

Chapter 4

Block copolymers

4.1 Block copolymer mesophases

Block copolymers are polymers constructed of two or more monomers, in which the monomers appear not randomly (as in ABAABBBABABBBB...), but in large unbroken sequences (as in AAA...ABBB...B). The simplest block copolymers are diblocks, in which an unbroken string of monomer A is followed by an unbroken string of monomer B. Diblock architectures are then characterized by two parameters, once the monomer types have been chosen: the total length N , and the fraction f of monomers of type A.

We have remarked earlier in our discussion of homopolymer blends, that even a very small repulsive interaction on a per monomer basis is sufficient to cause long polymers to demix into coexisting liquid phases. What then happens if we prepare a melt of sufficiently long diblocks, constructed from two incompatible homopolymers A and B by covalently bonding them end to end?

Evidently, the covalent bond prevents the two blocks from separating into macroscopic A-rich and B-rich regions. The most effective separation of A and B that can be achieved is for the system to undergo microphase separation; that is, for local regions rich in A or B to form, in some arrangement or other.

Immediately three questions arise: 1) What determines the length scale of the microdomains? 2) What sort of arrangements of microdomains are most stable (i.e., give the lowest free energy)? 3) How incompatible must the two blocks be for microphase separation to occur?

We shall give more precise answers to each of these questions below, but for now we discuss these three issues qualitatively, in turn. With regard to the length scale for microphase separation, the obvious first guess is that separation should first occur on a length scale comparable to the radius of gyration of the blocks. If the length scale were much smaller than this, blocks would lose entropy as a result of being confined to small regions; and if the length scale were much larger than this, blocks would lose entropy as a result of being greatly stretched.

Consider the challenge of imagining possible geometries for microphase separation. The simplest case is a symmetric diblock, in which the two blocks are “mechanically identical”, having the same number, flexibility, and volume of monomers. Whatever structure results would be expected to be symmetric with respect to interchange of the A-rich and B-rich regions. The simplest possibility that comes to mind is a lamellar phase, with alternating layers rich in A and B. The A-B junctions of the chains would tend to be located at the interfaces between A and B regions.

If the A and B blocks are short enough, or compatible enough, we expect to have a homogeneous single phase. Note that unlike a homogeneous one phase mixture of A and B homopolymers, there

cannot be concentration fluctuations of a large spatial scale, because there is no way to pile up a significant excess of A over B monomers in a large region without stretching the chains over a great distance. So the scattering from concentration fluctuations in the one phase region will be suppressed at small wavenumbers q , and will have a peak at length scales around R_g (i.e., qR_g of order unity).

As we increase the length or χ parameter of a symmetric diblock, the system will undergo microphase separation to the lamellar phase. At first, we might expect the separation of A and B monomers to be rather weak, with rather broad interfaces between A-rich and B-rich domains. To achieve such a weak segregation between A and B blocks would require both some localizing the junction points along the interfacial regions, as well as some orienting of the random-coil configurations so that the A and B blocks point in the right direction with respect to the interface normal.

We might guess that rather more entropy would be lost in making these arrangements than the typical $k \log 2$ in separating homopolymers into one-half of the system volume, and so expect that the critical value of χN for lamellar microphase separation should be somewhat larger than 2, which holds for the symmetric homopolymer critical point.

As the incompatibility between A and B (measured by the product χN) increases, we expect that the A-B interfaces in the microphase would sharpen — the segregation between A and B would become increasingly strong (i.e., complete). Of course, even if the concentration profile across the lamellar phase were nearly a square wave, there would still be unfavorable contacts between A and B along the interfaces. There would then be reason to increase the lamellar period, even at the expense of some entropy reduction due to chain stretching, to reduce the amount of interfacial area per unit volume.

Now imagine an increasingly asymmetric diblock, with a short A block and a long B block, under conditions of strong segregation. If an asymmetric diblock adopts a lamellar microphase structure, the A and B domains will each have thickness h_A and h_B proportional to the masses N_A and N_B of the A and B blocks respectively. This means that the stretch free energies $(h_A/R_A)^2$ and $(h_B/R_B)^2$ will be proportional to N_A and N_B respectively; the longer block will be paying a lot more stretch energy than the short block.

This observation suggests a geometry in which the minority component is confined to the inside of a curved domain, whether cylindrical or spherical, would afford a better compromise between chain stretching of the two blocks. The longer block, paying the larger portion of the stretching energy in the lamellar phase, could relax its stretching as a result of the greater volume available on the outside of a curved A-B interface. We might therefore guess that microphases in asymmetric diblocks would consist of regular packings of parallel cylinders or spheres.

By extensive experiments as well as theoretical calculations, a detailed picture of the ordering phase diagram for diblock copolymers has emerged, largely consistent with the qualitative arguments we have given. The phase diagram is represented in terms of the asymmetry f of the diblock, and the strength of the repulsive interactions per chain, measured by χN . Fig. ?? shows a theoretical version of the phase diagram.

For sufficiently weak repulsive interactions between A and B monomers, we find a homogeneous single phase, in which small-angle scattering from concentration fluctuations displays a peak around qR_g of order unity. (In the next lecture, we shall summarize the mean-field theory for calculating $S(q)$ for diblocks in the single phase.)

As χN is increased above about 10.5, the symmetric diblock microphase separates to a lamellar phase. Asymmetric diblocks undergo this microphase separation transition at somewhat higher values of χN ; sufficiently asymmetric diblocks transform not to a lamellar phase, but to a cylindrical or spherical phase. These turn out to consist of hexagonal packings of cylinders, and body-centered

cubic (BCC) packings of spheres respectively.

There is a surprise in the diblock phase diagram, not anticipated by our qualitative arguments; namely, a pocket of a three-dimensionally “bicontinuous” mesophase, called the gyroid. By bicontinuous, we mean that both the A and B domains are connected in all three dimensions; that is, there are continuous paths in any direction within both the A and B regions. The minority component in the gyroid phase is confined to an identical pair of mutually interpenetrating networks of “fattened tubes” connected by three-fold “junctions”, with the majority component filling the interstitial regions between the two networks. The gyroid phase is not immediately stable from the homogeneous phase, nor is it stable at sufficiently high χN . Understanding the stability of this structure is therefore subtle, beyond simple estimates and calculations we are prepared to give in this course.

