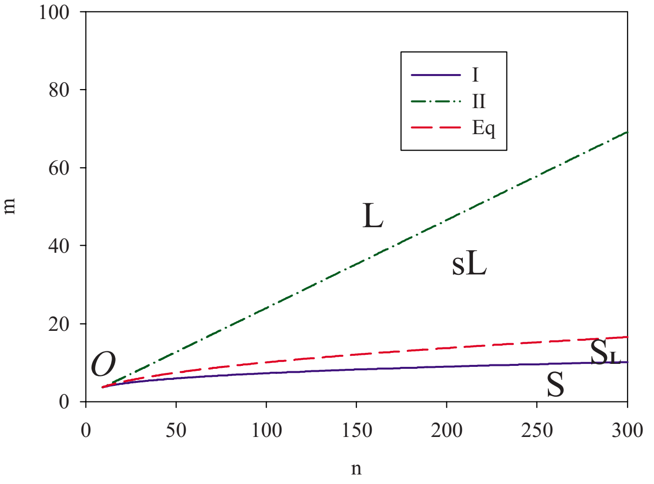

FIG. 6. (Color online) Classification diagram for $\alpha=0$. Symbol O denotes bifurcation point.

To specify which length scale of microphase separation realizes for a given set of parameters (α, m, n), it is necessary to construct so-called classification diagrams [17]. As it was already mentioned at value $\alpha=0$, our model coincides with model proposed by Nap *et al.* [17] except that in the latter the parameter t was set to zero. It comes as no surprise that classification diagram for value $\alpha=0$ presented in Fig. 6 agrees closely with one obtained previously [17]. It is worth to note that although m and n can have only positive integer values, it is more convenient to treat these parameters as the real variables and plot continuous curves at classification diagrams. The inverse structure factor in the S region and L region in Fig. 6 has a single minimum located at q_S^* and q_L^*, respectively. There are two minima if set of parameters (m,n) belongs to SL region or SL region. The q_S^* is the absolute minimum of function $\tilde{\Gamma}_2^{(0)}$ in first of these regions and q_L^* in the second one. Lines at Fig. 6 correspond to the boundaries between different regions in (m,n)-parameter space. At line equation, the condition $\tilde{\Gamma}_2^{(0)}(q_S^*)=\tilde{\Gamma}_2^{(0)}(q_L^*)$ holds. Below the bifurcation point O at which the boundary lines merge together (Fig. 6), the function $\tilde{\Gamma}_2^{(0)}$ has single minimum, above this point function $\tilde{\Gamma}_2^{(0)}$ can have two

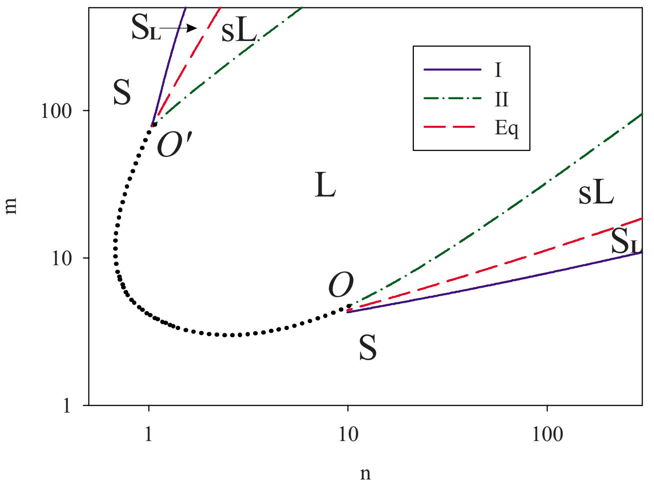

FIG. 7. (Color online). Classification diagram for $\alpha=0.1$. Symbols O and O' denote bifurcation points.

