Grafted rod–coil polymers in poor solvents: turnip and jellyfish surface micelles[1]

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Abstract

We consider a system of rod-coil diblock copolymers which are permanently tethered to a flat surface by the end of the coil block. This system is placed in a solvent which is poor for both the rods and the coils. At low grafting densities the polymers form separate globules on the surface. As the grafting density is increased these globules can fuse to form surface micelles. At intermediate grafting densities a 'turnip' should form, while at the higher grafting densities the system resembles a series of 'jellyfish'. © 1997 Elsevier Science B.V.

1. Introduction

Recently there have been several reports of successful syntheses of rod-coil diblock copolymers [1,2]. These consist of a flexible coil polymer joined irreversibly to the end of an inflexible rod-like polymer (Fig. 1). The combination of flexibility of one block and inflexibility in the second block imparts novel microphase behaviour and mechanical properties to melts and solutions of these rod-coil diblocks. Traditional diblock copolymers are comprised of two flexible homopolymers which would normally phase separate, but are limited by the chemical linkage of the blocks to phase separation on the microscale, forming domains of the order of 100 Å. Lamellar, cylindrical, spherical and bicontinuous microphases have

been found experimentally under a wide range of conditions [3] and are understood in terms of an energetic balance between deformation of the flexible components and the chemical incompatibility of the block constituents. The bulk behaviour of these coil-coil systems are now very well understood. While rod-coil diblocks have not been as extensively investigated experimentally, predictions of microphase separation in the bulk have been made with account of the different flexibility in the diblocks; however, no predictions or experiments have addressed the surface mediated microphase separation. Surface bound rod-coil diblock copolymers are expected to differ significantly from coil–coil diblocks as the lack of flexibility of the rod component becomes more significant as the dimension is reduced from three (bulk) to two (surface).

Several theoretical studies predict a wide range of bulk microphase morphologies for rod-coil

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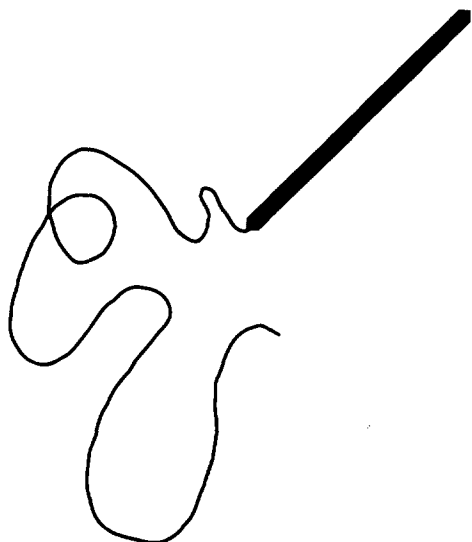[1] This paper is dedicated to Professor Barry Ninham on the occasion of his 60th birthday.

Fig. 1. A rod-coil diblock consisting of a flexible coil segment of N monomers attached to a rod-like segment of N_r monomers.

copolymers. The first of these was by Semenov and Vasilenko [4] who considered a melt of rod-coil diblocks and predicted some of the phases which could be formed: an isotropic phase, a nematic phase where the rods have orientational order but where there is no translational order, and two kinds of smectic phases, in which the rods pack into layers. The microphase behaviour was predicted via minimization of the free energy of the melt, which depends upon the rod packing entropy, the degree of incompatibility of the rods and coils, and the deformation energy of the flexible coil component. It was later shown that 'hockey-puck' cylindrical micelles could also form [5] as well as Smectic-C 'tilted' phases [6]. The phase behaviour of solutions of rod-coils have also been predicted by incorporating enthalpic contributions from the solvent; 'tilted' phases were predicted for rod-coils dissolved in a solvent which is good for the coils, but poor for the rods [7] and microdomains resembling 'plates', 'fences' and 'needles' were predicted for rod-coils in selective solvents [8].

