Plates, fences and needles: an example of the Skoulios effect

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We discuss some morphologies for triblock copolymers with a rigid, unsoluble part (R) at the center and two flexible, soluble parts (F) – plus a solvent (S). Aggregation may lead to plates of R, covered by brushes of F (the rod axis being tilted, as analyzed by A. Halperin). But, in certain conditions, because the F portions repel each other, the plates may be replaced by "needles" of R: the F chains can expand more freely near the tips of each needle, as first noticed (in a different context) by A. Skoulios. We show that this gives an energy drop proportional to the *perimeter* of the brush region. A third possibility is based on a "fence" of R rods, decorated at both ends by "bottle-brushes" of F. We also analyze the energy of these "bottle-brushes".

1. Introduction

1.1. Aims

Block copolymers with rigid pieces (R) and flexible pieces (F) may generate interesting new forms of rubbers, with segregated R regions acting as crosslinks between the F chains. For a given chemical system (R, F), it is of some interest to understand what form of aggregation should take place and what mechanical properties can be expected from them, without synthetizing too many examples of molecules. In the present note, we start with a simpler problem: namely a solution of triblock FRF molecules, in a solvent which is good for F and bad for R. They will then aggregate. We want to know which form of aggregation is preferred. We assume concentrations which are not too high, so that we can consider a single aggregate unit and ignore its interactions with other aggregates.

1.2. Driving forces

The simplest equilibrium form is the *plate* displayed in fig. 1. On both sides of the R region, we have a brush of F molecules. An essential feature is that the F molecules, which repel each other in good solvent solutions, favour arrangements where the interfacial area per chain Σ is large, while the R portions (because of the high interfacial energy γ between R and S (solvent)) prefer a small Σ ($\sim a$, a being a monomer size).
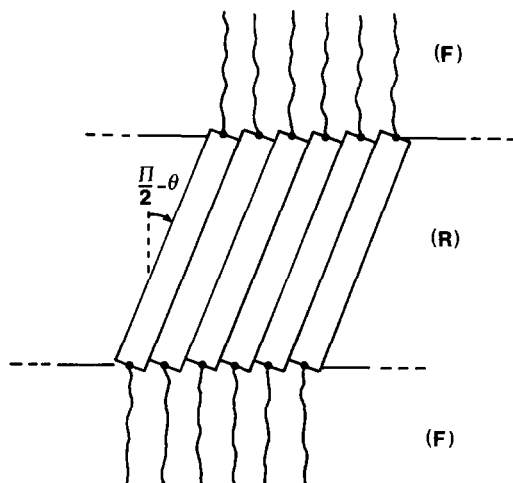
Fig. 1. A schematic cross-section of a plate formed by FRF molecules. The R portions are tilted by an angle $\frac{1}{2}\pi - \theta$. The separation between two adjacent grafting sites is $a/\sin\theta$ in the plane of the figure, but remains equal to a in the perpendicular direction.

One form of compromise is obtained by *tilting the R chains*; this has been discussed recently by Halperin [1], and can be summarized as follows:

(a) The free energy (per chain) of a brush, as analyzed by Alexander [2], has the scaling form

$$f_F = N_F k T \sigma^{5/6} , \tag{1}$$

where $\sigma = a^2/\Sigma$ is the surface density of stems, and $\Sigma = a^2/\sin\theta \sim a^2\theta^{-1}$, where θ is the complement of the tilt angle (it will turn out that $\theta \ll 1$).

(b) The interfacial energy (per chain) at small θ is

$$f_I = \gamma a^2 \theta^{-1} . \tag{2}$$

Optimizing the sum (1) + (2), one obtains the Halperin result:

$$\theta \cong \left(\frac{K}{N_F}\right)^{6/11} , \tag{3}$$

where $K = \gamma a^2 / kT$ is usually expected to be of order unity.

1.3. The Skoulios effect

Very long ago, Skoulios [3] encountered a related mismatch problem when studying the crystallography of dry soaps (where the polar heads tend to have a small area Σ, while the aliphatic tails would prefer a larger Σ). He found that in many cases, the polar heads segregate in the form of ribbons (or discs) with a finite radius, thus allow-

ing more freedom to the chains near the edge of the ribbons. We expect a very similar phenomenon to occur in some of our block copolymers; two forms then come to the mind: "needles" (fig. 2) and "fences" (fig. 3). A simplified form of needles is constructed in section 3, fences in section 4. All our discussion is restricted to the level of scaling laws.

