

AGGREGATION OF FLEXIBLE-RIGID-FLEXIBLE TRIBLOCK COPOLYMERS

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Abstract : We discuss the aggregation behavior of flexible-rigid-flexible triblock copolymers in a selective solvent of low molecular weight. Aggregation may lead either to plates of (R) covered by brushes of (F), or to large "needles" (as a consequence of the Skoulios effect). In the absence of anisotropic bonding between adjacent rods, the "fence" morphology is not expected.

I - INTRODUCTION

1.1. Aims

Block copolymers are the subject of considerable theoretical and experimental activity⁽¹⁾⁻⁽⁶⁾. Most of the existing studies focus on flexible chains and much less is known of the behavior of block copolymers incorporating both flexible (F) and rigid (R) pieces⁽⁷⁾⁻⁽⁹⁾. These systems may generate interesting new forms of rubbers, with segregated R regions acting as crosslinks between the F chains. In the present work - which extends the analysis of reference (9) - we study the aggregation behavior of FRF triblock copolymers in a selective solvent (good for F, bad for R) of low molecular weight.

1.2. The tilted plate

The simplest morphology is the plate (or lamellae) pictured on Fig. 1. On both sides of the R region, the F molecules form a brush. While the F molecules (which repel each other) favour arrangements where the interfacial area per chain Σ is large, the R portions (because of the high interfacial energy γ between R and the solvent) prefer a small Σ (of the order of the monomer size a). As discussed recently by A. Halperin⁽⁷⁾, one form of compromise is obtained by tilting the R chains :

a) the free energy (per chain) of a brush has the scaling form⁽¹⁰⁾

$$f_F \approx kT N_F \sigma^{5/6} \quad (1)$$

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

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

$$f_I \approx \gamma a^2 \theta^{-1} \quad (2)$$

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

$$\theta \approx \left(\frac{K}{N_F} \right)^{6/11} \quad (3)$$

where $K = \gamma a^2/(k/T)$ is usually expected to be of order unity.

Note that for $\theta < N_R^{-1}$ the plate breaks down and the preceding discussion is no longer meaningful. In all what follows we

shall therefore assume that

$$N_R > (N_F/K)^{6/11} \quad (4)$$

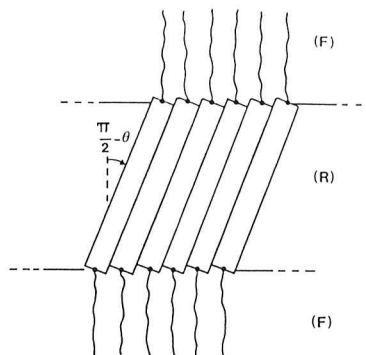


Fig. 1. A plate formed by FRF molecules. The R portions are tilted by an angle $\pi/2 - \theta$. The separation between two adjacent grafting sites is $a/\sin\theta$ in the plane of the figure but remains equal to a in the perpendicular direction.

1.3. The Skoulios effect

Thirty years ago, Skoulios studied the crystallography of dry alkaline soaps⁽¹¹⁾. He found that in many cases, rather than forming a lamella, the polar heads segregate in the form of indefinitely long ribbons (or in the form of discs with a finite radius), thus allowing more freedom to the chains near the edge of the ribbons (Fig. 2). We expect a very similar phenomenon to occur with our FRF copolymers, leading to equilibrium structures such as "fences" (Fig. 3) or "needles" (Fig. 4).

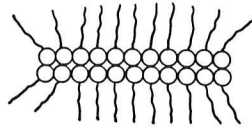


Fig. 2. A schematic cross section of an indefinitely long ribbon formed by alkaline soap molecules (after (11)). More freedom is allowed to the chains near the edge of the ribbons.

The present paper is organized as follows. In section II, we give an estimate of the edge energy of a brush describing the Skoulios effect. Fences are constructed in section III. Section IV is devoted to the construction of needles and to the relative stability of plates, needles and fences. We restrict our study to dilute solutions so that we can consider a single aggregate unit and ignore its interactions with other aggregates. Our analysis is based on scaling arguments: the exact prefactors in all our formulas remain unknown.

II - EDGE ENERGY OF A BRUSH

2.1. Mean field approximation

Consider 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" :

$$P = \frac{1}{D^2} \left\langle \sum_{i=1}^{N_F} x_i \right\rangle \quad (5)$$

where $1/D^2$ 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 $\partial P / \partial x$:

$$\Gamma = \Gamma_0 - \frac{\partial P}{\partial x} \quad (6)$$

with $\Gamma_0 = N_F / D^2$. Equation (6) is analogous to the relation between the local charge and the polarization in a dielectric.

