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Phase Behavior of Hydrogen-Bonding Polymer−Oligomer Mixtures

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ABSTRACT: The phase behavior of mixtures of flexible homopolymer chains with oligomers capable of hydrogen bonding with the monomer units of the polymer chains is analyzed in the weak segregation limit. A theoretical model is proposed to describe hydrogen bond (hb) formation depending on temperature, composition, and strength of hydrogen bonding. The conditions for macro- and microphase separation are studied. Microphase separation takes place if the tendency to segregate is not very strong and the degree of association X is large enough. The type of ordered structure depends not only on the composition and the temperature but also on the possibility to minimize the polymer−oligomer contacts. The period of the ordered structures D is minimal for stoichiometric composition of the mixture and increases with an increase of either component. Macrophase separation into ordered and homogeneous phases is typical for these kind of systems. The corresponding regions of phase coexistence occupy a significant part of the phase diagrams. Coexistence between different ordered phases such as lamellar and hexagonal can also take place. It was found that macrophase separation influences hb formation, reducing the average degree of association. The specific temperature dependence of the degree of association can result in the phenomenon of reappearing phases.

1. Introduction

Polymer systems consisting of polymers and low molecular weight components, oligomers or surfactants, have attracted considerable interest during the last decade.[1−26] This interest is due to a broad range of properties combined with a large variety of phase-separated morphologies, promising good perspectives for practical applications. Microphase separation is a common phenomenon in these systems and has been studied experimentally in some detail for various polymer/surfactant systems involving charged or uncharged surfactants.[1−6,15−21] Polymer systems involving hydrogen bond formation with surfactants or oligomers attracted the interest of specialists in this field relatively recently. However, a large collection of experimental observations has been obtained already.[15−18,21,25] Polymer systems capable of hydrogen bonding exhibit a wide variety of different specific properties, which is mainly due to the strong temperature dependence of hb formation. In the present paper we will limit our considerations to mixtures consisting of polymers and oligomers in the absence of solvent. This specific polymer system is interesting because it is well studied experimentally.[15−18,21,25] Besides, it can also be considered as a first step to the more common case of polymer/surfactant systems in the presence of solvent.

Mixtures of flexible homopolymer chains and oligomers capable of hydrogen bond formation with the monomer units of the polymers represent a class of systems exhibiting both macro- and microphase separation. The reasons for both types of separation is the same: incompatibility of the initial mixture components, polymers and oligomers. Microphase separation can take place if the degree of association is relatively high and the polymer chains resemble comb copolymers with oligomer side chains, but the incompatibility is not so strong as to induce separation on a macroscopic level.

In this case the formation of microdomain structures of alternating polymer-rich and oligomer-rich regions will be preferred by the system.

The specific feature of this polymer system is that the degree of association is temperature (and composition) dependent. It implies that the fraction of free oligomers, playing the role of "solvent" for the associated comb copolymer-like chains, changes as the temperature changes. Although it might seem reasonable to expect that the phase behavior will be similar to that of real comb copolymer melts studied theoretically,[27−30] the presence of the "solvent", in an amount that changes with temperature, makes the phase behavior of the system substantially different. This has already been observed experimentally[15−18,21,25] as well as numerically (i.e., by means of computer modeling[23,24]). One of the specific features of the polymer system under consideration, the reappearance of homogeneous phases, has been discovered experimentally only recently[25] and is confirmed by the present theoretical analysis.

The similarity of the present polymer system to comb copolymer systems[27−30] allows us to apply the random phase approximation (RPA) considerations developed for the present situation, taking into account the specific role of a temperature dependent "solvent" of free oligomers. It makes the analysis more complicated and hence requires special accuracy of the calculations. The theoretical investigation of these kinds of problems involving associating polymers was initiated by Tanaka and co-workers.[31] They derived spinodal curves for both macro- and microphase separation using the random phase approximation. However, the analysis presented[31] is incomplete in the part concerning the stability and the nature of the ordered structures. The phase diagrams were calculated by assuming the free energy of the ordered states to be the same as for the homogeneous state. The approach presented here is based on a slightly different model, the main objective of the paper is to apply the RPA technique for description of

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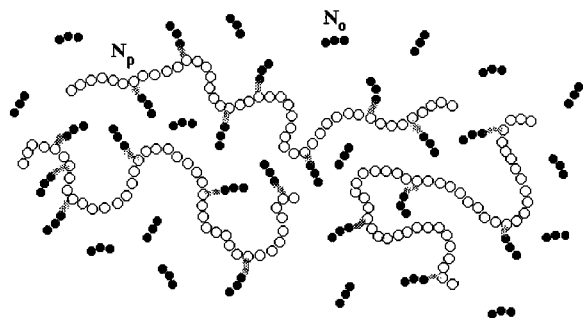
Figure 1. Schematic picture of a mixture consisting of polymer chains and oligomers capable of hydrogen bond formation. N_p is the length of homopolymer chains; N_o is that of oligomers.

the ordered structures in order to analyze phase behavior by taking also into account the possibility of phase coexistence between ordered and homogeneous phases.

The present paper is organized in the following manner. In the next section we introduce the model describing the most important features of the polymer system, such as hydrogen bond formation. The average fraction of hydrogen bonds per chain is calculated directly by minimization of the free energy of the homogeneous state. As a result, the expression obtained differs from that obtained by Tanaka,[31] who calculated the average degree of association by a multistage calculation involving the consideration of intermediate clusters. The third section is devoted to the analysis in the framework of the RPA approach of the stability of the polymer system toward macro- and microphase separation. The free energies of the different ordered structures are calculated and compared. In the subsequent section phase diagrams accounting for the possibility of macrophase separation into different phases are presented. Furthermore, the influence of macrophase separation on the average degree of association is discussed. Finally, the most important results of the present work are collected in the Conclusions.

2. Model

We will consider a mixture of flexible polymer chains and end-functionalized oligomers (amphiphiles) capable of reversible temperature dependent bond formation (hydrogen bonding) (Figure 1). The length of the polymer chains, N_p, is supposed to be much larger than that of the oligomers, N_o: $N_p \gg N_o$. The composition of the mixture can be characterized by the volume fraction of polymer Φ. Due to the assumed incompressibility, the volume fraction of oligomer chains is $1 - \Phi$.

Hydrogen bonding can occur between any monomer unit of the polymer chain and the head group of any oligomer (each oligomer possesses only one head group). Each group can only participate in one hydrogen bond. The present model assumes that hydrogen bonding between oligomers does not occur.

An alternative way to characterize the composition of the mixture is in terms of the number of oligomer chains per monomer unit of the polymer chains, X_o

$$X_o \equiv \frac{N_o}{N_p N_p} = \frac{1}{N_o}\left(\frac{1}{\Phi} - 1\right) \tag{1}$$

where N_i is the number of polymers (i = p) and oligomers (i = o). As this expression shows, the limit

$X_o \rightarrow 0$ corresponds to the case of pure polymer ($\Phi = 1$), whereas $X_o \rightarrow \infty$ corresponds to the pure oligomer case ($\Phi = 0$). The larger the length of the oligomer chains, the smaller the fraction of oligomer chains per monomer unit X_o for a fixed value of the polymer volume fraction Φ. The case $X_o = 1$ corresponds to stoichiometric composition, where the number of oligomers is exactly the same as the number of monomer units of polymer chains. The corresponding stoichiometric volume fraction of polymer Φ_{st} is

$$\Phi_{st} = \frac{1}{1 + N_o} \tag{2}$$

Free Energy of the Homogeneous State. Let us start the analysis of phase behavior by considering the homogeneous state of the polymer−oligomer mixture. Besides "free" polymer and oligomer chains, the mixture contains polymer chains with different numbers (and positions along the chain) of hydrogen bonds. These associated polymer chains are in fact annealed comb copolymers. Let us denote by N_n the number of comb copolymerlike chains with n hydrogen bonds per chain and by Φ_n the volume fraction of such chains. Then the probability to find a polymer chain with n hydrogen bonds, P_n, equals the ratio between the number of such chains N_n and the number of all polymer chains in the system $N_p - P_n = N_n/N_p$.

In the framework of the self-consistent field theory, the free energy of the homogeneous state can be written in the following form:

$$\frac{F}{kT} = \frac{1}{b^3} \int \left\{ \sum_n P_n \frac{\Phi}{N_p} \ln(\Phi_n/e) + \frac{\Phi_{fo}}{N_o} \ln(\Phi_{fo}/e) + \right.$$
$$\frac{\Theta}{2T}\Phi(1 - \Phi) + \sum_n P_n \frac{\Phi}{N_p} n \frac{\Delta F_{hb}}{kT} +$$
$$\left. \sum_n P_n \Phi\left\{ \frac{n}{N_p} \ln \frac{n N_s}{N_p} + \left(1 - \frac{n}{N_p}\right) \ln\left(1 - \frac{n}{N_p}\right) \right\} \right\} dV \tag{3}$$

where Φ_{fo} is the volume fraction of free oligomers, V is the volume of the system, b^3 is the volume per monomer, and $\Theta/2T$ is the χ parameter of polymer−oligomer interactions.