2. Edge energy of a brush

(i) Our starting point is to construct a free energy for a brush (parallel to the xy plane), in conditions where the chains may be tilted (along x). We describe this tilt in terms of a "polarization":

$$P = \left\langle \frac{1}{D_0^2} \sum_{i=1}^{i=N_F} x_i \right\rangle, \tag{4}$$

where $1/D_0^2$ is the density of chain ends at the surface, while the x_i are the positions (along x) of the various monomers along one chain. The number density of monomers is related to $\partial P/\partial x$:

$$\Gamma = \frac{N_F}{D_0^2} - \frac{\partial P}{\partial x} = \Gamma_0 - \frac{\partial P}{\partial x}. \tag{5}$$

(ii) The mean field energy (per unit area) is a combination of elastic and excluded volume energies, computed at the actual density Γ:

$$f = \frac{\Gamma}{N_F} kT \left(\frac{3}{2} \frac{h^2}{N_F a^2} + \frac{1}{2} \frac{N_F \Gamma a^3}{h} \right), \tag{6}$$

where h is the brush thickness. Minimization with respect to h leads to

$$h = a \left(\frac{a^2 N_F^2 \Gamma}{6} \right)^{1/3}, \tag{7}$$

$$f = f_0 - f' \left(\frac{\partial P}{\partial x} \right) + \tfrac{1}{2} f'' \left(\frac{\partial P}{\partial x} \right)^2 + \dots, \tag{8}$$

where

$$f' = \frac{15}{2 \cdot 6^{2/3}} kT \left(\frac{a}{D_0} \right)^{4/3}, \qquad f'' = \frac{5}{6^{2/3}} kT \frac{a^2}{N_F} \left(\frac{D_0}{a} \right)^{2/3}. \tag{9}$$

(iii) We must add to (8) a term describing the elastic energy associated to P, of the form

$$F = \tfrac{1}{2} \kappa P^2, \qquad \kappa = 12 kT N_F^{-3} \left(\frac{D_0}{a} \right)^2. \tag{10}$$

From the sum $f+F$, we can define a correlation length ξ for the P field:

$$\xi^2 = \frac{f''}{\kappa} = \tfrac{5}{12} h_0^2 , \tag{11}$$

where h_0 is the thickness for $P=0$.

(iv) Consider now a brush extending from $x=0$ to $x=+\infty$. The spillover of the brush near $x=0$ is described by a P field of the form

$$P(x) = -P_0 \exp(-x/\xi) . \tag{12}$$

We determine P_0 by returning to the free energy: integrating $f+F$ over the region $0 < x < \infty$, we find an edge energy

$$-f'P_0 + \tfrac{1}{2}\kappa\xi P_0^2 = -\Im . \tag{13}$$

We then optimize this with respect to P_0:

$$P_0 = \frac{f'}{k\xi} = \tfrac{1}{4}(15)^{1/2} h_0 \Gamma_0 , \tag{14}$$

and obtain a Skoulios energy correction $-\Im$, where $\Im$ is given by

$$\Im = \tfrac{1}{2}f'P_0 = \frac{3^{1/2}\,5^{3/2}}{32}\frac{kT}{a}N_{\mathrm{F}}^2\left(\frac{a}{D_0}\right)^4 . \tag{15}$$

3. The simplest "needle" form

A typical "needle" (with a cross section $am_1 \times am_2$) is shown in fig. 2. The needle contains $n = m_1 \times m_2$ molecules.

3.1. The naive model

The simplest form of needle that one can imagine corresponds to a *square* cross section ($m_1 = m_2 = n^{1/2}$). The needle energy is then

$$U(n) = 4an^{1/2}\gamma L + 2\times\mathrm{const}\times\gamma a^2 n/\sin\theta - 4an^{1/2}(1+1/\sin\theta)\,\Im . \tag{16}$$

The first term is the lateral energy of the hard core. The second term is associated with the two terminal caps: it contains both the R/solvent interfacial energy and the brush energy (which are comparable at the optimum θ). The last term is the Skoulios correction (taken on both square edges). We see from (16) that if

$$\gamma L < (1+1/\sin\theta)\,\Im \tag{17}$$

there is an optimum number of molecules n^* for the needle. The condition (17) is not unrealistic because $(1+1/\sin\theta)\,\Im \sim N_{\mathrm{F}}^{16/11}$, and can dominate over γL (propor-
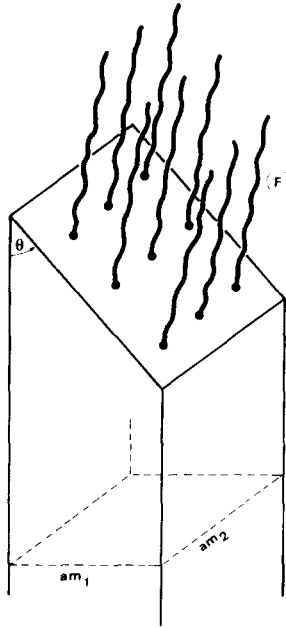
Fig. 2. A needle with a cross section $am_1 \times am_2$. Only one end of the needle is shown. More freedom is allowed to the chains near the edge of the brush (an effect not shown in the figure).

tional to N_R). Thus the Skoulios effect can generate aggregates of finite size.