A (crude) Landau-Ginsburg energy for the tilted brush has been recently constructed⁽⁹⁾ :

$$H = \int dx \left[\frac{1}{2} \kappa P^2 - \alpha \left(\frac{\partial P}{\partial x} \right) + \frac{\beta}{2} \left(\frac{\partial P}{\partial x} \right)^2 + \dots \right] \quad (7)$$

with

$$\kappa \approx \left(\frac{D}{a} \right)^2 N_F^{-3}, \quad \alpha \approx kT \left(\frac{a}{D} \right)^{4/3}, \quad \beta \approx kT \left(\frac{D}{a} \right)^{2/3} \frac{a^2}{N_F} \quad (8)$$

From (7) we can define a correlation length ξ for the P field

$$\xi = \left(\frac{\beta}{\kappa} \right)^{1/2} \approx h_0 \quad (9)$$

where $h_0 \approx a N_F^{2/3} (a^2 \Gamma_0)^{1/3}$ is the brush thickness for $P = 0$.

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

$$P(x) = -P_0 \exp(-x/\xi) \quad (10)$$

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

$$-\alpha P_0 + \frac{1}{2} \kappa \xi P_0^2 = -\zeta \quad (11)$$

We then optimize this with respect to P_0

$$P_0 = \frac{\alpha}{\kappa \xi} \approx h_0 \Gamma_0 \quad (12)$$

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

$$\zeta = \frac{1}{2} \alpha P_0 \approx \frac{kT}{a} N_F^2 \left(\frac{a}{D}\right)^4 \quad (13)$$

Note that eq.(13) can be rewritten as :

$$\zeta \approx \Pi \cdot h_0^2 \quad (14)$$

where

$$\Pi \approx \frac{kT}{a^3} \left(\frac{N_F a^3}{D^2 h_0}\right)^2 \quad (15)$$

is the osmotic pressure inside the brush (far away from the edge).

2.2. Scaling estimate of the Skoulios tension

A scaling estimate of ζ may be obtained by assuming that eq.(14) is still valid, provided that the scaling form of the osmotic pressure

$$\Pi \approx \frac{kT}{a^3} \left(\frac{N_F a^3}{D^2 h_0} \right)^{3/4} \quad (16)$$

is used instead of (15). This leads to :

$$\zeta \approx \frac{kT}{a} N_F^2 \left(\frac{a}{D} \right)^{13/3} \quad (17)$$

III - FENCES AND BOTTLE-BRUSHES

3.1. Structure of a bottle-brush

Figure 3 represents a "fence" of R chains, with flexible F chains starting from the tips of the fence. The F chains attached to the fence form a "bottle-brush" with a spacing $D = a \phi^{-1}$ and a radius R . The structure of this bottle-brush can be derived by the Edwards self consistent field method⁽¹²⁾. Starting from the basic equation

$$\frac{kT}{a^2} \left(\frac{dr}{dN} \right)^2 = kT a^3 c(r) \quad (18)$$

(where $c(r)$ is the concentration profile of F monomers at a distance r from the brush axis) and taking into account that

$$(2\pi r dr D) c(r) = dN \quad (19)$$

we get (for $r \geq D$) :

$$c(r) \approx a^{-3} \left(\frac{a}{D} \right)^{2/3} \left(\frac{a}{r} \right)^{2/3} \quad (20)$$

$$r(N) \approx a \left(\frac{a}{D}\right)^{1/4} N^{3/4} \quad (21)$$

In particular, the radius R of the bottle-brush is given by

$$R \approx a \phi^{1/4} N_F^{3/4} \quad (22)$$

The free energy (per F chain) may be obtained by integrating the energy density $kT \cdot a^3 \cdot c^2(r)$ over the bottle-brush region, leading to

$$f_F \approx kT N_F^{1/2} \phi^{1/2} \quad (23)$$

A more refined scaling approach, inspired by the Marques analysis of long copolymer micelles⁽¹³⁾ gives the same law for R , but a slightly different energy :

$$f_F \approx kT N_F^{3/8} \phi^{5/8} \quad (24)$$

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

$$\phi = k^{8/13} N_F^{-3/13} \quad (25)$$

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

3.2. Overall energy of a fence

A fence containing n molecules has an energy

$$F_f = 2a^2 N_R \gamma (n+1) + 2(\text{const}) a^2 \gamma \phi^{-1} n - 4\zeta \quad (26)$$

The first term in eq.(26) is the lateral contribution to the interfacial energy. The second term is associated with the two tips of the fence : it contains both the R/solvent interfacial energy and the bottle-brush energy (which are comparable at the optimum ϕ). The last term is a Skoulios correction (different from the one considered in section II) which is independent of n (for $n \gg 1$).

