Macromolecules **1997,** *30,* 577−583

Surface Enrichment from a Binary Polymer Blend

Ioannis G. Kokkinos and Marios K. Kosmas*

Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

Received April 17, 1996; Revised Manuscript Received October 4, 1996⊗

ABSTRACT: We study the quantitative behavior of a two-component polymer blend in the presence of an impenetrable interacting surface. A solution of the problem for ring chains is given, which can also describe the behavior of linear chains. While first-order perturbation theory is used for the interactions between the different monomers, the interactions between the monomers and the surface are taken into account to all orders. The monomer concentrations on the surface are found to be linear functions of the bulk concentrations only in the absence of interactions between the two components. The deviation from linearity between the surface and the bulk concentrations increases on increasing both the intensities of all three different interactions and the molecular weights of the polymers. Surface enrichment of one of the components is enhanced when the difference between the two surface interactions increases and reaches its largest value near the coexistence curve of the corresponding phase diagram of the blend. The theoretical predictions compare well with experimental results found by means of scattering and other spectroscopic techniques.

1. Introduction

The macroscopic behavior of polymeric blends near surfaces differs from that in the bulk[1] and has recently been the subject of many interesting studies, because of the control exerted by the surface composition on a variety of technologically important properties of blends. Applications in numerous fields such as adhesion of different polymeric phases,[2] colloidal stability,[3] and the design of composite and biocompatible materials[4] requires a fundamental understanding of the microstructure and composition of binary polymer blends in the vicinity of interacting surfaces. Mean-field theories with short and long range surface interactions[5−9] and self-consistent field methods in continuous space[10−12] and on lattices[13,14] as well as techniques based on computer simulations[15,16] have been employed to investigate mixtures of polymers at surfaces and interfaces. Many experimental techniques such as X-ray photoelectron spectroscopy,[17−19] forward recoil spectrometry,[20−22] secondary-ion mass spectrometry,[21,22] and surface-enhanced Raman scattering[23] have also been used to investigate the behavior of polymers interacting with various substrates. In the case of polymer blends, a multitude of surface phenomena have been explored including surface enrichment by one of the two polymeric species, which usually occurs on the surface of a mixed condensed phase when one of the components partitions preferentially to the surface. The surface composition, the quantity that indicates when enrichment is sufficient for certain purposes, has been found to depend strongly on the difference between the interactions of the two species with the surface.[5−19] It also depends on the magnitude of the interactions between the two polymer constituents which determines their degree of compatibility.[13−18] Other factors that affect the surface concentrations as well as the other properties of blends are the blend composition,[5−22] the molecular weights of the components,[13,14,19,23] and the thickness of the polymeric sample.[23,24]

The purpose of this work is to investigate the macroscopic behavior of a binary polymer blend in contact with an interacting surface. In particular, we describe the surface composition of the blend along with the surface enrichment of one of the blend components when in contact either with a solid or a liquid substrate or the air and has a sharp density profile across the interface. The difficulty connecting the macroscopic behavior with the microscopic characteristics of the system lies mainly in the fact that a polymer blend in contact with a surface is an inhomogeneous system along the perpendicular axis. The interactions between the polymer chains and the surface alter the conformational behavior of the nearby chains relative to those in the bulk far from the surface, leading to an enrichment of the surface region by the preferentially adsorbed component. A molecular model defined in terms of microscopic parameters is employed together with methods of statistical thermodynamics according to which the macroscopic properties of the systems of polymer chains are averages over the probabilities of the configurations of the chains. The surface properties of the blends are derived directly from the system's configurational Hamiltonian that describes an ensemble of two different kinds of chains, A and B . The chains interact with one another, through a monomer−monomer interaction equal to $u_{AB} = w$, but they also interact with an impenetrable surface with intensities of interactions between the monomers A and B and the surface equal to u_A and u_B, respectively. While the solution of the problem to all orders of u_A and u_B is possible, as far as the unit−unit interactions w are concerned, first-order perturbation theory is used, which, together with the filling of the whole available volume V with monomers, describes blends to the accuracy of the Flory−Huggins approximation.[25,26] An analytic solution for the surface interactions is given for the case of ring chains, permitting a detailed study of the surface segregation. The effects of molecular factors such as interaction parameters and molecular weights of the polymers and of macroscopic characteristics such as blend composition, annealing temperature, and thickness of the sample are also analysed. A qualitative description of the behavior of open linear chains is also gained from the presented solution because the properties of ring and linear chains of the same molecular weight as regards the free energy and density profiles have been shown to display similar trends.

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S0024-9297(96)00567-0 CCC: $14.00

2. The Partition Function

The n_A and n_B chains of the polymeric species A and B interact with each other and with a surface and they are free to belong to the available volume $V = SL$, where S is the area of the interacting surface on the XY plane restricting the blend to the positive half-space $z \geq 0$ and L is the length of the perpendicular dimension of the available space along the z axis, also representing the thickness of the polymeric sample. The flexible polymer chains are represented by the continuous lines $\mathbf{R}(s_k)$ ($k = 1, 2, ..., n_A$) and $\mathbf{R}(s_\lambda)$ ($\lambda = 1, 2, ..., n_B$), with s_k and s_λ being the contour lengths of the two kinds of chains, respectively. According to the Edward's continuous model of polymer chains used,[27] the partition function that describes the polymer mixture interacting with an impenetrable wall (at $z = 0$) is defined by the following path integral, where the impenetrability is achieved by reflecting boundary conditions:[28,29]

$$Z = \int \mathrm{D}[\mathbf{R}(s_k)]\, \mathrm{D}[\mathbf{R}(s_\lambda)] \exp\Bigg\{ -\frac{3}{2l} \sum_{k=1}^{n_\mathrm{A}} \int_0^{N_\mathrm{A} l} \left| \frac{\partial \mathbf{R}(s_k)}{\partial s_k} \right|^2 \mathrm{d}s_K - u_\mathrm{A} \sum_{k=1}^{n_\mathrm{A}} \int_0^{N_\mathrm{A} l} \delta[\mathrm{z}(s_k)]\, \mathrm{d}s_k - \frac{3}{2l} \sum_{\lambda=1}^{n_\mathrm{B}} \int_0^{N_\mathrm{B} l} \left| \frac{\partial \mathbf{R}(s_\lambda)}{\partial s_\lambda} \right|^2 \mathrm{d}s_\lambda - u_\mathrm{B} \sum_{\lambda=1}^{n_\mathrm{B}} \int_0^{N_\mathrm{B} l} \delta[\mathrm{z}(s_\lambda)]\, \mathrm{d}s_\lambda - w \sum_{k=1}^{n_\mathrm{A}} \sum_{\lambda=1}^{n_\mathrm{B}} \int_0^{N_\mathrm{A} l} \int_0^{N_\mathrm{B} l} \delta[\mathbf{R}(s_k) - \mathbf{R}(s_\lambda)]\, \mathrm{d}s_k\, \mathrm{d}s_\lambda \Bigg\} \quad (1)$$

