SEGREGATION OF POLYMER BLENDS

IN SMALL PORES

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INTRODUCTION

Many studies have been devoted to the subject of polymer blends,
mainly as a result of their major role in the processing of new high-
performance materials.
The thermodynamic properties of an A + B polymer mixture in the
fluid state are usually described by the Flory-Huggins model :[1] the chains
are inscribed on a lattice, all sites being filled either by a monomer
A (probability ϕ) or by a monomer B (probability $1 - \phi$). The free energy
per site is then given by :

$$F/kT = N_A^{-1} \phi \, \text{Log} \, \phi + N_B^{-1}(1 - \phi) \, \text{Log}(1 - \phi) + \chi\phi(1 - \phi) \quad (1)$$

(where N_A and N_B are the degrees of polymerization of A and B respectively).
The first two terms describe the translational entropy of the chains.
The last term corresponds to the energy of interaction. The Flory parameter
χ is generally positive and favors segregation.
The (mean-field) Flory-Huggins theory is expected to be qualitatively
correct, provided that both N_A and N_B are large.[2] For instance, in the
symmetric case ($N_A = N_B = N$), the critical value of χ is given by

$$\chi_c = 2/N \quad (2)$$

For $\chi < \chi_c$, the system is entirely miscible, while for $\chi > \chi_c$ the
system separates into two phases for a certain range of the relative
concentration ϕ .
Our aim here is to understand -by the use of scaling laws- how the
critical value (2) is modified when the blend is *confined* in a cylindrical
tube of diameter D.

Let us first recall the main results obtained by Brochard and
de Gennes for a monodisperse polymer melt of chemically identical chains
confined in a tube.[3] When the diameter D of the tube is large, we are
dealing with a three dimensional system : the chains are ideal spherical
coils of size $R_0 = aN^{1/2}$ (a being a monomer size). For $aN^{1/4} \ll D \ll aN^{1/2}$,
each chain is confined in two directions but still spans an unperturbed
length R_0 in the direction parallel to the tube axis. For $D \ll aN^{1/4}$,
the chains are *spatially segregated* : each chain occupies a given length
$R \sim Na^3D^{-2}$ of the tube and the chains lie in sequence one after the other.

We now consider the case of an A + B molten polymer blend confined in a tube of diameter D. For sake of simplicity, we restrict ourselves to the symmetric case $N_A = N_B = N$. We take the wall to be repulsive and assume that the interaction between a monomer and the wall is the same for the two polymer species. If $D >> aN^{1/2}$, the system is three dimensional and χ_c is given by $\chi_c \sim 1/N$ (Eq.(2)). On the other hand, if $D << aN^{1/4}$, we know (see section 1) that the chains lie in sequence one after the other (Fig. 1). The free energy per site is then given by

$$F/kT = N^{-1}\phi \, Log\phi + N^{-1}(1 - \phi) \, Log(1 - \phi) + 2N^{-1}\phi(1 - \phi)\varepsilon_{AB}/kT \quad (3)$$

where ε_{AB} represents the energy associated to the boundary between an A-chain and a B-chain. If we denote by L the thickness of this boundary, ε_{AB} can be written as

$$\varepsilon_{AB} \sim LD^2 a^{-3} kT\chi \quad (4)$$

where LD^2 represents the volume of the interfacial region. For a *non confined* system, the interfacial thickness was predicted to vary as $\sim a\chi^{-1/2}$.[4] This result can be qualitatively derived[5] by considering a sharp A - B boundary (Fig. 2). A portion (n monomers) of the A-chain will enter the B-phase if $n.(kT\chi) \lesssim kT$. Such a portion extending over a distance $\sim an^{1/2}$, we indeed recover the expression $a\chi^{-1/2}$.

If we assume that the interfacial thickness is not modified by the confinement, i.e. :

$$L \sim a\chi^{-1/2}, \quad (5)$$

Eqs.(3), (4) and (5) lead to a critical value of the Flory parameter[6]

$$\chi_c \sim (D/a)^{-4} \quad (1 < D/a << N^{1/4}) \quad (6)$$

Since for $D = aN^{1/4}$ we recover the 3d value $\chi_c \sim 1/N$, we conclude that χ_c departs from its 3d value only when D becomes smaller than $aN^{1/4}$ (see Fig. 3). For $D << aN^{1/4}$, χ_c increases, thus *increasing* the blend miscibility.

DISCUSSION

1. It can be shown that the approximation $L \sim a\chi^{-1/2}$ breaks down for $D < a\chi^{-1/4}$. However, the results derived in the previous section do remain valid.[7]

2. It is important to notice that the chains may have difficulty to re-arrange themselves : to pass through a B-chain, an A-chain must get over a potential barrier which becomes large with regard to kT for $D << aN^{1/4}$. In that case, equilibration times might thus become very long.

3. In the case of a polymer blend confined in a *slab*, the critical value of χ is expected to be given by the usual three dimensional expression (Eq.(2)), whatever the distance between the two walls.[7] To observe an increase of the blend miscibility, one must therefore confine the system at least along two directions (e.g. in a tube).