At relatively low values of χN , near the homogeneous phase, the segregation of A and B monomers is found to be weak; fluctuations of the average order are significant, interfaces are broad, and a quantitative theoretical description of the microphase separation is rather involved. At larger χN , however, the picture simplifies. The phase boundaries become increasingly vertical; in this strong segregation region, the microphase geometry depends only on the copolymer asymmetry, and not how strength of the A-B repulsions.

The nearly square-wave composition profiles in the strong-segregation regime imply that the junction points are essentially confined to sharp A-B interfaces, much as if the A and B blocks had been end-grafted to opposite sides of a thin sheet. This suggests a treatment of the free energy of these phases by the same methods we employed to describe grafted polymer brushes. There is one important difference: there is no solvent in the diblock melts we are considering; each block is a “melt brush”, in which the monomer density is uniform.

The degree of stretching in a melt brush is completely determined by the grafting density σ . The area per chain Σ is the inverse of σ , The constraint of constant density implies the volume per chain $h\Sigma$ must equal the displaced volume $N\Omega_0$ of a chain (in which Ω_0 is the displaced volume per monomer). Hence we have

$$h = N\Omega_0\sigma \quad (4.1.1)$$

If σ is large enough, the grafted chains in a melt brush are obliged to stretch, to avoid overfilling space.

Unlike in the grafted brush, the coverage in the lamellar mesophase is determined not by the polymer chemist but by the system, as a compromise between a longer period (which reduces the contact area per chain) and shorter period (which reduces chain stretching). To strike such a balance, we write a Flory argument: the free energy per chain is estimated as

$$\begin{aligned} \beta F/\text{chain} &= \frac{3h^2}{2Nb^2} + \frac{\beta\gamma}{\sigma} \\ &= \frac{3h^2}{2Nb^2} + \frac{\beta\gamma N\Omega_0}{h} \end{aligned} \quad (4.1.2)$$

In the above, γ is the interfacial free energy per unit area (surface tension) associated with the A-B interface; the interfacial energy per chain is γ/σ (read “free energy per area, divided by chains per area”).

The interfacial tension γ we obtain from the Helfand-Tagami argument. Although the blocks are stretched, they are not so strongly stretched that loops of chain near the junction points cannot stray across the A-B interface, broadening the interface by the same mechanism as described earlier

for immiscible homopolymers. Replacing γ with $kTb/\Omega_0\sqrt{\chi/6}$, we obtain

$$\beta F/\text{chain} = \frac{3h^2}{2Nb^2} + \frac{bN\chi^{1/2}}{\sqrt{6}h} \quad (4.1.3)$$

Minimizing leads to a scaling result for the lamellar period h :

$$h \sim bN^{2/3}\chi^{1/6} \quad (4.1.4)$$

which we can rewrite as

$$h/R_e \sim (\chi N)^{1/6} \quad (4.1.5)$$

Thus the lamellar period is controlled by the value of the incompatibility parameter χN , and grows, albeit weakly, as we make the blocks more incompatible. (But because the power $1/6$ is rather weak, it is roughly correct to say that the length scale of microphase separation is around R_g .)

4.2 Uses and structures of copolymer mesophases

As we showed in the last lecture, block copolymers form ordered mesophases in which the length scale of microphase separation is of order the radius of gyration, which for typical polymers is in the range of 100–500Å. This is a range of length scales for microstructure in materials not easily accessible otherwise, either in bulk materials or in thin films.

There are several existing applications of block copolymers in bulk — as well as considerable promise of applications as yet unrealized, in the 30-plus years that such polymers have been available synthetically. The most prevalent materials that rely on a block copolymer structure are styrene-isoprene-styrene (SIS) triblock copolymers (trade name Kraton), typically formulated with short polystyrene (PS) endblocks and a longer polyisoprene (PI) midblock.

It turns out to be the case that the microphases formed by ABA triblocks are very close to those that would be formed if the triblock were cut in the middle into two AB diblocks, because it is a relatively minor perturbation on the polymer conformations in the diblock mesophases to pair up the ends of diblocks in the B-rich region. So highly asymmetric SIS triblocks form a phase of spherical PS domains a few volume percent, with links between nearby domains formed by the PI chains. Now PS at temperatures below about 100C is a glassy, solid polymer with mechanical rigidity; whereas, PI is a rubbery polymer at temperatures down to about -30C.

So at normal use temperatures, the SIS microphase is mechanically equivalent to a crosslinked rubber, with the glassy PS domains forming the crosslinks. Thus the material is a thermoplastic elastomer; that is, a rubber that can be melted, flowed, and reformed on cooling into a rubbery solid part. Usual commercial rubbers, such as those used in tires, are chemically, irreversibly crosslinked (vulcanized); this is one of the reasons why tires are extremely difficult to recycle (into anything other than objects made from literal pieces of tires, like sandal soles). Note that the usefulness of Kraton does not depend on having an ordered packing of spherical domains, but only on the spontaneous formation of the domains above the T_g for PS.

Another category of uses for copolymer mesophases relies on the bicontinuous nature of the gyroid phase. This allows one block to determine the mechanical properties of the material (say, a strong glassy polymer) while the second block is chosen controls the transport of some solute or solvent. That is, one can imagine designing filters or membranes using copolymers in the gyroid phase. Again, the final properties depend not so much on the precise ordering of the mesophase, as the general aspect of three-dimensional connectivity.

Copolymer mesophases can also be potentially useful in thin-film geometries, in several ways. For example, ordered spherical mesophases can be used as templates for lithography on a length scale much smaller than can be achieved by optical lithography. (Of course, the structures that can be made this way are limited at present to various regular arrays, but some clever engineer may be able to think of useful devices that can be made using this technique.) Self-assembled templates made from copolymer thin films might be used also to arrange adsorbed particles, which were wetted by one of the two polymer blocks, again resulting in ordered arrays of perhaps magnetic or optically active particles. In applications such as these, the periodicity of the self-assembled structure would be critical.

Structure determination

Two experimental tools are chiefly used to determine the structure of copolymer microphases: transmission electron microscopy (TEM), and small-angle scattering (X-ray and neutron).