Though both penetrable and impenetrable walls can be described by the same solution up to a normalization constant, in this paper we confine ourselves to the study of an impenetrable surface. We aim in this way to study chains that cannot escape from the polymer phase. The reflecting boundary conditions which are used yield maximum density profiles for $u_\mathrm{A} = u_\mathrm{B} = 0$ and describe well sharp density profiles like those of polymers in contact with the air.[15,16,28] The factors N_A and N_B denote the numbers of monomeric units of the A and B chains and l is the effective Kuhn length considered for simplicity to be the same for both polymeric units. All three interaction parameters, w between the monomers A and B and u_A and u_B between the two kinds of monomers and the surface, are equal to the binary cluster integrals of the corresponding mean potentials, and they depend on the temperature and the nature of the monomers and the surface.[28−31] In order to make contact with similar molecular models, like those employing chains in lattices with interacting energies between the chain units at nearest possible positions, it must be mentioned that, for typical molecular potentials with hard cores and attractive wells of depths ϵ, these binary cluster integrals have been studied before.[28] There are critical values of ϵ, where the interaction parameters become zero. The general expressions given in section 3 easily yield results for these trivial subcases. On the other hand, the presented analysis also applies in the cases where the depths of the wells are zero and the interaction parameters u_A, u_B, or w become positive.

To first-order in w, Z can be written as

$$Z = Z_\mathrm{A}^{\mathrm{n_A}} Z_\mathrm{B}^{\mathrm{n_B}} - w Z_\mathrm{AB} Z_\mathrm{A}^{\mathrm{n_A}-1} Z_\mathrm{B}^{\mathrm{n_B}-1} \quad (2)$$

where

$$Z_i = \int \mathrm{D}[\mathbf{R}(s)] \exp\Bigg\{ -\frac{3}{2l} \int_0^{N_i l} \left| \frac{\partial \mathbf{R}(s)}{\partial s} \right|^2 ds - u_i \int_0^{N_i l} \delta[\mathrm{z}(s)]\, \mathrm{d}s \Bigg\} \qquad (i = \mathrm{A,B}) \quad (3)$$

and

$$Z_\mathrm{AB} = \int \mathrm{D}[\mathbf{R}(s)]\, \mathrm{D}[\mathbf{R}(s')] \times \exp\Bigg\{ -\frac{3}{2l} \int_0^{N_\mathrm{A} l} \left| \frac{\partial \mathbf{R}(s)}{\partial s} \right|^2 \mathrm{d}s - u_\mathrm{A} \int_0^{N_\mathrm{A} l} \delta[\mathrm{z}(s)]\, \mathrm{d}s - \frac{3}{2l} \int_0^{N_\mathrm{B} l} \left| \frac{\partial \mathbf{R}(s')}{\partial s'} \right|^2 \mathrm{d}s' - u_\mathrm{B} \int_0^{N_\mathrm{B} l} \delta[\mathrm{z}(s')]\, \mathrm{d}s' \Bigg\} \times \sum_{k=1}^{n_\mathrm{A}} \sum_{\lambda=1}^{n_\mathrm{B}} \int_0^{N_\mathrm{A} l} \int_0^{N_\mathrm{B} l} \delta[\mathbf{R}(s) - \mathbf{R}(s')]\, \mathrm{d}s\, \mathrm{d}s' \quad (4)$$

represent the configurational partition functions of single chains and that of the pairs of interacting chains, respectively. The behavior of a single chain and its surface adsorption has been studied before both for linear and ring polymers and many similarities between the two cases have been found.[30,31] The extension of this study to the evaluation of the partition function of the pairs of interacting chains is straightforward and an analytic solution with respect to u_A and u_B interactions is possible for the case of ring mixtures. This solution is presented here in order to investigate the behavior of both ring and linear polymer blends in the vicinity of an interacting surface. Indeed, the macroscopic behavior of ring and the corresponding open linear chains has already been found to be similar as far as properties related to the free energy and density profiles are concerned.[31] Properties that depend on the existence of the chain ends[13,32] or chain end effects of special chemical units able to give rise to strong interactions with the substrate[33] and differentiate linear from ring chains are not included in this study.

For the case of a penetrable surface the partition functions Z_i ($i = A$, B) of a single ring belonging to both half-spaces has been found in ref 31. When the surface is impenetrable and the available volume extends only to the half-space they are equal to

$$Z_i = \left(\frac{3}{2\pi N_i l^2} \right)^{3/2} V \left[1 - \frac{l \sqrt{\pi N_i}}{L \sqrt{6}} \left\{ \frac{1}{2} - \mathbf{K}(U_i) \right\} \right] \quad (5)$$

The only difference between the two cases being the normalization constant of $^1/_2$ inside the brackets, which is equal to 1 for the penetrable case. The parameters $U_i = u_i \mu_\mathrm{o} \sqrt{N_i}$ ($\mu_\mathrm{o} = \sqrt{3/2}$, $i = A,B$) and $L = V/S$ are the reduced surface interactions and the perpendicular dimension of the sample, respectively. The function $\mathbf{K}(U_i) = \exp(U_i^2)\, \mathrm{Erfc}(U_i)$ ($i = A$, B), the product of the exponential and the complementary error function,[34] is often met in this work. The prefactor $(3/2\pi N_i l^2)^{3/2} V$ is the number of configurations of a free ideal chain in the absence of the surface, and the second term in the brackets is the contribution from the surface. As in the case of Z_i, the function Z_AB can be found by means of its Laplace transforms with respect to N_A and N_B.[30,31] The derivation is given in the Appendix and the result for $N_\mathrm{A} = N_\mathrm{B}$ is equal to

$$Z_\mathrm{AB} = n_\mathrm{A} n_\mathrm{B} N^2 \left(\frac{3}{2\pi N l^2} \right)^3 V F(U_\mathrm{A}, U_\mathrm{B}, L)$$

$$U_\mathrm{i} = u_\mathrm{i} \mu_\mathrm{o} \sqrt{N} \qquad (i = A,B) \quad (6)$$

where the function $F(U_A,U_B,L)$ that includes the complementary error function is given in the Appendix. By means of Z_i of eq 5 and Z_{AB} of eq 6, the overall configurational partition function Z of eq 2 is written in terms of the interaction parameters, sample width, and molecular weight of the chains and permits the study of the effects of these factors on the system properties.