Our interest here is in rod-coils permanently grafted to repulsive surfaces by the end of the flexible coil. In a poor or bad solvent these rod-coils will form surface micelles, just as grafted

homopolymers in a poor solvent will form 'octopus' surface micelles [9-12] in order to reduce their surface energy. Surface micelles can be divided into two categories: micelles formed from reversible surface adsorption [13-18]; and micellization by irreversible end-grafting [9-12]. The latter category has been studied by several authors [19] who consider the rods to be attached by short flexible hinges such that the phase behaviour is determined by the repulsive excluded volume interactions of the rods. We consider irreversible end-grafted systems also; however, our system is different. We consider copolymers where the long and flexible coil block is tethered to the surface, and is in a solvent which is bad for the coil and rod components. In our system the rods and coils do not mix, and both components avoid the surface. The rod–rod interactions are thus attractive and the grafted coils play a significant part in controlling the aggregation of the rods and the domain size of rods. The surface microphase separation is driven in part by the tendency of the rods to aggregate and is opposed in part by the deformational elasticity of the coils.

The technique used in this paper to predict microphase morphologies is to guess a morphology and minimize the free energy of the morphology over any free parameters. This is the standard method for predicting copolymer microphases and relies heavily upon intuition. We thus cannot claim that our list of surface morphologies is exhaustive. It can only be used as a rough guide to what might be expected in experiments or computer simulations. Throughout the study we adopt a scaling approach. All numerical prefactors are neglected, except in cases where they are physically important. In particular we make the usual assumption that all surface tensions are roughly kT/a^2, where a is a monomer size. The paper is organized as follows. In Section 2 we re-examine the simplest case where there are no rods present and a flexible homopolymer is tethered to the repulsive surface. In Section 3 we consider the addition of a rod component and the formation of primitive two-chain 'micelles' from rod–coils at low grafting densities to many-chained 'turnip' micelles at higher densities. In Section 4 even higher grafting

densities are considered where the surface micelles appear as 'jellyfish'-like structures.

2. Octopus surface micelles of grafted homopolymers

We introduce our study by re-examining a simpler system, i.e. permanently grafted homopolymer coils in a bad solvent [9]. Each coil consists of N monomers, with a monomer length a and monomer volume a^3. The grafting density is ρ chains per unit area where we consider $\rho a^2 \ll 1$, so that chains are sparsely tethered and where the system energetics determine sensitively whether a tethered chain remains isolated on the surface, or whether it fuses with nearby chains. At this low density, since the solvent is bad and interaction with the surface is unfavourable, the coil will collapse to minimize its surface energy [20]. At low grafting densities they can form individual 'tadpoles' (Fig. 2a), i.e. small isolated spheres of polymer situated near the surface. The radius of a single coil sphere is $R^2 \sim aN^{1/3}$ and the surface energy is $\gamma_{cs} R^2 \sim \gamma_{cs} a^2 N^{2/3}$, where γ_{cs} is the solvent–coil surface tension. The energy per isolated chain is then $kTN^{2/3}$. However, for large enough N, isolated chains can combine with their neighbours by forming tethers which connect the fused sphere to each grafted end (Fig. 2b). This fusion reduces the surface energy, but also costs some stretching energy for the tethers plus some surface energy for each tether. If the distance between grafting sites is $d \approx \rho^{1/2}$, then the stretching energy per tether is $kTd^2/(N_{tether}a^2)$, where N_{tether} is the number of monomers in each tether. The most favourable tether is one which is one-monomer thick [21,22], so $N_{tether} = d/a$, and accordingly the stretching energy per tether is $kT(d/a)$. $kT(d/a)$ is also the surface energy of the tether. When two neighbouring coils fuse into a single globule, the number of monomers is conserved, and the surface area is reduced in the ratio $2:2^{2/3}$. Thus, there is a reduction in surface free energy of $\gamma_{cs} a^2 N^{2/3} \sim kTN^{2/3}$. Note that if $d > aN^{2/3}$, then the penalty for tether formation (stretching and surface energy of the tether) is $\sim kTN^{2/3}$ and is comparable to the reduction in stretching energy. Consequently, the
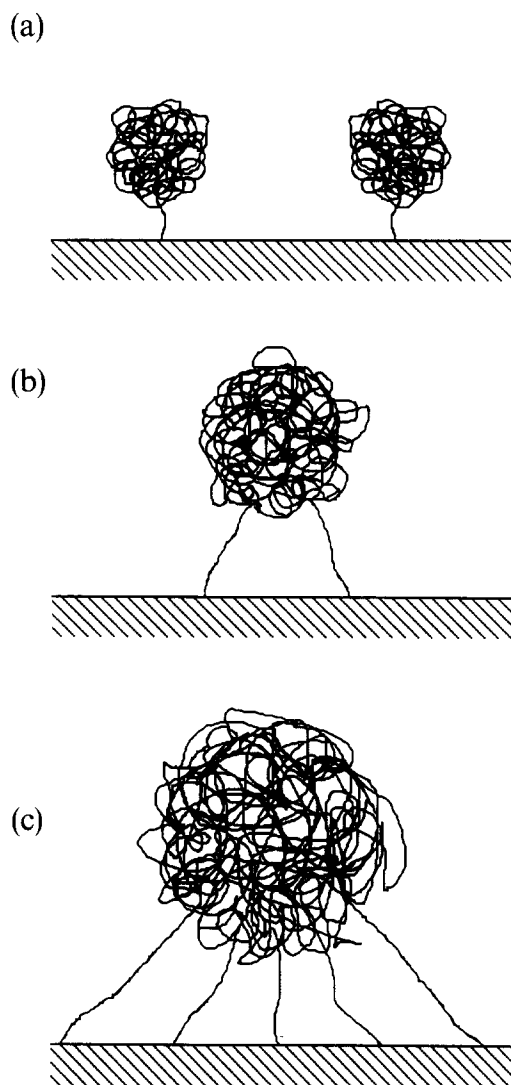

