Behavior of Isotopic, Binary Polymer Blends in the Vicinity of Neutral Surfaces: The Effects of Chain-Length Disparity

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Received July 9, 1990; Revised Manuscript Received January 25, 1991

ABSTRACT: The segregation of one component of a binary, isotopic polymer mixture to a neutral surface is affected by the difference in surface energy between the two components. We begin by showing that the surface energy differences between segments of isotopic polymers at neutral surfaces, in the mean-field approximation of Scheutjens and Fleer,[1] are caused by differences in their zero-point energies and are *independent* of the chain lengths of the two polymers. When this treatment is extended to include results obtained from lattice and off-lattice Monte Carlo simulations, however, additional terms have to be incorporated to account for the connectivity of the macromolecular chains. It is then shown that chain-length effects are particularly important in the case of a blend of hydrogenated and deuterated polymers and that the surface energy differences between the two components becomes small and approaches zero for specific values of the chain lengths of the two polymers. These results are in excellent agreement with recent neutron reflectivity data on such systems, which will be reported elsewhere. While these results restress the importance of chain connectivity, and the limitations of mean-field calculations in the context of the prediction of the thermodynamic properties of interfacial systems, they have important consequences on determining the surface segregation of a deuterated polymer from a protonated/deuterated mixture of different chain lengths.

1. Introduction

The behavior of a polymeric melt in the vicinity of a neutral surface has been studied recently by a number of theoretical models,[1-3] computer simulations,[4,5] and experiments.[6,7] Interest has focused on bimodal systems near a surface[1,6,7] to study the effects of polydispersity on surface behavior. In an earlier paper,[1] we showed that an athermal polymer melt with a bimodal molecular weight distribution in the vicinity of a hard, energetically neutral surface equilibrates to a state in which the shorter chains segregate to the surface, driven purely by entropic factors.

Here the effect of having a binary polymer blend in the vicinity of an energetically neutral surface is examined. Although the surface is neutral, we show that there is a surface energy difference between the two species in the blend and attribute this to two facts: First, the presence of the wall ensures that all species at the surface feel a loss of potential energy since they have no neighbors on one side. The difference in potential energy loss between the A and the B species at the surface thus results in a surface energy difference between the two species (or a chemical potential difference, μ, in the language of Jones et al.[6]). Second, the difference in the loss of potential for the A and B segments can be related directly to the energetic interactions between A–A and B–B segments in the bulk, respectively, if one adopts a mean-field lattice model like that of Scheutjens and Fleer.[1-3] Thus, the chemical potential difference of a binary isotopic polymer blend at a neutral surface (such as a vacuum), which determines the surface segregation of one component in the blend, can be calculated simply from knowledge of their bulk properties. This information is critical for understanding surface experiments that require labeling of one of the species, for example, by deuteration. It has been shown that,[6] in some cases, there is significant segregation of the deuterated component to the air (vacuum)–polymer interface. The initial calculations that we present here are obtained from the use of a mean-field lattice model for polymeric blends near surfaces[1-3] and enable us to highlight and quantify the physical parameters that cause these effects and to emphasize that these results are relevant even for systems that are far away from their upper critical solution temperature (UCST). Subsequently, we extend these calculations to account for the connectivity of chain molecules in a more accurate fashion through the use of results obtained from Monte Carlo simulations.[4,5] The more sophisticated calculations are thus able to derive the chain-length dependence of the chemical potential difference parameter, μ_1. The consequences of these results on the surface segregation of isotopic polymer blends of varying chain lengths will then be examined.

2. Calculation of Surface Energy Differences

2.1. Mean-Field Calculations. Consider the surface energy difference between small isotopic molecules or between segments of isotopic polymer chains at a neutral surface. Bates et al.[8] studied the energetic interactions between protonated and deuterated segments in the bulk and demonstrated that the relevant Flory–Huggins interaction parameter, χ, has two contributions. The first, χ_v, results from the slightly different segmental volumes between the two monomers. The second factor, χ_d, arises from the different polarizabilities between the two segments, which leads to a dispersive force between the isotopic monomers. To estimate the surface energy differences between deuterated and protonated monomers near a neutral surface, such as a hard wall or air at low temperatures (which behaves effectively as a wall with a root-mean-square roughness of 0.3–0.5 nm)[9] [characterized by $\chi_s = (U_{sD} - U_{sH})/k_BT$], it is assumed that changes in volume of mixing play a relatively small role in determining χ_s. The initial stages of the development presented herein follow the earlier work of Nakanishi and Pincus, who estimated the difference in surface energies between two species near an interacting surface,[10] and follow exactly