3. Surface Composition

The surface concentrations Y_A and Y_B of the two species, defined as the number of monomers attached to the surface per unit surface area, are equal to

$$Y_i = -\frac{1}{S}\frac{\partial(\ln Z)}{\partial u_i} \qquad (i = A, B)$$

and can be found by means of Z of eq 2. The surface concentration of the monomers A for example is given by

$$Y_A = \phi_A \frac{l\sqrt{\pi}}{\sqrt{6}}\left\{\frac{[2\pi^{-1/2} - 2U_A\mathbf{K}(U_A)]}{P_A(U_A,L)} + \frac{wN(1-\phi_A)}{P_A(U_A,L)\,P_B(U_B,L)}\left[\frac{[2\pi^{-1/2} - 2U_A\mathbf{K}(U_A)]}{P_A(U_A,L)} F(U_A,U_B,L) + H(U_A,U_B)\right]\right\} \quad (7)$$

where $\phi_A = n_A N_A V_o/V$ is the bulk volume fraction with the reference unit volume V_o considered to be equal to 1. $P_i(U_i,L)$ equals $P_i(U_i,L) = [1 - (l\sqrt{\pi N i}/L\sqrt{6})\{(1/2) - \mathbf{K}(U_i)\}]$, $(i = A,B)$, and the functions $F(U_A,U_B,L)$ and $H(U_A,U_B)$ are given in the Appendix. The first term of eq 7 is the contribution from the configurations of the isolated A chains near the surface,[31] and the remaining terms are contributions from chain correlations caused by the w interactions. The surface concentrations Y_A that express the values of the density profiles at $z \to 0$, together with the values of the density profiles far from the influence of the surface at $z \to \infty$ which can be obtained when $u_A = u_B = 0$, yield a picture of the density profiles that vary between these two limits. As no incompressibility constraints are imposed, adsorption and depletion states can occur for both components of the blend, depending on the values of the parameters of the system. Examination of the surface fractions of component A and B given by $\phi_{SA} = Y_A/(Y_A + Y_B)$ and $\phi_{SB} = Y_B/(Y_A + Y_B)$, respectively, facilitates the study of the main factors that determine the preferential adsorption at the surface. Surface concentrations and therefore surface fractions are controlled by the interactions u_A and u_B, the w interactions between the different monomers, the molecular weights of the chains, the thickness of the sample (L), and the bulk compositions ϕ_A and $\phi_B = 1-\phi_A$ of the two species. Illustrative graphs described in the following sections depict clearly these dependences. The surface concentration variations are studied first, having set, for simplicity, the effective Kuhn length l equal to unity, a convention that will be used throughout the rest of this paper.

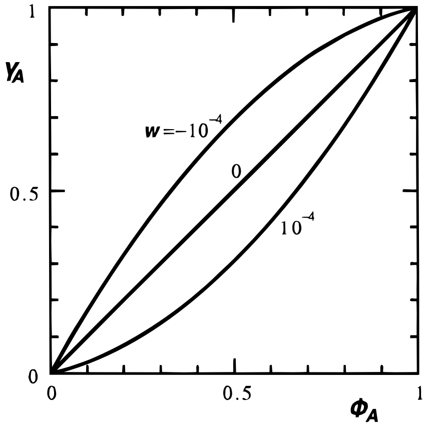

Figure 1. The surface concentration Y_A versus the bulk composition ϕ_A for surface interactions with $U_A = -3 \times 10^{-3}$ and $U_B = -3 \times 10^{-4}$, the chain length $N = 10^4$, and the perpendicular dimension $L = 7200$. Different curves correspond to various choices of the w parameter, as indicated.

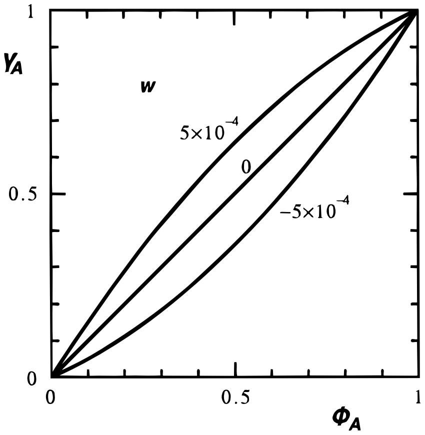

Figure 2. The surface concentration Y_A versus the bulk composition ϕ_A for various values of the w parameter. The reduced surface interaction parameters are equal to $U_A = -3 \times 10^{-3}$ (attractions) and $U_B = 0.8$ (repulsions). The chain lengths are $N = 10^4$ and the perpendicular dimension $L = 7200$.

3A. Composition Dependence. When the interaction parameter w is equal to zero, corresponding to negligible χ parameters between the two species, the surface concentration Y_A can be found from eq 7 and depends linearly on the bulk composition ϕ_A. It is given by $Y_A = \phi_A\pi^{1/2}[2\pi^{-1/2} - 2U_A\mathbf{K}(U_A)]/[6^{1/2}P_A(U_A,L)]$ and this expression with $\phi_A = 1$ also gives the surface concentration of pure A component.[31] Quite interesting is the trivial case $u_A = u_B = w = 0$, showing that even in the absence of net interactions, the concentrations $Y_i = 4lL\phi_i/(2\sqrt{6}L + l\sqrt{\pi N_i})$ ($i = A$, B), depend on the molecular weights N_i and also that, for a fixed bulk composition, shorter chains preferentially accumulate at the surface. The linear dependence of Y_A on ϕ_A, with a slope depending on the parameter U_A, is shown in Figures 1 and 2. For nonzero values, the w interactions between the monomers of the two components correlate the two different kinds of chains and lead to a deviation from the linear dependence. Depending on the values of w and u_B, the curves $Y_A(\phi_A)$ can be above or below the straight line. The curves above the ideal straight line in Figure 1 correspond to negative w interactions, representing regions of attraction between the two species. The surface interaction u_B is also negative, permitting excess B monomers to be found near the surface. These B monomers at the surface region attract more A monomers and result in an enhanced surface concentration Y_A compared to that of the ideal straight line. This is in accord with previous reports of Monte Carlo simulations in compressible systems, based on the ability of the surface to condense the system by adsorption.[15] Increasing ϕ_A further, though, results in less B monomers in the bulk and adsorbed at the surface, which attract less A monomers at the surface