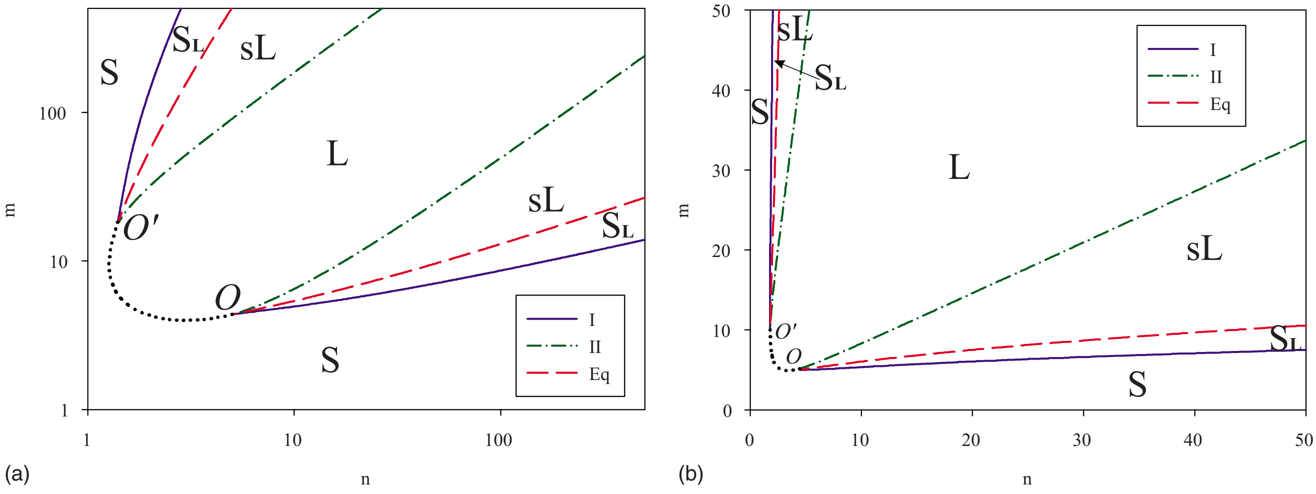

FIG. 8. (Color online) Classification diagrams for $\alpha=0.2$ (left panel) and $\alpha=0.25$ (right panel).

minima. Noteworthy that classification diagrams obtained previously for the linear-alternating block copolymer [Fig. 1(b)] [17], the linear-alternating-linear block copolymer [Fig. 1(c)] [24], and the linear-alternating-linear-alternating block copolymer [Fig. 1(d)] [29] have the appearance similar to diagram presented in Fig. 6.

The classification diagram changes qualitatively in comparison to previous case if the lengths of side chains of (m) block are distinct from zero, i.e., $\alpha>0$. The diagram that corresponds to the value $\alpha=0.1$ is presented in Fig. 7. In contrast to diagram for $\alpha=0$ (Fig. 6), the *two* bifurcation points (O and O') in (m,n)-parameter space appear. The length scale of microphase separation in S and SL regions is determined by the radius of gyration of the repeating fragment of (m) block if $m \gg n$ (absolute minimum of inverse structure factor is located at $q_S^* \approx q_S^{*(m)}$) and of (n) block (absolute minimum is located at $q_S^* \approx q_S^{*(n)}$) otherwise. Upon crossing in (m,n)-parameter space the curve OO' which connects bifurcation points, the position of single minimum $y^* > 1$ (in S region) changes to $y^* < 1$ (in L region).

The classification diagrams constructed for $\alpha=0.2$ and $\alpha=0.25$ (Fig. 8) show that curve OO' diminishes as parameter α increases. Size of the SL regions increases attended by the shrinking of L region. Upon reaching value $\alpha=\alpha_1^{(c)}=0.278$, the bifurcation points and curve OO' disappear. The boundary curves emerge that separate regions S, SL, SL, and L from each other (see Fig. 9). Further increase of parameter α that corresponds to the growth of side chain length in (m) block of macromolecules leads to substantial shrinking of L region (see Fig. 9).

At value $\alpha \geq \alpha_2^{(c)}=0.33$, L region disappears and classification diagrams assume the forms depicted in Fig. 10. As parameter α varies in the range $\alpha_2^{(c)} < \alpha < 1$, the sizes of regions S and SL increase substantially. At $\alpha \approx 1$, only these regions survive with SL region shifted in parameter space to very large values of m and n. Finally, at $\alpha=1$, the architecture of macromolecules transforms to one of regular *AB*-comb copolymer which contains side chains of the same length distributed regularly along the backbone. The periodical structures formed in melts of such copolymer are characterized by only one length scale which is of magnitude of gyration radius of repeating fragment of comb macromolecule [32,34]. This implies that only S region exists for this copolymer.