Fig. 2. The aggregation behaviour of a system of grafted homopolymers in a poor solvent. In (a) the grafting density is low and the chains form individual tadpoles. In (b) the grafting density is somewhat higher. The chains fuse together to form a surface micelle. This micelle lowers the surface energy of the globule but at the cost of an energy to form the tether. In (c) the grafting density is higher still and an 'octopus' micelle is formed.

free energy change for fusion is negative and favourable when $d < aN^{2/3}$ and unfavourable for larger d. Note that the critical grafting distance $d_c \sim aN^{2/3}$ is rather large, i.e. it is larger than the Flory radius for a single chain in a good solvent.

Thus, we expect surface micelles will not be very difficult to form. Indeed the 'octopus' surface micelles studied in reference [9] (Fig. 2c) have been seen in computer simulations [23,24] and more recently in experiments [11].

The number of homopolymer chains per micelle increases as the grafting density is further increased [9] (Fig. 2c) as a consequence of the driving force, surface tension, in opposition to the stretching of the chain tethers. At a high enough grafting density, a uniform collapsed layer will form [25]. Intermediate to these two regimes, the collapsed layer shows corrugations [26]. These regimes, surface micelles and collapsed layers, undulating or uniform, are determined by two variables: the dimensionless grafting density ρa^2 and the degree of polymerization N.