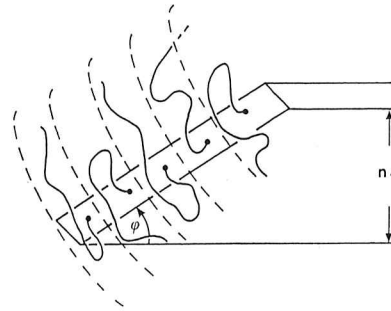


Fig. 3. A fence containing n molecules (only one end of the fence is shown). The F chains form a "bottle-brush". The separation between two adjacent grafting sites is $a/\sin\phi$.

IV - NEEDLES

A typical "needle" with a cross section $a_{m1} \times a_{m2}$ is shown on Fig. 4 ($m_1 \geq m_2$). The needle contains $n = m_1 \times m_2$ molecules and its energy is given by

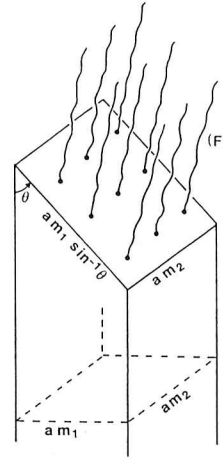
$$F_{\text{need}} = 2a^2 N_R \gamma (m_1 + m_2) + 2(\text{const}) a^2 \gamma \theta^{-1} n - 4 \zeta a (m_1 \theta^{-1} + m_2) \quad (27)$$

Note that a fence (section III) may be considered as an extreme case

of needle ($m_1 = n, m_2 = 1$).

The first term in eq.(27) 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 derived in section II.

Fig. 4 : a needle with a cross section $a m_1 \times a m_2$. More freedom is allowed to the F chains near the edge of the brush (an effect not shown on the figure).



Equation (27) is meaningful as long as the Skoulios correction is smaller than the brush energy. Comparing the last two terms, we can thus define a threshold value m_1^t above which the needle energy is no longer given by (27) :

$$m_1^t \sim \frac{K n}{[\zeta a / (kT)]} \sim K^{-2/11} N_F^{-9/11} n \quad (28)$$

(where we have used the scaling estimate of ζ , eq.(17)). In what follows we shall assume that the number n of molecules is such that $m_1^t > n^{1/2}$, i.e.

$$n > K^{4/11} N_F^{18/11} \quad (29)$$

The corresponding threshold value of m_2 is given by

$$a m_2^t = a \frac{n}{m_1^t} \approx \xi \quad (30)$$

where $\xi \approx a N_F \theta^{1/3}$ is the correlation length defined by (9). We therefore conclude that as long as the width $a m_2$ of the needle is smaller than the correlation length ξ (or, equivalently, smaller than the brush thickness) the Skoulios term is indeed a small correction and (27) is meaningful⁽¹⁴⁾. On the other hand, we know that for $m_1 = n$ the needle energy must correspond to the fence energy derived in section III :

$$F_f \approx kT [K N_R + K^{5/13} N_F^{3/13}] n \quad (31)$$

(all numerical prefactors being omitted).

The energy (27) can be rewritten as

$$F_{\text{need}} \approx X m_1 + Y \frac{n}{m_1} + Z n \quad (n^{1/2} \leq m_1 \leq m_1^t) \quad (32)$$

where

$$X = 2a (a N_R \gamma - 2\zeta\theta^{-1}) \approx 2kT (K N_R - 2K^{7/11} N_F^{15/11})$$

$$Y = 2a (a N_R \gamma - 2\zeta) \approx 2kT (K N_R - 2K^{13/11} N_F^{9/11}) \quad (33)$$

$$Z = 2 (\text{const}) \gamma a^2 \theta^{-1} \approx 2kT K^{5/11} N_F^{6/11}$$

According to the sign of X and Y , various cases must be considered (K being of order unity, Y is always larger than X).

(1) $X < 0 < Y$

This regime corresponds to

$$2K^{13/11} N_F^{9/11} < K N_R < 2K^{7/11} N_F^{15/11} \quad (34)$$

(intermediate N_R regime). The needle energy (32) is then a monotonous, decreasing function of m_1 . For $m_1 = m_1^t$ the needle energy is roughly given by :

$$F_{\text{need}}^t \equiv F_{\text{need}}(m_1 = m_1^t) \sim kT [K^{9/11} N_R N_F^{-9/11} + K^{5/11} N_F^{6/11}] n \quad (35)$$

Using eqs.(31) and (35), we find that as long as N_R is larger than the critical value

$$N_R^* = \frac{K^{5/11} N_F^{6/11} - K^{5/13} N_F^{3/13}}{K [1 - K^{-2/11} N_F^{-9/11}]} \approx (N_F/K)^{6/11} \quad (36)$$

then the two energies F_{need}^t and F_f satisfy

$$F_{\text{need}}^t < F_f \quad (37)$$

Taking into account eq.(4), we conclude that the inequality (37) is fulfilled (whatever the regime under consideration 1, 2 or 3).