TEM images are made on extremely thin samples, prepared with a microtome (think of a sample filling a nut, pushed through with a fine-thread bolt, thin slices taken with a razor blade). The

images have the appearance of cross-sections, or rather projections of the density into the viewing plane. The contrast, which is intrinsically very low for hydrocarbon samples such as copolymer mesophases, is typically enhanced by chemical staining with a reagent (such as osmium tetroxide, OsO_4) that attaches a heavy atom (e.g., osmium) preferentially to one of the two blocks.

To examine ordered microphases with TEM, it is a great advantage to have a single well-ordered crystal, in which the microphase structure is continuous without defects across the sample. (We shall discuss various ways to achieve this happy state of affairs in the next section.) Given a single crystal, it is then very revealing to slice the sample normal to different axes. Lamellar phases are of course the simplest; if the slice is made at an oblique angle to the layers, a regularly spaced array of parallel lines results in the micrograph. A cylindrical phase when sliced with a plane nearly perpendicular to the cylinders results in a hexagonal array of spots in the micrograph; if sliced with a plane closer to containing the cylinders, a distorted hexagonal array of elongated spots results.

A spherical phase, consisting of a regular (BCC) packing of spherical domains, is more complicated. However, even sample thick enough to contain several planes of packed spheres, when a viewed from certain well-chosen, high-symmetry directions — such that the spheres in one layer appear to sit atop spheres in layers below — results in a micrograph showing a simple periodic arrangement of spots.

Most complicated of all are the micrographs resulting from bicontinuous phases; even when sliced in high-symmetry directions, such that the fattened tubes and junctions in one layer appear to lie atop analogous structures in layers below, rather complicated periodic patterns result. It is challenging to identify the bicontinuous structure consistent with a given set of TEM images; so much so, that when bicontinuous phases were first identified and studied, the structure was for several years misidentified as “ordered bicontinuous double diamond” (OBDD), in which the interpenetrating networks of the minority phase are diamond lattices (with tetrahedral junctions), when the correct structure is in fact the gyroid (with triangular junctions).

The correct identification was first made with small-angle X-ray scattering, using techniques developed for identifying crystal structures, that we shall describe in the next section.

Scattering from periodic structures

A crystal structure, in the context of scattering, is any three-dimensional periodic arrangement of scatterers. In other words, if there is a scatterer at the origin, than another identical copy of that scatterer at every lattice vector \mathbf{R} , defined by

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (4.2.1)$$

in which \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are three non-coplanar vectors, and n_1 , n_2 , and n_3 are any integers. The set of points \mathbf{R} forms a regular lattice. (Varying a single n_i over the integers produces a regularly spaced line of points; varying two different n_i over the integers produces a two-dimensional planar array of points.)

In a regular lattice as defined above, there are many families of regularly spaced parallel planes, each family of planes with the property that every point is located on some plane in the family. If we scatter X-rays from a crystal, we can envision orienting the crystal, incoming beam, and detector, so that the incoming beam reflects off some family of planes, just as in a thin-film reflectivity experiment. If we choose the angle of the incoming and outgoing beams correctly, the reflected beams from different planes of scatterers will be in phase at the detector.

So we would like to identify and label the sets of planes corresponding to a given crystal structure. Equivalently, we can ask for the set of wavevectors \mathbf{k} of plane waves $\exp(i\mathbf{k} \cdot \mathbf{r})$, such

that the plane waves have the same periodicity as the lattice, i.e.,

$$e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (4.2.2)$$

or equivalently

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 1 \quad (4.2.3)$$

which implies that $\mathbf{k}\cdot\mathbf{R} = 2\pi n$, where n is some integer.

The reason such plane waves have anything to do with planes of atoms is this: if such a plane wave “lights up” (i.e., has a strong amplitude on) a scatterer at the origin, it also lights up a scatterer at every location in the lattice. In other words, its wavefronts (where the plane wave has maximum amplitude) pass through all the points in the lattice. So the wavefronts of such a plane wave define a family of planes.

Reciprocal lattice

Thus we set about constructing the set of wavevectors \mathbf{k} such that $\mathbf{k}\cdot\mathbf{R} = 2\pi n$, where n is some integer. It turns out that the set of these wavevectors themselves form a regular periodic lattice, called the reciprocal lattice. The wavevectors \mathbf{k} can be written as

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 \quad (4.2.4)$$

in which k_i are all integers, and \mathbf{b}_i are the basis vectors of the reciprocal lattice.

The set of \mathbf{b}_i are “dual” to the set of \mathbf{a}_i in the sense that

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad (4.2.5)$$

in which δ_{ij} is the Kronecker delta symbol, equal to unity if $i = j$ and zero otherwise. With this property of the vectors \mathbf{b}_i it is easy to verify that

$$\mathbf{k}\cdot\mathbf{R} = 2\pi(n_1k_1 + n_2k_2 + n_3k_3) \quad (4.2.6)$$

which is of the form 2π times an integer, as required.

The explicit construction of the \mathbf{b}_i is given by

$$\mathbf{b}_1 = \frac{2\pi\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (4.2.7)$$

and similarly for \mathbf{b}_2 and \mathbf{b}_3 (permuting the roles of the index values 1, 2, and 3 appropriately). Thus \mathbf{b}_1 is perpendicular to \mathbf{a}_2 and \mathbf{a}_3 (by virtue of being proportional to the cross product $\mathbf{a}_2 \times \mathbf{a}_3$, which is normal to the plane containing \mathbf{a}_2 and \mathbf{a}_3), and is explicitly constructed to give $\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$ as required (because numerator and denominator cancel after the dot product with \mathbf{a}_1).

So for every wavevector in the reciprocal lattice, there is a corresponding family of regularly spaced parallel planes in the original lattice of scatterers, which are the wavefronts of the plane wave with this wavevector, which contain all the lattice points in the lattice of scatterers. The wavevector itself is normal to the family of planes. The families of planes can be indexed by the integers $[k_1 k_2 k_3]$.