The first two terms in eq 3 correspond to the translational entropy of the polymer chains with hydrogen bonds (comb copolymers) and free oligomers. The third term represents the homopolymer−oligomer interactions, $\Theta/2T$ is the corresponding χ parameter. The next term describes the free energy of hydrogen bonding in the system. The free energy of hydrogen bonding consists of two contributions:

$$\frac{\Delta F_{hb}}{kT} \equiv \frac{\Delta F_e}{kT} - \Delta S \equiv -\frac{E}{T} + S \tag{4}$$

On the one hand, the formation of a hydrogen bond leads to an energetic gain $\Delta F_e/kT$ ($\Delta F_e/kT \equiv -E/T < 0$, $E > 0$). For high temperatures, where the thermal motion dominates, the hb energy ΔF_e is small in comparison with kT and the probability of hydrogen bonding becomes negligible. At low temperatures, where the thermal motion is restricted, ΔF_e can be much larger than kT and many hydrogen bonds can be formed.

Furthermore, there is an entropy loss associated with hb formation S ($S > 0$). This entropy loss is connected

with the fact that in order to form a hydrogen bond, the head group of the oligomer should have the "correct orientation" with respect to a monomer. The "permitted" angle range for hb formation is rather small.[32] So, the above mentioned entropy loss is in fact the loss of orientational entropy of the oligomer head group. This entropy loss is rather insensitive to temperature, and we will consider it to be temperature independent.

The competition between the above mentioned two factors, energy gain and entropy loss, determines the hb formation and hence the behavior of the system. The E and S parameters are related to the experimentally measured equilibrium constant of hydrogen bond formation K (see below).

The last term in the equation for the free energy of the homogeneous state of the polymer system, eq 3, is due to the entropy of distributing a given number of oligomers over the monomer units of the polymer chain. We will assume that the hydrogen bonds are formed independently of each other. There is experimental evidence that in many cases, hydrogen bonding is noncooperative in contrast to ionic bonding.[4] Hence, a hydrogen bond can appear at any "vacant" place of the polymer chain independent of the presence or absence of "neighboring" hydrogen bonds. They can arise spontaneously whenever the correctly oriented oligomer chain head group runs into a vacant monomer unit of a polymer chain. Due to the noncooperativity of hydrogen bond formation, the probability to find a polymer chain with n hydrogen bonds, P_n, satisfies the binomial law

$$P_n \equiv \frac{N_n}{N_p} = \frac{N_p!}{n!(N_p - n)!}\left(\frac{\langle n \rangle}{N_p}\right)^n\left(1 - \frac{\langle n \rangle}{N_p}\right)^{N_p - n} \quad (5)$$

where $\langle n \rangle$ is the average number of hydrogen bonds per chain, which can be obtained from the minimization of the free energy, eq 3. It is convenient to introduce another characteristic quantity of the polymer system, the average fraction of hb per chain, X:

$$X \equiv \frac{\langle n \rangle}{N_p} = \frac{1}{2}\{A - \sqrt{A^2 - 4X_o}\} \quad (6)$$

$$A = 1 + X_o + (1 + X_o N_o)\exp\left(\frac{\Delta F_{hb}}{kT}\right)$$

where X_o is the number of oligomer chains per monomer unit of the polymer chains, eq 1.

As can be seen from eq 6, in the limit of low temperatures $T \to 0$, where the formation of hydrogen bonds prevails, the average fraction of hb per chain X tends to the maximal possible degree of association X_m.

$$X_m = \begin{cases} X_o & \text{if } X_o < 1 \quad (\Phi > \Phi_{st}) \\ 1 & \text{if } X_o \geq 1 \quad (\Phi \leq \Phi_{st}) \end{cases} \quad (7)$$

The volume fraction of free oligomers in the system depends on the average degree of association via the relation $\Phi_{fo} = 1 - \Phi(1 + XN_o)$. The equilibrium constant of hydrogen bond formation can be defined as

$$\Phi_{hb} = K\Phi_{fo}\Phi_m \quad (8)$$

where $\Phi_m = \Phi(1 - X)$ is the volume fraction of "free" monomer units of polymer chains and Φ_{hb} is the volume fraction of hydrogen-bonded oligomers. A comparison of eq 8 with eq 6 gives the connection between the
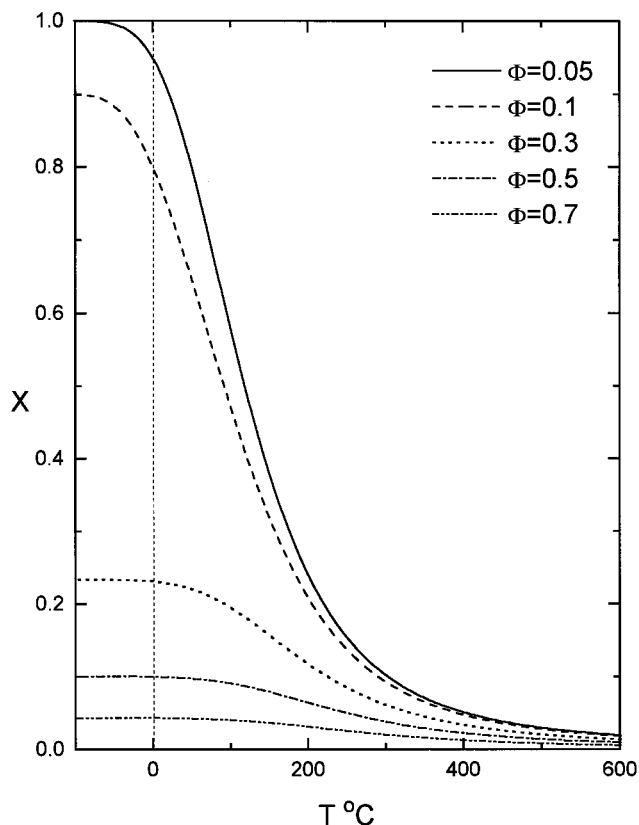

Figure 2. Temperature dependence of the average fraction of hydrogen bonds per chain X for the polymer systems ($N_p = 10^3$, $N_o = 10$, $E = 3000$ K, $S = 5$, $\Theta = 270$ K) with different values of polymer volume fraction Φ.

equilibrium constant K and the parameters E and S:

$$K = \exp\left(-\frac{\Delta F_{hb}}{kT}\right) = \exp\left(\frac{E}{T} - S\right) \quad (9)$$

As can be seen from eq 9, low temperatures correspond to a large equilibrium constant K and hence a large degree of association.

In the framework of our model only flexible polymer chains will be considered. The possibility of side chain induced "rigidity" of comb copolymer-like chains is typical for polymer solutions (see, e.g., ref 33) and less important for the case of melts considered here. Hence, it will not be taken into account.

The dependence of the average fraction of hydrogen bonds per polymer chain on the temperature for different values of the volume fraction of polymer Φ is shown in Figure 2. For relatively small volume fractions of polymer, the degree of association X changes dramatically with temperature. The formation of hb occurs abruptly in a relatively small temperature range and the maximum value of association X_m tends to unity. So, for low temperatures, the polymer system is a mixture of completely associated polymer chains (comb copolymers) and free oligomers. The high degree of association is ensured by the presence of an oligomer excess. For a volume fraction of polymer Φ exceeding the stoichiometric volume fraction Φ_{st}, the average fraction of hb per polymer chain X changes less strongly with temperature. Even for very low temperatures, when almost all oligomers take part in hydrogen bond formation, the average hb fraction X remains relatively small due to a lack of oligomers.
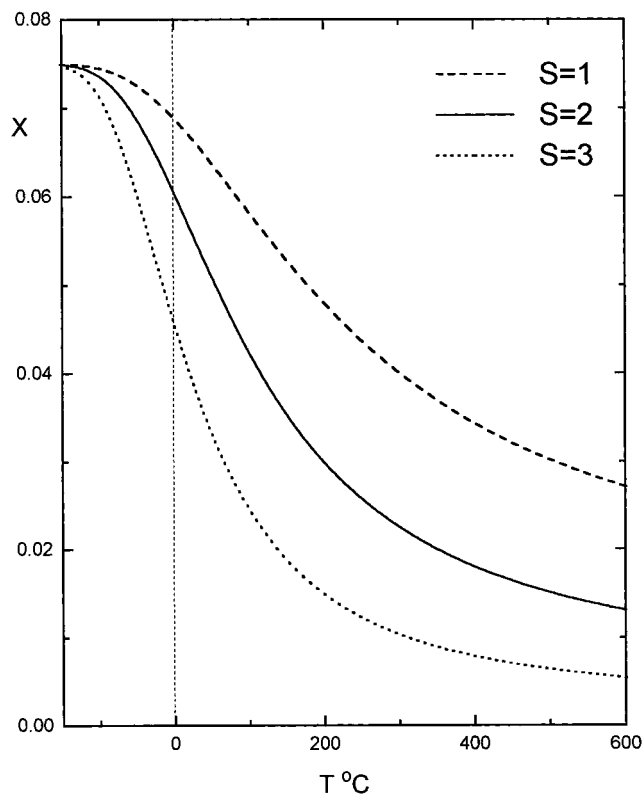
Figure 3. Temperature dependence of the average fraction of hydrogen bonds per chain X for the polymer systems ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $\Theta = 90$ K, $\Phi = 0.4$) with different strengths of hydrogen bonding (different values of entropy parameter S).

