Orientation-Dependent Interactions in Polymer Systems. 2. Segmental Orientation in Binary Blends

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ABSTRACT: On the basis of the Di Marzio-type lattice model and the freely-jointed-chain model with a statistical distribution of segment length, there were obtained analytical equations that describe the segmental orientations in a weakly deformed system containing two polymers of arbitrary length and arbitrary flexibility. The equations include several new predictions: for example, when a cross-linked polymer 1 swollen by an un-cross-linked polymer (diluent) 2 is deformed by a stretch, the excluded-volume or packing effect brings about an excess orientation of segment 1 over that which would be observed in the absence of the volume effect. This excess orientation increases as the rigidity and/or the contour length of the diluent as well as the rigidity of polymer 1 increase. At the same time, the diluent is also oriented. The amount of this "induced" orientation of the diluent also depends on the lengths and flexibilities of the two components as well as on the composition. The theory suggests that the amount of excess or induced orientation can be very large, in general. Some reported experimental results were discussed in light of the theory.

On the basis of lattice theories and gas-of-rods theories, we previously examined the effects of orientation-dependent intermolecular interactions on the segmental orientation in weakly deformed polymer systems.[1] There we showed in a somewhat general fashion that the orientation-dependent excluded-volume effect could give rise to a considerable amount of excess orientation over that expected for a "gaslike" system in which intermolecular interactions are absent. For example, a system of freely-jointed chains comprising rodlike segments of axial ratio 2, which would approximate the flexibility of common vinyl polymers like polyethylene, was predicted to show a relative excess orientation ranging roughly from 30 to 100%, depending on the theories and models.

In this paper, we extend the theory to weakly deformed systems containing two polymers differing in flexibility and/or chain length. The second polymer can be an oligomeric chain, a rodlike particle, or an asymmetric solvent. Examination of such binary systems is important not only for the interest in themselves but also for designing powerful experiments to directly test the reality of the predicted effects of intersegmental interactions. Unlike the previous work,[1] the theory developed here will be based solely on the lattice model of the Di Marzio type.[2] This model has been shown to provide a moderate and perhaps reasonable estimate of the packing entropy.[1] In addition, it is simple enough to be extended to a multicomponent system of any order. Even though there is no essential difficulty in extending the theory to systems with more than two components or in developing a theory based on a different chain model and/or a different packing model, the results given here will suffice to demonstrate essential features of multicomponent systems. Some comparison will be made between theory and published experimental data.

Theoretical Section

Molecular Model. Previously,[1] we considered the freely-jointed chain comprising m rodlike segments of uniform length b ($m \gg 1$). Here we modify the model so that we can treat long as well as short chains including small rodlike molecules. The chain considered here also comprises rodlike segments linearly connected by freely rotating joints, but the joints are assumed to be randomly distributed along the chain. The reciprocal population density of joints defines the mean segment length or persistence length b of long enough chains. The "effective" segment length b', the expectancy of the segment length of a chain with a finite length L, is

$$b' = b(1 - e^{-m}) \quad (1)$$

$$m = L/b \quad (2)$$

where m is the number of segments measured by the persistence length. The parameter m should not be confused with the number of "submolecules" n defined by

$$n = L/D \quad (3)$$

where D is the diameter of the rodlike segment.

The "effective" number of segments m' per chain

$$m' = m + 1 \quad (4)$$

represents the degree of orientational freedom of the chain ($m' - 1$ is the mean number of joints per chain; note that $m' \neq L/b'$ because of the difference in the averaging process), which is important in the discussion of the orientational entropy (see below). Clearly, when $L \rightarrow 0$ or $m \rightarrow 0$, b' tends to L, and m' to unity. When $m \rightarrow \infty$, b' and m' equal b and m, respectively, consistent with the previously used model.[1] It can be shown that the model introduced here is equivalent to the Kratky-Porod wormlike chain,[3] insofar as mean dimensions such as the mean-square end-to-end distance and the mean-square radius of gyration are concerned. They are different in orientational entropy, however.[1]

Packing Entropy. Consider a cubic lattice XYZ with N_0 sites, in which a total of N molecules are being packed. The molecules can be different in length but are assumed to be the same in diameter. The ith molecules, whose length is L_i, are divided into n_i submolecules each of the same size as a lattice site; hence the number of "bonds" in this molecule is $n_i - 1$. Here we have implicitly assumed that n_i is identical with the number of submolecules given

