Theory of microphase separation of homopolymer–oligomer mixtures

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Microphase separated structure consisting of the periodic alternation of the layers of stretched homopolymer chains surrounded by perpendicularly oriented oligomeric (surfactant) tails is studied for the systems with strong ionic) as well as weak (hydrogen) interaction. Our approach is based on the fact that the structure period is determined by alternating associations between the head groups of the oligomer molecules and interacting groups of the homopolymer chains. Distribution of oligomers along the homopolymer chains is described by the effective equation of motion with the segment number playing the role of time. As a result, experimentally observed temperature dependence of the structure period, as well as the dependence of the point of order–disorder transition are determined as functions of the oligomeric fraction.

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I. INTRODUCTION

Various mesomorphic structures can be prepared using the strong (ionic) or weak (hydrogen) bonding, respectively, between homopolymers and head–functionalized oligomers or surfactants. The interaction between the head group of the oligomeric molecule and suitable groups on the homopolymer chain, on the one hand, and unfavorable polar–nonpolar interactions between the non–polar tail of the oligomer and the rest of the system, on the other one, can cause the microphase separation. The latter effect results in a periodic alternation of the layers of stretched homopolymer chains surrounded by perpendicularly oriented oligomeric tails as it is shown in Figure 1. An example of the ionically bonded system is represented by the homopolymer-oligomer mixture of atactic poly(4-vinyl pyridine) (P4VP) and dodecyl benzene sulfonic acid (DBSA) where due to a very strong interaction the microphase separation is realized over the whole temperature region. The peculiarity of the systems of this kind is an increasing long space period $L$ as a function of the oligomeric fraction $x$ defined as the number of the oligomeric (DBSA) molecules per one pyridine ring (see Figure 2). More complicated behavior is inherent in the hydrogen bonded systems where the weak interaction causes an order–disorder transition to homogeneous high–temperature state. An example of the system of this kind represents the mixture P4VP–(PDP)$_x$ of the same homopolymer P4VP with the surfactant 3-pentadecyl phenol (PDP). Here, contrary to the ionically bonded systems, the long space period de-
creases with increasing $x$ (see Figure 3). As it is shown in Figure 2, an intermediate behavior (non-monotonous $x$-dependence of the long space period) was found in the system P4VP-(Zn(DBS)$_2$)$_x$ where the ionic interaction between zinc dodecyl benzene sulfonate Zn(DBS)$_2$ and P4VP is somewhat weaker than in the P4VP-(DBSA)$_x$ system[4].

Principally important for our considerations is the decreasing character of the temperature dependence of the long period found experimentally for all the systems mentioned above[1]—[4]. However, such a character of the dependence appears in the hydrogen bonded systems only within a finite temperature interval limited by the temperatures of crystallization (or glass transition $T_g$) from below and of the order–disorder transition $T_c$ from above (see Figure 4). As it is shown in Figure 5, an increase of the oligomeric fraction leads to a non–monotonous dependence of the temperature $T_c$ with a maximum occuring near $x = 0.85$. The aim of this paper is to explain peculiarities of the microphased separated homopolymer–oligomer mixtures with both, strong and weak bonding, within a framework of the unified scheme of stochastic systems[5].

Our consideration is based on the obvious equality for the long period $L = 2l + D$ where $l$ is the oligomeric chain length and $D$ is the thickness of the homopolymer layer being fixed due to sharing of the surfactant molecules by homopolymer chains (see Figure 1). Physically, this share is reduced to the inverse magnitude $2\pi/\omega$ of the circular frequency of the alternation of the oligomer heads along the homopolymer chain. Then, the long period can be expressed by the following equation

$$L = 2l + D_0\omega^{-1}, \quad D_0 \equiv 2\pi \left(\chi^{1/6}n_0^{-1/3}\right)b \sim b \quad (1)$$

where $\chi \sim 10/N$ is the Flory interaction parameter ($N \sim 10^3$ is the degree of polymerization of the homopolymer chains), $n_0 \sim 10$ is the number of segments in the oligomer chain, $b$ is the segment length. The frequency $\omega$ will be found from the effective equation of motion which is stochastic in nature and where the segment number $n$ ($n \leq N$) plays the role of imagined time.