The temperature dependence of the average fraction of hydrogen bonds per chain is also influenced by the energetic gain E and the entropic loss S per hb (Figure 3). A decrease of S (increase of E) not only leads to an increase of the degree of association X ("strong" hydrogen bonding) but also makes the dependence more smooth in comparison to large S (small E) (weak hydrogen bonds) where the dominant part of the association process occurs in a relatively small temperature interval.

The oligomer length also influences the temperature dependence of X (Figure 4). For a fixed volume fraction of polymer Φ, an increase in oligomer length results in a decrease in the number of oligomer chains N_o. The average fraction of hb X as well as the fraction of oligomers per monomer unit X_o decrease (and hence, the maximal possible degree of association X_m for polymer systems with a volume fraction of polymers Φ exceeding Φ_{st} is reduced).

It is worthwhile to emphasize that the above mentioned dependencies have been obtained for the case of a homogeneous mixture. If macrophase separation takes place, for instance coexistence of two homogeneous phases, such dependencies will be valid for each of the coexisting phases, but the behavior of the system as a whole can be different. This effect will be considered in more detail below (section 4).

It follows from the above considerations that the polymer system in the homogeneous state represents a mixture of free oligomers and associated polymer chains. The average degree of association X and hence the fraction of free oligomers $\Phi_{fo} \equiv 1 - \Phi (1 + X N_o)$ changes with temperature. The character of this dependence is determined by the composition of the system Φ, the
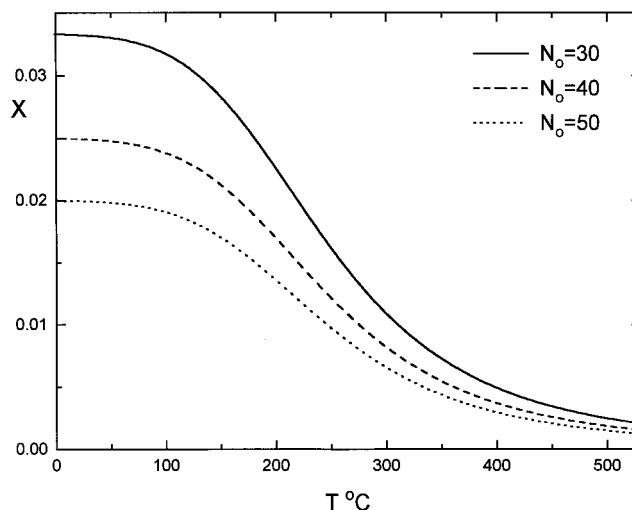

Figure 4. Temperature dependence of the average fraction of hydrogen bonds per chain X for the polymer systems ($N_p = 10^4$, $E = 4000$ K, $S = 7$, $\Theta = 80$ K, $\Phi = 0.5$) with different fractions of oligomers (different oligomer length N_o for a fixed value of polymer volume fraction Φ).

energetic E and entropic S parameters, and the oligomer length N_o. As we will see below, these specific features determine an uncommon phase behavior of the polymer system.

3. RPA Considerations

Next the RPA approach will be applied to analyze the phase behavior of the polymer–oligomer mixture in the weak segregation limit. As discussed in the previous section, the polymer system under consideration is in fact a mixture of free oligomers and comb copolymers with "side chains" identical to the oligomers. Furthermore, the average fraction of "side chains" is temperature dependent. Keeping in mind these specific features, the behavior of our polymer system can be discussed along the lines used previously for conventional comb copolymer systems.[27–30]

The RPA approach is based on a free energy expansion in power series of the order parameter, such as the volume fraction of polymer Φ. The second-order terms provide information about the structure factor $S(q)$.

$$S(q) = \cfrac{1}{S^0(q) - \cfrac{\Theta}{T}} \tag{10}$$

$$S^0(q) = \frac{S_{pp} + S_{oo} + 2S_{po}}{S_{pp}S_{oo} - S_{po}^2} \tag{11}$$

where S_{ij} are the second-order correlation functions (i = p, for polymer units, i = o, for oligomer units). The second-order correlation functions of polymer–polymer S_{pp}, polymer–oligomer S_{po}, and oligomer–oligomer S_{oo} interaction can be represented in the following form (cf. refs 34, 29, 30, 23):

$$S_{pp} = \Phi N_p\, g(r_p) \tag{12}$$

$$S_{po} = \Phi N_o \langle n \rangle\, S(r_o)\, g(r_p) \tag{13}$$

$$S_{oo} = (1 - \Phi) N_o\, g(r_o) +$$
$$\Phi \frac{N_o^2}{N_p} \langle n(n-1) \rangle\, S^2(r_o)\, g(r_p) \tag{14}$$

where $g(r_i)$ is the Debye function $g(r_i) = 2(r_i + \exp(-r_i) - 1)/r_i^2$, $S(r_i) = (1 - \exp(-r_i))/r_i$, and $r_i = N_i q^2 a^2/6$ for i = p, o.

The polymer−polymer correlation function S_{pp} has the standard form, as for other block copolymer systems.[29,34] The polymer−oligomer correlation function S_{po} depends on the probability to find a hydrogen bond and as a result it is temperature dependent through the average number of hydrogen bonds per chain $\langle n \rangle$. The oligomer−oligomer correlation function S_{oo} consists of two terms. The first term is related to the correlations between monomers belonging to the same oligomer chain (intraoligomer correlations), whereas the second term describes the correlations between monomers belonging to different "side chains" of the same polymer chain (interoligomer correlations). This term is connected with the probability to find two hydrogen bonds on the same polymer chain and is therefore proportional to the average value $\langle n(n - 1) \rangle$.

Since the average values in eqs 13 and 14 are determined by the binomial distribution eq 5 and, hence, they are temperature and composition dependent, these correlation functions as a whole are also complex functions of temperature, composition, and other parameters of the system, in contrast to the case of the covalent bonded comb copolymer systems.[27−30]

3.1. Spinodals of Micro- and Macrophase Separation. The value of the critical wave vector q^* and the critical temperature T^* corresponding to the boundary of the region of instability with respect to microphase ($q^* \neq 0$) and macrophase ($q^* = 0$) separation (i.e., spinodal curves) can be obtained from the set of equations

$$\begin{cases} \dfrac{\partial S(q)}{\partial q}\bigg|_{q=q^*} = 0 \\ S^0(q^*) - \theta/T = 0 \end{cases} \quad (15)$$

The spinodal of macrophase separation can also be obtained from the direct differentiation of the free energy of the homogeneous phase eq 3: $d^2 F/d\Phi^2 = 0$. Both ways result, as expected, in the same equation for the spinodal of macrophase separation:

$$\frac{\Theta}{T} = \frac{1}{N_p\Phi} + \frac{(1 + X N_o)^2}{N_o(1 - \Phi(1 + N_o X^2))} \quad (16)$$

The stability of the homogeneous state of the system depends on the following main factors: the degree of incompatibility of the components (Θ temperature), the strength of hydrogen bonding (interaction E and entropy S parameters), and the length of the oligomer chains.