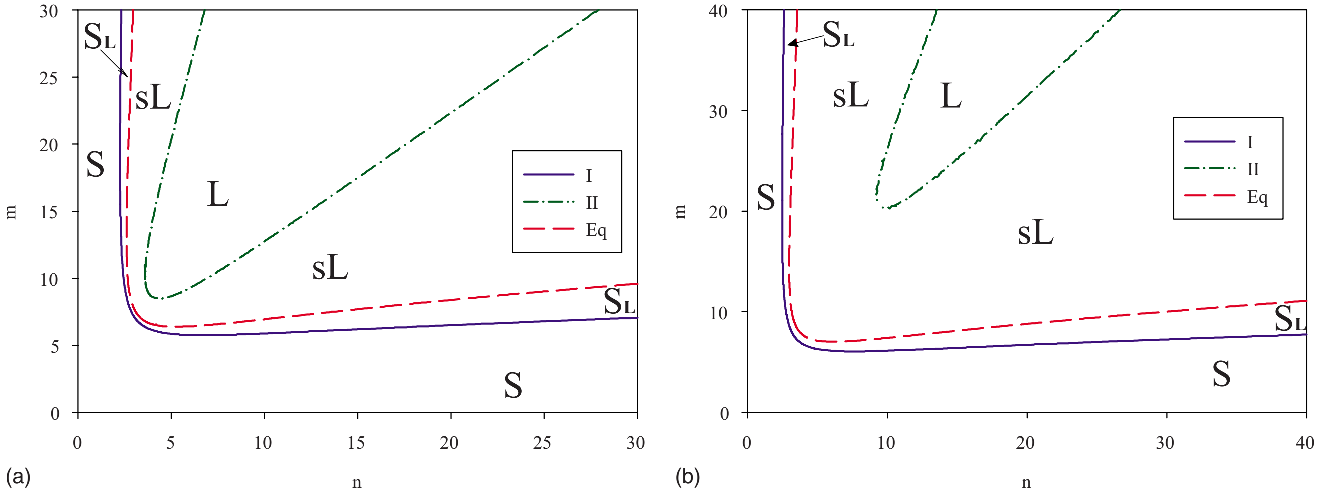

FIG. 9. (Color online) Classification diagrams plotted for (a) $\alpha=0.3$ and (b) $\alpha=0.32$.