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from the lattice treatments of Scheutjens and Fleer[1] when extended to the case of a polymer blend near a neutral surface.[2,3] In this model one treats the polymer–neutral wall interface through the device of a cubic lattice model, and the total energy of the system in the mean-field approximation includes a surface energy parameter, χ_s, which can be represented *independent of the chain length of the two species* as

$$\chi_s = \zeta(\epsilon_{DD} - \epsilon_{HH})/k_B T \qquad (1)$$

where ϵ_{DD} and ϵ_{HH} are the net interaction energies experienced by deuterated and hydrogenated monomers in the bulk, respectively, and ζ $(={}^1/_6)$ characterizes the fraction of missing neighbors for a segment in the immediate vicinity of the surface. Equation 1 can be physically understood as follows: when a purely protonated (deuterated) material is placed near a neutral surface, a segment in the vicinity of the wall feels a loss of potential energy due to the fact that it has neighbors on one side but a noninteracting wall on the other. Thus, χ_s, the dimensionless surface energy difference is a measure of the dissimilarity in the interactions of the segments of the two pure polymers and dictates that the component with lower segment–segment interaction will be preferentially adsorbed on the surface to minimize the free energy of the composite system.

Since the systems of interest interact only through dispersive forces, the total interaction energy experienced by a monomer can be evaluated through the London formula for dispersive interactions between a pair of monomers.[11] To simplify the final result and to contrast them with bulk properties, we scale the expression obtained for χ_s with the expression for χ_d (the dispersive contribution to the interaction parameter in the bulk) as reported by Bates et al.[8]

$$\chi_s/\chi_d = (\alpha_H/V_H + \alpha_D/V_D)(\alpha_H/V_H - \alpha_D/V_D)^{-1}(2\zeta) \qquad (2)$$

where α_H and α_D represent the polarizabilities of hydrogenated and deuterated monomers, respectively, and V_H and V_D represent the segmental molar volumes of the two isotopes. For the case of a deuterated polystyrene/normal polystyrene mixture near a neutral surface, eq 2 predicts that χ_s assumes a value that is ca. 50 times larger than χ_d in the bulk, independent of the chain length of the constituent polymers. At 454 K, therefore, χ_s assumes a value that is ca. 18 J/mol, which in the notation of Kramer and his co-workers also results in a μ_1 $(=a\chi_s$, where a is the segment size) value of 0.0033 nm.[6,7] This result should be compared to the value of 0.0024 nm obtained from the experimental results on PSH/PSD systems of molecular weight $1.80 \times 10^6/1.03 \times 10^6$. The calculations presented above and the experimental results for the chemical potential difference, μ_1, are in reasonable agreement.

It should be emphasized, however, that eq 1 has been derived in the framework of an extremely coarse grained, mean-field description of the interfacial polymer blend.[2] In such an approximation chain connectivity is lost to the extent that conformations involving immediate reversal of chain trajectory, and hence the double occupancy of a lattice site, are only precluded in a probabilistic, mean-field sense. The same reasoning therefore predicts that the surface energy differences between protonated and deuterated chain segments will be constant, independent of chain length of the two polymers. Below we will present a treatment that incorporates the chain-length dependence of this quantity to a zeroth order and show that this quantity is strongly affected by the variation of the chain lengths of the two polymers in the system.

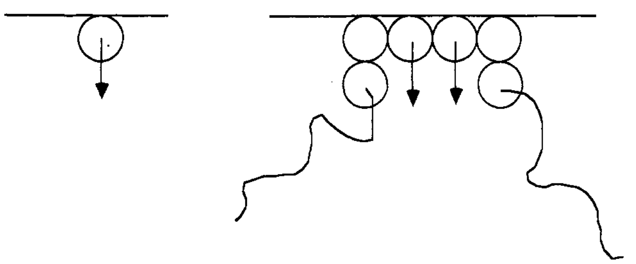

Figure 1. Schematic sketch of the structure and interactions experienced by a polymer chain in the vicinity of a wall. A small molecule at a surface is also shown for comparison.