Scattering condition

Having identified the possible planes of scatterers from which incident radiation can scatter coherently, we now write a criterion for the coherence of the scattered beam from the different scatterers. Consider just two scatterers at \mathbf{R}_1 and \mathbf{R}_2 , separated by some lattice vector \mathbf{R} . Let the incident beam be a plane wave $\exp(i\mathbf{k} \cdot \mathbf{r})$; the amplitude at the first scatterer is then $\exp(i\mathbf{k} \cdot \mathbf{R}_1)$.

The scattered wave from this scatterer along the outgoing wavevector \mathbf{k}' will have an amplitude

$$I_1 \propto e^{i\mathbf{k} \cdot \mathbf{R}_1} e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{R}_1)} \quad (4.2.8)$$

(as the product of the incident intensity, times an outgoing wave whose phase depends on the distance from the scatterer at \mathbf{R}_1 , along the direction of the outgoing wavevector).

A similar expression holds for the scattered amplitude from the second scatterer. For the two scattered waves to add coherently, they need to be in phase, which implies

$$e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_1} = e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_2} \quad (4.2.9)$$

or, using $\mathbf{R}_1 = \mathbf{R}_2 + \mathbf{R}$,

$$e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = 1 \quad (4.2.10)$$

For the scattered wave from *every* scatterer to add coherently at the detector, the above condition must hold for every lattice vector \mathbf{R} . In other words, $\mathbf{k}' - \mathbf{k}$, which is the scattered wavevector \mathbf{q} , must be a reciprocal lattice vector.

Single crystal and powder samples

Now suppose we arrange the incident and scattered wavevectors so as to scatter from planes oriented with normals in a particular direction. For a single crystal oriented in some arbitrary direction, there will typically be no planes of atoms lined up exactly right to scatter, never mind whether the spacing of the planes would be correct to scatter coherently. So for a single crystal, observing the coherent scattering means rocking the crystal back and forth to hunt for the right orientation of planes, and then varying the scattering angle (equal incidence and reflection angles of the beam and detector) to match the spacing of the planes once they are properly oriented. This tedious process is necessary for single crystal samples.

Much simpler is to use a polycrystalline or “powder” sample, made from a large number of macroscopically small crystallites, oriented randomly in all possible directions. For such a sample, for every possible plane of atoms, there will be some crystallites within the sample that are oriented properly with respect to the chosen normal direction so that the plane can scatter coherently. It then remains only to vary the scattering angle, by observing the scattered beam in different directions, which varies the wavevector \mathbf{q} .

Only the magnitude of \mathbf{q} matters for a powder scattering; we can rotate the scattered wavevector \mathbf{k}' about the incident beam and there will be some crystallites lined up appropriately with the same family of planes scattering coherently. The scattering pattern on a detector from a powder sample for a given reciprocal lattice vector is a ring of scattering intensity, centered on the incident beam.

Note that for the periodic reciprocal lattice, there is a finite sequence of possible wavenumbers (lengths of the scattering wavevectors). The wavenumbers can be given as multiples of the shortest value, which depends on the overall size scale of the lattice. For the simple square lattice in two dimensions, for example, the wavenumbers come in the ratios $\sqrt{k_1^2 + k_2^2}$ where k_1 and k_2 are integers, which is to say $1, \sqrt{2}, \sqrt{4}, \sqrt{5}, \sqrt{8}, \sqrt{10}, \dots$

Other reciprocal lattices, which result from periodic arrangements of scatterers of different symmetry, have different sequences of possible wavenumbers. Different periodic lattices can be

identified by the sequences of wavenumber ratios (and to some extent the intensities of the rings of scattering; particularly their absence or “extinction”, see below). This is how the gyroid phase, for example, was first properly identified.

Lattice with a basis; extinctions

So far in our discussion of scattering from periodic structures, we have implicitly assumed pointlike scatterers located at the lattice points. But the scatterer in general will not be pointlike; we may have a structure consisting of some arbitrary blob of scattering contrast, periodically repeated.

If the scatterer is not pointlike, the sum of the scattered amplitudes at wavevector \mathbf{q} will be proportional to

$$S(\mathbf{q}) = \int d^3\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (4.2.11)$$

in which the integral is performed over the “unit cell”, i.e., the region of space containing the scatterers in the immediate vicinity of one lattice point. This integral is just the generalization of the sum over two scatterers at \mathbf{R}_1 and \mathbf{R}_2 performed in the previous section, except that now the scattering contributions within the unit cell will not be completely in phase.

Note that even some periodic arrays of identical points that might at first sight be thought of as “lattices”, are not simple lattices of repeated single points. A simple example is the body-centered cubic lattice. The lattice vectors are $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, $a\hat{\mathbf{z}}$, where a is the length of the side of a cube with points at the corners and in the center as well, at location $a(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})/2$. To represent this arrangement of points as a periodic set of copies, we must declare the object to be copied to be not a single point at the origin, but a “basis” of two points, one at the origin and one at $a(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})/2$.

Thus the scattering from a BCC lattice is proportional to

$$S(\mathbf{q}) = 1 + e^{i\mathbf{q}\cdot a(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})/2} \quad (4.2.12)$$

Now the reciprocal lattice of the cubic lattice of side a , is a cubic lattice of side $2\pi/a$, so the wavevectors take the form

$$\mathbf{q} = 2\pi/a(k_1\hat{\mathbf{x}} + k_2\hat{\mathbf{y}} + k_3\hat{\mathbf{z}}) \quad (4.2.13)$$

which implies

$$S(\mathbf{q}) = 1 + e^{i\pi(k_1+k_2+k_3)} \quad (4.2.14)$$

So we see that if $k_1 + k_2 + k_3$ is odd, $S(\mathbf{q})$ will vanish.

These reflections, which would have been present for a simple cubic lattice of pointlike scatterers, are extinguished for the BCC because the scattering from the two identical points in the basis for BCC are exactly out of phase for the corresponding wavevectors. The pattern of extinctions is an important part of structure determination for periodic structures composed of more complicated objects.

Defects and annealing

TEM studies of microphase geometry, as well as some applications of block copolymer mesophases (such as templating regular patterns), rely on the availability of large well-ordered single crystal samples. If we simply quench a block copolymer sample from the disordered phase, by rapidly lowering the temperature or removing a common solvent for the two blocks, well-ordered microphases do not result. Instead, we typically obtain a “polycrystalline” sample, in which local regions are ordered, but distant regions are oriented differently, and not in phase with respect to the periodic order.