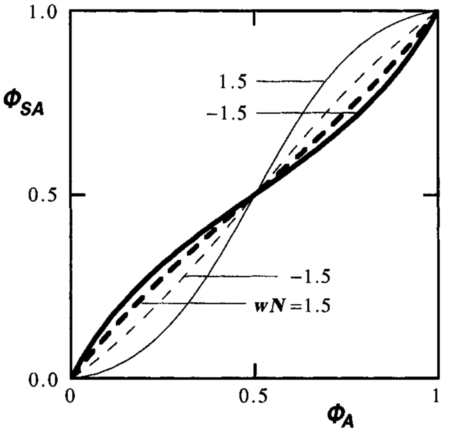

Figure 3. Plot of the surface fraction ϕ_{SA} versus the bulk composition ϕ_A for a symmetric blend of degree of polymerization $N = 10^3$, thickness $L = 7200$, and equal surface interactions $U_A = U_B = U$. The solid curves correspond to $U = 0.1$ (low adsorption) and the dashed curves to $U = 1.1$ (depletion). In each case the product wN is 1.5 and −1.5, as indicated. Enrichment of the minority species is displayed in the bold curves and enrichment of the majority species is shown in the normal curves. All the inversion points are at $\phi_{SA} = \phi_A = 0.5$.

leading to a reduction of the gradients of the $Y_A(\phi_A)$ curves. In the same plot in Figure 1 the case of positive w interactions is included, where the A monomers are repelled from the surface region and the surface concentration Y_A is reduced, leading to curves below the straight line of Figure 1. On the other hand, in Figure 2 the case of positive surface interaction u_B (repulsion) is illustrated where less B monomers are adsorbed at the surface, with the largest B concentration being away from the surface region. When the w interactions are positive, the B monomers repelled from the surface force the A monomers toward the surface, and consequently, the concentration Y_A near the surface increases above the straight line, leading to the upper curves of Figure 2. As the composition ϕ_A of the A units in the bulk increases further, $\phi_B = 1\text{-}\phi_A$ decreases and less B units in the bulk force less A units to the surface, explaining the reduction of the gradient of the $Y_A(\phi_A)$ curves. For negative w interactions, the nonadsorbed B monomers drag A monomers away from the surface and reduce the surface concentration Y_A, leading to curves below the straight line of Figure 2.

The variations of the surface compositions can be studied in terms of the surface fraction $\phi_{SA} = Y_A/(Y_A + Y_B)$ of the A component. Of interest is the trivial case of zero interactions $u_A = u_B = w = 0$, where ϕ_{SA} is found to depend both on N_A, N_B and ϕ_A, giving no enrichment ($\phi_{SA} = \phi_A$) when $N_A = N_B$. For $N_A < N_B$, the relation $\phi_{SA} > \phi_A$ is predicted, proving that, in the absence of interactions, enrichment of the species with the smaller molecular weight takes place, in agreement with other theoretical works.[35] Another trivial but interesting case is shown in Figure 3, where enrichment due to bulk composition variations is illustrated for various values of the interaction parameter w and equal values of the surface interactions $u_A = u_B = u$. Opposite behavior of surface enrichment by the majority chains with bulk volume fraction $\phi_A > 0.5$ and the minority chains with $\phi_A < 0.5$ is shown in the corresponding parts of the graphs which are above the straight line $\phi_{SA} = \phi_A$ of no enrichment. There is a critical value of $U = u(3N/2)^{1/2} = 0.65$ above which larger repulsions w favor the enrichment of the majority chains and larger attractions favor the enrichment of the minority species, while the contrary happens for $U < 0.65$, in agreement with previous theoretical observations.[36] For nonzero interactions, ϕ_{SA} depends both on the difference between the surface interactions u_A and u_B and the parameter w, which expresses the interactions between the different species. These two factors can be counteractive or cooperative, and the effectiveness of the action depends on their sign and intensity. When w is small, regardless of its sign, the driving force for surface enrichment is always the difference between the surface interactions. The macroscopic Flory−Huggins parameter χ, related to the enthalpic component of the free energy and used normally to characterize interactions between the polymeric components, has recently been calculated for a blend to all orders in w and composition.[25,26] It must be mentioned here that in order to interprete quantitatively the experimental observations this χ parameter can be set equal to w, which is its first-order approximation. As far as the difference between the surface interactions is concerned, this is similar to surface energy difference and the related difference between the surface tensions of the pure components. The larger this difference is, the larger the enrichment, and this is shown in Figure 4, where ϕ_{SA} is plotted versus ϕ_A for various differences $\Delta U = (u_A - u_B)(3N/2)^{1/2}$ between the reduced surface interactions. This is in agreement with the theoretical results of refs 7 and 13. Upon increasing the bulk volume fraction ϕ_A of the most adsorbed component A, its surface fraction ϕ_{SA} increases, and the increase is more rapid when the absolute difference between the surface interactions is larger. Such observations have been reported for miscible blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) of almost equal molecular weights both on a solid substrate of aluminum[17] and in contact with the air,[19] where the polymer density profile is extended beyond its maximum value into the air phase only to a small distance compared to the average chain size.[15,16] This system is characterized by a very small interaction parameter w or χ between the PS and PVME in the miscible state, in the range from -10^{-4} to $+10^{-4}$. On the other hand, the difference between the two surface interactions is large, amounting to a value of −7.8 dyn/cm at 150 °C in terms of the surface tensions of the two species, and this is the driving force for the preferential surface adsorption of PVME.

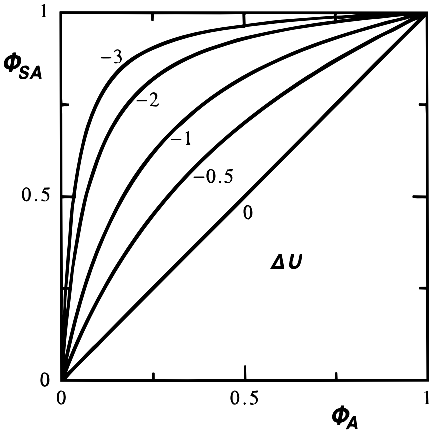

Figure 4. Surface fraction ϕ_{SA} of the enriched species as a function of bulk composition ϕ_A for five different values of $\Delta U = (u_A - u_B)(3N/2)^{1/2} = 0, -0.5, -1, -2, -3$. The w parameter equals $w = -10^{-4}$, $N = 10^3$, the perpendicular dimension $L = 7200$, and $U_A = -0.3$.