2.2. Results Incorporating Chain Connectivity. Before we proceed to consider the case of polymers, we must reexamine the assumptions made in deriving μ_1 $(=a\chi_s$, where a is the segment size) above. In it we have assumed that ζ, the parameter that relates the potential energy lost by a monomer at the surface compared to the bulk value of the energy of interaction per monomer, will assume a value of ${}^1/_6$. This will continue to be approximately true in the case of a polymer, a result that we have also verified recently through off-lattice Monte Carlo simulations.[12] One may now proceed to derive the density distribution of monomers along the x, y, and z directions, utilizing a classical approach such as a lattice model[1-3] or utilizing the self-consistent-field method as proposed by Edwards[13] and de Gennes.[14] Most models for polymer chains near surfaces,[15] however, assume that the distribution of monomers in the x–y directions (parallel to the plates) is isotropic and thus solve only for the density distribution of monomers in the z direction (perpendicular to the plates). A necessary criterion for this to be true is that the potential of mean force between segments of polymer chains[16] should be unaffected in the x–y direction and that all the effects of the surface should manifest themselves as variations in the potential of mean force along the z direction.

As can be seen in Figure 1, however, such an assumption will be valid only in the case of a monomer fluid in the vicinity of a neutral surface. In the case of polymer chains, the total potential energy of the interfacial system is essentially independent of the chain lengths of the constituent chains. When we consider polymeric species, however, an important factor that has to be considered is that macromolecular structure in the vicinity of a surface is a combination of surface walks, as well as loops and tails. As shown in Figure 1, the presence of such a structure will modify the potential of mean force along the z direction since the two beads at either end of the surface walk, being bonded to beads on the next layer, will not experience any attraction into the film. The potential of mean force along the z direction is thus a strong function of the length of the surface walks associated with the polymer chains in the system. Since the total potential energy of the interfacial system is essentially independent of the length of the constituent chains (and hence the length of surface walks, loops, and tails), this statement implies that the potential of mean force along the x–y direction is also a function of z. An accurate solution to the concentration profile for the segments of the isotopic polymer chains in the vicinity of the surface could then only be obtained if one solved the problem in a three-dimensional self-consistent-field approximation, with a value for the loss of potential energy that is essentially independent of the constituent chains. On the other hand, if one were to resort to a one-dimensional calculation such as the one proposed by Schmidt and Binder,[15] then one can no longer adopt the total loss of potential energy as the driving force for determining the concentration profile for the segments of the polymer chains in the vicinity of the surface. Rather, it would be more accurate if one utilized the potential of mean force along the z direction as the driving force that would cause the segregation of one component of the isotopic mixture to segregate to the neutral surface. In this context, it should be strongly stressed that the use of the potential of mean force along the z direction is necessarily an approximation that allows one to treat this problem as a one-dimensional case. The most accurate solution would necessarily preclude this approximation but would entail the calculation of monomer density in three dimensions in a coupled fashion, a problem that is more complicated and not easily amenable to analytical solution.

We now proceed to evaluate the potential of mean force along the z direction for the monomers in the immediate vicinity of the surface. Monomers in other lattice layers are assumed to be unaffected by the surface as suggested by our earlier off-lattice Monte Carlo simulations on the structure and conformations of polymer melt chains in the vicinity of a neutral surface.[4] These Monte Carlo simulations on a polymer melt near a surface[4] have also established the functional form for the variation of surface walk sequences as a function of polymer chain length, a result that is in quantitative agreement with results obtained from a mean-field cubic lattice model for the same system.[12]

$$\langle l \rangle = 4.64 - 5.59n^{-1/2} \; (n \geq 50) \tag{3}$$

Here $\langle l \rangle$ denotes the ensemble-averaged value for the length of surface walks for a system comprised of chains of length n and is valid only for chains of length 50 repeat units or higher. Clearly, this equation does not approach its proper lower limit of 1 when the chain length approaches 1. Therefore, such a result can only be utilized for the case of a polymeric system and must not be used for oligomeric systems. In all further usage this minimum chain-length criterion will be maintained and thus establishes the approximate region of validity of the resultant equations. The results for $\langle l \rangle$, as mentioned above, were obtained from an off-lattice simulation[4] and were shown to be in good agreement with the results obtained from a mean-field lattice model for a polymer melt near a surface. This result further establishes that it is appropriate for one to model a neutral wall–polymer melt interface with a cubic lattice model.