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by eq 3. It holds that

$$N_0 = \sum_{i=1}^{N} n_i \tag{5}$$

The ith molecules are packed in the lattice XYZ in such a manner that a fraction p_i of the bonds lie in the direction X and a fraction q_i of the bonds with

$$q_i = (1 - p_i)/2 \tag{6}$$

lie in each of the directions Y and Z. Following Di Marzio,[1,2] we readily obtain the probability ν_{r+1} that the $(r+1)$th molecule is successfully placed in the lattice after r molecules have been placed.

$$\nu_{r+1} = \left(\frac{N_0 - \sum_{i=1}^{r} n_i}{N_0}\right)\left[\frac{N_0 - \sum_{i=1}^{r} n_i}{N_0 - \sum_{i=1}^{r}(n_i - 1)p_i}\right]^{p_{r+1}(n_{r+1}-1)} \times \left[\frac{N_0 - \sum_{i=1}^{r} n_i}{N_0 - \sum_{i=1}^{r}(n_i - 1)q_i}\right]^{2q_{r+1}(n_{r+1}-1)} \tag{7}$$

On the right-hand side of eq 7, the first term refers to the first submolecule, the second term to the bonds in the direction X, and the last term to the bonds in the other two directions. Note that this counting process does not ask in which order the bonds in the three directions are placed. That is, it is independent of the chain conformation or rigidity. This is commonly the case with all packing entropy theories devised so far.[1]

The total number of ways to place N molecules is proportional to

$$\Omega = \prod_{r=1}^{N} \nu_r \tag{8}$$

The packing entropy S_p is obtained from $k \ln \Omega$, where k is the Boltzmann constant. Use of the standard approximations[1,2,4] to eqs 7 and 8 gives the orientation-dependent terms of S_p, which reads

$$S_p/k = N_0[1 - N_0^{-1}\sum_{i=1}^{N}(n_i - 1)p_i] \times \ln [1 - N_0^{-1}\sum_{i=1}^{N}(n_i - 1)p_i] + 2N_0[1 - N_0^{-1}\sum_{i=1}^{N}(n_i - 1)q_i] \ln [1 - N_0^{-1}\sum_{i=1}^{N}(n_i - 1)q_i] \tag{9}$$

For a binary mixture of a polymer ($n > 1$) and a symmetrical solvent ($n = 1$), eq 9 reduces to the Di Marzio result.[1,2]

Orientation in Weakly Deformed Binary Systems. As previously,[1] the excess free energy ΔF of a "real" system over that of the hypothetical gaslike system is written

$$\Delta F/T = (E_0/T) - (S_p + \Delta S_0) \tag{10}$$

where T is the temperature, E_0 is the orientation-dependent terms of internal energy, and ΔS_0 is the excess orientational entropy. The ΔS_0 of the system composed of N long freely-jointed chains each comprising m segments is given by

$$\Delta S_0/k = -(5/2)mN(\eta - \eta^*)^2 \quad \text{(eq 12, ref 1)} \tag{11}$$

where η is the order parameter, $\eta = (3/2)\langle\cos^2\theta\rangle - 1/2$, and an asterisk denotes the gaslike system. The energy term is given in the form

$$E_0/k = -N_0\phi^2 B\eta^2 \quad \text{(eq 24, ref 1)} \tag{12}$$

where ϕ is the volume fraction of the polymer.

Here we consider an incompressible binary mixture composed of N_1 molecules of type 1 and N_2 molecules of type 2.

$$N = N_1 + N_2 \tag{13}$$

$$N_0 = n_1N_1 + n_2N_2 \tag{14}$$

$$\phi_1 = n_1N_1/N_0 = 1 - \phi_2 \tag{15}$$

Now we assume that the system is weakly deformed by an external force field so that the segments in the gaslike system become oriented to the extent η_1^* and η_2^*, and those in the real system, to the extent η_1 and η_2. By analogy to eqs 11 and 12, the associated orientational entropy and internal energy may be given by

$$\Delta S_0/k = -(5/2)[m_1'N_1(\eta_1 - \eta_1^*)^2 + m_2'N_2(\eta_2 - \eta_2^*)^2] \tag{16}$$

$$E_0/k = -N_0[\phi_1^2B_{11}\eta_1^2 + \phi_2^2B_{22}\eta_2^2 + 2\phi_1\phi_2B_{12}\eta_1\eta_1] \tag{17}$$

where B_{ij} is a constant characterizing the dispersive interaction between submolecules i and j ($i,j = 1$ or 2). Equation 17 was introduced rather intuitively without a rigorous justification but should be useful to describe the system, at least phenomenologically. Note that m' instead of m is used in eq 16 to take account of the short-chain effect (see eq 4 and the statements following it).