3.1.1. Influence of Θ Temperature. For low values of the Θ temperature the polymer system becomes unstable with respect to macro- and microphase separation only for relatively low temperatures (Figure 5, $\Theta = 165$ K, which corresponds to $\chi = 0.275$ at $T = 300$ K). The form of the spinodal curves for macro- (dotted curve) and microphase separation (solid curve) are similar; however, the spinodal of microphase separation is somewhat above the macrophase separation spinodal. This type of behavior is similar to that of block copolymer or polyelectrolyte systems exhibiting microphase separation. Microphase separation can take place if there is a tendency to segregate, but this tendency is not strong enough to induce separation on a macroscopic level.
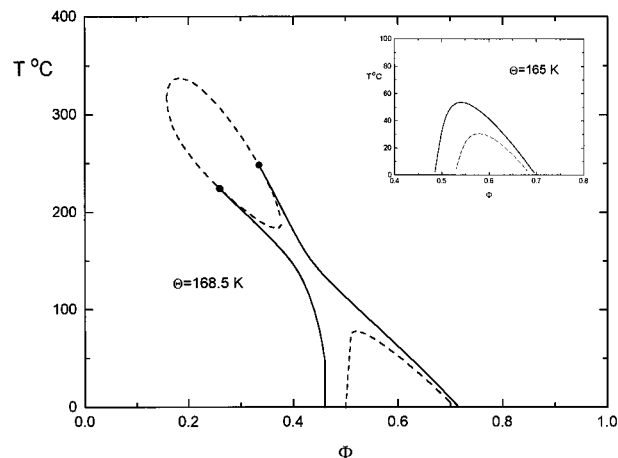

Figure 5. Spinodal curves for macro- (dotted curve) and microphase separation (solid curve) for the polymer−oligomer mixture ($N_p = 10^3$, $N_o = 10$, $E = 1000$ K, $S = 2$, $\Theta = 165$ K, $\Theta = 168.5$ K). Large solid points are the Lifshitz points.
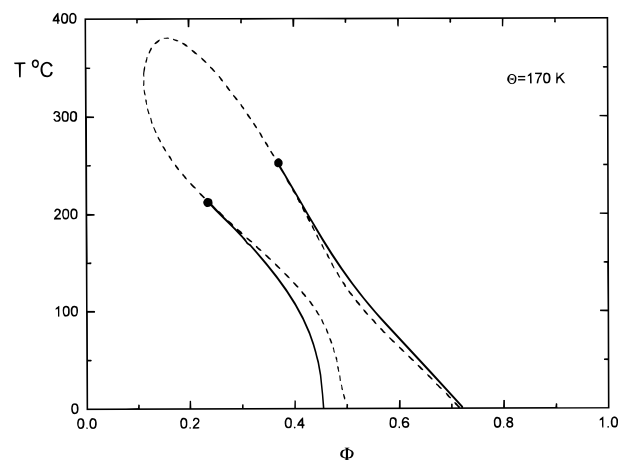

Figure 6. Spinodal curves for macro- (dotted curve) and microphase separation (solid curve) for the polymer−oligomer mixture ($N_p = 10^3$, $N_o = 10$, $E = 1000$ K, $S = 2$, $\Theta = 170$ K). Large solid points are the Lifshitz points.

An increase of the Θ temperature (i.e., stronger repulsion) leads to the instability enhancement and an additional instability region with respect to both micro- and macrophase separation appears at elevated temperatures (Figure 5, $\Theta = 168$, and 5 K, which corresponds to $\chi = 0.281$ at 300 K). An interesting feature of the phase behavior is the possibility of reappearance of a stable homogeneous phase at intermediate temperatures. This phenomenon will be discussed in detail in the next subsection. Spinodals for microphase separation belonging to the high- and low-temperature regions of instability can form joint curves in the way presented in Figure 5. The area between the two spinodals for microphase separation is the region available for microphase separation. At elevated temperatures the average degree of association is too small to ensure the formation of ordered structures and the spinodal of microphase separation terminates in Lifshitz points, where ordered and disordered states become indistinguishable.

For a still higher Θ temperature the regions of instability expand further and the instability regions for macrophase separation at high and low temperatures merge (Figure 6). The region available for microphase separation increases as well. The regions of instability with respect to macrophase separation con-
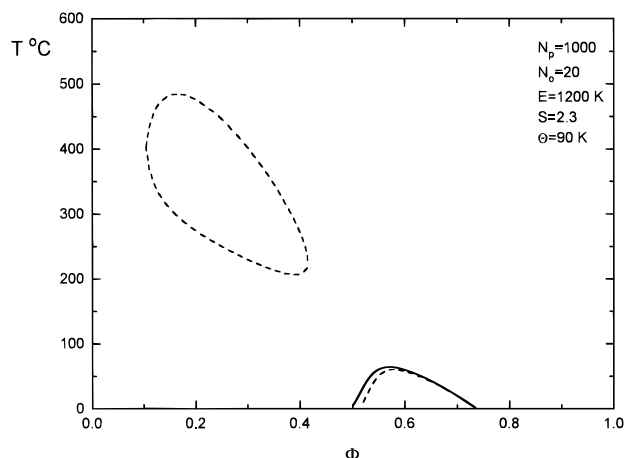
Figure 7. Spinodal curves for macro- (dotted curve) and microphase separation (solid curve) for the polymer−oligomer mixture ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $S = 2.3$, $\Theta = 90$ K).

tinue to increase to higher temperatures with a further increase of the Θ temperature. The spinodal of microphase separation survives mainly in the region of low temperature and low polymer concentration, i.e., in the region where the average degree of association is large.

3.1.2. Influence of the Strength of Hydrogen Bonding. A decrease in the strength of hydrogen bonding (a decrease of E and/or an increase of S) influences the phase behavior similarly to that discussed in the previous subsection for an increase in the Θ temperature. Thus, polymer−oligomer mixtures with strong hydrogen bonding (large value of E and small S) remain stable until relatively low temperature, depending on the Θ temperature. The corresponding spinodal curves are qualitatively similar to those in Figure 5 for $\Theta = 165$ K.

Another type of phase behavior is characteristic for polymer systems where an increase in the average fraction of hb, X, occurs abruptly enough. As discussed in section 2, this might happen when both the energetic gain E and the entropic loss S are relatively large. In this case, the energetic gain dominates below some critical temperature, where association occurs very rapidly. Spinodal curves for these kinds of situations are presented in Figure 7. Besides a low-temperature region of instability, there is also a loop-like instability region (with respect to macrophase separation) for elevated temperatures. These instability regions are separated by a region of a stable homogeneous phase. The reason for this behavior is clear from the following considerations. With a decrease in temperature the polymer/oligomer incompatibility increases and the homogeneous state becomes unstable. Further cooling results in a significant increase of the average fraction of hydrogen bonds per polymer chain X (see Figures 2−4). The comb copolymer-like chains with a large number of side chains become compatible with a "solvent" of free oligomers, resulting in the stabilization of the homogeneous state. For even lower temperatures, the incompatibility becomes very strong and the homogeneous state is unstable again. This sequence of phase transformations is very similar to recent experimental observations[25]: a closed loop region of macrophase separation at elevated temperatures, a homogeneous state in the intermediate range, and ordered structures at low temperatures.

The smaller the temperature range over which the association takes place (larger S), the smaller the region
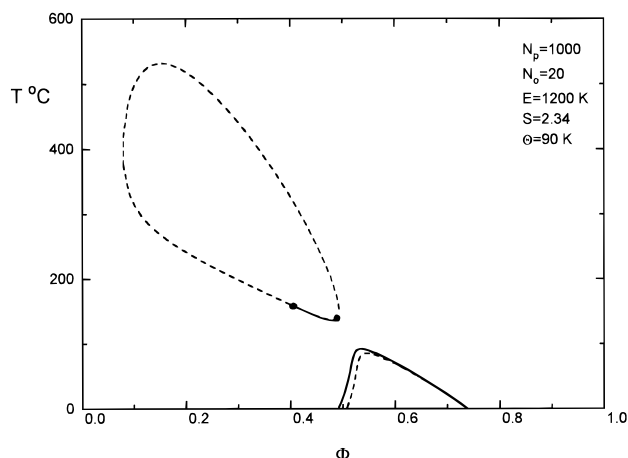

Figure 8. Spinodal curves for macro- (dotted curve) and microphase separation (solid curve) for the polymer−oligomer mixture with larger entropy loss S under hb formation ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $S = 2.34$, $\Theta = 90$ K). Large solid points are the Lifshitz points.
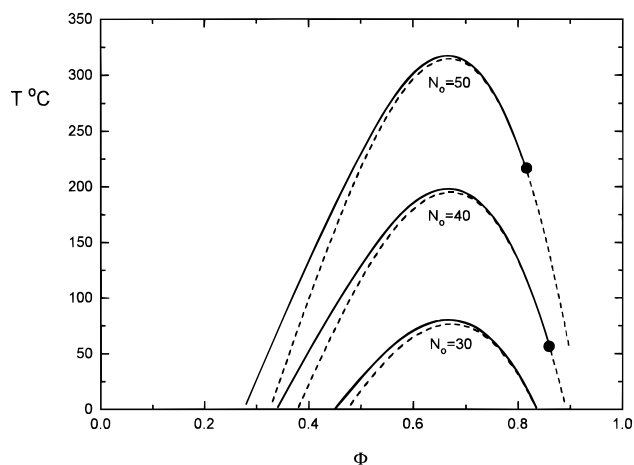

Figure 9. Spinodal curves for macro- (dotted curve) and microphase separation (solid curve) for the polymer−oligomer mixtures with different oligomer lengths ($N_p = 10^4$, $E = 4000$ K, $S = 1$, $\Theta = 80$ K). Large solid points are the Lifshitz points.

of the stable homogeneous phase in between the high- and low-temperature regions of instability (Figure 8). A comparison between Figures 7 and 8 shows that the low-temperature instability region remains almost the same, whereas the region of instability for elevated temperatures expands substantially due to a decrease in the average degree of association for the system with larger S (Figure 8). Since the instability region extends to relatively low temperatures, where association is already considerable, a spinodal for microphase separation belonging to this incompatibility region appears. Spinodals of micro- and macrophase separation coincide in Lifshitz points.

