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On the miscibility of chemically identical linear homopolymers of different size

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Abstract

The effects of asymmetry due to the chain-size differences on the miscibility of linear polymer blends composed from the same monomers are studied by means of an analytical theory. The partition function of the blend and the resulting free energy are obtained through the summation of the series of the one-loop diagrams at any dimensionality d. From the stability conditions, no macrophase separation is found at $d = 3$ for any size disparity or volume fractions in agreement with other recent theoretical calculations. At $d = 2$, the effective repulsions between the two different species are much larger leading to macrophase separation. This result strongly indicates that a way to observe de-mixing of chemically identical homopolymer, is to increase the two-dimensional character of the chains like in the cases of strong adsorption or ultra-thin polymeric films.

Keywords: Linear polymers; Size disparity; Effective interaction parameter

1. Introduction

In recent years, there is an increasing interest in the study of asymmetric polymer blends consisting of two kinds of chains of the same type of monomers but with differences in the chain-size or the chain architecture. This is because of both the extensive use of these materials in industry but also of the need to understand whether sole entropic effects can lead to phase separation in these mixtures. There is experimental evidence that thermodynamic interactions, purely entropic in nature, are present in systems of asymmetric chains [1–5], capable to cause even de-mixing. In the case of blends, for example, consisting of linear and branched (comb) polyethylenes though the melt mixture is homogenous when the branch content is low, for higher branch content (typically 8 branches/100 backbone carbons), the blends phase separate [1–3]. For mixtures of star branched polymers with linear analogs, the experimental literature is scarce [4,5] but theoretical results based on the Gaussian approximation method suggest that the thermodynamic interactions are increasing on increasing the number of arms, or the disparity between the size of linear chains and the size of star arms [6]. These effects are weak in three-dimensional blends and for a modest number (up to 20) of arms of polymeric length the theoretical results suggest that phase separation is unlikely. The simplest case is that of chemically identical linear blends due to the presence of only one asymmetric parameter, the chain-size disparity. Theoretical results based on different models [6,7] indicates that linear blends are always miscible at $d = 3$. However, nothing is known in the best of our knowledge for the miscibility in chemically identical two-dimensional blends like in the case of ultra-thin polymeric films where the consistent polymer chains have a two-dimensional character. Is de-mixing possible under such circumstances?

In this paper, we attempt to clarify the macroscopic behavior of asymmetric linear blends of chemically identical linear homopolymers of different size using a molecular model and describing long chain correlations at any space dimensionality. The polymer chains in the mixture are considered Gaussian with excluded volume interactions between units located at different chains. The partition function and the resulting free energy and stability conditions are obtained through the summation of the series of the one-loop diagrams, which represent long chain correlations among many chains. This model has successfully described dense systems of many chains explaining, for example, the cancellation of the excluded volume interactions in a homopolymer melt [8].

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2. Model

We consider a system composed of two macromolecular species A and B with population n_A and n_B differing only in their molecular weights N_A and N_B. The chains fully occupy a volume V and are represented by continuous curves in d dimensions. In the canonical ensemble, the configurational partition function can be written as $Z = V^{n_\mathrm{A}+n_\mathrm{B}}/n_\mathrm{A}!n_\mathrm{B}! \int D\vec{R}\exp[-H(\vec{R})/k_\mathrm{B}T]$, where $\int D\vec{R}$ denotes integration over the positions of all statistical segments of each species and $H(\vec{R})$ is an Edwards type Hamiltonian for a collection of n_A and n_B interacting chains.