3. Turnip micelles of grafted rod–coils

We now consider the microphase behaviour of rod–coil diblock copolymers, which are similarly end-tethered to a repulsive surface. It is instructive to construct our arguments from the most dilute surface tethering where isolated diblocks exist, and to consider higher grafting densities where single chain fusion and then multiple chain fusion occurs, leading to micelles which appear as 'turnip' and then 'jellyfish'. Our model diblock is one containing N monomers in the coil block and N_r cubical monomers in the rod block, with the size of both rod and coil monomers being a. Association between rod components and coil components is driven by the rod–solvent and coil–solvent surface tensions, γ_{rs} and γ_{cs}, respectively. We assume throughout this paper that the rod–coil surface tension is large, so the rod and coil always remain separate. At very low grafting densities each grafted rod–coil system will form individual 'tadpoles' (Fig. 3a). The smallest grafting density at which diblocks can associate is also that point at which the rods can touch, without forming tethers, i.e. $d/2 < N_r a + N^{1/3} a$ (Fig. 3b). The first term, $N^{1/3} a$, accounts for the extent of the coil part and $N_r a$ the length of the oriented rods. There is an orientational entropy penalty for aligning two neighbouring rod components: it is $\sim kT \ln(\delta\theta)$
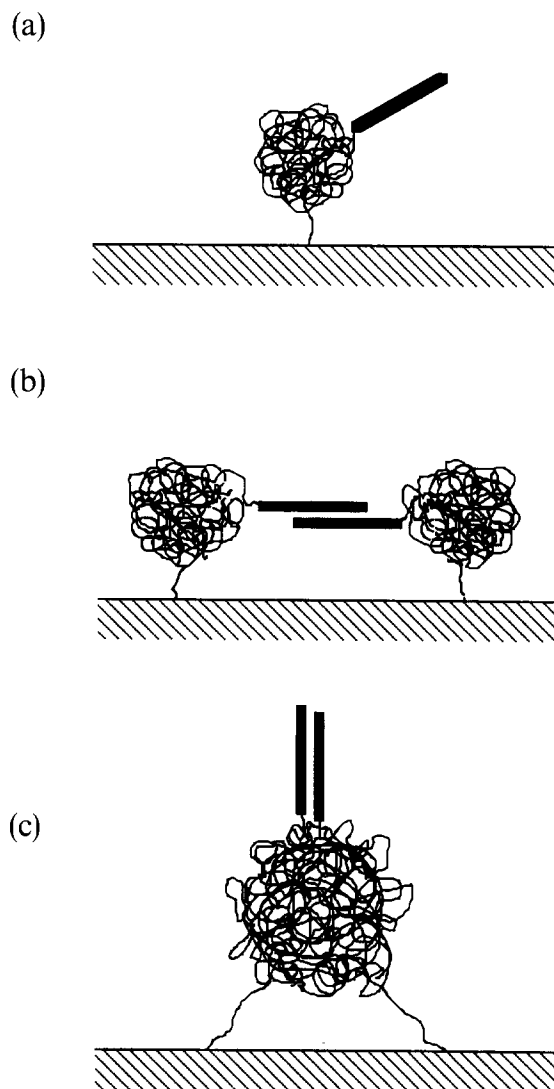

Fig. 3. The formation of surface micelles for grafted rod–coil diblocks in the low grafting density regime. In (a) we see an isolated rod–coil; in (b) two rod–coils have fused to form a prototype micelle by overlapping the rod regions; in (c) both the coil and rod regions have overlapped.

where $\delta\theta$ is the angle to which each rod is confined, $\delta\theta \sim a/(N_r a)$. The entropic term thus increases with rod alignment as $\ln(N_r)$, a small and negligible term in comparison with the surface energies of the coil and rod components, $\gamma_{cs} N^{2/3} a^2$ and $4\gamma_{rs} N_r a^2$, respectively. Note that the critical grafting distance required for incipient contact can be much greater than in the simple homopolymer coil

system, because the rods act as effective tethers, for which there is no extra stretch or surface penalty when fusing. Indeed, it is the rod surface term which drives the fusion. In the extreme case where the rod–solvent surface tension is much larger than the coil–solvent surface tension, then rods from multiple tethered diblocks might still associate, even at these low grafting densities, but only at great expense of tether penalty.