Assume that between m_1^t and n the needle energy is a monotonous increasing function of m_1 . In the range

$n^{1/2} \leq m_1 \leq n$ the needle energy is then minimal for $m_1 = m_1^t$. To find the optimal aggregation number in a needle, we minimize the grand potential

$$\Omega = F_{\text{need}}^t - n \mu \quad (38)$$

where μ is the chemical potential of an isolated molecule. For a dilute solution with volume fraction ϕ

$$\mu = kT \log_e \phi + 4a^2 N_R \gamma \quad (39)$$

whence

$$\Omega = kT [c - \log_e \phi] n \quad (40)$$

$$c = K^{5/11} N_F^{6/11} - K N_R (1 - K^{-2/11} N_F^{-9/11}) < 0 \quad (41)$$

We thus find a critical concentration

$$\phi_{cr} \approx \exp c \quad (42)$$

For $\phi < \phi_{cr}$, no aggregation occurs [a word of caution is needed : eq.(40) is valid only for $n \geq K^{4/11} N_F^{18/11}$; to be sure that no aggregation occurs below ϕ_{cr} one would have to compute the free energy of a needle containing less than $K^{4/11} N_F^{18/11}$ molecules]. For $\phi > \phi_{cr}$, large needles ($n \rightarrow +\infty$) show up. The length $a m_1^t$ of these needles tends to infinity (see eq.(28)) while their width remains finite and equal to the correlation length ξ .

This regime corresponds to

$$2 K^{7/11} N_F^{15/11} < K N_R \quad (43)$$

(large N_R regime).

a) If $n < (Y/X) N_F^{18/11}$, the energy (32) is a monotonous, decreasing function of m_1 . In the range $n^{1/2} < m_1 < m_1^t$ the needle energy is thus minimal for $m_1 = m_1^t$.

b) If $n > (Y/X) N_F^{18/11}$, the energy (32) passes through a minimum for

$$m_1 = \tilde{m}_1 \equiv n^{1/2} (Y/X)^{1/2} \quad (44)$$

In the range $n^{1/2} \leq m_1 \leq m_1^t$, the needle is thus minimal for $m_1 = \tilde{m}_1$.

The Ω potential is given by

$$\frac{\Omega}{kT} = \begin{cases} (c - \log_e \phi)n + \text{constant} & n < (Y/X) N_F^{18/11} \\ A n^{1/2} + (B - \log_e \phi)n + \text{constant} & n > (Y/X) N_F^{18/11} \end{cases} \quad (45)$$

where c is given by (41) and

$$A = 2 \left(\frac{X}{kT} \right)^{1/2} \left(\frac{Y}{kT} \right)^{1/2} > 0 \quad (46)$$

$$B = \frac{Z}{kT} - 4 K N_R < 0 \quad (47)$$

For $\phi < \phi^* \equiv \exp B$, no aggregation occurs. For $\phi > \phi^*$, plates show

up. (Note that ϕ^* is slightly smaller than ϕ_{cT}).

(3) $X < Y < 0$

This regime corresponds to

$$K N_R < 2 K^{13/11} N_F^{9/11} \quad (48)$$

(small N_R regime). The energy (32) is then a monotonous decreasing function of m_1 : above the critical concentration (42) large needles (length $\rightarrow +\infty$, width = ξ) show up.

V - CONCLUDING REMARKS

1) The aggregation behavior of FRF copolymers in a selective solvent depends mainly on the lengths of (R) and (F). We have seen that for large N_R the stable equilibrium form is the plate, while for smaller values of N_R large needles (length $\rightarrow +\infty$, width = ξ) are preferred. Within our model fences are never expected.

2) Sometimes in nature the fence structure can be stabilized by anisotropic bonding between adjacent rods: this occurs for instance (via H bonds) in the β sheets of polypeptides such as silk. We have also considered such FRF molecules with anisotropic bonding and showed that in this case the fence structure can indeed occur (these results will be described elsewhere).

3) Our discussion is fragile since the analysis of section IV is oversimplified. A more rigorous analysis would require the computation of the free energy of a needle containing less than $(\xi/a)^2$ mole-

cules.

4) The present study was restricted to the case of a low-molecular-weight solvent. The behavior of FRF copolymers in a sea of F molecules will be published elsewhere.

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- (14) Note that eq.(26) implicitly assumes that the complement of the tilt angle of the needle remains equal to θ (eq.(3)). This hypothesis is justified by the coherence of the result (30). It is likely that for $m_1 > m_1^t$ the complement of the tilt angle of the needle increases and reaches the value ϕ (eq.(25)) for $m_1 = n$.