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Notes

Orientation-Dependent Interactions in Polymer Systems. 6. Effect of Segmental Orientation on Polymer Miscibility

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Introduction

Almost all molecules are more or less anisotropic in shape at a molecular or segmental level. Shape anisotropy brings about anisotropy of excluded-volume interaction, causing various cooperative phenomena that cannot be observed in systems of symmetrical molecules. The most drastic of those phenomena is the spontaneous or liquid crystalline ordering of rodlike molecules and stiff-chain polymers.[1,2] The effect of orientation-dependent excluded volume, or simply the packing entropy effect, is usually unexplicit in systems of flexible polymers and nonmesogenic compounds. However, once the system is oriented by, e.g., a stretch or flow, it explicitly appears, affecting whatever properties in which orientation matters. For example, it has been shown that segments of a probe polymer dispersed in the orientated network of a matrix polymer become oriented even at equilibrium, the degree of orientation depending on the flexibility and molecular weight of the probe polymer.[3,4] The purpose of this work is to draw attention, for the first time, to the fact that the packing entropy effect can have a large influence also on the phase behavior of oriented polymer systems. This work is therefore relevant also to the phenomenon of flow-induced mixing or demixing of polymer solutions and blends, a subject that has attracted much attention in recent years[5,6] but has never been discussed from the standpoint of the packing entropy effect. As in the previous work,[1−4] any information that will be gained here is gained at no expense, since the present treatments include no new assumptions or parameters other than those already introduced.

Theoretical Section

This work is a simple extention of the previous one,[3] where we considered an *incompressible* one-phase mixture of polymers 1 and 2 with their segments *weakly* oriented by some means. The free energy F_a of the system in excess over that of the hypothetical "gaslike" system, in which there is no orientation-dependent interaction among polymer segments, was written (note that F_a was written ΔF previously[3])

$$F_a = E_O - T(S_P + \Delta S_O) \qquad (1)$$

where E_O is the energetic term, which we will not consider in this work ($E_O = 0$), T is the absolute temperature, S_P is the packing entropy, and ΔS_O is the excess orientational entropy. Both S_P and ΔS_O are zero for the gaslike system. To evaluate S_P and ΔS_O, we employed the cubic lattice model and the random freely-jointed (RFJ) chain, respectively. This lattice model is an extension of the Di Marzio model[7] to a multicomponent system, and we specifically considered the case of a cubic lattice. The RFJ chain consists of rodlike segments of variable lengths with a mean length or persistence length of q and is equivalent to the wormlike chain with respect to the mean-square dimensions.[3] The expressions for S_P and ΔS_O derived for a weakly oriented system were[3]

$$S_P/kN_0 = A(\eta_1\phi_1' + \eta_2\phi_2')^2 \qquad (2)$$

$$\Delta S_O/kN_0 = -(5/2)[(\phi_1/x_1')(\eta_1 - \eta_1^*)^2 + (\phi_2/x_2')(\eta_2 - \eta_2^*)^2] \qquad (3)$$

with

$$A = (3 - \phi_1' - \phi_2')^{-1} \qquad (4)$$

$$\phi_i' = \phi_i(1 - n_i^{-1}) \qquad (5)$$

$$x_i' = x_i/(1 + x_i n_i^{-1}) \qquad (6)$$

$$x_i'' = x_i'(1 + n_i^{-1}) \qquad (7)$$

where N_0 is the total number of submolecules (lattice sites), k is the Boltzmann constant, ϕ_i is the volume fraction, $n_i = L_i/D_i$, and $x_i = q_i/D_i$ with L_i, D_i, and q_i being the contour length, diameter, and persistence length, respectively, of polymer i(=1 or 2): η_i and η_i^* are the order parameters of the real and gaslike systems, respectively; $\eta = (3/2)\langle\cos^2\theta\rangle - (1/2)$. The equilibrium orientation η_i was obtained, by minimizing eq 1 with respect to both η_1 and η_2, as

$$\eta_1 = \frac{[1 - (2/5)Ax_2''\phi_2']\eta_1^* + (2/5)Ax_1''\phi_2'\eta_2^*}{1 - (2/5)A(x_1''\phi_1' + x_2''\phi_2')} \qquad (8)$$