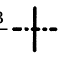
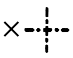
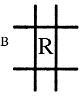
$$H/k_\mathrm{B}T = \sum_{i=\mathrm{A;B}}\sum_{j=1}^{n_i}\int_0^{N_i}\mathrm{d}s\left(\frac{\mathrm{d}\vec{R}_j(s)}{\mathrm{d}s}\right)^2 + \sum_{i,j=\mathrm{A;B}}\sum_{i'=1}^{n_i}\sum_{j'=1}^{n_i} \times \int_0^{N_i}\mathrm{d}s\int_0^{N_j}\mathrm{d}s'\,\delta^d((\vec{R}_{i'}(s)-\vec{R}_{j'}(s'))w_{ij}. \quad (1)$$

The first term counts for the connectivity of the chains, with the $\vec{R}_j(s)$ representing the spatial position of the sth statistical segment of the jth chain, while the second stands for the interactions between nonadjacent parts of the chains. Notice that strictly speaking N in Eq. (1), is defined as a contour chain length and it is equal to the number of units N/ℓ ($\ell =$ length of the unit) of each chain, ℓ considered, however, for simplicity to be equal to 1. The excluded volume interaction parameters in all cases w_AA, w_BB, w_AB are taken in the present work equal to u due to the chemically identical species A and B. Following previous works [8,9] and expanding the configurational partition function with respect to inter-excluded-volume interactions we take

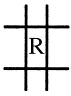
$$Z = \frac{V^{n_\mathrm{A}+n_\mathrm{B}}}{n_\mathrm{A}!n_\mathrm{B}!}\left\langle 1 - u\sum_{i,j=\mathrm{A;B}}\sum_{i'=1}^{n_i}\sum_{j'=1}^{n_j}\int_0^{N_i}\mathrm{d}s\int_0^{N_j}\mathrm{d}s'\,\delta^d((\vec{R}_{i'}(s)-\vec{R}_{j'}(s')) + \sum_{m>2}\frac{(-1)^m u^m}{m!}\left[\sum_{i,j=\mathrm{A;B}}\sum_{i'=1}^{n_i} \times \sum_{j'=1}^{n_{ji}}\int_0^{N_i}\mathrm{d}s\int_0^{N_j}\mathrm{d}s'\,\delta^d((\vec{R}_{i'}(s)-\vec{R}_{j'}(s'))\right]^m\right\rangle. \quad (2)$$

Each delta function of Eq. (2) brings into contact segments of different chains and diagrams to all orders of u are produced. These diagrams can be classified in three major categories according to the number of contacts i, and the number of chains m involved in them. The case $i = m - 1$ corresponds to the well known RPA open connected diagrams with no loops while the cases $i < m - 1$ and $i = m$ correspond to the open-disconnected and ring diagrams, respectively. Every line of these diagrams stand for a chain either of the species A or B. The RPA diagrams in Eq. (2) sum into an exponential permitting ℓnZ to be written as

$$\ell nZ = \ell n\frac{V^{n_\mathrm{A}+n_\mathrm{B}}}{n_\mathrm{A}!n_\mathrm{B}!} - u\left[\frac{n_\mathrm{A}^2}{V}\right.$$

$$+ 2\frac{n_\mathrm{A}n_\mathrm{B}}{V}$$

$$+ \frac{n_\mathrm{B}^2}{V} \times$$

$$\left.\vphantom{\frac{1}{V}}\right] + \sum_{m>1}\frac{(-u)^m}{m!}2^{m-1}(m-1)!\frac{1}{V^{m-1}}\sum_{m_\mathrm{A}=0}^{m} \times \binom{m}{m_\mathrm{A}} n_\mathrm{A}^{m_\mathrm{A}} n_\mathrm{B}^{m_\mathrm{B}}$$

$$\left.\vphantom{\frac{1}{V}}\right]. \quad (3)$$

Among all connected diagrams, which survive in the expression of ℓnZ the ring diagrams play a dominant role and are represented by the last summation of Eq. (3). The number of these ring diagrams involving $m = m_\mathrm{A} + m_\mathrm{B}$ chains from species A and B, comes: (a) from the $(m_\mathrm{A})n_\mathrm{A}^{m_\mathrm{A}}n_\mathrm{B}^{m_\mathrm{B}}$ different ways, the m chains can be chosen among all the $n_\mathrm{A} + n_\mathrm{B}$ of chains, (b) from the different $(m - 1)!$ arrangements of the m chains to form the ring and (c) from the two ways that each chain can be placed in a position inside a ring, totally 2^{m-1} ways. As in the previous works [8,9] we write the ring diagrams in terms of the Debye functions J_A and J_B as:


$$= (N_\mathrm{A}^{2m-d/2}r^m/\Gamma(d/2))\int_0^\infty \mathrm{d}pp^{d/2-1}J_\mathrm{A}^{m_\mathrm{A}}J_\mathrm{B}^{m_\mathrm{B}}, \quad (4)$$

where p is a dummy integration variable, $r = N_\mathrm{B}/N_\mathrm{A}$ is the size asymmetry ratio of the two polymer species, and

$$J_\mathrm{A} = \int_0^1 \mathrm{d}x(1-x)\mathrm{e}^{-px} = (\mathrm{e}^{-p} - 1 + p)/p^2;$$

$$J_\mathrm{B} = \int_0^1 \mathrm{d}x(1-x)\mathrm{e}^{-prx} = (\mathrm{e}^{-pr} - 1 + pr)/p^2r^2.$$

Using the values of ring diagrams and the respective N_A^2, N_A,N_B, N_B^2 of the cross ones in Eq. (3) we evaluate the partition function of the blend up to an integral

$$\ell nZ = \ell n\frac{V^{n_\mathrm{A}+n_\mathrm{B}}}{n_\mathrm{A}!n_\mathrm{B}!} - uV[\varphi_\mathrm{A}^2 + \varphi_\mathrm{B}^2 + 2\varphi_\mathrm{A}\varphi_\mathrm{B}] + \frac{V}{2}\sum_{m>1} \times \sum_{m_\mathrm{A}}^{m}\frac{1}{\Gamma(d/2)N_\mathrm{A}^{d/2}}\frac{m!}{m_\mathrm{A}!(m-m_\mathrm{A})!}\int_0^\infty \mathrm{d}pp^{d/2-1}[(-4uN_\mathrm{A}^2J_\mathrm{A}n_\mathrm{A}/V)^{m_\mathrm{A}} \times(-4uN_\mathrm{A}^2r^2J_\mathrm{B}n_\mathrm{B}/V)^{m_\mathrm{B}}]/m, \quad (5)$$

where φ_A,φ_B, the volume fractions of the A and B species equal to $n_\mathrm{A}N_\mathrm{A}v_\mathrm{A}/V$ and $n_\mathrm{B}N_\mathrm{B}v_\mathrm{B}/V$, respectively. v_A and v_B are the effective volumes of the A and B units considered for simplicity to be both equal to unity $v_\mathrm{A} = v_\mathrm{B} = 1$, without changing the analysis and the conclusions which follow. This of course makes V equal to $V = n_\mathrm{A}N_\mathrm{A}v_\mathrm{A} + n_\mathrm{B}N_\mathrm{B}v_\mathrm{B} = n_\mathrm{A}N_\mathrm{A} + n_\mathrm{B}N_\mathrm{B}$ and appears to be dimensionless though it has the units of volume. What we notice here is that the first order u term is equal to $uV(\varphi_A + \varphi_B)^2$ and assuming that the system is incompressible ($\varphi_A + \varphi_B = 1$), it becomes independent of the volume fractions. This independence is not possible for the case of different species and different interactions between them. The summation of the ring diagrams is trivial and leads to the following expression of ℓnZ

$$\ell nZ = \ell n \frac{V^{n_A+n_B}}{n_A! n_B!} - uV + \frac{V}{2\Gamma(d/2)N_A^{d/2}} \times \int_0^\infty \mathrm{d}p p^{d/2-1}[-\ell n[1 + (4uN_A\varphi_A J_A) + (4uN_A r\varphi_B J_B)]]. \tag{6}$$

This expression is very similar to that Fredrickson [6] has given based on a quadratic interaction Hamiltonian model, without a 1 into the logarithmic term in his results. The presence of this unity though is crucial for the existence of the p integral in the spinodal expression in Eq. (8). In the limit of $p \longrightarrow \infty$ where the Debye function goes as $J \sim 1/p$ no cutoffs are necessary in the expression Eq. (8). A thing to note is that though the classical treatment up to the first two terms of Eq. (6) does not depends on the dimensionality d of the system the third term coming from long chain correlations does depend on d differentiating the behaviors of the three- and the two-dimensional blends.