**II. BASIC EQUATIONS**

The problem under consideration is addressed by the definition of effective law of motion $c(n)$ that determines the sequence of the alternation of oligomers along the homopolymer chain by means of the occupation number, $c(n)$, being $c(n) = 1$ if the oligomer is attached to the
segment \(n\), and \(c(n) = 0\) otherwise. In the limit \(N \to \infty\), the argument \(n\) may be considered as a continuous one, and the behavior of the system is governed by the action and the dissipative functional

\[
S = T \int_0^N L(c(n), \dot{c}(n)) \, dn, \quad R = \frac{\Theta}{2} \int_0^N (\ddot{c}(n))^2 \, dn
\]  

(2)

with dimensionless Lagrangian

\[
L = K – \Pi; \quad K \equiv \frac{m}{2} (\dot{c}(n))^2, \quad \Pi \equiv \frac{\tau}{2} (c(n))^2.
\]  

(3)

Here dot denotes the derivative with respect to the segment number \(n\), \(T\) is temperature in energy units, \(\Theta\), \(m\) and \(\tau\) are inverse kinetic coefficient, inhomogeneity and interaction parameters, respectively. The key point in our consideration consists in that the effective mass \(m\) in Eq. (3) is a fluctuating parameter with the mean value \(\bar{m}\) and the variance \((\bar{m} - \bar{m})^2 \equiv \sigma^2\) (bar denotes the average, as usually). Then, after the averaging of the exponent \(\exp(-S/T)\) over Gaussian distribution of the bare mass \(m\), we obtain renormalized inhomogeneity energy

\[
K = \frac{1}{2} \left( \bar{m} - \Delta \right) (\dot{c}(n))^2, \quad \Delta \equiv \frac{\sigma^2}{2} \int_0^N (\dot{c}(n'))^2 \, dn'.
\]  

(4)

As a result, taking into account the stochastic source \(\zeta\), relevant Euler equation arrives at non–linear Langevin equation

\[
\bar{m} \ddot{c} + n_c \dot{c} + \tau c = \zeta
\]  

(5)

where the effective mass \(\bar{m} \equiv \bar{m} \{c(n)\}\), characteristic number of correlating segments \(n_c\) and \(\delta\)–correlated noise \(\zeta(n)\), respectively, are introduced in accordance with definitions:

\[
\bar{m} \equiv \bar{m} - \Delta, \quad n_c \equiv \frac{\Theta}{\bar{m}}, \quad \langle \zeta(n) \rangle = 0, \quad \langle \zeta(n) \zeta(n') \rangle = \delta(n - n').
\]  

(6)

(7)

To linearize the equation of motion \(\bar{E}\) within the self–consistent approach, it is necessary to replace the fluctuational term \(\Delta\) of the renormalized mass in Eq. \(\bar{E}\) by the averaged expression

\[
\Delta = \int S(\nu) \nu^2 \, d\nu
\]  

(8)

where \(S(\nu) \equiv \langle |\zeta(\nu)|^2 \rangle\) is the structure factor in the frequency representation (angle brackets denote average over noise \(\zeta\)). Then, the Green function \(G \equiv \langle \delta c/\delta \zeta \rangle\) and the structure factor \(S \equiv |G|^2\) take the forms:

\[
G = \frac{\tau(\nu) - in_c \nu}{\tau(\nu) + n_c^2 \nu^2}, \quad S = \frac{\tau(\nu) + n_c^2 \nu^2}{\tau(\nu) - in_c \nu}
\]  

(9)

where renormalized interaction parameter is introduced by equalities

\[
\tau(\nu) \equiv \tau - m_{ef} \nu^2, \quad m_{ef} \equiv \bar{m} - \Delta.
\]  

(10)

### III. Determination of the Period of Microphase Structure

To obtain physically observable values, at first one has to determine the effective mass \(m_{ef}\) given by Eqs. (10), (3). On the basis of the theory of residues, using the structure factor, Eq. (11) arrives at the expression for renormalization mass parameter

\[
\Delta = \frac{\sigma^2}{n_c m_{ef}}.
\]  

(11)

Inserting here Eqs. (10), (1), we obtain the effective inhomogeneity parameter

\[
m_{ef} = \mu(T) \bar{m}, \quad \mu \equiv \frac{1}{2} \left( 1 + \sqrt{1 - \frac{T}{T_c}} \right)
\]  

(12)

where the temperature domain is bounded above by the characteristic temperature

\[
T_c = \left( \frac{\bar{m}}{2 \sigma^2} \right)^2 \Theta.
\]  

(13)

According to Eq. (12) the effective mass decreases monotonously with increasing temperature from the bare magnitude \(\bar{m}\) at \(T = 0\) to \(\bar{m}/2\) at \(T = T_c\).

The divergency condition of the Green function \(\bar{G}\) arrives at the proper frequency of the oligomer alternation

\[
\nu_0 = -i \omega \pm \omega
\]  

(14)

with imaginary and real parts

\[
\omega^2 = \omega_0^2 - \omega^2, \quad \omega_0^2 \equiv \frac{\tau}{m_{ef}}, \quad \omega \equiv \frac{n_c}{2 m_{ef}}.
\]  

(15)

Insertion of Eqs. (10), (12) gives the temperature dependence of the proper frequency

\[
\omega^2 = \frac{\omega_0^2}{\mu^2} \left( \mu - \frac{T_0^2}{T^2} \right)
\]  

(16)

where the bare frequency \(\omega_0\) and another characteristic temperature \(T_0\) are introduced as follows:

\[
\omega_0^2 = \frac{\tau}{m}, \quad T_0 = \frac{\Theta}{2 \sqrt{m \tau}}
\]  