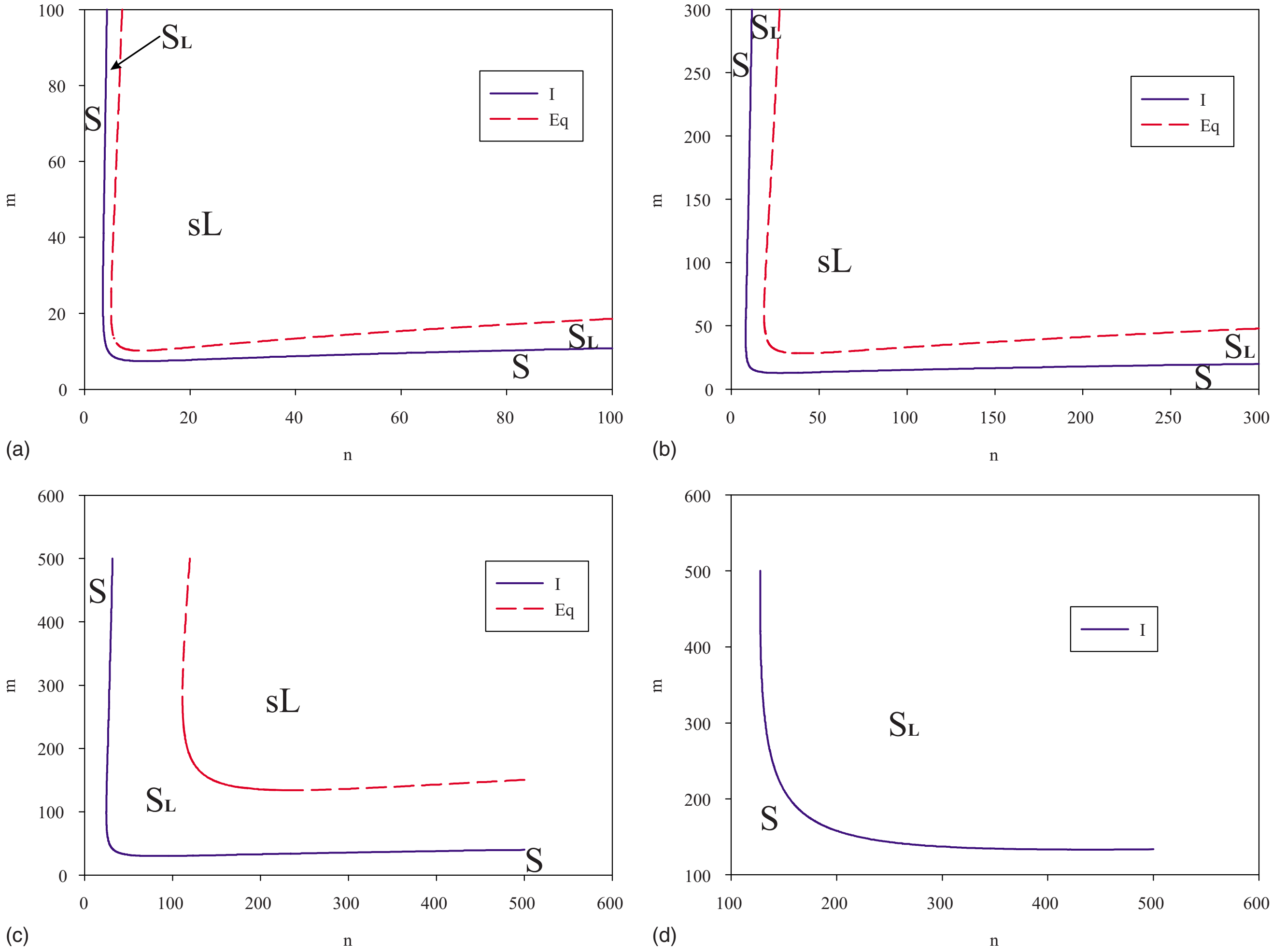

FIG. 10. (Color online) Classification diagrams plotted for (a) α=0.4, (b) α=0.6, (c) α=0.8, and (d) α=0.95.

V. CONCLUSION

The phase behavior of binary copolymer melt contained the comb macromolecules whose side chains can be of the two unequal lengths is discussed. The dependence of the behavior of the inverse structure of melt on the parameters of chemical structure of macromolecules is investigated. It is shown via analysis of stability limit of disordered state of melt that two different length scales of microphase separation can be realized. The large length scale D_L is due to the microphase separation between (m) block and (n) block of macromolecule and the small length scale D_S is due to microphase separation of chemically distinct monomers in repeating fragments of (n) block and (m) block. To determine which length scale is preferred for a given set of parameters of chemical structure, the classification diagrams are constructed. It is shown that for nonzero lengths of side chains in (m) block (i.e., $0<\alpha<1$) classification diagrams are qualitatively unlike those obtained previously for copolymers presented in Fig. 1. The existence of two bifurcation points for some values of parameters of chemical structure is found.

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[1] I. W. Hamley, *The Physics of Block Copolymers* (Oxford University Press, Oxford, 1998).
[2] M. Maldovan, A. M. Urbas, N. Yufa, W. C. Carter, and E. L. Thomas, Phys. Rev. B **65**, 165123 (2002).
[3] C. Park, J. Yoon, and E. L. Thomas, Polymer **44**, 6725 (2003).
[4] I. W. Hamley, Nanotechnology **14**, R39 (2003).
[5] N. P. Balsara and H. Hahn, in *The Chemistry of Nanostructured Materials*, edited by P. Yang (World Scientific, Singapore, 2003), pp. 317–328.
[6] U. Breiner, U. Krappe, E. L. Thomas, and R. Stadler, Macromolecules **31**, 135 (1998).
[7] J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Makela, R. Serimaa, G. ten Brinke, and O. Ikkala, Science **280**, 557 (1998).
[8] J. Ruokolainen, G. ten Brinke, and O. Ikkala, Adv. Mater. **11**, 777 (1999).
[9] J. Ruokolainen, M. Saariaho, O. Ikkala, G. ten Brinke, E. L.