For still larger values of S these two high- and low-temperature regions of instability merge in a similar way as presented in Figures 5 and 6.

3.1.3. Influence of Oligomer Length. The influence of oligomer length will be discussed by using the example of a polymer−oligomer mixture with strong hydrogen bonding (Figure 9). The spinodal curves are qualitatively similar to that of Figure 5 ($\Theta = 165$ K): the spinodal of microphase separation is above that for macrophase separation. For increasing oligomer length,
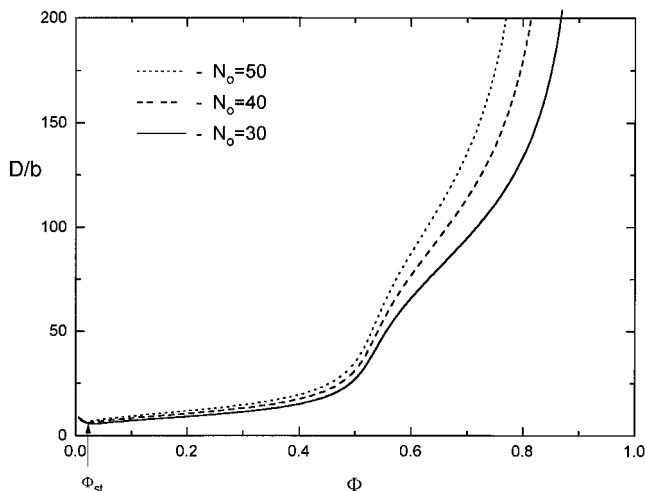
Figure 10. Dependence of the period of ordered structures D (per monomer volume b) on the volume fraction of polymer Φ for the polymer−oligomer mixtures ($N_p = 10^4$, $E = 4000$ K, $S = 1$, $\Theta = 80$ K) with different oligomer lengths N_o.

the polymer system becomes less stable with respect to both macro- and microphase separation. This comes as no surprise. Even for a mixture of two homopolymers an increase in the length of one of the components results in an increase of the instability. For the present polymer system there is an additional reason for the instability enhancement. As discussed in section 2 (Figure 4), an increase of the oligomer length leads to a decrease in the average degree of association, promoting the instability. A further increase in oligomer length can result in the appearance of an additional instability region at elevated temperatures, as in Figures 5−8. The larger the oligomer length, the higher the temperature at which the system becomes unstable.

An increase in the order−disorder temperature for increased oligomer lengths has been observed recently for polymer systems with the same composition but different oligomer lengths.[26] The origin of the phenomenon is the same as discussed above. The reduction of the degree of association results from the decrease of polymer volume fraction for the experimentally studied system.

3.2. Period of Ordered Structures. In the framework of RPA the period of the microdomain structure D is defined by the value of the critical wave vector q^* corresponding to the spinodal of microphase separation: $D = 2\pi/q^*$.

For polymer systems with low Θ temperature (Figure 5) or "strong" hydrogen bonding (large E, relatively small S) (Figures 7 and 9), where the spinodal for microphase separation is somewhat above that for macrophase separation, the period of the ordered structure D increases as a function of the polymer volume fraction Φ for $\Phi > \Phi_{st}$ (decreases for $\Phi < \Phi_{st}$) (Figure 10). The set of curves corresponds to the spinodals presented in Figure 9. The minimal value of the period is attained at the stoichiometric condition $\Phi = \Phi_{st}$, where full complexation is possible. An increase of the volume fraction of one of the components gives rise to the increased domain size of this component, resulting in the increase of the period of the structure as a whole. An increase in the oligomer length N_o leads to an increase of instability in the system, as discussed above (Figure 9). Order−disorder transitions at higher temperatures result in an increase of the period D for $\Phi >$

Φ_{st} (Figure 10). This effect is connected with the fact that for larger oligomer lengths the number of oligomer chains for a fixed polymer volume fraction is smaller. For $\Phi < \Phi_{st}$, there is an oligomer excess so a decrease in the number of oligomers leads to a decrease in the fraction of free oligomers, resulting in a decrease of the period. For $\Phi > \Phi_{st}$, the situation is the opposite, a reduction in the number of oligomer chains makes the polymer excess even larger and the period of the structure increases. The regions of very large or very small Φ correspond to nearly one-component systems, where the period of the structure tends to infinity (as well as in the vicinity of Lifshitz points).

3.3. Free Energy of Ordered Structures. To obtain the free energy of the ordered structures (such as lamellar, hexagonal, BCC) the higher order correlation functions (third G_{ijk} and fourth G_{ijkl} order) should be taken into account.[34] We will not present the exact expressions for the higher order correlation functions here to avoid overcomplicating the paper by technical details. Instead, we will emphasize the most characteristic features of the correlation functions.

The higher order correlation functions can be calculated in a similar way as for conventional block copolymer systems.[28,34] As mentioned above, the correlation functions (with exception of the polymer−polymer one) depend on the probability to find one, two, etc. hydrogen bonds on a polymer chain. So, the third G_{ijk} and fourth G_{ijlk} order correlators are complex functions (depending on the type of correlator) of the average values $\langle n \rangle$, $\langle n(n-1) \rangle$, $\langle n(n-1)(n-2) \rangle$, $\langle n(n-1)(n-2)(n-3) \rangle$. These average values can be expressed using the binomial distribution eq 5 as a function of the average fraction of hydrogen bonds X (eq 6), which depends on the temperature T, composition (volume fraction of polymer Φ), strength of hydrogen bonds (energy E and entropy S), and oligomer length N_o. The specific feature of the present polymer system is that the fraction of free oligomers and a composition of comb-like copolymers changes with temperature. As a result, the correlation functions are temperature dependent as well.

The free energy of the ordered structures can be represented in the framework of RPA in the following form:[34]

$$\frac{F_i}{kT} = \frac{F_0}{kT} + \left(\frac{\theta}{T^*} - \frac{\theta}{T}\right)\Psi_i^2 - \alpha_i\Psi_i^3 + \beta_i\Psi_i^4 \quad (17)$$

where Ψ_i is the amplitude of an ordered phase, F_0/kT is the free energy of the homogeneous phase (eq 3), and the coefficients α_i and β_i depend on the symmetry of the ordered structure ($i = 1$ corresponds to lamellar, $i = 3$ to hexagonal, and $i = 6$ to BCC structures):

$$\alpha_1 = 0; \quad \beta_1 = \Gamma_4(0,0)/4$$

$$\alpha_3 = -\frac{2}{3\sqrt{3}}\Gamma_3; \quad \beta_3 = (\Gamma_4(0,0) + 4\Gamma_4(0,1))/12$$

$$\alpha_6 = -\frac{4}{3\sqrt{6}}\Gamma_3; \quad \beta_6 = (\Gamma_4(0,0) + 8\Gamma_4(0,1) +$$

$$2\Gamma_4(0,2) + 4\Gamma_4(1,2))/24$$

The coefficients Γ_3 and Γ_4 are connected with the higher order correlation functions G_{ijk} and G_{ijkl} and the second-order ones G_{ij} via the relations

$$\Gamma_3(q_1,q_2,q_3) = -G^3(q_1,q_2,q_3)/\prod_{i=1}^{3}G^2(q_i,-q_i) \quad (18)$$

$$\Gamma_4(q_1,q_2,q_3,q_4) = G^4(q_1,q_2,q_3,q_4)/\prod_{i=1}^{4}G^2(q_i,-q_i) -$$
$$\{\sum_{q'}[G^3(q_1,q_2,q')\ G^3(-q',q_3,q_4) +$$
$$G^3(q_1,q_3,q')\ G^3(-q',q_2,q_4) + G^3(q_1,q_4,q')\ \times$$
$$G^3(-q',q_2,q_3)]/G^2(q',-q')\}/\prod_{i=1}^{4}G^2(q_i,-q_i) \quad (19)$$

The expression for the free energy, eq 17, differs from the corresponding expressions for that of other polydisperse systems as, e.g., random copolymers by the absence of the so-called nonlocal term.[35,36] The latter originates from the entropy of mixing induced by the chain redistribution inside the domains. This term, accounting for chain polydispersity, can be important for quenched comb copolymer systems. Since we deal in fact with annealed comb copolymers capable of composition changing, the nonlocal effects are assumed to be less important.