3. Results and discussion

By means of Eq. (6) and the partition functions of the polymeric melts of the A and B species, $Z_A = V_A^{n_A}/n_A!$ and $Z_B = V_B^{n_B}/n_B!$ the Helmholtz free energy density of mixing $\Delta F/K_B TV = -\ell nZ + \ell nZ_A + \ell nZ_B$ becomes equal to

$$\frac{\Delta F}{K_B TV} = \frac{\varphi_A}{N_A}\ell n\varphi_A + \frac{\varphi_B}{N_A r}\ell n\varphi_B + u + \frac{1}{2\Gamma(d/2)N_A^{d/2}} \times \int_0^\infty \mathrm{d}p p^{d/2-1}\ell n[1 + (4uN_A\varphi_A J_A) + (4uN_A r\varphi_B J_B)], \tag{7}$$

which depends on V only through the volume fractions $\varphi_?$ and $\varphi_?$ and exactly reproduces the first two ideal terms in the well known Flory–Huggins expression. The third u term due to the absence of a prefactor that depends on the second order of the volume fractions is eliminated in the spinodal, which takes the form

$$\frac{\partial^2 \Delta F}{\partial \varphi_A^2} = \frac{1}{\varphi_A N_A} + \frac{1}{(1-\varphi_A)N_A r} - \frac{1}{2\Gamma(d/2)N_A^{d/2}} \times \int_0^\infty \mathrm{d}p \frac{p^{d/2-1}(\lambda_A J_A - \lambda_B J_B)^2}{[1 + \lambda_A J_A\varphi_A + \lambda_B(1-\varphi_A)J_B]^2} = 0,$$

$$\lambda_A = 4uN_A, \lambda_B = 4uN_A r, r = N_B/N_A. \tag{8}$$

The spinodal can obtain an analytic form if we replace the Debye functions with the approximants [9] $J_A = (p+2)^{-1}$, $J_B = (pr+2)^{-1}$. This approximation reproduces correctly the $p \longrightarrow 0$ and $p \longrightarrow \infty$ limits of the exact expression of the Debye functions introducing an error that lies about 3% of the true values. Thus performing the integration at $d = 3$ we get for the spinodal the following expression

$$\frac{1}{\varphi_A N_A} + \frac{1}{(1-\varphi_A)N_A r} - 2\chi_{\mathrm{eff}} = 0, \tag{9}$$

where χ_{eff} is defined according to Flory expression and is equal to

$$\chi_{\mathrm{eff}} = \frac{\sqrt{2\pi r}(\lambda_A - \lambda_B)^2}{N^{3/2}\Delta^{3/2}}\left[-\frac{2x + \sqrt{\Delta}}{\sqrt{x + \sqrt{\Delta}}} + \frac{2x - \sqrt{\Delta}}{\sqrt{x - \sqrt{\Delta}}}\right], \tag{10}$$

where $\Delta = x^2 - 4ry$ with $x = (2r + 2 + \lambda_B)$ and $y = (2\lambda_A\varphi_A + 2\lambda_B - 2\lambda_B\varphi_A + 4)$. χ_{eff} does not include a first order interaction term giving a first indication that it is smaller compared to the case of different species where terms in small orders in u yield phase separation [10]. In Fig. 1 we plot χ_{eff} as a function of the asymmetry ratio r for different volume fraction of the short chains φ_A. Theoretical methods furnish the value of the excluded volume parameter at the fixed-point to be equal to $u^* = \epsilon/16$, where $\epsilon = 4 - d$. It depends on the dimensionality d of the space and describes the region of full repulsion between the same monomeric units. The excluded volume parameter u have been set in this work equal to the fixed-point value of $u = 1/16$ in $d = 3$ and $u = 2/16$ in $d = 2$, considered as upper limits. For $r = 1$ all the chains in the blend are of equal length and $\chi_{\mathrm{eff}} = 0$ indicating full mixing of the two species. Increasing the asymmetry ratio, the effective interactions are increasing taking maximum values for the case we have few long chains into a 'sea' of short chains ($\varphi_A \longrightarrow 1$) and this is in agreement to the notion of the depletion potential [11]. The molecular weight dependence of the short chains on χ_{eff} is illustrated in Fig. 2 for constant asymmetry ratio r and excluded volume parameter values equal to 5 and 1/16, respectively. It can be observed that the