In the case of small differences between the surface interactions, preferential adsorption and surface enrichment is governed by the magnitude of the w parameter

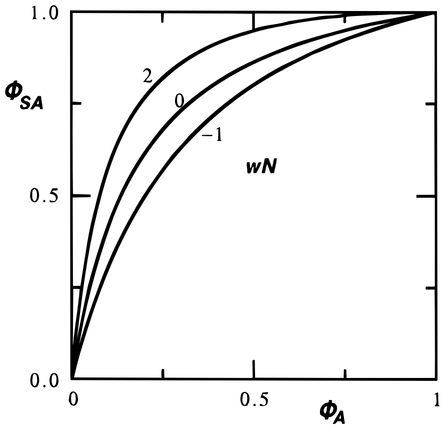

Figure 5. The surface fraction ϕ_{SA} of the enriched species plotted versus bulk composition ϕ_A for three values of the product wN. The difference between the surface interactions is kept small at $\Delta u = u_A - u_B = -1.225 \times 10^{-2}$, while the degree of polymerization is fixed at $N = 10^4$ and the perpendicular dimension at $L = 7200$.

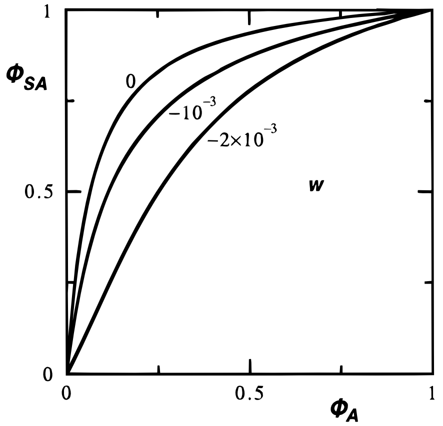

Figure 6. The surface fraction ϕ_{SA} as a function of the bulk composition ϕ_A for three values of the w parameter. The difference between the reduced surface interactions is kept constant at $\Delta U = U_A - U_B = -2$ while the degree of polymerization is $N = 1000$; the perpendicular dimension is equal to $L = 7200$ and $U_A = -0.3$.

and the product wN. The difference between the surface tensions, for example, of isotopic blends of PS and deuterated polystyrene (DPS) is only about −0.1 dyn/cm or less.[20−23] The w parameter between PS and DPS is also small and positive, on the order of 1.0×10^{-4}. In these systems, surface enrichment of the deuterated component that has slightly lower surface energy than the protonated one can be achieved by using large molecular weight polymers in order to induce the preferential adsorption of DPS by enlarging the product wN. The plots of ϕ_{SA} versus ϕ_A in Figure 5, where $\Delta u = u_A - u_B$ is fixed at the value of -1.225×10^{-2} and $N = 10^4$, show that enrichment is indeed gained for more positive values of w, where chains from the two different species repel each other, shifting to smaller values for more negative w interactions, where the chains are forced to interrelate.[13]

In a fully compatible blend with more negative w interactions, the bulk thermodynamics overcomes differences in the surface interactions and the samples are relatively homogeneous. The two components attract each other more strongly in these cases and the difference in the two surface concentrations and the enrichment is smaller. Such reduction of the fraction ϕ_{SA} with negative w is seen in Figure 6, where ϕ_{SA} is depicted versus ϕ_A for various values of w and for a fixed difference between the reduced surface interactions $\Delta U = U_A - U_B = -2$, a trend that has also been reported in the theoretical calculations of ref 7. A similar lack of difference in the two surface compositions has been observed experimentally at the surfaces of totally miscible polymer blends, such as the blends poly(ethylene oxide)/poly(methyl methacrylate),[18] in which the large negative χ parameter is on the order of -10^{-2}, compared to the value 10^{-4} of the PS/DPS and PS/PVMA systems, indicating greater miscibility. Despite the significant differences in the surface interactions of the two polymers, only a slight surface enrichment has been detected because of the strongly negative interactions between themselves. Similar conclusions have been derived from an analysis of the surface region of the poly(vinyl chloride)/poly(methyl methacrylate) blend.[37] This system, when casted from the mutual solvent of the two components, methyl ethyl ketone, exhibits a high degree of miscibility, possibly at the molecular level, which balances the difference in surface interactions, amounting to about −1 dyn/cm, and thus exhibits a surface composition almost equivalent to that of the bulk.

3B. Dependence on the Form of the Phase Diagram, Molecular Weight and Sample Thickness. A further understanding of the behavior of blends characterized by an upper (UCST) or a lower (LCST) critical solution temperature can be derived by means of the present study. The preceding analysis makes it clear that the maximum enrichment at the surface of a miscible blend is expected to occur near the corresponding coexistence curve, where the w parameter obtains its maximum positive value, as indicated in Figures 5 and 6. With this in mind, one can explain the observations at the surface of the widely studied PS/DPS blend, where the surface fraction of DPS increases rapidly near the coexistence curve, although the difference between the surface interactions of the two species is small.[20−23] Considering that binary systems have a UCST behavior when w (or χ) is a decreasing function of temperature, enhanced surface enrichment is expected at lower temperatures in the one-phase region of these systems. On the other hand, in LCST systems where w increases with temperature, enhanced enrichment occurs with higher annealing temperatures. When two phases with different fractions of components are possible, the phase preferentially adsorbed by the surface moves to the surface away from the bulk, increasing the adsorbed amount. Thus, in phase-separated systems enrichment is even further enhanced. Significant surface enrichment after annealing a polystyrene/poly(ethylene oxide) blend[18] comprises an illustrative example, as the PS-rich phase preferentially localizes at the surface. Also, a direct comparison of a miscible with a phase-separated sample of PS/PVME demonstrates a greater surface enrichment by PVME in the case of the second blend,[17] simply because the PVME-rich phase preferentially accumulates at the surface.