It is worthwhile to emphasize that the coefficients α_i and β_i are connected with the higher order correlation functions and hence are temperature dependent as well. As a result, in contrast to the conventional diblock copolymer case,[28,34] the equilibrium value of the amplitude of the ordered phase Ψ_i is a more complex function of temperature, so the temperature of a transition between different ordered phases and between homogeneous and ordered phases cannot be obtained analytically.

The numerical comparison between the free energies of the different ordered phases and the homogeneous phase allows us to define the regions where the corresponding phase has the lowest free energy. It is necessary to point out that the phase diagram containing such regions of different phases with lowest free energy cannot provide the complete information about the behavior of the polymer system, since coexistence between different phases in the framework of macrophase separation has to be taken into account. The free energy of the macrophase-separated state can happen to be smaller than that of an ordered or homogeneous state. Macrophase separation into different phases will be analyzed in the next section. Here we will consider one example of a phase diagram containing regions of different phases having lowest (in comparison with others phases) free energy (Figure 11). This kind of phase diagram can give important information about the qualitative features of the polymer system under consideration. For instance, even if the macrophase-separated state has a lower free energy than an ordered one, the latter can still exist as a metastable state and hence it can be realized under changing the external conditions or during the equilibration process.

The phase diagram presented in Figure 11 was obtained by a numerical comparison between the free energies of the different ordered (lamellar, hexagonal, BCC) phases and the homogeneous phase for the case
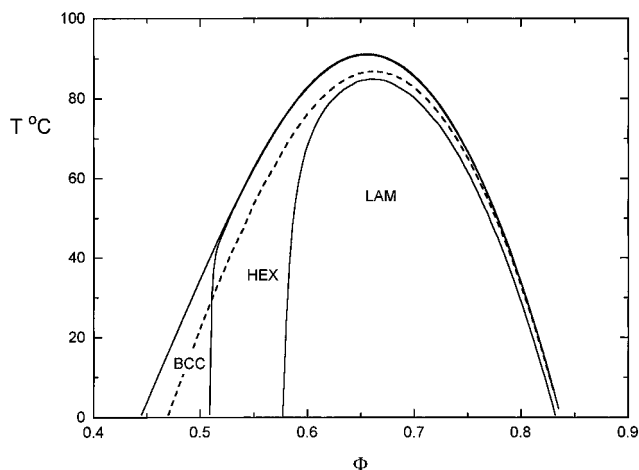

Figure 11. Phase diagram for polymer–oligomer mixture with strong hydrogen bonding ($N_p = 10^4$, $N_o = 30$, $E = 2000$ K, $S = 2$, $\Theta = 80$ K) obtained from a comparison between the free energies of the different phases. The diagram contains regions of body-centered-cubic (BCC), hexagonal (HEX), and lamellar (LAM) ordered phases. In these regions the corresponding phases have the lowest free energy. The dotted curve is the spinodal for macrophase separation.

of relatively strong hydrogen bonding (large E, small S). The dotted curve corresponds to the spinodal for macrophase separation into two homogeneous phases. As can be seen from Figure 11, the polymer system becomes unstable with respect to both micro- and macrophase separation in the region of a slight (or considerable) excess of the polymer volume fraction. For this region the average degree of association is not so high as for the case of an oligomer excess (low Φ), which is the reason for the instability. A comparison between the free energies of the different ordered phases (lamellar, hexagonal, BCC) shows that a lamellar structure can be formed if there is a polymer excess and the degree of association is close to the maximal value. The hexagonal structure is preferred by the polymer system with a larger oligomer volume fraction or when the segregation tendency is weaker, i.e., in the vicinity of the spinodal curve. The BCC phase can be formed if the volume fraction of oligomers is still larger or in the very vicinity of the spinodal. For the present case (Figure 11) the BCC phase can exist only for comparable polymer/oligomer volume fractions at low temperature. Note, however, that stoichiometric conditions correspond to $\Phi \cong 0.032$, implying that the whole phase diagram presented corresponds to the region where all oligomers can be hydrogen bonded at least at low temperatures. For larger polymer volume fraction a direct transition from the homogeneous to the hexagonal structure can be expected unless macrophase separation takes place. The uncommon behavior of the polymer system is connected with the temperature dependence of the association as well as with the complex "architecture" of the comb copolymer-like chains. Indeed, in contrast to conventional block copolymer systems, where a decrease of the temperature influences only the interactions in the systems, in the present case cooling of the system results also in a "composition" change: the fraction of free oligomers decreases due to the increase in the number of hb ("side-chains") per polymer chain. This effect has been taken into account in the free energy of the ordered phases through the temperature dependent coefficients α_i and β_i.

Since the length of the oligomers influences the degree of association, the common "order" of different phase appearance can be somewhat different for shorter oligomers. For instance, a homogeneous phase−BCC phase transition becomes possible for a broader (or even whole) composition range. This result is not a surprise, since it is reasonable to expect that spherical micelles can be more easily formed from shorter oligomer chains. For lower temperatures the influence of the "architecture" of the polymer chains on the type of ordered structure becomes even more important since the degree of association reaches the maximum value and further cooling does not change the "composition" of the system. It is important to note that not only the initial composition of the system but also the possibility to minimize polymer/oligomer contacts has to be taken into account. For instance, as can be seen from Figure 11, a lamellar structure is preferable for the polymer system with a large fraction of polymer, whereas for comparable polymer/oligomer volume fractions the hexagonal (or BCC) phase has a lower free energy. In the latter case, the degree of association is larger and hence the average distance between the "side-chains" becomes smaller. Then the lamellar structure can be less favorable, since it would be more difficult to avoid polymer−oligomer contacts inside polymer layers. To this end, hexagonal or BCC structures can be more appropriate.

It is worthwhile to emphasize that we took into consideration only the most standard types of ordered structures. So, some other structures like the bicontinuous ones are also possible. Taking into account the complex "architecture" of associated polymer chains, it is possible to expect also the formation of vesicles or hollow spherical, hollow cylindrical, or even more exotic polymer micelles.

4. Macrophase Separation into Different Symmetry Phases. Phase Diagrams

As mentioned above, the phase diagrams obtained from a comparison between the free energies of the different phases (Figure 11) cannot provide complete information about the behavior of the polymer system until we take into consideration the possibility of macrophase separation as well.

To obtain the equilibrium composition of a macrophase-separated system, the set of equations of phase equilibrium can be solved for all possible combinations of coexistent phases:

$$\begin{cases} \dfrac{\mathrm{d}F_i}{\mathrm{d}\Phi}\bigg|_{\Phi=\Phi_1} = \dfrac{\mathrm{d}F_j}{\mathrm{d}\Phi}\bigg|_{\Phi=\Phi_2} \\ \left\{\Phi\dfrac{\mathrm{d}F_i}{\mathrm{d}\Phi} - F_i\right\}\bigg|_{\Phi=\Phi_1} = \left\{\Phi\dfrac{\mathrm{d}F_j}{\mathrm{d}\Phi} - F_j\right\}\bigg|_{\Phi=\Phi_2} \end{cases} \quad (20)$$

The first equation corresponds to the condition of equality of "chemical potentials" of the coexistent phases. The second equation results from the condition of equality of osmotic pressures of the phases.