Several techniques have been developed to obtain a well-aligned single crystal sample. One approach is to “anneal” the sample; that is, to hold the sample for a long time at a temperature just below the microphase separation transition, where segregation is weak and chain mobility is at its highest. This is a painfully slow process for high molecular weight copolymers, for which the chain mobility is very low. If the sample was prepared by “solvent casting”, i.e., removal of a common solvent, annealing can also be effectively performed by removing the solvent very slowly, because the solvent both controls the location of the microphase separation, as well as enhancing chain mobility.

A different way of producing aligned samples is to perform annealing in conjunction with the application of some external field that prefers one microphase orientation over another. For copolymers with a high dielectric contrast between the two blocks, application of strong electric fields will prefer orientations in which the electric field lines can pass through the sample entirely contained within the high-dielectric blocks; this will tend to align cylindrical phases parallel to the field, for example.

Another more general field that can strongly influence the microphase orientation is an applied shear flow, either steady or oscillatory. Some orientations of an ordered phase are deformed by a large amplitude shear, in such a way that the spacings and angles of the periodic structure are altered, resulting in an increase in free energy. For example, for a lamellar phase, if the layer normal is perpendicular to the velocity direction, shear does not affect the oscillatory concentration profile (think of shearing a pack of cards resting on a table). However, if the lamellar normal points in the velocity direction, shearing the sample results in a decrease in the layer spacing, which shifts the compromise between chain stretching and interfacial tension away from its optimum point.

Misaligned regions of a mesophase undergoing shear can then either melt and regrow, or progressively shrink as better-aligned neighboring regions grow at their expense. Using this technique, samples aligned and essentially free of defects over macroscopic distances (cm) have been produced.

To this point, we have not actually said much about what the polycrystalline samples themselves look like, other than to say that they are only locally ordered. It is useful and interesting to consider more precisely what sort of defects can appear in various microphases. Studying defects in ordered structures is useful if one wants to prepare structures without defects, because you learn what you’re up against — what do the defects look like, how do they move and interact, how do external fields couple to them to cause them to disappear or move out of the sample.

So what do defects look like? The simplest example appropriate to mesophases is provided by a close examination of a fingerprint, which provides a pretty good approximation to the appearance of a two-dimensional lamellar phase (or equivalently, of parallel cylinders confined to a plane). The lines in a fingerprint are quite regularly spaced, but not globally aligned. There are two important kinds of defects present in fingerprints. The first is relatively subtle: lines in a fingerprint sometimes terminate. Viewed in isolation, a single terminating line gives rise to a strain field in adjacent lines, as they swerve around the extra half-line, trying to maintain a constant spacing without bending too abruptly.

This defect is called a “dislocation”, the location of which we associate with the end of the terminated line. Dislocations can also be defined for regular arrays of points (as in a plane of atoms, or of spherical domains in the BCC microphase), as an extra half-row of points (in three dimensions, an extra half-plane). Note that a dislocation has the effect of disturbing the phase of the concentration pattern — if we look to the left and to the right of a dislocation somewhat above or below the extra line, we are on different lines — but the lines remain more or less parallel. We say that a finite density of dislocations disturbs the translational order, but preserves the orientational order, of a lamellar phase.

Note that it is not possible to make purely local rearrangements at the dislocation point to make

it disappear. The defect is “topological”, meaning informally that it survives any rearrangement that only involves stretching or distorting the material without any cutting or reattaching. A precise way of stating how a dislocation disturbs the arrangements of lines is provided by the Burger’s construction. On any simple closed path surrounding a dislocation, count the number of times a line is crossed as we traverse the path counterclockwise, with a count of +1 if the line is crossed “heading upwards” (i.e., the tangent to the path has a positive projection on the vertical axis) and -1 if the line is crossed “heading downwards”. For closed paths that contain a dislocation, there will be a net number of lines crossed, equal to the number of extra lines injected from the right.

There are two ways to move the dislocation: 1) we can “evaporate” minority phase from the end of the line or condense more minority phase onto the end of the line, to shorten or lengthen the line; or 2) we can locally melt an adjacent line (thereby cutting the line), and attach the half-line to the newly formed half-line — which leaves behind half of the line we cut, so the dislocation persists. The first process is called “climb” — the extra line climbs into or out of the sample — and the second process, “glide” — the extra line moves perpendicular to itself.

The more pronounced defect in fingerprints are the large-scale patterns of folds, circles, and triangular-shaped gatherings of lines that we first notice. These, too, can be described in terms of pointlike topological defects called disclinations. There are two types of disclinations possible in an array of parallel lines, which we may denote as + and - disclinations. To produce a - disclination, remove an entire half-plane of lines above a given line, and then stretch the remaining half-plane (as if it were a very stretchy sheet of rubber, but confined to be flat) so that the line bounding the half-plane is folded onto itself. The folded line becomes a single terminated line, the terminus of which is the location of the - disclination. Finally, allow the pattern of lines to relax in the plane without breaking, to minimize the free energy of the pattern subject to the presence of the disclination.

To produce a + disclination, make a cut from infinity between two lines, up to some point, and stretch the sheet open (while keeping it flat) until the two sides of the cut are opened into a straight line. Now, bring up a half-plane of lines, and join it to the cut so that the line bounding the half-plane lies alongside the cut. As before, finally allow the pattern of lines to relax without breaking, subject to the presence of the disclination, which we may regard as located at the terminus of the cut.

It is intuitively clear that a finite density of disclinations destroys both the orientational and translational order of the pattern of lines in the sample. Disclinations are thus in fact easier to get rid of than dislocations, by applying a field (such as shear flow) that discriminates between orientation directions of the microphase pattern.

Notice that a + and - disclination reasonably close to each other, when viewed from far away, look like a dislocation of large Burger’s number (number of extra lines injected). Indeed, if we consider the process of cutting and patching described above for producing + and - disclinations, this observation may be made precise; a disclination pair n lines away corresponds to the insertion of $2n$ extra half-lines.

With disclinations paired in this way, the distortion of the pattern of lines far from the pair is much reduced. From this we can infer that disclinations of opposite sign will tend to attract each other and annihilate. This argument also suggests how disclinations can move, mediated by dislocations. For every pair of half-lines that climbs from within the disclination pair out to infinity, the disclination moves one line-width forward towards its mate.