The packing entropy of the binary system is obtained from eq 9, which is expanded around $p_i - 1/3 = (3/2)\eta_i = 0$ ($i = 1$ or 2) to yield

$$S_p/k = AN_0(\eta_1\phi_1' + \eta_2\phi_2')^2 \tag{18}$$

$$A = (3 - \phi_1' - \phi_2')^{-1} \tag{19}$$

with

$$\phi_i' = \phi_i(1 - n_i^{-1}) \quad (i = 1 \text{ or } 2) \tag{20}$$

$$\phi_1 + \phi_2 = 1 \tag{21}$$

Equilibrium orientation is obtained by minimizing eq 10 with eqs 16–18 with respect to both η_1 and η_2:

$$\left(\frac{\partial \Delta F}{\partial \eta_1}\right)_{T,V,\eta_2} = \left(\frac{\partial \Delta F}{\partial \eta_2}\right)_{T,V,\eta_1} = 0 \tag{22}$$

Solving these equations for η_1, we have

$$\eta_1 = \{[1 - (2/5)(Ax_2''\phi_2' + \tilde{B}_{22}x_2'\phi_2)]\eta_1^* + (2/5)(Ax_1''\phi_2' + \tilde{B}_{12}x_1'\phi_2)\eta_2^*\}/ \{1 - (2/5)A(x_1''\phi_1' + x_2''\phi_2') - (2/5)(\tilde{B}_{11}x_1'\phi_1 + \tilde{B}_{22}x_2'\phi_2)\} \tag{23}$$

$$x_i' = x_i/(1 + m_i^{-1}) \tag{24}$$

$$x_i'' = x_i(1 - n_i^{-1})/(1 + m_i^{-1}) \tag{25}$$

$$\tilde{B}_{ij} = B_{ij}/T \quad (i,j = 1 \text{ or } 2) \tag{26}$$

where x_i is the segmental axial ratio

$$x_i = b_i/D_i \tag{27}$$

or equivalently (cf. eqs 1–4)

$$x_i = n_i/m_i \tag{28}$$

To obtain η_2, exchange 1 and 2 in eq 23.

Discussion

On the basis of the modified freely-jointed-chain model and the Di Marzio-type lattice theory, we have obtained an analytical expression for the segmental orientations in weakly deformed systems containing two polymers of arbitrary length and flexibility. For generality, we have taken into account energetic or "soft" interactions as well as the excluded-volume or "hard" interactions. In what follows, we will neglect soft interactions or assume that $B_{ij} = 0$, for simplicity. This of course will not generally be true, but presently it is difficult to estimate the magnitude of B_{ij}. Equation 23 indicates that the B_{ij} terms contribute to orientation just like other terms that derive from the excluded-volume interactions. It should therefore be noted that any estimate of segmental orientation that will be gained by neglecting the B_{ij} terms can still be too low.

Particularly interesting is the case in which only polymer 1 is externally deformed through, e.g., cross-links, while no external force field is applied to polymer 2; viz., $\eta_1^* > 0$ and $\eta_2^* = 0$. From eq 29 (with $B_{ij} = 0$) we have the equilibrium orientations η_1 and η_2 of the two types of segments relative to the external deformation η_1^*:

$$\eta_1/\eta_1^* = 1 + \frac{(2/5)Ax_1''\phi_1'}{1 - (2/5)A(x_1''\phi_1' + x_2''\phi_2')} \tag{29}$$

$$\eta_2/\eta_1^* = \frac{(2/5)Ax_2''\phi_1'}{1 - (2/5)A(x_1''\phi_1' + x_2''\phi_2')} \tag{30}$$

with $\phi_1 + \phi_2 = 1$ (see also eqs 19, 20, and 25). These equations include several interesting predictions, as will be discussed below.

Blends of Two Long Polymers. When n_1, n_2, m_1, and m_2 are all large enough, eqs 29 and 30 reduce respectively to

$$\eta_1/\eta_1^* = 1 + \frac{x_1\phi_1}{5 - (x_1\phi_1 + x_2\phi_2)} \tag{31}$$

$$\eta_2/\eta_1^* = \frac{x_2\phi_1}{5 - (x_1\phi_1 + x_2\phi_2)} \tag{32}$$

Equations 31 and 32 should be compared with the previous results[1] for a system with one long polymer and one symmetrical solvent, which can be recovered from eqs 29 and 30 with $n_1^{-1} = m_1^{-1} = 0$ and $n_2 = 1$:

$$\eta_1/\eta_1^* = 1 + \frac{2x_1\phi_1}{15 - (5 + 2x_1)\phi_1} \tag{33}$$

$$\eta_2/\eta_1^* = 0 \tag{34}$$

Both eqs 31 and 33 show that $\eta_1/\eta_1^* > 1$; i.e., polymer 1 becomes more oriented due to the excluded-volume effect, as has been already noted.[1] Comparison of the two equations, however, provides the new prediction that polymer 1 is more oriented when mixed with a polymer, particularly with a less flexible polymer, than with a symmetrical solvent. In Figure 1, eqs 31 and 33 are compared for several different x_2 values with a fixed x_1 value of 2, a typical value of flexible polymers.[1] When $\phi_1 = 1$, the ratio η_1/η_1^* amounts to $^8/_5$. When compared at a common value of ϕ_1 between 0 and 1, polymer 1 becomes more and more oriented as x_2 or the rigidity of polymer 2 increases.

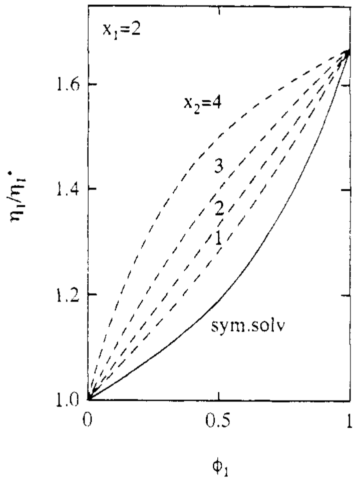

Figure 1. Plot of η_1/η_1^* vs ϕ_1 for $x_1 = 2$ and several values of x_2 (broken curves). The solid curve is for a symmetrical solvent ($n_2 = 1$): see eqs 31 and 33.

Equation 32 predicts that polymer 2 itself becomes also oriented due to the orientation of polymer 1. The amount of this induced orientation is a function of x_1, x_2, and ϕ_1. For $\phi_1 = 1$ and $x_1 = x_2 = 2$, η_2 amounts to $^2/_3$ of η_1^*. The ratio η_2/η_1 which reads

$$\eta_2/\eta_1 = x_2(1 - \phi_2)/(5 - x_2\phi_2) \tag{35}$$

is perhaps more easily accessible experimentally. This ratio has a maximum of $x_2/5$ for $\phi_2 = 0$.

Blends of a Long Polymer and a Short Polymer. One of the most striking effects of the excluded-volume interaction may be observed in the stress-optical coefficient of a polymer network swollen by an asymmetric solvent. Let us assume that the cross-linked polymer 1 is swollen in solvent 2 and weakly deformed uniaxially. The strength of the birefringence of the hypothetical gaslike system would be proportional to $\phi_1\Gamma_1\eta_1^*$, while that of the real system is proportional to $\phi_1\Gamma_1\eta_1 + \phi_2\Gamma_2\eta_2$, where Γ_1 and Γ_2 represent the optical anisotropies of submolecules 1 and 2, respectively. Hence the (apparent) stress-optical coefficient of the real system, C, would be larger than that of the gaslike system, C^*, by a factor Λ:[5]

$$C = \Lambda C^* \tag{36}$$

$$\begin{aligned}\Lambda &= (\phi_1\Gamma_1\eta_1 + \phi_2\Gamma_2\eta_2)/(\phi_1\Gamma_1\eta_1^*) \\ &= (\eta_1/\eta_1^*) + (\Gamma_2/\Gamma_1)(\phi_2\eta_2/\phi_1\eta_1^*)\end{aligned} \tag{37}$$

where η_1/η_1^* and η_2/η_1^* are given by eqs 29 and 30 with $n_1^{-1} = m_1^{-1} = 0$. The factor Λ can take any value, positive or negative, large or small, depending on the length and rigidity of the solvent and, above all, the ratio Γ_2/Γ_1. Figure 2 demonstrates the plot of Λ as a function of ϕ_1 for the case with $x_1 = x_2 = 2$ and $\Gamma_2/\Gamma_1 = 5$. It can be seen that Λ changes drastically with the length n_2 of the "flexible" solvent, especially when ϕ_1 is small.

Also practically interesting is a system in which a small number of short molecules 2 are dispersed in the matrix of the oriented polymer 1. Equations 29 and 30 with $n_1^{-1} = m_1^{-1} = 0$ and $\phi_2 = 0$ give

$$\eta_2/\eta_1 = (1/5)x_2'' = (1/5)x_2(1 - n_2^{-1})/[1 + (x_2/n_2)] \tag{38}$$

Figure 3 shows the plot of η_2/η_1 vs the chain length n_2 for several values of x_2. The broken line is for rigid rods ($x_2 = \infty$), for which η_2/η_1 is proportional to $n_2 - 1$. For flexible molecules ($x_2 = \infty$), η_2/η_1 increases with n_2 but approaches the limiting value of $x_2/5$ for sufficiently large n_2.