Let us consider the phase diagram obtained by the solution of these equations (eq 20) for the case of strong hydrogen bonding (Figure 12). Accounting for phase coexistence (eq 20) changes the overall appearance of the phase diagram dramatically (cf. Figure 11). Instead of large regions of ordered structures, broad regions of macrophase separation into homogeneous and ordered phases appear. Of course, the presence of large regions of macrophase separation is not a unique characteristic
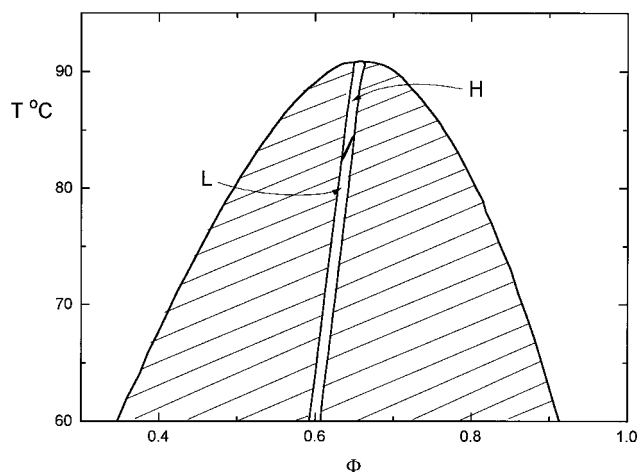

Figure 12. Phase diagram for the polymer−oligomer mixture with strong hydrogen bonding ($N_p = 10^4$, $N_o = 30$, $E = 2000$ K, $S = 2$, $\Theta = 80$ K). The diagram contains regions of stability of hexagonal (H) and lamellar (L) ordered phases as well as regions of macrophase separation (shaded areas).

of the polymer system under consideration. Large regions of macrophase separation are typical for various polymer systems in the presence of low molecular weight components,[37−41] be it polymer solutions or mixtures. For the present case the role of this low molecular weight component is played by free oligomers. The unique feature of the system is that the fraction of free oligomers changes with temperature.

As can be seen from the diagram (Figure 12), the "surviving" region of stable ordered phase is rather narrow. It corresponds to the composition range for which microphase separation occurs first upon decreasing the temperature. The coexistence of homogeneous and hexagonal phases takes place in the temperature region where the hexagonal phase has the lowest free energy (among the ordered phases). For lower temperatures, where the lamellar phase has the lowest free energy, the coexistence occurs between lamellar and homogeneous phases. Separation into hexagonal and lamellar phases takes place in a rather narrow temperature and composition interval in the vicinity of the boundary between these phases. The peculiar feature of the diagram is that the composition range of the stable ordered phase is very narrow from the "beginning" and remains almost the same during cooling. Upon cooling, this composition range shifts to somewhat smaller values of Φ, implying an increase in the average oligomer fraction and a decrease in the period of the structure. However, it is important to realize that, since the applied approach is valid only in the weak segregation limit, we cannot expect our results to remain valid for temperatures 20−30 °C lower than the highest order−disorder transition temperature.

Another example of a possible phase diagram obtained for the polymer system with shorter oligomer chains, smaller energy of hydrogen bonding ($E = 1200$ K), and somewhat larger entropy loss ($S = 2.3$) is presented in Figure 13. As discussed (Figure 3), the larger the entropy loss S (or smaller E) the less the average degree of association X and the more abruptly the association occurs as the temperature decreases. For such polymer systems the presence of reappearing homogeneous phases is typical, as already noted from the analysis of the spinodal curves for the same system (Figure 7). The order of phase transformation with
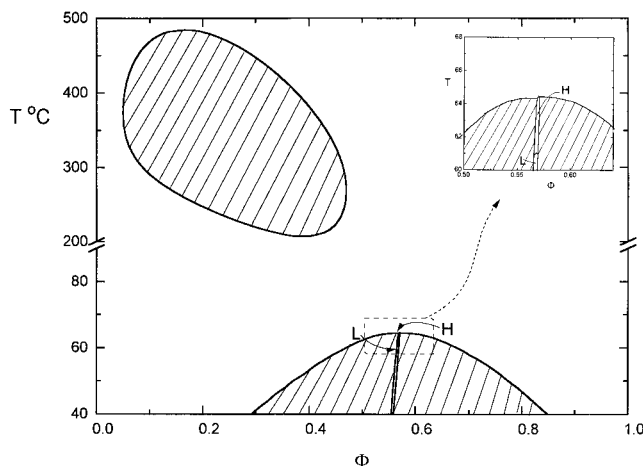
Figure 13. Phase diagram for the polymer–oligomer mixture ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $S = 2.3$, $\Theta = 90$ K). The diagram contains regions of stability of hexagonal (H) and lamellar (L) ordered phases as well as regions of macrophase separation (shaded areas).

Figure 14. Phase diagram for the polymer-oligomer mixture ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $S = 2.34$, $\Theta = 90$ K). Diagram contains regions of stability of lamellar (L) and hexagonal (H) ordered phases as well as regions of macrophase separation (shaded areas).

changing temperature is in good agreement with the experimental observations,[25] as mentioned before. There is a region of macrophase separation into homogeneous phases at elevated temperatures, the lamellar ordered structure (at least as one of the coexistent phases) at low temperatures, and a region of reappearing homogeneous phase for the intermediate temperature range. The high-temperature region of instability (Figure 7) is transformed into the (larger) region of macrophase separation into two homogeneous phases of different volume fraction of polymer. One of the coexistent phases contains practically pure oligomer component—the volume fraction of polymer in this phase is rather low. As might be expected, the region of reappearing homogeneous phase does not change substantially (cf. Figures 7 and 13). The low-temperature region of instability with respect to both micro- and macrophase separation is transformed into a large region of ordered-homogeneous phase coexistence. As for the case presented in Figure 12, the coexistence of hexagonal and homogeneous phases occurs in the vicinity of the spinodal and, for lower temperatures, lamellar structures coexist with the homogeneous one. The low-temperature regions of both diagrams (Figures 12 and 13) are similar. So, all comments made above apply for the present case as well.

Yet another phase diagram (Figure 14) can be obtained for polymer systems with larger values of the entropy loss S than for the case considered in Figure 13. The spinodal curves for this system are presented in Figure 8. The increase of the entropy loss S results in a decrease of the average degree of association (Figure 3), leading to an expansion of the instability regions. The sequence of temperature phase transformations is similar to the case of Figure 13. However, the region of the reappearing homogeneous phase becomes more narrow. There are also remarkable changes in the regions of the ordered phases. For the present case (Figure 14), there are regions of ordered structures belonging to the elevated temperature region of instability (above the region of reappearing homogeneous phase). As can be seen from Figure 14, lamellar and hexagonal ordered structures can be formed in the system both above and below the region of reappearing homogeneous phase. As for the cases considered above (Figures 12 and 13), macrophase separation into homo-
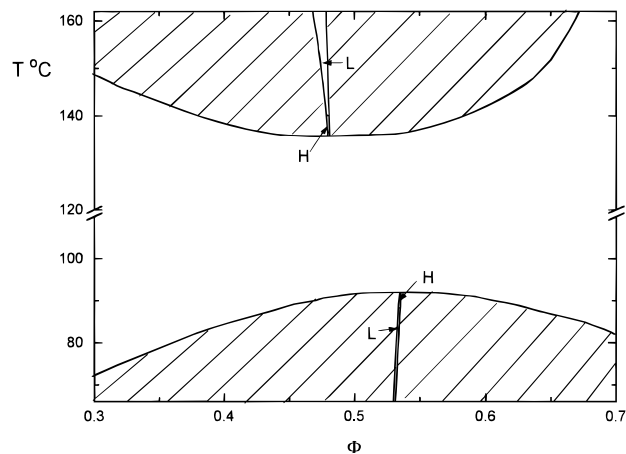
geneous and ordered structures occupies large regions. The regions of stable ordered structures are located near the points of the highest (lowest) order–disorder transition temperature. Since the results of RPA approach are valid in a relatively narrow temperature interval in the vicinity of these points, we present only the corresponding part of the diagram in Figure 14. The rest of the diagram is similar to that considered in Figure 13.

Let us consider the phase transformations for decreasing temperatures for the case of equal volume fractions of polymer and oligomer ($\Phi = 0.5$). For elevated temperatures the homogeneous state of the system is stable. As the temperature decreases, macrophase separation into two homogeneous phases of different polymer concentrations occurs. For lower temperatures, the coexistent phase with the lower concentration of polymer becomes ordered; a lamellar structure is formed. Then the lamellar structure transforms into a hexagonal one, which is still in coexistence with the homogeneous phase. For lower temperatures, the homogeneous phase becomes stable again, and finally, for still lower temperatures, macrophase separation into the lamellar and the homogeneous phases takes place again. Now the lamellar structure forms in the phase with the larger polymer concentration.