Under these conditions one can write that a segment of a protonated chain (from a homopolymer melt) will, on average, feel an attractive force into the film, and the corresponding potential of mean force along the z direction can be represented by

$$\epsilon_{s,HH} = \epsilon_{HH}\zeta(1 - 2/\langle l \rangle_H) \tag{4}$$

$$= \epsilon_{HH}\zeta(1 - 2[4.64 - 5.59n_H^{-1/2}]^{-1}) \tag{5}$$

where $\zeta = {}^1/_6$, and ϵ_{HH} represents the interaction potential experienced by a protonated monomer in the bulk. Here, account has been taken of the fact that the two end beads on a surface walk do not feel any attractive force into the bulk. We can then write an equation, analogous to eq 1, that will be valid for a system comprised of protonated and deuterated chains of different lengths

$$\chi_s = (\epsilon_{s,HH} - \epsilon_{s,DD})/k_BT \tag{6}$$

$$= \zeta\{\epsilon_{HH}(1 - 2[4.64 - 5.59n_H^{-1/2}]^{-1} - \epsilon_{DD}(1 - 2[4.64 - 5.59n_D^{-1/2}]^{-1}\}/k_BT \tag{7}$$

wherein we have assumed that the average length of surface walks for one species is unaffected by the presence of a second component. Since the systems of interest only interact through dispersive forces, one may then utilize the London formula to relate the bulk interaction potentials (ϵ_{HH} and ϵ_{DD}, respectively) to the polarizabilities of the C–H and the C–D bonds.[8,11] To make this conversion easier, we scale χ_s with χ_d, the dispersive component of bulk interaction parameter as calculated by Bates et al.[8] Thus, eq 7 can now be rewritten as

$$\frac{\chi_s}{\chi_d} = \frac{1}{3(\alpha_H/V_H - \alpha_D/V_D)^2}\left\{\alpha_H^2V_H^{-2}\left(1 - \frac{2}{[4.64 - 5.59n_H^{-1/2}]}\right) - \alpha_D^2V_D^{-2}\left(1 - \frac{2}{[4.64 - 5.59n_D^{-1/2}]}\right)\right\} \tag{8}$$

Alternately, eq 8 can thus be rewritten for the case of a PSH/PSD system at 184 °C, in the notation of ref 6 (where $\mu_1 = a\chi_s$), as

$$\mu_1 = 0.0034 - 0.256[4.64 - 5.59n_H^{-1/2}]^{-1} + 0.246[4.64 - 5.59n_D^{-1/2}]^{-1} \tag{9}$$

where μ_1 is in units of nanometers. Equation 9 therefore represents the final expression for the variation of the chemical potential difference for a PSH/PSD system of varying chain lengths of the two components. It should be noted that our results do not include any temperature or composition dependence for the surface energy difference. We do not have detailed information for the variation of the surface walk lengths as a function of temperature and composition and therefore cannot make predictions regarding these effects. However, as has been noted in earlier work,[4] the results for the $\langle l \rangle$, obtained for an energetically interacting melt at 400 K near a neutral wall, smoothly approach the value obtained for an infinitely long, athermal system (i.e., temperature-independent value) when one examines the limit $n \rightarrow \infty$ for eq 3.[17] We therefore surmise that eq 8 is temperature independent, thus allowing χ_s (or μ_1/a) to have the same temperature dependence as the dispersive part of χ_d. We note further that Bates and his co-workers[18] have derived a chain length and composition dependence for the bulk interaction parameter, χ. A similar analysis for χ_s should, in principle, yield the appropriate composition and chain-length dependence for this parameter.[21] We have not attempted to perform such an analysis since such a model is beyond the scope of the work that is reported here. However, as suggested by these authors,[18] the numerical values for χ_s derived in this work should be valid in the case where one has approximately equal amounts of each of the isotopic polymers in the bulk and corrections due to variation in composition will only play a significant role in cases where one has a large amount of either one of the two components. It should also be noted that several other factors have not been incorporated in the calculation of χ_s:

(i) We have ignored any volume (or area) changes on mixing the H and D components. As noted by Bates et al.,[8] these effects can be significant and can in some cases account for ca. 33% of the calculated value of χ_d. It is thus anticipated that such effects will affect the chemical potential difference but will not alter the general conclusions that are drawn here. However, quantitative predictions are expected to be affected significantly.