As the surface composition of symmetric polymer blends has been found to be sensitive to molecular weight changes, a detailed analysis of this dependence is of interest. In the case of equal chain lengths, $N_A = N_B = N$, the bulk compositions $\phi_A = n_A N_A/(n_A N_A + n_B N_B)$ and $\phi_B = n_B N_B/(n_A N_A + n_B N_B)$ do not depend on N. In the analytic solution of eq 7, the molecular weight N appears both in wN, expressing chain correlations, and in $U_i = u_i \mu_o \sqrt{N}$, expressing polymer−surface interactions, suggesting that longer chains interact more times with each other and with the surface, thus enhancing the phenomena. These trends are illustrated in Figure

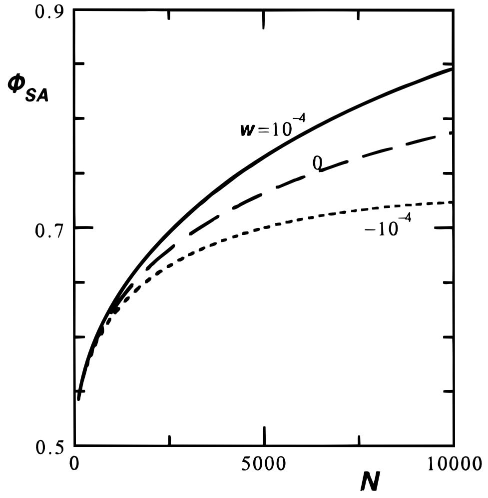

Figure 7. The surface fraction ϕ_{SA} as a function of the chain length N for various values of w . The perpendicular dimension is $L = 10^3$, the bulk composition is $\phi_A = 0.5$, and the interactions with the surface are equal to $u_A = 10^{-3}$ and $u_B = 1.1 \times 10^{-2}$.

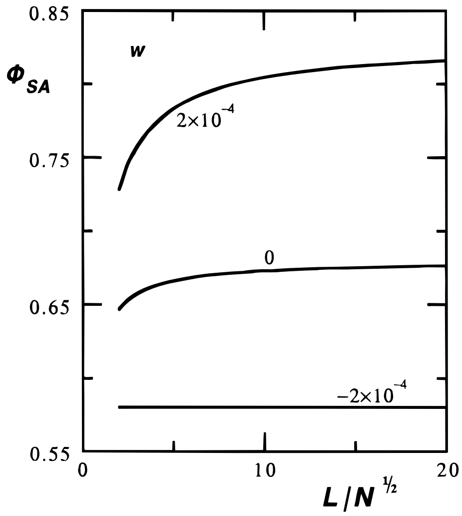

Figure 8. The surface fraction ϕ_{SA} of the enriched species as a function of the ratio $L/N^{1/2}$. The difference between the reduced surface interactions is kept constant at $\Delta U = U_A - U_B = -0.5$, $N = 10^4$, $U_A = 0.1$, and $\phi_A = 0.5$. Different curves correspond to various values of the w parameter, as indicated.

7, where the surface fraction ϕ_{SA} of an A/B blend with bulk composition $\phi_B = \phi_A = 0.5$ is plotted versus the chain lengths $N_A = N_B = N$ for various choices of w interactions, also illustrative of the ϕ_{SA} dependence on the various degrees of blend miscibility. Other theoretical results also suggest that one can achieve substantial increases in the surface enrichment by increasing the degrees of polymerization of the chains in the blend.[13] Recent experimental measurements justifying the above theoretical conclusions concern experiments on isotopic PS/PDS systems characterized by small values of the w parameter and very small differences between the surface interactions u_A and u_B, where surface enrichment of the deuterated constituent is accomplished only through the use of longer chains.[20-22] Also supportive are experimental studies of symmetrical blends, where a systematic variation of the equal chain lengths of the two components was performed and a surface composition dependence on molecular weight was found.[14,23] Indeed, enrichment is gained at the surface of the longer chains, and the theoretical curves from eq 7 shown in Figure 7 reveal the same trends as those of the experimental observations.

Another interesting factor that can be studied by means of the present analysis is the thickness of the polymeric sample, which is expressed with the length L of the perpendicular dimension of the available space, along the z axis. A plot of the surface fraction versus the length L in Figure 8 shows that the amount of the enriched component increases, as the thickness L of the sample increases, and approaches a limit, indicating that thicker systems exhibit larger enhancement of surface composition. This is in accord with recent experimental observations on the surface of PS/DPS and PS/PVME blend films that have equal weight fractions, nearly equal chain lengths, and various thicknesses. The surface composition of these films has been studied systematically, and a continuous enrichment has been obtained from thinner to thicker films up to a point of critical thickness, where the samples gain no further enrichment.[23,24]

4. Conclusions

Surface enrichment in mixed condensed phases of a system of two polymers has been studied in the framework of a continuous model and described by means of an analytic solution. The surface fractions of the two components are found to depend on two major factors: the product wN that controls the thermodynamic state of the blend and ΔU that characterizes the difference between the interactions of the chains and the surface. Moreover, our results demonstrate that the segregation at the surface can be enhanced by varying the blend composition, the molecular weights of the polymers, the annealing temperature, and the thickness of the sample. Surface composition plays a key role in determining the final use of polymeric blends, and the present theory suggests many new experiments to clarify the relation of surface composition to the molecular and macroscopic characteristics of the blends.

Acknowledgment. This work was funded partially by grants from the Greek General Secretary of Research and Technology.

Appendix

Expanding eq 4 to all orders of the parameters u_A and u_B and evaluating the terms in the two Laplace variables S_A and S_B of N_A and N_B, respectively, yields the following expression for Z_{AB} of two ring chains:

$$\begin{aligned}Z_{AB} = n_A n_B \left(\frac{3}{2\pi l^2}\right)^3 V L_A{}^{-1} L_B{}^{-1} \biggl\{ & \frac{\pi}{\sqrt{S_A S_B}} - \frac{l\pi\sqrt{6}}{12L\sqrt{S_A S_B}} \\ & \biggl[\frac{2u_B\mu_o}{\sqrt{S_B}(\sqrt{S_B} + u_B\mu_o)} + \frac{2u_A\mu_o}{\sqrt{S_A}(\sqrt{S_A} + u_A\mu_o)} - \frac{1}{\sqrt{S_B}} - \\ & \frac{1}{\sqrt{S_A}} - \frac{1}{(\sqrt{S_A} + \sqrt{S_B})} + \frac{2u_B\mu_o}{(\sqrt{S_B} + u_B\mu_o)\,(\sqrt{S_A} + \sqrt{S_B})} + \\ & \frac{2u_A\mu_o}{(\sqrt{S_A} + u_A\mu_o)(\sqrt{S_A} + \sqrt{S_B})} - \\ & \frac{4u_A u_B \mu_o{}^2}{(\sqrt{S_A} + u_A\mu_o)(\sqrt{S_B} + u_B\mu_o)(\sqrt{S_A} + \sqrt{S_B})}\biggr]\biggr\} \end{aligned} \quad (A.1)$$