To obtain η_2, exchange subscripts 1 and 2 in eq 8. Equation 8 gives the degree of orientation in the real system (with the excluded-volume interaction) as a function of the externally given orientations η_1^* and η_2^*, the flexibility parameters x_1 and x_2, the chain length indices n_1 and n_2, and the composition ϕ_1 (=1 − ϕ_2). Obviously, we obtain the relation $\eta_i = \eta_i^*$ for the gaslike system by setting $S_P = 0$ in eq 2 or $x_i = 0$ in eq 8 (in the flexible limit, polymers show no excess orientation, since $|\Delta S_O|$ in eq 3 becomes infinitely large).

Now, eq 8 with eqs 1−3 gives the value of F_a for the one-phase system:

$$g(\phi_1) = \frac{F_a}{N_0kT} = -\frac{A(\phi_1'\eta_1^* + \phi_2\eta_2^*)^2}{1 - (2/5)A(\phi_1'x_1'' + \phi_2'x_2'')} \qquad (9)$$

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Putting $\phi_1 = 1 - \phi_2 = 1$ in eq 9, we obtain the excess free energy for the pure polymer 1:

$$g(1) = -\frac{(2 + n_1^{-1})^{-1}(1 - n_1^{-1})^2\eta_1^{*2}}{1 - (2/5)(2 + n_1^{-1})^{-1}(1 - n_1^{-1})x_1''} \quad (10)$$

The relevant function for the pure polymer 2, $g(0)$, is obtained by replacing subscript 1 with 2 in eq 10. The contribution, ΔF_a, of the anisotropic interaction to the free energy of mixing may thus be given by

$$\frac{\Delta F_a}{N_0 kT} = g(\phi_1) - [\phi_1 g(1) + \phi_2 g(0)] \quad (11)$$

Now we define the generalized interaction parameter χ as the residual free energy function, reduced by $\phi_1\phi_2N_0kT$, which includes all contributions but the Flory–Huggins combinatorial entropy term[8] (for the isotropic system):

$$\frac{\Delta F_M}{N_0 kT} = \frac{\phi_1}{n_1}\ln \phi_1 + \frac{\phi_2}{n_2}\ln \phi_2 + \phi_1\phi_2\chi \quad (12)$$

where ΔF_M is the total free energy of mixing. Then this χ comprises two terms

$$\chi = \chi_i + \chi_a \quad (13)$$

where χ_i is the (conventional) interaction parameter for the isotropic system and the anisotropic contribution χ_a is obtained from

$$\chi_a = \Delta F_a/(\phi_1\phi_2N_0kT) \quad (14)$$

with ΔF_a given by eq 11 with eqs 9 and 10. When the two polymers are long enough ($n_i^{-1} = 0$), $\phi_i' = \phi_i$, $x_i'' = x_i' = x_i$, and χ_a is simplified to

$$\chi_a = \frac{(5/2)[(5 - x_2)\eta_1^* - (5 - x_1)\eta_2^*]^2}{(5 - \phi_1x_1 - \phi_2x_2)(5 - x_1)(5 - x_2)} \quad (15)$$

Discussion

The previous work[4] showed that segments of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) sparsely dispersed in a stretched network of polystyrene (PS) are oriented by two different mechanisms. One is related to the entanglement interaction, and accordingly, PPO chains longer than a critical length (about 10^4 in molecular weight) are relevant to this mechanism. The other mechanism is related to the interaction at a segmental level, and hence it works on both long and short probe molecules. The orientation induced by the former mechanism eventually relaxes to null, while that induced by the latter mechanism does not relax, so far as the matrix is kept oriented. The equilibrium or unrelaxing orientation of PPO segments was observed to well agree with the theoretical prediction

$$\eta_2/\eta_1 = (1/5)x_2(1 - n_2^{-1})/(1 + x_2n_2^{-1}) \quad (16)$$

which is obtained from eq 8 and the partner equation for η_2 with $\eta_2^* = 0$ and $\phi_2 \approx 0$. This result lends support to the reality and reliability of the F_a and χ_a expressions given above, as they are of the same origin as eq 16.