4. We have here studied the segregation of two, chemically different, polymers of the same length in a confined geometry. The somewhat related

problem of a confined mixture of long and short -chemically identical-
chains will be discussed elsewhere. [8]
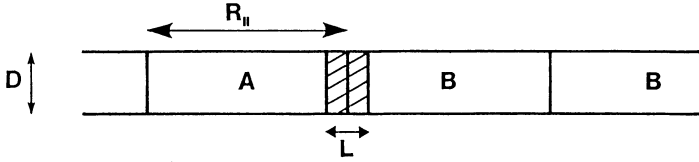
Figure 1. A+B polymer blend confined in a tube of
diameter D in the regime $1 \leqq D/a \ll N^{1/4}$.
Each chain occupies a given length $R_{\parallel}$ of
the tube and the chains lie in sequence
one after the other. Two adjacent chains
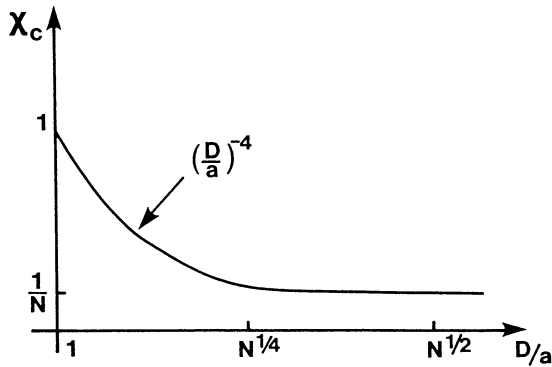A and B overlap in a region of thickness
L (shaded area).

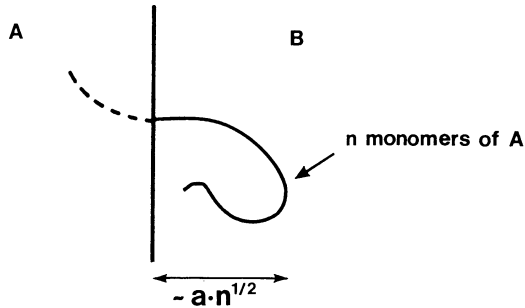Figure 2. Variation of the critical value of the Flory
parameter with the diameter D of the tube.

Figure 3. An interface between A and B polymers. A portion
of an A-chain (n monomers) may enter the B phase
if $n \cdot \chi \leqq 1$. Such a portion of the chain extends
over a distance $a n^{1/2}$ and the overall thickness
of the interface is given by $a \cdot \chi^{-1/2}$.

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4. E. Helfand and Y. Tagami, J. Polym. Sci. B29:741 (1971).
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6. Since we are now dealing with a one dimensional system and short range couplings we cannot strictly define a critical point and a critical value of ε_{AB}. However, there is at least a crossover-point between an uncorrelated mixture and a situation with long correlated "trains" of identical chains. The crossover point corresponds to $\varepsilon_{AB} \sim kT$, which leads to Eq.(6).
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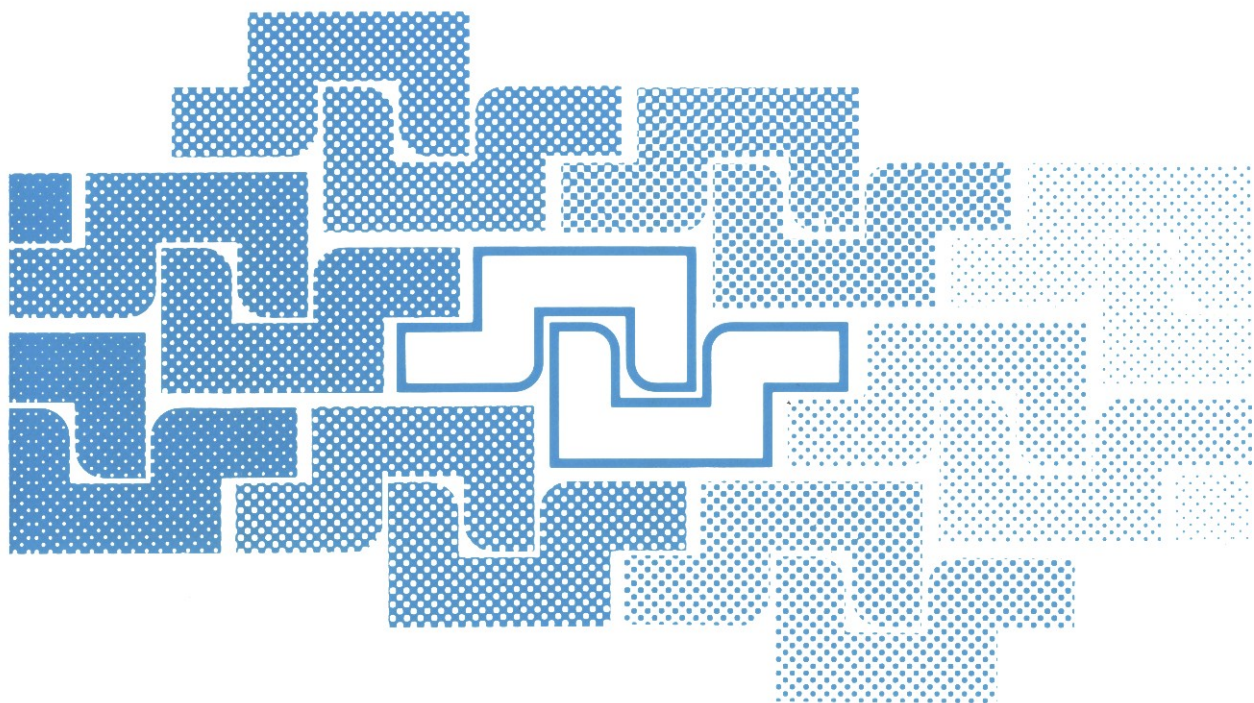
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