(ii) In the calculation of χ_{HD} (the interaction parameter between H and D segments in the bulk, including dispersive contributions and volume change effects) Bates et al.[8] point to the presence of a noncombinatorial entropy term that contributes to the final value of this parameter. It is clear that such terms, which may also be thought of as corrections to the Flory–Huggins equation for the free energy of mixing polymers, will play a role in determining the final value of the surface energy differences. Such factors cannot be accommodated in the framework of the model developed here but could possibly be accounted for if one chose to model the system of interest through the use of integral equation techniques.[19]

(iii) In this context we have assumed that the air surface will behave in a fashion that is similar to a hard, flat two-dimensional surface. It should be emphasized that such a surface will not be flat due to thermal fluctuations, a result that is consistent with experimental findings that suggest that the air surface has a root-mean-square roughness of 0.3–0.5 nm. Clearly, the assumption of the air surface as flat makes the quantitative validity of the proposed theory questionable.

In light of these factors it is stressed that the proposed theory should be used carefully if one desires to model such interfacial systems quantitatively. However, the trends predicted by this theory are expected to be qualitatively correct in modeling situations of interest. Further, it should be stressed that the predicted values are extremely sensitive to the values utilized in eq 8 for the polarizabilities as well as molar volumes for the two isotopic polymers and that even small errors in their determination can lead to predictions for μ_1 that may not be quantitatively accurate.

3. Results and Discussion

Before examination of the predictions of eq 9 at finite molecular weights, it is interesting to inspect its behavior when both chains are of infinite molecular weight. It should be recognized that such a situation is unattainable in reality since such a protonated/deuterated mixture will be immiscible. At this limit, for a PSH/PSD mixture eq 8 predicts that μ_1 (alternately $a\chi_s$) assumes a value of 0.0029 nm. It may be seen that moving from a monomer fluid to an infinite molecular weight system has reduced the chemical potential difference. The origin of the lower value of μ_1 in the case of a polymeric fluid can be attributed to the fact that some of the C–H and C–D bonds at the surface do not feel an attractive force into the bulk since they are bonded to other monomers in the interlayers of the lattice. Thus, the net attraction for the C–H and C–D bonds is lower than in the case of a monomeric fluid, leading to a surface energy difference that is somewhat reduced in magnitude in the case of polymers as compared to a monomeric mixture near a surface.

We now examine the predictions of eq 9 for finite molecular weights. For the system examined in ref 6 corresponding to a system of PSH/PSD of molecular weights $1.8 \times 10^6/1.03 \times 10^6$ (i.e., chain lengths 17 300/9900), eq 9 yields $\mu_1 = 0.0021$ nm. Consequently, finite molecular weights of the polymers do influence the chemical potential difference.

Having examined the behavior of eq 9 for one PSH/PSD system, we proceed to inspect its behavior over a range of chain lengths. In Figure 2 we plot the variation of μ_1 with $n_H^{-1/2}$ (where n_H is the chain length of the protonated polymer) for deuterated chains of length 500, 1000, and 10 000 repeat units, respectively. It can be seen that reducing the chain length of the protonated species, in all cases, reduces the chemical potential difference. In one case (corresponding to $n_D = 10\,000$) the surface energy difference becomes negative for relatively large values of n_H (i.e., for $n_H <$ ca. 700) suggesting that the presence of hydrogenated segments at the surface is energetically preferred. While this represents a surprising result, it reemphasizes the delicate balance of forces at the surface, dictating which species will preferentially segregate to a neutral surface at equilibrium.