Macrophase separation is a common phenomenon for many polymer systems. As mentioned above, one of the specific features of the present polymer system is the temperature dependence of the association (and hence the fraction of free oligomers). It is possible to expect that macrophase separation can influence the association. Let us consider this influence for the example of the high-temperature region of separation into two homogeneous phases of Figure 13. Obviously, the conditions for hydrogen bond formation in the coexistent phases are different. As a result, although the distribution of polymer chains with given number of hydrogen bonds remains binomial in both phases, the average fraction of hydrogen bonds per chain X will be different in the two phases. (As is clear from eq 6, X depends on the composition of the phase Φ.) In the phase with a small number of polymer chains (small Φ), the formation of hydrogen bonds is stimulated by the presence of a large number of free oligomers; the degree of association X is large (dash-and-dot curve of Figure
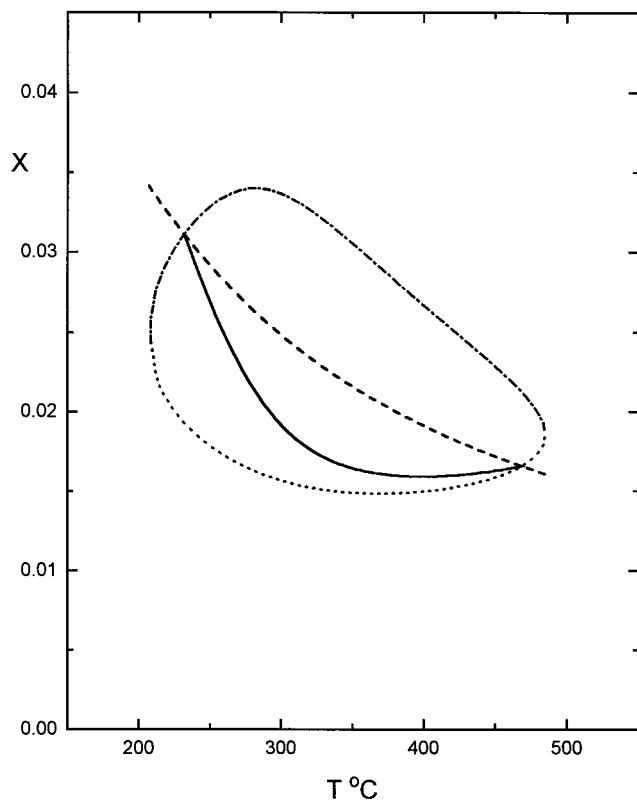
Figure 15. Temperature dependence of the average fraction of hydrogen bonds per chain X for a macrophase-separated polymer−oligomer mixture ($N_p = 10^3$, $N_o = 20$, $E = 1200$ K, $S = 2.3$, $\Theta = 90$ K, $\Phi = 0.25$). The dashed curve corresponds to the overall degree of association for the homogeneous state; the solid curve corresponds to that for the macrophase-separated state. Dotted and dot-and-dash curves represent the values of X in the coexisting phases.

15). It is larger than in the homogeneous state under the same temperature (dashed curve in Figure 15). In the other phase, the fraction of free oligomers is much smaller and, as a result, the degree of association X is smaller too (dotted curve in Figure 15). It is also smaller than in the homogeneous state. The average fraction of hydrogen bonds in the phase-separated system X_{mac} is

$$X_{mac} = X_1 \frac{\Phi_1}{\Phi} \frac{(\Phi_2 - \Phi)}{(\Phi_2 - \Phi_1)} + X_2 \frac{\Phi_2}{\Phi} \frac{(\Phi - \Phi_1)}{(\Phi_2 - \Phi_1)} \quad (21)$$

where X_i and Φ_i are the average fraction of hb per chain and the volume fraction of polymer in ith phase ($i = 1$, 2); Φ is the volume fraction of polymer in the system as a whole.

As can be seen from Figure 15, macrophase separation leads to a substantial decrease in the average fraction of hb per chain X_{mac} (solid line) in comparison with the homogeneous state of the polymer system (dashed line). The explanation of this effect is that under macrophase separation most of the polymer chains are in the same phase, where the fraction of free oligomers and hence the degree of association is much smaller than in the corresponding homogeneous state. The degree of association in the other phase can be very high; however, the number of polymer chains is rather small. So, the degree of association in the system as a whole X_{mac} (eq 21) is only somewhat larger than in the polymer-rich phase. Of course, the difference between

the degree of association in the phase-separated state and in the homogeneous state is very small near the boundaries of the region of macrophase separation. A decrease in the degree of association X as a result of macrophase separation can lead to the following effect. In contrast to the common tendency (Figures 2−4), a decrease of the temperature can result in a reduction in the degree of association of the polymer system as a whole in some temperature interval belonging to the macrophase separation region.

We have considered the influence of macrophase separation on the average degree of association for the example of homogeneous phase coexistence (Figure 15). However, this effect can also take place for the case of macrophase separation into different symmetry phases, since it results from the difference in composition of the coexistent phases.

It is reasonable to wonder whether microphase separation may influence the association process as well. The answer to this question can be as follows. Microphase separation, in contrast to macrophase, means segregation on a microscopic level. So, the microenvironment of different polymer chains can be different. Due to this, the redistribution of oligomers inside the layers is possible, especially for the case of a large period of the ordered structure. However, since polymer-"rich" layers alternate with oligomer-"rich" layers, the possibility of hydrogen bonding as a whole is practically the same as in the homogeneous state until the phase boundaries become very sharp. But this case corresponds to strong segregation limit and hence is outside the scope of the present considerations.

It is worthwhile to note that the RPA approach is valid in the limit of weak segregation only; so, the results obtained are valid as long as we are not very far from the spinodal of phase separation. We cannot expect that our results are still valid for very low temperatures, where an analysis in the framework of the strong segregation limit is required. Furthermore, fluctuation corrections have not been taken into consideration here. We believe, however, that they will not influence significantly the main results of the present paper.

5. Conclusion

In the present paper a theoretical model describing the formation of reversible temperature dependent bonds in polymer−end-functionalized oligomer mixture has been formulated and applied to analyze the phase behavior of the hydrogen-bonding mixture.[42] Two parameters, energetic E and entropic S, related to the experimentally measured equilibrium constant of hydrogen bonding K, have been used (eq 4) to describe the strength of hydrogen bonding.

One of the most important features of the system is the temperature dependence of hydrogen bond formation. The polymer system can be considered as a mixture of random comb copolymers, with the number and position of side chains and free oligomers varying. The set of associated polymer chains (random comb copolymers) satisfies the binomial distribution P_n (eq 5) resulting from the assumed noncooperative nature of the association. The average fraction of hb per chain X is a function of temperature T, strength of hb (E, S), oligomer length N_o, and composition Φ (eq 6).

It has been found that macrophase separation decreases the overall degree of association X. Due to the

difference in polymer concentration in the coexisting phases, the average degree of association in the polymer-rich phase is much smaller than that in the homogeneous state, which results in a decrease of the overall degree of association. It might even happen that the overall degree of association (for a fixed volume fraction of polymer Φ) decreases with a decrease of the temperature in some temperature range.

Microphase separation can take place in the polymer system if the tendency to segregate is not very strong and the degree of association X is large enough. The larger the incompatibility of the components, the broader the regions of macrophase separation and the smaller the probability to have stable ordered structures in the whole volume of the system.

An increase in the length of the oligomers for a fixed volume fraction of polymer Φ (or fixed X_0) results in a decrease of the number of oligomer chains (or decrease of polymer volume fraction), reducing the average degree of association. As a result, the polymer system becomes less stable with respect to both macro- and microphase separation. Recently, this phenomenon has been observed experimentally.[26]

For polymer systems characterized by rapidly changing degree of association X as a function of temperature and large incompatibility of the components (relatively high Θ temperature), the presence of a reappearing homogeneous state is typical (Figures 7, 8, 13, and 14) in accordance with experimental observations.[25] For high temperatures, the degree of association is low but the incompatibility is already strong. As a result, macrophase separation takes place. Cooling leads to an abrupt increase of the average number of hb per chain X and the comb copolymer-like chains become compatible with a "solvent" of free oligomers due to the presence of many "side-chain" oligomers. For very low temperatures, incompatibility becomes very strong and the polymer system separates again.

The type of ordered structure depends not only on the composition (polymer volume fraction Φ) and temperature (degree of association) but also on the possibility to minimize polymer−oligomer contacts. Due to that, hexagonal or even BCC structures can be realized for relatively high values of Φ.

The minimum value of the period of the ordered structures, $D = 2\pi/q^*$, corresponds to the stoichiometric volume fraction, Φ_{st}, where full complexation is possible at low temperatures ($X_0 = 1$). With an increase in volume fraction of one of the mixture components, the period of the structure increases.

The analysis of thermodynamic equilibrium between different phases shows that coexistence of homogeneous and ordered phases is typical for the polymer system under consideration. A large part of the phase diagrams is occupied by regions of macrophase separation into homogeneous and ordered phases, lamellar or hexagonal. This result is of considerable interest for the recent experimental observations. It indicates that the ordered structures invariantly observed most probably correspond to metastable rather than thermodynamic equilibrium states.[15−18] The coexistence of different ordered phases such as lamellar and hexagonal can also take place. Ordered structures of different symmetry can be formed both above and below the regions of the reappearing homogeneous phase.

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(42) In fact, the model proposed can also be applied for studying of any other polymer systems with reversible bonds, for instances, associated polymers.

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