As the grafting density increases, multiple chain fusion, i.e. aggregation of both the rod and coil components, is likely. The resulting micelle is shaped like a turnip (Figs. 3c and 4a). These turnip micelles are driven by the surface tension of the
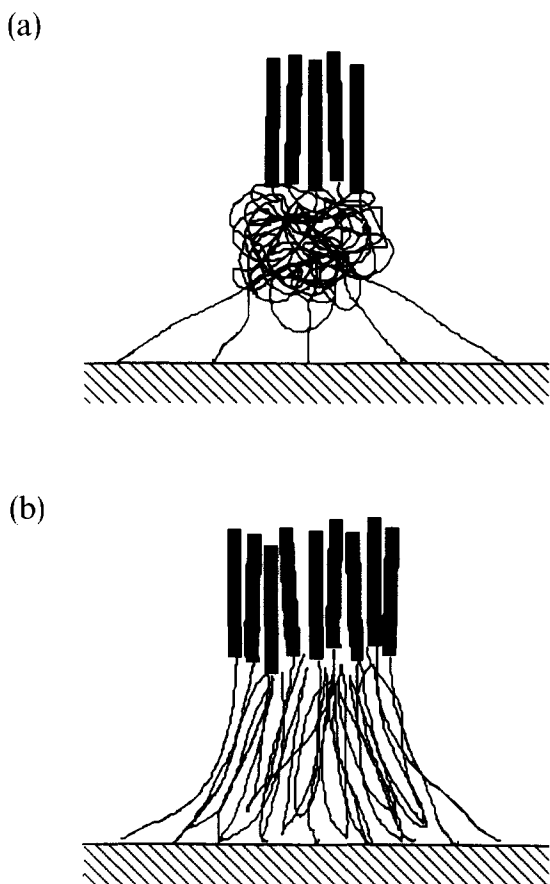
(a)

(b)

Fig. 4. Surface micelles of rod–coil diblocks in the intermediate and high grafting density regimes. In (a) we see a 'turnip' micelle, with the body of the turnip attached to the surface by several tethers; in (b), at a higher grafting density the tethers and the body have merged and we have a 'jellyfish' micelle.

coils and the rods, and opposed by the tether penalty. The decrease in surface energy per chain is $\gamma_{rs}N_r a^2 \sim kTN_r$, for the rod component, and $kTN^{2/3}$ for the coil component. As the tether penalty is kTd/a, the critical grafting distance above which turnip micelles are energetically favourable is:

$$d_c = a(N^{2/3} + N_r).\qquad(1)$$

For long rods, $N_r \gg N^{2/3}$, this can be much larger than the critical grafting distance for coil homopolymers.

The number of tethered chains comprising a turnip micelle as a function of diblock sizes and grafting density and surface tensions is found from scaling of the free energy. Let n_c be the number of tethered chains per micelle. Then the dimensions of the micelle are as follows: the radius of the coil globule is roughly $(n_c N)^{1/3}a$, and the radius of the crown of rods is $R_{crown} = a\sqrt{n_c}$. Provided that $N > n_c$, the radius of the crown will always be smaller than the radius of the globule. The chains within a circle of radius $R_{capture} \sim \sqrt{n_c/\rho}$ on the grafting surface will form the micelle. The total tether energy of the coils is then $kT\rho \int_0^{R_{capture}} (r/a)r dr = kT\rho a^{-1} R_{capture}^3$. The surface energy contributed by the coil globule is $kT(n_c N)^{2/3}$. The rod portions of the micelle contribute surface energy $kTN_r n_c^{1/2}$ (for the lateral surface of the crown) plus kTn_c (for the crown's top surface). One other energetic contribution to consider is the stretching of the coil segments which reside near the rod–coil interface (the bottom surface of the crown). The grafting density at this interface is high, $\sim a^{-2}$, such that the chains are stretched similarly to a densely grafted polymer brush [27]. The area of high stretch is R_{crown}^2, and so we can approximate the high stretching energy in this region with the free energy of brush grafted to a sphere of radius R_{crown}, i.e. $kT\sigma^2 a R_{crown}^3 \approx kTa^{-3}R_{crown}^3$ [28]. Alternatively, we can regard the region as part of a planar brush. The free energy per unit volume in such a brush is $kTa\sigma^2$ [28] giving a free energy for the region of $kTa^{-3}R_{crown}^3 \sim kT\rho^{3/2}R_{capture}^3$. The ratio of this term to the tether penalty is $\rho^{1/2}a$, and is negligible;

consequently, we neglect the stretching energy of the coils near the base of the crown.