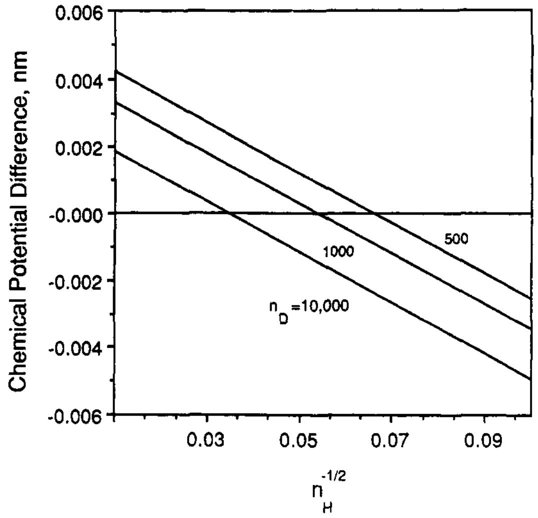

Figure 2. Variation of the chemical potential difference, μ_1, as a function of $n_H^{-1/2}$ (n_H is the chain length of the protonated polystyrene) for three different values of n_D = 10 000, 1000, and 500.

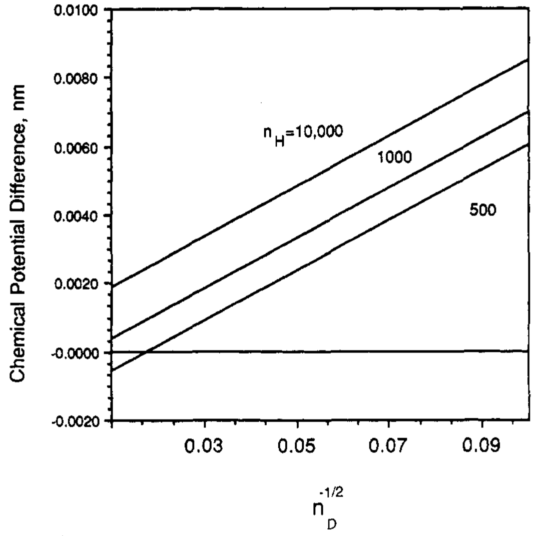

Figure 3. Variation of the chemical potential difference, μ_1, as a function of $n_D^{-1/2}$ (n_D is the chain length of the deuterated polystyrene) for three different values of n_H = 10 000, 1000, and 500.

An important result that emerges from this analysis is that the chemical potential difference assumes a value of 0 for a specific combination of a high molecular weight deuterated chain and a low molecular weight protonated polymer. This result is particularly interesting, if accurate, since it permits the examination of preferential segregation to the surface due to chain-length effects alone without perturbations due to labeling.

We have also examined the case where the variation of μ_1 with n_D is examined for fixed values of n_H. This is shown in Figure 3 where results for three different values of n_H are shown. In contrast to Figure 2, it is seen that the μ_1 increases as one decreases n_D for all values of n_H.

The major conclusion of this analysis is that the chemical potential difference, μ_1, is strongly influenced by the chain lengths of the two isotopic polymers. Further, by tuning the chain lengths of the protonated and deuterated chains, one can make μ_1 approach a value of zero, in which limit there will be no energetic preference to place protonated or deuterated segments at the neutral surface. We have recently performed neutron reflectivity measurements on PSH/PSD mixtures of different chain lengths and find that there is indeed a reversal as predicted by the theory and that for a PSD of molecular weights 500K and 100K one finds a PSH of molecular weights less than 52K and 30K, respectively, partitioning preferentially to the air surface. (These experiments were conducted for a 50% volume mixture of each species in the bulk.[20]) These preliminary experimental results thus verify the validity of the theory that has been presented in this work, since it predicts a crossover at PSH molecular weights of ca. 60K and 30K for the two different PSD molecular weights employed in these experiments.

Acknowledgment. We gratefully recognize the financial support provided by the IBM Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CTS-9009949).

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(21) We have examined the calculations of Bates et al.[18] to probe the possibility that the chemical potential difference between the monomers may reverse in sign due to monomer–monomer correlations and fluctuations. It was found that the bulk Flory parameter reversed sign at 50% by volume of PSH (ca. 18K) and PSD (1000K). Since this number does not agree with the results reported here, we cannot conclude if the same effects may contribute to the reversal in sign of μ_1. However, it is to be noted that sequence lengths at surface obtained from the Monte Carlo simulations automatically account for monomer fluctuations and hence, in principle, should be devoid of any artifacts inherent in Flory theories of polymer solutions.

Registry No. PS, 9003-53-6.