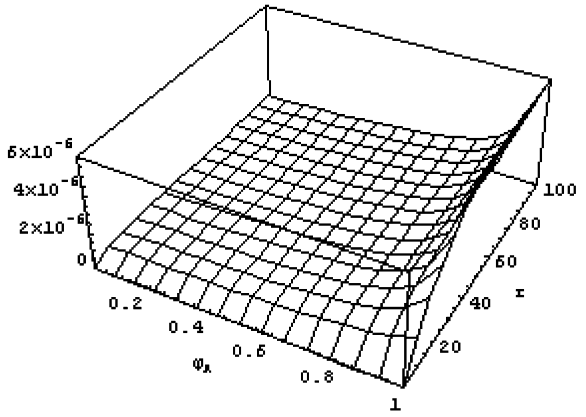


Fig. 1. χ_{eff} as a function of φ_A and r. The number of segments $N_A = 100$ and $u = 1/16$.

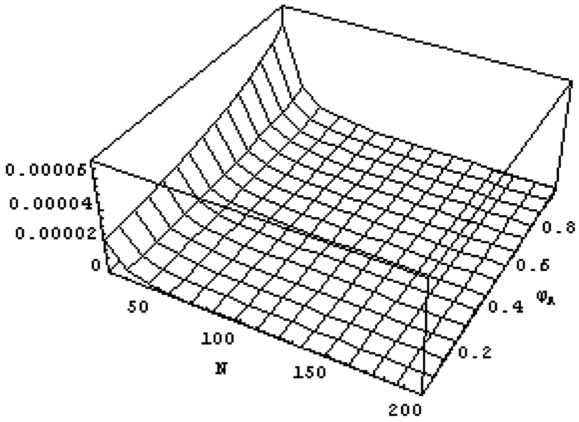


Fig. 2. χ_{eff} as a function of φ_A and N_A. $r = N_B/N_A = 5$, $u = 1/16$.

effective interactions are stronger in the case of short chains. However, their negative contribution to Eq. (9) is always smaller compared to the ideal term for any size disparity, volume fraction and molecular weight of the short chains as we have verified numerically for $d = 3$. Thus our theory predicts that a blend of chemically identical chains of any size is always miscible in agreement with previous theoretical findings [6,7] and with the experimental results on linear polyethylenes where no de-mixing of the two species was found [12]. χ_{eff} for the case of chemically identical species is generally smaller compared to that of different species and only large differences coming from different architectures, for example, could lead to phase separation at $d = 3$. We notice though that the effective interactions strongly depends on the dimensionality of the system taking the highest values at low d and decreasing as the dimensionality increasing, up to $d = 4$.

Using in Eq. (8), the same Debye approximants as previously we calculate χ_{eff} analytically at $d = 2$ as

$$\chi_{\text{eff},d=2} = \frac{(\lambda_A - \lambda_B)^2}{N_A}\left[\frac{x}{y\Delta} + \frac{2r}{\Delta^{3/2}}\ell n\left(\frac{x-\sqrt{\Delta}}{x+\sqrt{\Delta}}\right)\right]. \quad (11)$$

From the spinodal equation we found that at $d = 2$ when the size disparity r is higher than 6 and the volume fraction of the short chains is around 0.85, the blend separates in two phases. Further increase in size disparity increases the de-mixing window as it can be seen in Fig. 3. In Fig. 4 we plot $\partial^2\Delta F/\partial\phi_A^2$ for two different interaction parameters $u^* = 2/16$ and $u^* = 1/16$ while the asymmetry ratio r and the size of short species remain constant and equal to $r = 10$ and $N_A = 100$. It can be seen from this figure that the dependence of the de-mixing window on u is rather small. From the comparison of Figs. 3 and 4 the effect of the size of short species N_A is seen to be negligible.