A closer examination of fingerprints reveals something interesting about the interactions of disclinations and dislocations; namely, dislocations tend to be found in close proximity to the inner core of disclinations, arranged in such a way as to ease the far-field strain of the disclination.

For example, an isolated $-$ disclination in absence of any dislocations must either bend the lines in semicircles of increasing radius all the way out to infinity, or make large adjustments in the spacing of the lines. But if additional half-lines are brought in from the unbent (“tail”) side of the $-$ disclination, the bending at far distances can be relieved, and the corresponding distortion of the optimal pattern of parallel lines reduced.

4.3 Quantitative theory for diblock phase behavior

The work we did for deriving the RPA for scattering from miscible homopolymer blends is directly applicable to scattering from copolymer melts in the homogeneous one-phase region.

$$\begin{aligned}
 S(q) &= (\Sigma/D - 2\chi)^{-1} \\
 \Sigma &= \sum_{i,j} S_{ij} \\
 D &= \det S_{ij}
 \end{aligned} \tag{4.3.1}$$

The free-chain structure factors are

$$\begin{aligned}
 S_{11}(q) &= \frac{2}{N} \int_0^{fN} ds \int_0^s ds' e^{-(s-s')q^2 a^2/6} \\
 S_{12}(q) = S_{21}(q) &= \frac{2}{N} \int_{fN}^N ds \int_0^{fN} ds' e^{-(s-s')q^2 a^2/6} \\
 S_{22}(q) &= \frac{2}{N} \int_{fN}^N ds \int_{fN}^s ds' e^{-(s-s')q^2 a^2/6}
 \end{aligned}$$

Carrying out these integrals results in

$$\begin{aligned}
 S_{11}(q) &= Ng(f, x) \\
 S_{12}(q) = S_{21}(q) &= N/2(g(1, x) + g(f, x) - g(1 - f, x)) \\
 S_{22}(q) &= Ng(1 - f, x) \\
 g(f, x) &= 2(fx + \exp(-fx) - 1)/x^2
 \end{aligned} \tag{4.3.2}$$

in which we have defined $x = q^2 Na^2/6$.

The final result for the structure factor is $S(q) = N/(F(x) - 2\chi N)$, where

$$F(x) = \frac{g(1, x)}{g(f, x)g(1 - f, x) - (1/4)(g(1, x) - g(f, x) - g(1 - f, x))^2} \tag{4.3.3}$$

Weak segregation regime of phase diagram calculated by building on this result for fluctuations, to say what happens when the system becomes linearly unstable to the formation of inhomogeneous concentration fluctuations, i.e., sinusoidal variations in the concentration difference between A and B monomers.

Strong segregation for curved phases

Setup: round unit cell approximation. Simple approximation: stretching controlled by filling.

Problem with Flory: if we require all chains to have the same trajectories, then for inwardly curved domains such as occupied by the minority block in a cylindrical or spherical phase, the chains must all stretch to reach the innermost point (the centerline for the cylinder, or the center for a sphere), because this point must be filled with something. But if all the chains must reach the center (because we are assuming they have identical trajectories), then it turns out there is a divergence in the stretching free energy at the center of the domain.

For the particular case of a cylindrical domain, we may write

$$(2\pi a f^{1/2} L)(\sigma N \Omega_0) = \pi a^2 L \tag{4.3.4}$$

which expresses the fact that the displaced volume of the chains rooted on the interface (of area equal to the circumference of the interfacial circle $2\pi a f^{1/2}$ times the cylinder length L) is sufficient to fill the entire cylinder of length L .

Likewise, we can write

$$(\pi a^2 f - \pi r_{in}^2(s))L = s\Omega_0\sigma(2\pi a f^{1/2}L) \quad (4.3.5)$$

which expresses the fact that the space occupied by the chains from the zeroth through the s th monomer must equal the displaced volume of those monomers ($s\Omega_0$ per chain, times σ chains per area, times the interfacial area).

Combining these two expressions gives

$$r_{in}(s) = a f^{1/2} (1 - s/fN)^{1/2} \quad (4.3.6)$$

Then the stretching free energy per chain can be computed as

$$\begin{aligned} \beta F/\text{chain} &= \frac{3}{2b^2} \int_0^{fN} ds \left(\frac{\partial r}{\partial s} \right)^2 \\ &= \frac{3a^2}{8b^2 f N^2} \int_0^{fN} ds (1 - s/fN)^{-1} \end{aligned} \quad (4.3.7)$$

whereupon we recognize that the integral diverges at $s = fN$ in absence of some cutoff. We can impose a cutoff (arguing that the integral should stop “at the last monomer”, for which the integrand does not strictly speaking diverge), but this behavior is the result of the artificial singularity of requiring all the chains to do the same thing, and hence to all reach the center of the cylinder.

These problems are overcome by treating the inner and outer domains of the cylindrical phase as composed of melt brushes on curved surfaces.

Outer brush:

$$\pi r_{out}^2(\sigma') - \pi a^2 f = \pi a^2 (1 - f) \sigma' / \sigma \quad (4.3.8)$$

Difference in area between the circle to which we have filled, and the interface where we started, is the total amount of stuff to be filled in, times the fractional coverage. The height $h_{out}(\sigma')$ of the outer brush as we go along is the difference between the radius to which we have filled, and the radius of the interface:

$$h_{out} = r_{out} - a f^{1/2} \quad (4.3.9)$$

The stretching free energy per chain we compute as for the flat brush, by summing the energy to add each chain in turn, taking advantage of the observation that the chains in the brush are degenerate, and the easy chain to evaluate the addition energy is one with free end near the grafting surface:

$$\begin{aligned} \beta F_{str}^{(out)}/\text{chain} &= 1/\sigma \int_0^\sigma d\sigma' (1 - f) N A(\sigma') \\ &= (1 - f) N B((1 - f)N) 1/\sigma \int_0^\sigma d\sigma' h_{out}^2(\sigma') \end{aligned} \quad (4.3.10)$$

in which we have used $A = B h^2$, and recall that $B(N) = 3\pi^2/(8N^2 b^2)$ depends on the chain length.