According to eq 15, χ_a is either positive or negative depending on the flexibilities of the two polymers. Equation 8 with $\phi_2 = 0$ and $n_1^{-1} = 0$ indicates that a pure, long polymer with $x = 5$ will be oriented to an infinitely high degree. Since $0 \le \eta \le 1$ by definition, this means that a polymer with $x \ge 5$ will order by itself forming a nematic liquid crystal. Thus the segmental axial ratio of 5 is a measure of nematicity, according to the present models.[9] In this regard, we may mention that when both polymers are flexible (x_1 and $x_2 < 5$), χ_a is positive and hence the blend miscibility will be lowered by orientation: when a rigid ($x_2 > 5$) polymer is mixed as a minor component with the matrix of a flexible polymer ($x_1 < 5$), their miscibility will be enhanced by orientation, since $\chi_a < 0$ in this case. Systems containing a rigid polymer as a main component can have a nematic phase with or without an external force field, and they require an independent treatment. On the basis of his own lattice model, Flory[10] has shown that in a quiescent state, a flexible polymer is hardly miscible with the nematic phase formed by a rigid polymer. The present treatments show that the miscibility can be changed when the two components are externally oriented into a weak "nematic" state. Clearly, the phenomenon discussed by Flory is the same in origin as the ones predicted here.

Practically important is the magnitude of the effect of segmental orientation on the threshold temperature of blend miscibility. In order to estimate this, we need know the temperature dependence of χ_i of the blend in question. Regarding systems with PS and poly(vinyl methyl ether) (PVME), Nishi[11] has determined the lower critical solution temperatures (LCSTs) of several blends with differing PS molecular weights to deduce the following relation:

$$\frac{\partial(\chi_i/v_0)}{\partial T^{-1}} = -0.10 \quad (17)$$

where v_0 is the molar volume of the submolecule (or lattice site). According to the more recent neutron scattering work due to Shibayama et al.,[12] the χ_i of a PS/PVME blend at its critical composition varies approximately like

$$\frac{\partial(\chi_i/v_0)}{\partial T^{-1}} = -0.30 \quad (18)$$

The difference between eqs 17 and 18 may be ascribed to the dependence of χ_i on composition, molecular weight, and molecular weight distribution.[12] A rigorous calculation of the phase diagram of a PS/PVME blend by use of eqs 12, 13, and 15 requires these details on χ_i, which is out of the scope of this work. A rough estimate of the change ΔT caused on the LCST of the blend by the anisotropic contribution χ_a may be given by

$$\Delta T \cong \frac{\chi_a}{(\partial\chi_i/\partial T)} \quad (19)$$

Here we tentatively assume that $x_1 = x_2 = 1.5$, $\eta_1^* = 0.1$, and $\eta_2^* = 0$, which would simulate, e.g., a uniaxially stretched system comprising a very long (hardly relaxing) matrix polymer and a very short (nonentangling, hence quickly relaxing[3]) guest polymer, both of which are flexible to the same degree. Letting $v_0 = 150$ cm^3/mol and $T = 400$ K, we obtain, from eqs 15 and 19, $\Delta T = -75$ K and -25 K for eqs 17 and 18, respectively. Thus the theory predicts quite a large effect of orientation on the blend miscibility.

According to our preliminary result,[13] the cloud point of the PS ($M_n = 2.6 \times 10^6$)/PVME ($M_n = 1.1 \times 10^4$) blend was lowered by as much as 20 °C when a uniaxial stretch of 400% ($\eta_1 \approx 0.1$)[3] was applied to the blend film above its glass transition temperature. It has also been known for some time that PS/PVME blends show flow-induced demixing under certain conditions.[5d] This work suggests that at least an important part of these phenomena is interpretable from the viewpoint of packing entropy, i.e., equilibrium thermodynamics.

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(9) A rigorous calculation would show that the critical value of x for the isotropic−nematic transition is somewhat smaller than 5 (cf. ref 1). Equation 8 as well as all other equations in this paper are valid only for weak orientations. They cannot be used when either or both components are in a highly oriented state, e.g., a nematic liquid crystalline state.

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