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Notes

Effect of Chain Architecture on the Cloud Point Curves of Binary Blends of Star Polymers

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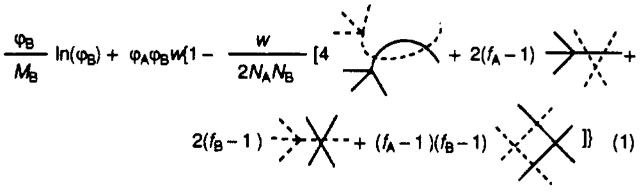
The Flory–Huggins expression of the free energy of mixing of two polymers i = A and B, of molecular weights and volume fractions N_i and $\varphi_i = V_i/V$, respectively, is given by[1] $\Delta G/kTV/v_0 = (\varphi_A/N_A)\ln(\varphi_A) + (\varphi_B/N_B)\ln(\varphi_B) + \chi\varphi_A\varphi_B$. It describes an incompressible system of total volume $V = V_A + V_B$, with $V_i = n_iN_iv_0$ the volume of the two species, n_i the number of chains of the two polymers, and v_0 a reference monomer volume considered for simplicity to be the same for the two monomeric units. The last term is quadratic in the volume fractions of the two components and comes from the interactions between pairs of chains. The χ parameter is not a constant at a specific temperature as initially considered but depends on the molecular weights and volume fractions of the two species[2] because of the correlations between two or more polymer chains at long chain distances. Starting with a continuous molecular model and keeping interactions between two or more chains,[3] the dependence of the χ parameter not only on volume fractions and molecular weights[4,5] but also on the architecture of the chains can be seen. Experimentally, architecture effects are seen in the cases with a lower critical solution temperature where the critical temperatures of mixtures of stars with an enhanced macromolecular topology, with linear chains, are found higher than those of mixing of linear chains.[6,7] The connection of ΔG with molecular models and the determination of the effects of the chain correlations are therefore necessary for the proper description of systems of chains of complicated architectures and the explanation of their experimental behavior. We show in this paper that, keeping correlations between the chains even, the quadratic dependence of ΔG on volume fractions can explain experiments.

If $w = \int \mathrm{d}r\,\{1 - \exp[-V(r)/kT]\}$ is a molecular parameter describing the intensity of interactions between approaching monomeric units, to first order in w, only single encounters between different chains are taken into account and the χ parameter is equal to w, leading to an independence in the case of stars from the chain molecular weights and architecture. To second order in w, correlations between the chains turn in and the cases of stars differentiate. If f_i and N_i are the numbers of branches and the molecular weights per branch of the two polymers, then the star molecular weights are $M_i = f_iN_i$. The volumes of the two species are given by $V_i = n_iM_iv_0$ and that of the incompressible system by $V = V_A + V_B$, and considering v_0 as unity ΔG can be written as

$$\frac{\Delta G}{kTV} = \frac{\varphi_A}{M_A}\ln(\varphi_A) +$$



The diagrams of one loop describing two point correlations between Gaussian chains are easily determined.[8] At the critical dimension $d = 4$ they yield an expression of ΔG of the form

$$\frac{\Delta G}{kTV} = \frac{\varphi_A}{M_A}\ln(\varphi_A) + \frac{\varphi_B}{M_B}\ln(\varphi_B) + \varphi_A\varphi_B w\{1 - w[2\ln(M) + F]$$

$$\begin{gathered} F = \frac{(f_A - f_Ax + xf_B)^2(3f_A + 3f_B - 2f_Af_B - 5)}{x(1-x)f_Af_B} \\ \ln\left(\frac{1-x}{f_B} + \frac{x}{f_A}\right) + \frac{(f_B - 1)(f_A - 2)(2f_A - 2f_Ax + xf_B)^2}{2x(1-x)f_Af_B} \\ \ln\left(2\frac{1-x}{f_B} + \frac{x}{f_A}\right) + \frac{(f_A - 1)(f_B - 2)(2xf_B + f_A - f_Ax)^2}{2x(1-x)f_Af_B} \\ \ln\left(2\frac{x}{f_A} + \frac{1-x}{f_B}\right) + \frac{3f_A - 3f_Ax - (1-x)f_A^{\,2} + 4x}{2x} \\ \ln\left(\frac{1-x}{f_B}\right) + \frac{3xf_B + 4 - 4x - xf_B^{\,2}}{2(1-x)}\ln\left(\frac{x}{f_A}\right) + \\ 2\left[(f_B - 1)\left(\frac{(1-x)f_A}{xf_B} + 1\right) - (f_A - 1)(f_B - 1)\left(\frac{xf_B}{f_A(1-x)} + \right.\right. \\ \left.\left.\frac{(1-x)f_A}{xf_B} + 1\right) + (f_A - 1)\left(1 + \frac{xf_B}{(1-x)f_A}\right)\right] \\ \ln(2) - 1, \quad M = M_A + M_B, \quad x = \frac{M_A}{M_A + M_B} \quad (2) \end{gathered}$$

where F depends solely on the architectural parameters which in the present case of stars are the number f_i of the branches of the two stars and the molecular weight ratio $x = M_A/(M_A + M_B)$. At the fixed point value $w^* = \epsilon/4$, with $\epsilon = 4 - d$, where d is the dimensionality of the space, the exponentiation of the series $1 - w[2\ln(M) + F] + \ldots \approx M^{-\epsilon/2}e^{-\epsilon F/4}$ takes place[8] and the M dependence comes from the $\ln(M)$ term, yielding an exponent in the limit of large M equal to $-\epsilon/2$, $\chi \sim M^{-\epsilon/2}$. This critical exponent is the same for stars and linear chains as well as for chains