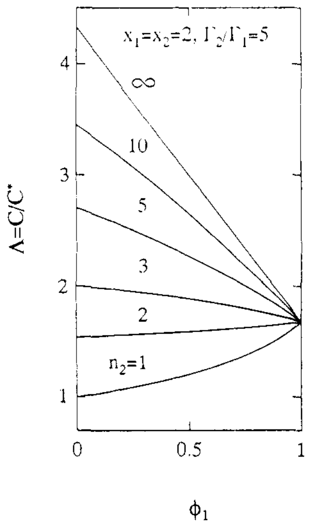

Figure 2. Plot of Λ ($=C/C^*$) vs ϕ_1 for several values of n_2: $x_1 = x_2 = 2$ and $\Gamma_2/\Gamma_1 = 5$ (see eq 37).

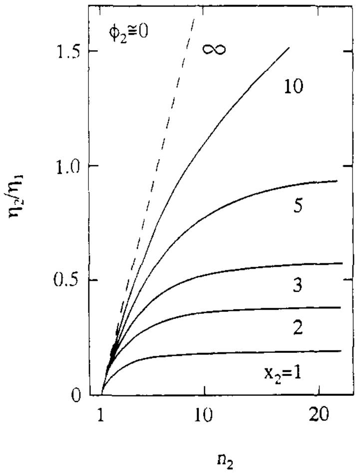

Figure 3. Plot of η_2/η_1 vs n_2 for several values of x_2: $\phi_2 \cong 0$ (see eq 38).

Concluding Remarks. Rigid or semirigid polymers in solution or in the bulk often spontaneously order by themselves to form a liquid crystal. A number of theories have been developed to describe the order–disorder transition.[4,6] The Di Marzio-type lattice model coupled with the freely-jointed-chain model used here also predicts the occurrence of a liquid crystalline phase in solution as well as in the bulk, when the chain parameters are appropriate.[7] This indicates that the mentioned models, albeit simple, are capable of describing orientational properties of multicomponent as well as single-component systems essentially correctly, at least in a qualitative sense.

In a previous paper,[8] we theoretically showed for the first time that polymer segments can be more oriented in the real system than in the gaslike system, due to the excluded-volume effect, and pointed out some experimental observations that appeared to be interpretable from this viewpoint. However, comparison of the orientation in the real system, η_1, with that in the gaslike system, η_1^*, requires an accurate knowledge of η_1^*, which is another difficult problem. Hence the reality of the predicted effect seems to have been experimentally verified still not conclusively. The theory developed here enables us to design many experiments to test the reality of the effect of "induced" orientation more or less directly. For example, the observation of the orientation of small molecules 2 embedded in a deformed polymer network will give a quick answer: in the absence of the excluded-volume and other interactions, molecules 2 should show zero orientation *in equilibrium*.

There seem to be many relevant observations already reported in the literature. For example, according to Thulstrup and Michl,[9] who have compiled the results of UV–visible dichroism on over a hundred aromatic molecules embedded in a stretched swollen polyethylene, the orientation factors were dominated primarily by molecular shape: molecules which are long and narrow and hence large in axial ratio showed a particularly high degree of orientation along the stretching direction. This seems to be consistent with our result (cf. eq 38 and Figure 3).

Also notably, Erman and Flory[10] have determined the stress-optical coefficients of poly(dimethylsiloxane) networks swollen by various diluents and noted that the (apparent) coefficient C depends very seriously on the diluents. More precisely, when the solvent was symmetrical, C decreased with decreasing polymer concentration ϕ_1, while when the solvent was highly asymmetrical, C increased with decreasing ϕ_1. Particularly noteworthy is the fact that higher C values were observed for hexadecane than for decane, a shorter solvent. These results qualitatively agree very closely with the prediction of this work (compare Figure 2 in this paper with Figure 6 in ref 10). Erman and Flory[10] attributed, perhaps correctly, the observed dependence of C on the diluents to intermolecular correlations that effectively enhance the very small intrinsic anisotropy of the dimethylsiloxane unit; viz., $\Gamma_2/\Gamma_1 \gg 1$ in our terms.

Observations of the orientation of polymer 2 embedded in polymer 1 have been made by some authors, but mostly in a nonequilibrium state.[11] In progress in our laboratory is an infrared dichroism (IRD) study on a cross-linked polystyrene containing a small amount of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). By IRD, independent determination of η_1 and η_2 of this compatible pair of polymers is possible.[11] A preliminary result does confirm eq 35.[12] Also see note 13.

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