The total free energy per unit area of the grafting surface is:

$$F/kT = a^{-1}\rho R_{capture} + N_r \rho^{1/2} R_{capture}^{-1}$$
$$+ (\rho N)^{2/3} R_{capture}^{-2/3} + \rho. \qquad (2)$$

The first term is the tether penalty, which opposes the formation of large micelles. The second term is the rod surface term, which favours large micelles. The third term is the coil surface term, which also favours large micelles. The final term is the contribution from the top surface of the crown, which is a constant and can thus be ignored. There are, then, two regimes, depending on whether the rod surface or the coil surface term is dominant. If the rods play the dominant role, then $R_{capture} \ll N_r^3 N^{-2}\rho^{-1/2}$, and the minimum of the free energy lies at $R_{capture}^* \sim a^{1/2}\rho^{-1/4}N_r^{1/2}$, $n_c = N_r a\rho^{1/2}$. In the second regime, the rods are irrelevant and $R_{capture} \gg N_r^3 N^{-2}\rho^{-1/2}$. We then have $R_{capture}^* = a(\rho a^2)^{1/5}N^{2/5}$ and $n_c = (\rho a^2)^{3/5}N^{4/5}$. Since in this regime the rod makes a negligible contribution we reproduce the results of [9].

4. Surface micelles at higher grafting densities: jellyfish

In Section 3 we have examined the micelles which will form at intermediate grafting densities. These are turnip-like objects [Fig. 4(a)], consisting of a crown and body tethered to the surface by a series of roots. At higher grafting densities the roots and body will fuse into one, and the above analysis becomes inaccurate. In this high grafting density regime we will have 'jellyfish' micelles [Fig. 4(b)]. The crossover between the turnip and jellyfish regimes occurs approximately where the capture radius is equal to the radius of the body of the micelle.

Each jellyfish micelle is a cone of coils of base radius R_{tail} and top radius R_{crown} crowned by a cylindrical crown of rods with base radius R_{crown} and height $N_r a$. The height of the cone is H. The free energy of each micelle consists of five terms: (1) the stretching energy of the chains in the cone,

$F_{stretch}$; (2) the surface energy of the cone–solvent interface; (3) the surface energy of the crown–cone interface; (4) the surface energy of the top of the crown–solvent interface; and (5) the surface energy of the curved side surface of the crown. Only the first term provides any difficulties which we address as follows. To model $F_{stretch}$, we approximate the cone as a section of a brush grafted onto a spherical surface of inner radius R_{in} and outer radius R_{out}. We let the angle formed by the apex of the cone be θ (Fig. 5). From elementary geometry, the fraction of a sphere taken up by the cone is $\phi_{sphere} = \frac{1}{2}(1 - \cos\frac{\theta}{2})$. In each cone there are $R_{tail}^2\rho$ chains and each rod has area a^2. Thus, $R_{crown} = R_{tail}a\rho^{1/2}$. We choose R_{in} to be the height of the cut-off part of the cone. This satisfies:

$$(H + R_{in})/R_{tail} = \cot\frac{\theta}{2}. \qquad (3)$$

We also choose $R_{out} = R_{in} + H$. By counting the volume of the chains in the part-cone and equating this to the volume of the cone we have:

$$\frac{1}{3}\pi(R_{tail}^2 H - R_{crown}^2 R_{in}) = \pi R_{tail}^2 \rho N a^3. \qquad (4)$$

By similar triangles $(R_{in} + H)/R_{tail} = R_{in}/R_{crown}$. Using these two equations, and noting that $a^2\rho \ll 1$, we have $R_{in}\sigma^4\rho^{3/2}N$ and $H \sim \rho a^3 N$ (roughly the size of the undistorted layer). We also have $\tan\theta/2 = R_{tail}/(H + R_{in}) = R_{tail}/(\rho N a^3)$. This implies
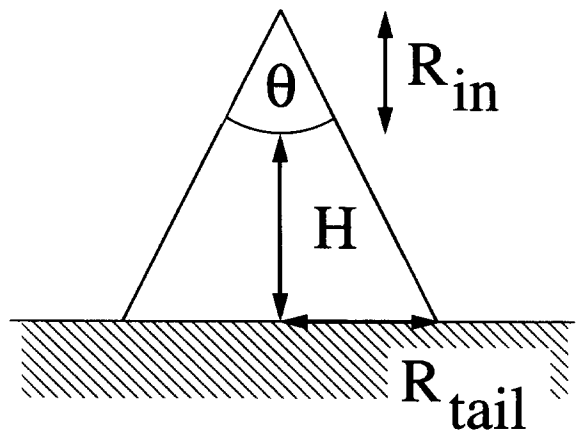