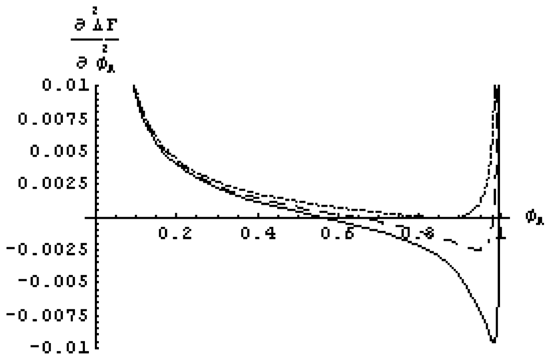


Fig. 3. $\partial^2\Delta F/\partial\phi_A^2$ as a function of φ_A with $N_A = 1000$ and $u = 2/16$. (Dot line) $r = 6$; (dash line) $r = 10$; (continuous line) $r = 20$. Zero and negative values indicate phase separation.

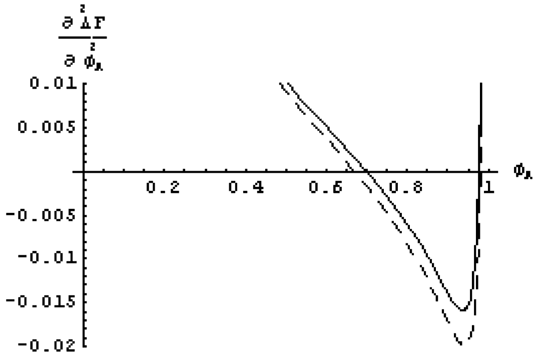


Fig. 4. $\partial^2\Delta F/\partial\phi_A^2$ as a function of φ_A with $N_A = 100$ and $r = 10$. (Dash line) $u = 2/16$; (continuous line) $u = 1/16$. Zero and negative values indicate phase separation.

4. Conclusions

Using a molecular model, we found that a blend of chemically identical linear homopolymers is always miscible for any size disparity between chains, at $d = 3$, in agreement with previous theories. At $d = 2$, a novel result was obtained, indicating a phase separation when the size disparity is higher than six times and the volume fraction of short chains is around 0.85. Increasing the size disparity the immiscibility window is increasing. This result strongly indicates that a way to observe de-mixing of chemically identical homopolymer is to increase the two-dimensional character of the chains like in the cases of strong adsorption or ultra-thin polymeric films. This observation will inspire further experiments of film blends of the same homopolymers having different size.

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References

[1] Barham P, Hill M, Keller A, Rosney C. J Mater Sci Lett 1988;7:1271.
[2] Hill M, Barham P. Polymer 1997;38:5595.
[3] Alamo R, Graessley W, Wignall G. Macromolecules 1997;30:561.

[4] Greenberg C, Foster M, Turner C, Corona S, Cloutet E, Butler P, Hammouda B, Quirk R. Polymer 1999;40:4713.

[5] Greenberg C, Foster M, Turner C, Corona S, Cloutet E, Quirk R, Butler P, Hawker C. J Polym Sci Part B: Polym Phys 2001;39:2549.

[6] Fredrickson G, Liu A, Bates F. Macromolecules 1994;27:2503.

[7] Gujrati P. Phys Rev E 2001;63:21504.

[8] Kosmas MK. Macromolecules 1989;22:720.

[9] Garas G, Kosmas MK. J Chem Phys 1995;103:10790.

[10] Garas G, Kosmas MK. Macromolecules 1994;27:6671.

[11] Asakura S, Oosawa F. J Chem Phys 1954;22:1255.

[12] Hill M, Barham P. Polymer 1995;36:1523.