Thomas, M. Torkkeli, and R. Serimaa, Macromolecules **32**, 1152 (1999).

[10] V. Abetz and P. F. W. Simon, Adv. Polym. Sci. **189**, 125 (2005).

[11] A. Werner and G. H. Fredrickson, J. Polym. Sci., Part B: Polym. Phys. **35**, 849 (1997).

[12] I. Ya. Erukhimovich, V. Abetz, and R. Stadler, Macromolecules **30**, 7435 (1997).

[13] E. W. Cochran, D. C. Morse, and F. S. Bates, Macromolecules **36**, 782 (2003).

[14] J. Masuda, A. Takano, Y. Nagata, A. Noro, and Y. Matsushita, Phys. Rev. Lett. **97**, 098301 (2006).

[15] Y. Matsushita, Macromolecules **40**, 771 (2007).

[16] G. ten Brinke, J. Ruokolainen, and O. Ikkala, Adv. Polym. Sci. **207**, 113 (2007).

[17] R. J. Nap, C. Kok, G. ten Brinke, and S. I. Kuchanov, Eur. Phys. J. E **4**, 515 (2001).

[18] R. J. Nap and G. ten Brinke, Macromolecules **35**, 952 (2002).

[19] R. J. Nap, Ph.D. thesis, Groningen University, 2003.

[20] L. Wang, J. Lin, and L. Zhang, Langmuir **25**, 4735 (2009).

[21] R. J. Nap, I. Ya. Erukhimovich, and G. ten Brinke, Macromolecules **37**, 4296 (2004).

[22] R. J. Nap, N. Sushko, G. ten Brinke and I. Ya. Erukhimovich, Macromolecules **39**, 6765 (2006).

[23] Yu. G. Smirnova, G. ten Brinke, and I. Ya. Erukhimovich, J. Polym. Sci. A **47**, 430 (2005).

[24] Yu. G. Smirnova, G. ten Brinke, and I. Ya. Erukhimovich, J. Chem. Phys. **124**, 054907 (2006).

[25] Yu. G. Smirnova, Ph.D. thesis, Groningen University, 2006.

[26] Yu. A. Kriksin, I. Ya. Erukhimovich, P. G. Khalatur, Yu. G. Smirnova, and G. ten Brinke, J. Chem. Phys. **128**, 244903 (2008).

[27] Yu. A. Kriksin, I. Ya. Erukhimovich, Yu. G. Smirnova, P. G. Khalatur, and G. ten Brinke, J. Chem. Phys. **130**, 204901 (2009).

[28] V. Pichugin and S. I. Kuchanov, J. Stat. Mech.: Theory Exp. (2005) P07009.

[29] S. Kuchanov, V. Pichugin, and G. ten Brinke, e-Polymers **12**, 1 (2006).

[30] V. V. Palyulin and I. I. Potemkin, J. Chem. Phys. **127**, 124903 (2007).

[31] Y. Nagata, J. Masuda, A. Noro, D. Cho, A. Takano, and Y. Matsushita, Macromolecules **38**, 10220 (2005).

[32] A. Shinozaki, D. Jasnow, and A. C. Balazs, Macromolecules **27**, 2496 (1994).

[33] I. Ya. Erukhimovich, Polym. Sci. U.S.S.R. **24**, 2223 (1982).

[34] H. Benoit and G. Hadziioannou, Macromolecules **21**, 1449 (1988).

[35] L. Leibler, Macromolecules **13**, 1602 (1980).

[36] R. Holyst and T. A. Vilgis, Macromol. Theory Simul. **5**, 573 (1996).

[37] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, Cornell, 1979).

[38] S. I. Kuchanov and S. V. Panyukov, in *Comprehensive Polymer Science, 2nd Supplement*, edited by G. Allen (Pergamon, New York, 1996), Chap. 13, pp. 441–496.

[39] M. A. Aliev and S. I. Kuchanov, Eur. Phys. J. B **43**, 251 (2005).