The integral with respect to coverage is most easily performed by changing variables to the height itself:

$$\pi a^2 (1 - f) d\sigma' / \sigma = 2\pi r_{out}(\sigma') dh_{out} \quad (4.3.11)$$

which enables us to write the stretch free energy per chain as

$$\begin{aligned} \beta F_{str}^{(out)}/\text{chain} &= \frac{2(1 - f) N B((1 - f)N)}{a^2 (1 - f)} \int_0^{1-f^{1/2}a} (h + a f^{1/2}) h^2 dh \\ &= \frac{2(1 - f) N B((1 - f)N) a^2}{(1 - f)} \int_0^{1-f^{1/2}} (x + f^{1/2}) x^2 dx \end{aligned} \quad (4.3.12)$$

which is reduced to a simple integral.

The same approach works for the inside of the cylinder. Now, because we are not obliging all the chains to do the same thing, we find no spurious singularity as for the simple Flory-style estimate above. For completeness, the corresponding equations are

$$\pi a^2 f - \pi r_{in}^2(\sigma') = \pi a^2 f \sigma' / \sigma \quad (4.3.13)$$

$$h_{in} = a f^{1/2} - r_{in} \quad (4.3.14)$$

$$\begin{aligned} \beta F_{str}^{(in)} / \text{chain} &= 1/\sigma \int_0^\sigma d\sigma' f N A(\sigma') \\ &= f N B(f N) 1/\sigma \int_0^\sigma d\sigma' h_{in}^2(\sigma') \\ &= \frac{2f N B(f N)}{a^2 f} \int_0^{f^{1/2}a} (a f^{1/2} - h) h^2 dh \\ &= \frac{2f N B(f N) a^2}{f} \int_0^{f^{1/2}} (f^{1/2} - x) x^2 dx \end{aligned} \quad (4.3.15)$$

Putting everything together, the complete stretch free energy per chain (sum of the inner and outer blocks) is

$$\beta F_{str} / \text{chain} = \frac{\pi^2 a^2}{16b^2 N} \left[\frac{(1 - f^{1/2})^3 (3 + f^{1/2})}{(1 - f)^2} + 1 \right] \quad (4.3.16)$$

To this we must add the interfacial free energy per chain γ/σ , in which we replace the coverage in terms of the cylinder radius a using Eqn. ?? above, for a total of

$$\beta F / \text{chain} = \frac{\pi^2 a^2}{16b^2 N} \left[\frac{(1 - f^{1/2})^3 (3 + f^{1/2})}{(1 - f)^2} + 1 \right] + \frac{2f^{1/2} N \Omega_0 \gamma}{a} \quad (4.3.17)$$

Now we can minimize the free energy per chain with respect to the cylinder radius, to optimize with respect to the overall scale of the mesophase. (The minimization is simple, as the function is of the form $C_1 a^2 + C_2/a$; we just need to take care with transcribing and combining the ‘‘constants’’ C_1 and C_2 .) Carrying out the algebra gives

$$\beta F / \text{chain} = \frac{3}{2^{2/3}} \left(\frac{\pi N^{1/2} \Omega_0 \gamma}{2b} \right)^{2/3} \left[\frac{f(1 - f^{1/2})^3 (3 + f^{1/2})}{(1 - f)^2} + f \right]^{1/3} \quad (4.3.18)$$

To find the value of asymmetry at which the cylindrical phase becomes favorable with respect to the lamellar phase — which determines the cylindrical-lamellar phase boundary, in the strong segregation limit — we need to compute the corresponding free energy of an asymmetric diblock in the lamellar phase.

We use the same basic approach as for the cylindrical phase. Let a now be the lamellar period (combined thickness of A and B layers for a single diblock). The lamellar period satisfies

$$a/\sigma = a\Sigma = N\Omega_0 \quad (4.3.19)$$

which expresses the fact that the volume per chain $a\Sigma$ is equal to its displaced volume $N\Omega_0$.

The thickness of the A block brush satisfies

$$h_A(\sigma') = fa\sigma'/\sigma \quad (4.3.20)$$

The stretch free energy per chain of the A blocks is

$$\begin{aligned} \beta F_{str}^{(A)}/\text{chain} &= fNB(fN)(1/\sigma) \int_0^\sigma d\sigma' h_A^2(\sigma') \\ &= fNB(fN)f^2a^2/3 \\ &= f\pi^2a^2/(8N^2b^2) \end{aligned} \quad (4.3.21)$$

The result is the same for the B block, with f and $1-f$ exchanged. The sum of the two is then simply $\pi^2a^2/(8N^2b^2)$, independent of f . To this we add the interfacial free energy per chain γ/σ , for a total of

$$\begin{aligned} \beta F/\text{chain} &= \frac{\pi^2a^2}{8N^2b^2} + \frac{\gamma}{\sigma} \\ &= \frac{\pi^2a^2}{8N^2b^2} + \frac{\gamma N\Omega_0}{a} \end{aligned} \quad (4.3.22)$$

in which we have as before replaced σ in terms of a , this time using Eqn. ??.

We once again have an expression for the free energy per chain of the form $C_1a^2 + C_2/a$, which we optimize with respect to a to find the lamellar period. Evaluating the free energy at the minimum, we have

$$\beta F/\text{chain} = \frac{3}{2} \left(\frac{\pi N^{1/2} \Omega_0 \gamma}{2b} \right)^{2/3} \quad (4.3.23)$$

Finally — we can evaluate the ratio of the free energy per chain for the optimized cylindrical and lamellar phases. We find

$$F_{cyl}/F_{lam} = \left[\frac{2f(1-f^{1/2})^3(3+f^{1/2})}{(1-f)^2} + 2f \right]^{1/3} \quad (4.3.24)$$

When this function equals unity at $f = f_{CL}$, the free energies of lamellar and cylindrical phases are equal. For $f < f_{CL}$ ($f > f_{CL}$), the cylindrical phase has lower (higher) free energy, and is (not) preferred. We find, with just a bit more algebra, $f_{CL} = (9 + 4\sqrt{2})/49 \approx 0.3$, in good agreement with experimental findings for strongly segregated diblocks.