(17)

As a result, combination of Eqs. (1), (14) leads to the final result

\[
L = 2l + \frac{\mu(T)}{\sqrt{\mu(T) - T_0^2/T^2}} L_0
\]  

(18)

where the characteristic length, \(L_0\), is defined as

\[
L_0 \equiv \frac{D_0}{\omega_0} \sim \sqrt{\frac{m}{\tau}} b.
\]  

(19)
IV. DISCUSSION

The behavior of the system is determined by the relation
\[
\kappa = \frac{T_c}{T_0} = \frac{\sqrt{m_T}}{2} \left( \frac{\bar{m}}{\sigma} \right)^2 \geq 1
\]
(20)

where the minimal magnitude \( \kappa = 1 \) fixes the choice of the theory parameters according to the condition: \( \sigma \leq 2^{-1/2} \bar{m}^{3/4} \tau^{1/4} \). It would seem from Eq. (20) that the decrease of the temperature \( T_c \) with weakening interaction when passing from the ionically bonded system (such as P4VP–(DBS)\( \bar{x} \)) to the hydrogen bonded one (e.g., P4VP–(PDP)\( \bar{x} \)) is caused only by the growth of the fluctuation parameter \( \sigma \) with respect to the mean magnitude of the inhomogeneity parameter \( \bar{m} \). It appears, however, that the main reason for such behavior is a decrease of the mean–geometrical magnitude \( \sqrt{m_T} \) of the principle coefficients in the generic Lagrangian (3).

To clarify this problem, assume the three–parametric \( x \)-dependencies for the above parameters
\[
\bar{m} = m_0 + Ax(x_m - x), \quad \tau = \tau_0 + Bx(x_T - x)
\]
(21)

with positive constants \( m_0, \tau_0, A, B, x_m, x_T \). In limiting case, \( \kappa \gg 1 \) relevant to the ionically bonded systems, when \( m_{cf} \approx \bar{m}, \mu(T) \approx 1 \), the temperature \( T_c \) is so large that the temperature dependence \( \Theta \) takes the form
\[
L = 2l + \frac{L_0}{\sqrt{1 - T_0^2/T^2}}, \quad L_0 \sim \sqrt{\frac{\bar{m}}{\tau} b}.
\]
(22)

Then, fitting of the experimental data shown in Figure 2 according to Eq. (22) arrives at the following results. The system P4VP–(DBS)\( \bar{x} \): \( m_0 = 49, A = 21, x_m = 0.5; \tau_0 = 1, B = 1.1, x_T = 0.5; b = 1 \) nm; \( l = 10 \) nm. The system P4VP–(Zn(DBS))\( \bar{2} \): \( m_0 = 18, A = 55, x_m = 1.8; \tau_0 = 1, B = 0.1, x_T = 2; b = 1 \) nm; \( l = 10 \) nm. Respectively, for \( x = 1 \) Eq. (24) gives values \( \kappa = 10^3, 10^2 \) at ratios \( \sigma/\bar{m} \approx 0.045, 0.203 \).

A much more complicated situation occurs in hydrogen bonded system P4VP–(PDP)\( \bar{x} \), where the reduction of the parameter \( \sigma/\bar{m} \) leads to a more narrow temperature domain \( T_0 = T_c \). As a result, the temperature dependence of the period \( L(T) \) obtains a more complicated form (18) which keeps the decreasing character as shown in Figures 3 and 4. The dependence \( L(x) \) at a fixed temperature may be described by the estimation
\[
L \approx 2l + \sqrt{\bar{m}/\tau} b
\]
(23)

following from Eqs. (18) and conditions \( \mu \approx 1, T_0 \ll T \). Then, the experimental data shown in Figure 3 give the following constrains: \( \sqrt{m_0/\tau_0} = 33.5, B/\tau_0 = 1.6, x_T = 3.1 \). Respectively, the comparison of the experimental data shown in Figure 4 with the fitting results using Eqs. (12), (13), (17) and (18) yields \( \Theta/\sqrt{m_0\tau_0} = 1517, l = 8.7 \) nm. Finally, Figure 5 and Eq. (13) give \( A/m_0 = 0.16, x_m = 1.6, \Theta m_0^2/4\sigma^2 = 276 \).

As a result, taking \( m_0 = 1 \) at \( x = 1 \) the magnitudes \( A = 0.16, \Theta = 5.5, \sigma = 0.07 \) are obtained and they provide the value of \( \tau_0 \) smaller than \( 10^{-3} \) which arrive at the parameter \( \kappa \approx 6.7 \) and ratio \( \sigma/\bar{m} = 0.069 \). It is worth to mention that the value of the parameter \( \tau_0 < 10^{-3} \) is extremely small that guarantees the validity of the Flory–Huggins approach.

To conclude, the model described above can explain successfully all peculiarities obtained experimentally for various homopolymer–oligomer mixtures with interaction of different strength.

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