Fig. 5. The geometry used in the brush free energy calculation for a jellyfish micelle.

that we have:

$$\phi_{\text{sphere}} = \frac{1}{2}(1 - (1 + R_{\text{tail}}^2/(\rho^2 N^2 a^6))^{-1/2}). \quad (5)$$

We can now calculate the stretching energy. For a spherical shell with grafting density σ on the inner radius, the stretching energy is:

$$kTa\sigma^2 R_{\text{in}}^4(R_{\text{in}}^{-1} - R_{\text{out}}^{-1}). \quad (6)$$

In our case, $\sigma \sim n_c/(\phi R_{\text{in}}^2)$ where $n_c \sim R_{\text{tail}}^2 \rho$. Noting that we have a fraction, ϕ_{sphere}, of a sphere we find:

$$F_{\text{stretch}} = aR_{\text{tail}}^4 \rho^2 \phi_{\text{sphere}}^{-1} R_{\text{in}}^{-1}(1 - R_{\text{in}}/R_{\text{out}}). \quad (7)$$

We also have $1 - R_{\text{in}}/R_{\text{out}} \approx 1 - a\sqrt{\rho} \approx 1$ so the only difficult term, the stretching energy of the coils, is:

$$F_{\text{stretch}} = aR_{\text{tail}}^4 \rho^2 \phi_{\text{sphere}}^{-1} R_{\text{in}}^{-1}$$
$$\sim a^{-3} N^{-1} R_{\text{tail}}^4 \rho^{1/2} \phi_{\text{sphere}}^{-1}. \quad (8)$$

The remaining energy terms are as follows. The energy of the top and bottom surfaces of the crown are simply $(\gamma_{\text{rs}} + \gamma_{\text{rc}})R_{\text{crown}}^2 \sim kTR_{\text{tail}}^2 \rho$. The energy of the side of the crown is $2\pi R_{\text{crown}} \gamma_{\text{rs}} N_r a \sim kTR_{\text{tail}} N_r \rho^{1/2}$. Finally, the surface energy of the side of the cone is:

$$\gamma_{\text{rs}} 2\pi H \sec(\theta/2)\left(R_{\text{tail}} - \frac{H}{2}\tan\frac{\theta}{2}\right)$$
$$\sim kT\rho Na R_{\text{tail}}(1 + R_{\text{tail}}^2/(\rho^2 N^2 a^6))^{1/2}. \quad (9)$$

The free energy, expressed per unit area, is then:

$$F/(kT) = R_{\text{tail}}^2 \rho^{1/2} a^{-3} N^{-1} \phi_{\text{sphere}}^{-1} + \rho + N_r \rho^{1/2} R_{\text{tail}}^{-1}$$
$$+ \rho Na R_{\text{tail}}^{-1}(1 + R_{\text{tail}}^2/(\rho^2 N^2 a^6))^{1/2}. \quad (10)$$

The first term is the coil stretching energy, the second term is the (constant) energy of the rod ends and the third term is the lateral surface energy of the rods and the final term is the surface energy of the coils.

Having constructed the free energy expression, we can now investigate two different regimes, corresponding to the unperturbed brush height of the tethering coils: (i) $R_{\text{tail}} \gg H_0 \equiv \rho Na^3$, and (ii) $R_{\text{tail}} \ll H_0 \equiv \rho Na^3$.