The evaluation of the inverse Laplace transforms $L_A{}^{-1}$and $L_B{}^{-1}$ of eq A.1 is possible and yields

$$\begin{aligned}
Z_{\mathrm{AB}} = {} & n_{\mathrm{A}}n_{\mathrm{B}}\left(\frac{3}{2\pi l^2}\right)^3 V\biggl\{\frac{1}{\sqrt{N_{\mathrm{A}}N_{\mathrm{B}}}} - \frac{l\pi\sqrt{6}}{12L}\biggl[\frac{1}{\sqrt{\pi N_{\mathrm{A}}}} + \\
& \frac{1}{\sqrt{\pi N_{\mathrm{B}}}} - \frac{1}{\sqrt{\pi(N_{\mathrm{A}} + N_{\mathrm{B}})}} - \frac{2\mathbf{K}(U_{\mathrm{A}})}{\sqrt{\pi N_{\mathrm{A}}}} - \frac{2\mathbf{K}(U_{\mathrm{B}})}{\sqrt{\pi N_{\mathrm{B}}}} + \\
& \frac{4u_{\mathrm{A}}u_{\mathrm{B}}\mu_{\mathrm{o}}}{(u_{\mathrm{A}} + u_{\mathrm{B}})}\mathbf{K}(U_{\mathrm{A}})\,\mathbf{K}(U_{\mathrm{B}}) + \mu_{\mathrm{o}}\biggl(2u_{\mathrm{B}} - \frac{4u_{\mathrm{A}}u_{\mathrm{B}}}{(u_{\mathrm{A}} + u_{\mathrm{B}})}\biggr) \\
& \biggl(\int_0^{N_{\mathrm{B}}}\frac{[(\pi x)^{-1/2} - u_{\mathrm{B}}\mathbf{K}(u_{\mathrm{B}}\mu_{\mathrm{o}}\sqrt{\mathrm{x}})]}{\sqrt{\pi(N_{\mathrm{A}} + N_{\mathrm{B}} - x)}}\,\mathrm{d}x\biggr) + \mu_{\mathrm{o}}\biggl(2u_{\mathrm{A}} - \\
& \frac{4u_{\mathrm{A}}u_{\mathrm{B}}}{(u_{\mathrm{A}} + u_{\mathrm{B}})}\biggr)\biggl(\int_0^{N_{\mathrm{A}}}\frac{[(\pi x)^{-1/2} - u_{\mathrm{A}}\mathbf{K}(u_{\mathrm{A}}\mu_{\mathrm{o}}\sqrt{x})]}{\sqrt{\pi(N_{\mathrm{A}} + N_{\mathrm{B}} - x)}}\,\mathrm{d}x\biggr)\biggr]\biggr\} \qquad \text{(A.2)}
\end{aligned}$$

Though the numerical evaluation of the remaining integrals of eq A.2 is a simple one and furnishes results for $N_{\mathrm{A}} \neq N_{\mathrm{B}}$, we use here the symmetrical case with $N_{\mathrm{A}} = N_{\mathrm{B}} = N$ for which the above integrals can be solved analytically. We use the integral

$$\int_0^{N}\frac{[(\pi x)^{-1/2} - u_i\mathbf{K}(u_i\mu_{\mathrm{o}}\sqrt{x})]}{\sqrt{\pi(2N - x)}}\,\mathrm{d}x = \mathbf{K}(\sqrt{2}U_i) - \frac{\mathbf{K}^2(U_i)}{2} \qquad (i = A, B)$$

and we take eq 6 with

$$\begin{aligned}
F(U_{\mathrm{A}},U_{\mathrm{B}},L) = {} & 1 - \frac{l\sqrt{\pi N}}{L\sqrt{6}}\biggl\{1 - \frac{\sqrt{2}}{4} - \mathbf{K}(U_{\mathrm{A}}) - \mathbf{K}(U_{\mathrm{B}}) + \\
& \frac{2U_{\mathrm{A}}U_{\mathrm{B}}\sqrt{\pi}}{(U_{\mathrm{A}} + U_{\mathrm{B}})}\mathbf{K}(U_{\mathrm{A}})\,\mathbf{K}(U_{\mathrm{B}}) + \frac{U_{\mathrm{B}}(U_{\mathrm{B}} - U_{\mathrm{A}})\sqrt{\pi}}{(U_{\mathrm{A}} + U_{\mathrm{B}})} \\
& \biggl[\mathbf{K}(\sqrt{2}U_{\mathrm{B}}) - \frac{\mathrm{K}^2(U_{\mathrm{B}})}{2}\biggr] + \\
& \frac{U_{\mathrm{A}}(U_{\mathrm{A}} - U_{\mathrm{B}})\sqrt{\pi}}{(U_{\mathrm{A}} + U_{\mathrm{B}})}\biggl[\mathbf{K}(\sqrt{2}U_{\mathrm{A}}) - \frac{\mathbf{K}^2(U_{\mathrm{A}})}{2}\biggr]\biggr\} \qquad \text{(A.3)}
\end{aligned}$$

For the evaluation of the function $H(U_{\mathrm{A}},U_{\mathrm{B}})$ of eq 7 we start from the definition

$$Y_i = -\frac{1}{S}\frac{\partial(\ln Z)}{\partial u_i} \qquad (i = A, B)$$

and Z of eq 2, and using the Z_i of eq 5 and Z_{AB} of eq 6. The surface concentration of the monomers A is then found to be given by eq 7, which includes the function $H(U_{\mathrm{A}},U_{\mathrm{B}})$ given by

