Weak Segregation in Molten Statistical Copolymers

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Summary : we present a qualitative argument suggesting that a statistical (AB) copolymer should display a certain form of weak segregation, with A rich and B rich regions of size comparable to the coil radius. This should occur if the Flory parameter χ is larger than *unity* (much larger than for the phase separation of A and B of homopolymers) in agreement with detailed calculations by Frederikson, Milner and Leibler. We achieve a certain qualitative insight for the resulting microphase.

Keywords : microphase separation; polymer melts; segregation; statistical copolymers;

Introduction

Two distinct homopolymers (A…A) and (B…B) are usually non miscible, when the product of the Flory parameter χ by the polymerisation index N is large ($\chi N > 2$).[1-3] This may be understood qualitatively through the work of transfer W of one A chain from a pure A medium to a pure B medium. This work is proportional to the chain length W = NU, where U is the enthalpy increase for the transfer of one A monomer ($U = \chi$ kT, where T is the temperature). Segregation will occur when W >> kT, or $\chi N \gg 1$.

In this note, we consider the more complex problem of a melt based on a statistical linear polymer AB AA B… with N monomers, and a completely random chemical sequence. Here, the average enthalpy of mixing is trivial: what matters is the fluctuations of composition inside one chain. This question has been analysed recently by A. D. Litmanovich and coworkers[4] on a model with *two* chains in close contact: for this model, ref. [4] provides a detailed statistical analysis.

Our aim here is to extend the discussion to a real melt, in 3 dimensions, with many chains in interaction. This problem was solved long ago, at the level of the random phase approximation [5], by Frederikson, Milner and Leibler. [6] They set up a Landau theory, where

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the order parameter is the deviation from average of the A/B concentration. For our case, with no correlations along the chemical sequence, they find a spinodal threshold when $\chi > 2$.

Our main aim, in the present note, is to present a poor man's approach to this segregation problem. This is crude, but possibly helpful, because it gives a certain insight for the resulting mesophase.

Weak segregation

We assume that the sequence A…BB…A of each chain is generated independently. (This is very different from a melt of polypeptides obtained from one same protein, where all the chains have the same sequence). The fraction ϕ of monomers A on one chain has a gaussian distribution around $\phi = 1/2$, with a r.m.s. width

$$\Delta = N^{-1/2} \tag{1}$$

We divide this distribution into two pieces:

(α) with $\phi > ½$

(β) with $\phi < - 1/2$

The (r.m.s.) excess fraction of A in the (α) group is Δ. In the (β) group it is $-\Delta$.

We call $\psi(r)$ the local volume fraction of the (α) chains (ranging from 0 to 1). The average Flory Huggins energy [1] f of the $\alpha\beta$ mixture (per monomer site) is given by:

$$f/kT = N^{-1} [\psi \clubsuit n\ \psi + (1 - \psi) \clubsuit n\ (1 - \psi)] - \chi\Delta^2 (\psi - ½)^2 \tag{2}$$

This leads to a transition for:

$$\chi > 2N\Delta^{-2} \equiv 2 \tag{3}$$

Spinodals

Let us now focus on the case where χ is slightly larger than 2. We start at time 0, with a completely disordered melt. Then we expect to observe a spinodal decomposition [5] with a certain caracteristic correlation length ξ_s. The formula for ξ_s may be obtained by adding to eq. (2) a term of order $a^2 (\nabla\psi)^2$ (where a is the size of one unit in the Flory picture). The coefficient of this gradient term is unaltered by our transformation from ϕ to ψ: in the language of ref. [5], the unperturbed correlation function for one chain is always the Debye function $g_D(r)$ [7].

The result (for χ slightly above 2) is:

$$\xi_s = a/3[2 - \chi]^{-1/2} \tag{4}$$

This gives the size of the regions which should nucleate initially. Indeed, a recent simulation of Houdayer and Muller [8] (with $N \sim 20$)shows A rich and B rich regions which may correspond to this.

At very long times, the α and β regions should grow into droplets, which swell by Ostwald ripening. But it is important to realise that the diffusion constants D should be slowed down by the weakness of the constant between A and B. We expect:

$$D \sim D_0 (\chi - 2) \Delta^2 \qquad (5)$$

where D_0 is a diffusion constant for $\chi = 0$, which may be of the Rouse type (for small N) or of the reptation type (for large N).

Discussion

1) We see from eq. (3) that weak segregation should occur only for large values of the Flory parameter $\chi > 2$. This corresponds to very strong enthalpies of mixing. Thus all our discussion should be relevant only for some very special AB pairs, possibly using ionic components.

2) We should emphasize the weakness of the proposed segregation: the contrast between (α) and (β) regions is of order $\Delta << 1$, and the scattering intensities vary like $\Delta^2 \sim N^{-1}$.

3) We consider spatial variations in connection with eq. (4).But we can treat only wave vectors q which are small ($q R_0 < 1$, where $R_0 = N^{1/2} a$ is the size of one coil). At $q R_0 > 1$, the physically relevant value of Δ is $\Delta = g^{-1/2}$, where g is the number of monomers in a blob of size $q^{-1} = g = (qa)^{-2}$.

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[1] P. Flory, *Principles of Polymer Chemistry*, Cornell U. Press (Ithaca, NY), **1971**.
[2] R. L. Scott, *J. Chem. Phys.* **1949**, 17, 179.
[3] H.Tompa, *Trans. Faraday Soc.***1949**, 45, 1142.
[4] A. D. Litmanovich, Ya. V. Kudryavtsev, Yu. A. Kriksin, O. A. Kononenko, 4th Intern. Symp. "Molecular Order and Mobility in Polymer Systems", St Petersburg, June 3-7 2002, Book of Abstracts, 0-018, *"Macromol. Theory and Simul.*" (to be published).
[5] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell U. Press (Ithaca , NY), 2nd printing, **1985**.
[6] G. Frederikson, S. Milner, L. Leibler, *Macromolecules*, **1992**, 25, 6341.
[7] P. Debye, J. Phys. Colloid. Chem., **1947,** 51, 18.
[8] J. Houdayer, M. Müller, *Europhys. Lett.* **2002**, 58, 660.