We first look at regime (i) where the cone of coils is 'squat', i.e. the extent of the cone is greater

along the surface than perpendicular to it. In this case $\phi_{\text{sphere}} = \frac{1}{2}$, and

$$F/kT \sim R_{\text{tail}}^2 \rho^{1/2} a^{-3} N^{-1} + \rho + N_r \rho^{1/2} R_{\text{tail}}^{-1}$$
$$+ \rho^2 N^2 a^4 R_{\text{tail}}^{-2}. \quad (11)$$

Depending upon the relative magnitude of the rod surface and coil (tail) surface energies, $N_r \rho^{1/2} R_{\text{tail}}^{-1}$ and $\rho^2 N^2 a^4 R_{\text{tail}}^{-2}$, respectively, we find two possible regimes. If $R_{\text{tail}} \gg N^2 a^4 \rho^{3/2} N_r^{-1}$, the coil surface energy is insignificant and the system has to balance the stretching energy of the tails against the side line-tension of the rods. The free energy is:

$$F/kT \sim R_{\text{tail}}^2 \rho^{1/2} a^{-3} N^{-1} + N_r \rho^{1/2} R_{\text{tail}}^{-1}, \quad (12)$$

which has a minimum at $R_{\text{tail}}^* = a(N_r N)^{1/3}$. Note that this is independent of the grafting density since both terms in the free energy scale as ρ. If, on the other hand, $R_{\text{tail}} \ll N^2 a^4 \rho^{3/2} N_r^{-1}$, i.e. the rod surface energy is insignificant, then the free energy arises from the tail stretching energy and the surface energy of the cone:

$$F/kT \sim R_{\text{tail}}^2 \rho^{1/2} a^{-3} N^{-1} + \rho^2 N^2 a^4 R_{\text{tail}}^{-2}. \quad (13)$$

This has a minimum at $R_{\text{tail}}^* = a(\rho a)^{3/8} N^{3/4}$. Note that here the rods play no part, so in practice the geometry will be more like the undulational instability discussed in [26].

Now we consider regime (ii), $R_{\text{tail}} \ll H_0 \equiv \rho Ha^3$, where the cone is tall and slender. In this case:

$$\phi_{\text{sphere}} \sim \left(\frac{R_{\text{tail}}}{H_0}\right)^2\left[1 - \frac{3}{4}\left(\frac{R_{\text{tail}}}{H_0}\right)^2\right] \quad (14)$$

and the free energy is

$$F/kT \sim \rho^{1/2} R_{\text{tail}}^2(Na^3)^{-1} + (N_r \rho^{1/2} + \rho Na)R_{\text{tail}}^{-1}. \quad (15)$$

Minimizing yields $R_{\text{tail}}^* = aN^{1/3}(N_r + Na\rho^{1/2})^{1/3}$. If the rod contribution is negligible, then $N_r = 0$ and we have $R_{\text{tail}}^* = aN^{2/3}(\rho a^2)^{1/6}$. On the other hand, if the rod contribution is dominant, then $R_{\text{tail}}^* = aN^{1/3} N_r^{1/3}$.

5. Discussion and conclusion

In this paper we have discussed the possibility of surface micelle formation for rod–coil diblock copolymers tethered to a flat surface. We have shown that micelles can form at much lower grafting densities than for the case of the corresponding homopolymers because the rod blocks can readily fuse without a tether penalty. We have calculated the expected size of the micelles and argued that there should be at least three regimes. At low grafting densities we expect individual tadpoles. As the grafting density is increased, the rods overlap and eventually the coils fuse to form turnip micelles. At even higher grafting densities jellyfish micelles are formed.

It is interesting to contrast the situation for rod–coil diblock with coil–coil diblocks. In the later case there is a great deal of theory, but this is matched by a large number of experiments, which have generally been ahead of the theory, especially in the prediction of microphase morphology. For rod–coil diblocks the situation is much more biased. There are a number of theoretical predictions, but very few experimental studies on bulk systems [1,2] and most of these are in disagreement with the existing theories. It is hoped that in future there will be experiments confirming the existence of rod–coil micelles just as there have been for octopus micelles of homopolymers [11].

In this paper we have studied only one particular case of the diblock problem, where the solvent is bad for both the rods and the coils, and where the interaction between the rods and the coils and each of these and the surface is repulsive. There remain a whole series of problems which can be envisaged for this system by choosing different surface interactions and selective solvents. These remain an area for future work.

Acknowledgment

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