$$\begin{aligned}
H(U_{\mathrm{A}},U_{\mathrm{B}}) = {} & 2 - \frac{4U_{\mathrm{A}}U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})}\mathbf{K}(U_{\mathrm{A}}) - \\
& \frac{2U_{\mathrm{A}}\sqrt{2}(U_{\mathrm{A}} - U_{\mathrm{B}})}{(U_{\mathrm{A}} + U_{\mathrm{B}})} + \biggl(1 - \frac{2U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})} + \\
& \frac{4U_{\mathrm{A}}^{\ 2}(U_{\mathrm{A}} - U_{\mathrm{B}})}{(U_{\mathrm{A}} + U_{\mathrm{B}})} + \frac{2U_{\mathrm{A}}U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})^2}\biggr)\sqrt{\pi}\biggl[\mathbf{K}(\sqrt{2}U_{\mathrm{A}}) - \\
& \frac{\mathbf{K}^2(U_{\mathrm{A}})}{2}\biggr] + \biggl(\frac{2U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})} + \frac{4U_{\mathrm{A}}^{\ 2}U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})} - \\
& \frac{(2U_{\mathrm{A}}U_{\mathrm{B}})}{(U_{\mathrm{A}} + U_{\mathrm{B}})^2}\biggr)\sqrt{\pi}\mathbf{K}(U_{\mathrm{A}})\,\mathbf{K}(U_{\mathrm{B}}) - \frac{2U_{\mathrm{A}}U_{\mathrm{B}}}{(U_{\mathrm{A}} + U_{\mathrm{B}})}\mathbf{K}(U_{\mathrm{B}}) - \\
& \frac{2U_{\mathrm{B}}^{\ 2}\sqrt{\pi}}{(U_{\mathrm{A}} + U_{\mathrm{B}})^2}\biggl[\mathbf{K}(\sqrt{2}U_{\mathrm{B}}) - \frac{\mathbf{K}^2(U_{\mathrm{B}})}{2}\biggr] \qquad \text{(A.4)}
\end{aligned}$$

References and Notes

(1) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(2) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978; Vols. 1 and 2.

(3) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; John Wiley & Sons: New York, 1988.

(4) Mittermayer, C.; Lorenz, G.; Klee, D. *J. Apll. Polym. Sci.* **1995**, *57*, 391. Schroeder, K.; Klee, D.; Mittermayer, C. *Ibid.* **1995**, *58*, 699.

(5) Schmidt, I.; Binder, K. *J. Phys.* (*Paris*) **1985**, *46*, 1631.

(6) Nakanishi, H.; Pincus, P. *J. Chem. Phys.* **1983**, *79*, 997.

(7) Jones, R. A. L.; Kramer, E. J. *Polymer* **1993**, *34*, 115.

(8) Chen, Z. Y.; Noolandi, J.; Izzo, D. *Phys. Rev. Lett.* **1991**, *66*, 727. Yeung, C; Desai, R. C.; Noolandi, J. *Macromolecules* **1994**, *27*, 55.

(9) Jones, R. A. L. *Phys. Rev. E* **1993**, *47*, 1437.

(10) Carmesin, I.; Noolandi, J. *Macromolecules* **1989**, *22*, 1689.

(11) Genzer, J.; Faldi, A.; Composto, R. J. *Phys. Rev. E* **1994**, *50*, 2373.

(12) Cohen, S. M.; Muthukumar, M. *J. Chem. Phys.* **1989**, *90*, 5749.

(13) Hariharan, A.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1991**, *24*, 4909.

(14) Hariharan, A.; Kumar, S. K.; Russell, T. P. *J. Chem. Phys.* **1993**, *98*, 4163.

(15) Cifra, P. *J. Chem. Phys.* **1992**, *96*, 9157.

(16) Cifra, P.; Bruder, F.; Brenn, R. *J. Chem. Phys.* **1993**, *99*, 4121.

(17) Pan, D. H.- K. ; Prest, W. M. *J. Appl. Phys.* **1985**, *58*, 2861.

(18) Sakellariou, P. *Polymer* **1993**, *34*, 3408.

(19) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166.

(20) Sokolov, J.; Rafailovich, M. H.; Jones, R. A. L.; Kramer, E. J. *Appl. Phys. Lett.* **1989**, *54*, 590.

(21) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Composto, R. J.; Stein, R. S.; Russell, T. P.; Mansour, A.; Karim, A.; Felcher, G. P.; Rafailovich, M. H.; Sokolov, J.; Zhao, X.; Schwarz, S. A. *Europhys. Lett.* **1990**, *12*, 41.

(22) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.

(23) Hong, P. P.; Boerio, F. J.; Smith, S. D. *Macromolecules* **1994**, *27*, 596.

(24) Tanaka, K.; Yoon, J. S.; Takahara, A.; Kajiyama, T. *Macromolecules* **1995**, *28*, 934.

(25) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.

(26) Garas, G. E.; Kosmas, M. K. *Macromolecules* **1994**, *27*, 667; *J. Chem. Phys.* **1995**, 103, 10790.

(27) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613; **1966**, *88*, 265. Freed, K. F. *Adv. Chem. Phys.* **1972**, *22*, 1.

(28) Kosmas, M. K. *Macromol. Chem. Commun.* **1981**, *2*, 563. Stratouras, G.; Kosmas, M. K. *J. Chem. Phys.* **1995**, *102*, 2239.

(29) Kosmas, M. K. *J. Phys. A: Math. Nucl. Gen.* **1985**, *18*, 539; **1986**, *19*, 3087. Kosmas, M. K.; Douglas, J. F. *J. Phys. A: Math. Gen.* **1988**, *21*, L155. Douglas, J . F.; Kosmas, M. K. *Macromolecules* **1989**, *22*, 2412.

(30) Stratouras, G.; Kosmas, A. M.; Kosmas, M. K. *J. Phys. A* **1990**, *23*, L1317. Stratouras, G.; Kosmas, M. K. *J. Chem. Phys.* **1991**, *95*, 4656.

(31) Stratouras, G.; Kosmas, M. K. *Macromolecules* **1991**, *24*, 6754; Stratouras, G.; Kosmas, M. K. *Macromolecules* **1992**, *25*, 3307.

(32) Reiter, J.; Zifferer, G.; Olaj, O. F., *Macromolecules* **1990**, *23*, 224.

(33) Kosmas,M.; Ten Brinke,G.; Hadziioannou, G., *J. Phys. II Fr.* **1994**, *4*, 501.

(34) Abramowitz, M.; Stegun, I. *Handbook of Mathematical Functions*; Dover: New York, 1970.

(35) Hariharan, A; Kumar, S. K.; Russel, T. P. *Macromolercules* **1990**, *23*, 3584.

(36) Cifra, P.; Karasz, F.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4895. Kumar, S. K.; Tang, H.; Szleifer, I. *Molecular Physics* **1994**, *81*, 867. Rouault, Y.; Dunweg, B.; Baschnagel, J.; Binder, K. *Polymer* **1996**, *37*, 297.

(37) Schmitt, R. L.; Gardella, J. A.; Salvati, L. *Macromolecules* **1989**, *22*, 4489.

MA960567T