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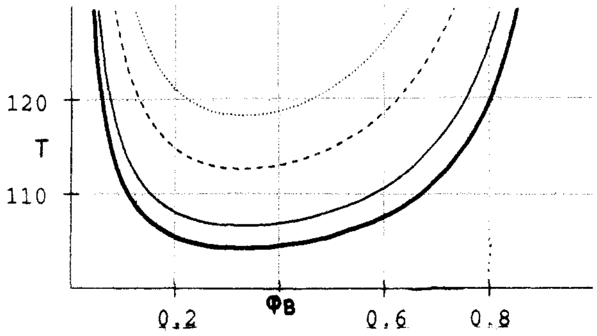

Figure 1. Spinodal lines of stars of the same molecular weights $M = 10^4$, $x = M_A/M = 0.2$, but different numbers f_A and f_B of branches: (▬) $f_A = 1$, $f_B = 1$; (—) $f_A = 1$, $f_B = 4$; (- - -) $f_A = 4$, $f_B = 4$; (· · ·) $f_A = 5$, $f_B = 4$.

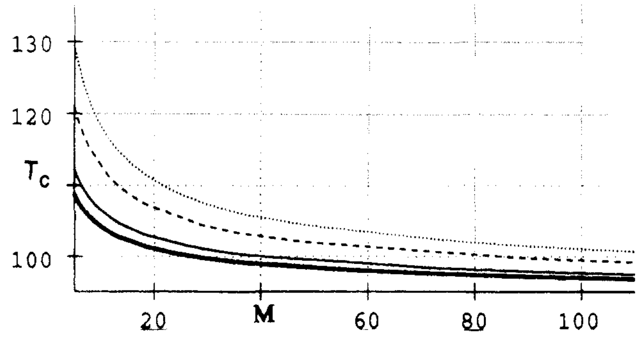

Figure 2. Critical temperatures T_c (°C) as a function of the molecular weight parameter M in thousands for various numbers f_A and f_B of branches of the two species: (▬) $f_A = 1$, $f_B = 1$; (—) $f_A = 1$, $f_B = 4$; (- - -) $f_A = 4$, $f_B = 4$; (· · ·) $f_A = 5$; $f_B = 4$. All lines tend to the same limit $T_c = b/a$ for $M \to \infty$.

of other architectures, and it is in agreement with previous results on linear chains.[4,5] Notice that the exponent $-\epsilon/2$ corresponds to ideal chains of dense systems like those of melts or concentrated solutions, and it is different from the exponent $-\epsilon/4$ which characterizes expanded chains like those of dilute solutions in good solvents.[9]

The spinodals are obtained by applying the criterion $\partial\Delta\mu_A/\partial\varphi_B = 0$ on the chemical potential $\Delta\mu_i = \partial\Delta G/\partial n_i$, $i = A$, which for the present case of stars yields the relation

$$\frac{1-2x}{1-x}(1-\varphi_B) + 2\varphi_B(1-\varphi_B)xw\mathrm{e}^{-\epsilon F/4}M^{1-\epsilon/2} - 1 = 0, \text{ spinodal lines} \quad (3)$$

In order to draw the spinodals $T(\varphi_B)$ by means of eq 3, a relation between w and T is necessary and this can be obtained from the connection of w with the potential $V(r)$ of monomer interactions. In the range of small values of w and for realistic molecular potentials $V(r)$ of the type including a hard core and an attractive well w comes out to depend on the temperature T with the function $w = a - b/T$ where a in units of volume and b in units of temperature × volume are positive constants determined from the molecular parameters of $V(r)$. In Figures 1 and 2 we take the values of these constants equal to $a = 0.45$ and $b = 165$ in order to produce the results in a realistic temperature window, while $\epsilon = 1$ for $d = 3$. In Figure 1 we draw spinodal line for linear and star chains where we see that an elevation of the spinodals of chains of enhanced topology takes place. This agrees with the experimental observation of a 12° elevation in the cloud point curve of a mixture of a four-armed star polystyrene with linear poly(vinyl methyl ether) relative to the cloud point curve of a mixture of linear polystyrene and linear poly(vinyl methyl ether).[6] This is of course with the reservation of the simplification we made considering the two different monomeric units to be of equal effective length.

For the determination of the critical point the second derivative of $\Delta\mu_A$ with respect to φ_B must also vanish $\partial^2\Delta\mu_A/\partial\varphi_B{}^2 = 0$, and this provides another condition which combined with eq 3 yields the critical value $w_c = (\mathrm{e}^{\epsilon F/4}/2M^{1-\epsilon/2})[1 + 2[x(1-x)]^{1/2}/x(1-x)]$. The critical temperature $T_c = b/(a - w_c)$ is then given by

$$T_c = \frac{2bx(1-x)M^{1-\epsilon/2}}{2ax(1-x)M^{1-\epsilon/2} - [1 + 2[x(1-x)]^{1/2}]\mathrm{e}^{\epsilon F/4}} \quad (4)$$

We plot these critical temperatures in Figure 2, and we see that enhanced topologies yield larger critical temperatures coming from the dependence on the architecture factor F. This explains the difference of 4° between the minima of the cloud point curves of a mixture of 22-armed star polystyrene and linear poly(vinyl methyl ether) and a mixture of linear polystyrene and linear poly(vinyl methyl ether) seen experimentally.[7] These experiments have been done with molecular weights of a rank of magnitude higher than those of four-armed stars, and the smaller difference can also be explained by means of relation 4 where we see that upon increasing the molecular weight M the architectural effects from F decrease. This reduction of the architectural effects on increasing M is general, and from eq 4 a special limit is revealed that of T_c for $M \to \infty$ where the critical temperatures of mixing of all macromolecular systems regardless of their architecture tend to the same value $T_c = b/a$ for $M \to \infty$.

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