3.2. Criticism of the model

Despite its apparent simplicity, the above model is not correct since it assumes a priori a square cross section for the needle. In fact, in order to minimize its free energy, the needle tends to flatten ($m_2 < m_1$). This leads to a rather lengthy discussion of stabilities, which will be reported elsewhere. Here we will only consider the extreme case $m_2 \sim 1$, which we call a *fence*.

4. Fences and bottle-brushes

4.1. Structure of a bottle-brush

In fig. 3 we see a fence, with flexible chains F starting from the tips of the fence. The F chains attached to this fence form a "bottle-brush" [1] with a spacing $D = a\varphi^{-1}$.

[1] The work "bottle-brush" has been (to our knowledge) introduced first in connection with block copolymers consisting of long styrene midblocks and much shorter 4-vinyl pyridine endblocks quaternized with iodo alkanes; see ref. [4].
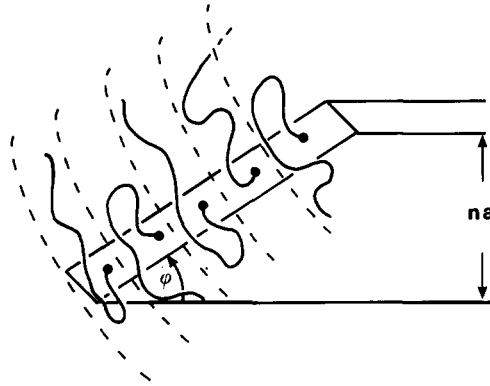
Fig. 3. A fence containing n molecules. Only one end of the fence is shown. The F chains form a "bottle-brush". The separation between two adjacent grafting sites is $a/\sin\varphi$.

The concentration profile of F monomers at a distance r from the brush axis can be derived by the Edwards self-consistent field method [5] and scales like $r^{-2/3}$. Here, to save space, we use a more compact argument of the Flory type [6] where each F coil is confined in a disc of radius R and length D. The energy per F chain (for an athermal solvent) is then

$$f_F \cong kT\left(\frac{R^2}{N_F a^2} + \frac{N_F^2 a^3}{R^2 D}\right) \tag{18}$$

and the optimum radius is $R \sim a N_F^{3/4}\varphi^{1/4}$, giving an energy $\sim kT(N_F\varphi)^{1/2}$. A more refined scaling approach, inspired by the Marques analysis of long copolymer micelles [7] gives the same law for R, but a slightly different energy:

$$f_F = kT N_F^{3/8}\varphi^{5/8} . \tag{19}$$

To the energy f_F, we must add a capillary term $\gamma a^2\varphi^{-1}$. This leads to an optimum angle

$$\varphi = K^{8/13} N_F^{-3/13} . \tag{20}$$

(Note that the fence angle φ is larger than the plate angle θ.)

4.2. Overall energy of a "fence"

A fence containing n molecules has an energy

$$U_n = na^2\gamma(2N_R + \text{const} \times \varphi^{-1}) - 4\mathfrak{I}_1 , \tag{21}$$

where the last term is another Skoulios correction, and is independent of n (for $n \gg 1$).

5. Concluding remarks

(1) In the present note, we do not discuss the relation stability of plates, needles and fences – because this involves many cases. But we hope to have shown what are the basic ingredients.

(2) The most important feature is the edge energy of a brush ($-\Im$) describing the Skoulios effect (for brushes of linear size larger than ξ). Our estimate of $\Im$ is based on a very crude Landau–Ginzburg description of tilted brushes, but it does show that $\Im$ can be quite large.

(3) Another facet of this problem is obtained with copolymers which can act as cross links in a rubbery structure: here the basic chemical unit is the triblock RFR. A complete discussion of the aggregation forms of these triblocks would be very complex. One first (naive) step towards it amounts to investigate FRF triblocks in a sea of F molecules: this will be described in a separate publication.

Acknowledgements

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