4.4 Diblock copolymers in preferential solvents

Up to now, we have considered diblock copolymers either as mesophases without solvent, or as a means by which we can construct end-grafted polymer brushes in a preferential solvent (i.e., a solvent for one block which is a nonsolvent for the other block). Diblock copolymers in a preferential solvent can also form a variety of self-assembled structures in solution, without adsorbing to an interface. Diblocks in preferential solvents can form spherical or cylindrical micelles, or lamellae closed up into vesicles.

Micelles and vesicles are important in many contexts in complex fluids. The equilibrium between micelles and single chains in solution controls the availability of single chains for absorption to a surface to be coated with a brush. Spherical micelles in solution lead to induced forces between colloidal particles via the “depletion interaction”, which we shall describe in later lectures. Long cylindrical micelles can entangle at sufficient concentration, leading to non-Newtonian flow behavior similar to that of polymer melts and solutions. Finally, the core regions of micelles can serve as “protected spaces” in which molecules may be sequestered and carried, in an otherwise incompatible solvent.

In extremely dilute solution, individual copolymer chains adopt configurations in which the insoluble block is a collapsed globule of volume $N_A\Omega_0$, and the soluble block is a random coil of radius $l_s(N/n_s)^{3/5}$. We can state a rough criterion for the solubility of single diblocks in this way, relative to some melt mesophase which would be formed in the absence of the preferential solvent.

The free energy of the single chain in solution (here neglecting translational entropy) is

$$\beta F/\text{chain} = \beta\gamma(N_A\Omega_0)^{2/3} - wN_B \quad (4.4.1)$$

We have written this free energy relative to a melt mesophase reference state, in which the interfacial tension and stretching terms would both scale as $(\chi N)^{1/6}$, which is small compared to the above contributions. Thus, the rough criterion for solubility is simply that the solvation energy of the B block is larger than the interfacial tension contribution of the surface of the A globule.

Spherical micelles

Now we consider the structure of a spherical micelle, constructed from p diblocks. The core is a melt of A blocks; the corona is a Daoud-Cotton spherical brush of B blocks in solvent. In equilibrium, the aggregation number p is determined by the system to minimize the free energy per chain. Depending on the value of p , the chains in the core may be compressed (if the core radius is much smaller than the melt radius R_{gA} of the A block), or stretched (if the core radius is much larger than R_{gA}), or neither. Likewise, depending on the length of the B block, the radius of the Daoud-Cotton brush may be larger than, smaller than, or comparable to the core radius.

We now treat the simplest case, in which we assume that the core is neither very much compressed or stretched, and that the corona radius is large compared to the core. In this regime, the micelle free energy per chain is the sum of two terms, the interfacial tension of the core against solvent and the corona free energy.

To calculate the corona free energy, we recapitulate the Daoud-Cotton scaling, this time with a finite core radius (which we will need shortly). The blob dimension $\xi(r)$ at a distance r from the core satisfies

$$4\pi r^2 = p\xi^2 \quad (4.4.2)$$

The free energy per corona chain can be written as “ kT per blob”, hence

$$\beta F_B/\text{chain} = \int_0^R dr/\xi = (p/4\pi)^{1/2} \log R/a \quad (4.4.3)$$

Finally, the radius of the brush can be found from the requirement that all the monomers get used up in getting to the end of the chain. That is,

$$N_B = \int_0^s ds = \int_a^R dr ds/dr = \int_a^R dr g(r)/\xi(r) \quad (4.4.4)$$

in which the last equality holds because the monomers get laid down at a rate ds/dr equal to one blob worth of monomers ($g(r)$) every blob diameter ($\xi(r)$).

To evaluate this, we use the blob scaling expression

$$\xi/l_s = (g/n_s)^{3/5} \quad (4.4.5)$$

After a bit of algebra, we have

$$R = \left(a^{5/3} + (5/3)(N_B/n_s)(p/4\pi)^{1/3}l_s^{5/3} \right)^{3/5} \quad (4.4.6)$$

which in the limit of long B blocks scales as $N_B^{3/5}p^{1/5}$ (as we found before when we introduced Daoud-Cotton scaling).

In the limit that the corona is much larger than the core, the stretching free energy of the corona depends only weakly on R (logarithmically). So roughly speaking, the free energy per chain in the corona scales as $p^{1/2}$.

Now we estimate the interfacial tension term. The volume of the core is equal to the total displaced volume of the A blocks:

$$4\pi/3a^3 = pN_A\Omega_0 \quad (4.4.7)$$

The core surface area is $4\pi a^2$. The number of chains per unit area σ then scales as

$$\sigma = p/(4\pi a^2) \sim (N_A\Omega_0)^{-2/3}p^{1/3} \quad (4.4.8)$$

As usual, we add the interfacial and stretching terms, to arrive at a Flory-style estimate for the free energy per chain:

$$\beta F/\text{chain} = \beta\gamma p^{-1/3}(N_A\Omega_0)^{2/3} + p^{1/2} \quad (4.4.9)$$

Minimizing with respect to p gives

$$\begin{aligned} p &\sim (N_A\Omega_0)^{4/5}(\beta\gamma)^{6/5} \\ \beta F/\text{chain} &\sim (N_A\Omega_0)^{2/5}(\beta\gamma)^{3/5} \end{aligned} \quad (4.4.10)$$

If we assume that the interfacial tension is of a typical magnitude, which is to say about kT per the area of a monomer $\Omega_0^{2/3}$, then we have p of order $N_A^{4/5}$ (which may be hundreds, say). The most important energy is the formation energy of the micelle, which compares the free energy per chain in the micelle to that of isolated chains:

$$\begin{aligned} \beta\Delta F/\text{chain} &= \beta F(p^*)/\text{chain} - \beta F(1)/\text{chain} \\ &\sim (N_A\Omega_0)^{2/5}(\beta\gamma)^{3/5} - (N_A\Omega_0)^{2/3} \end{aligned} \quad (4.4.11)$$

For large N_A , this is essentially the interfacial energy of the isolated chain, which can be many kT .

Coexistence between micelles

Copolymers in solution may be found in any number of different kinds of micelles. Most simply, we may label the different species of micelles by their aggregation number p . In equilibrium, we may regard the different species as able to exchange chains with each other, or with a dilute population of single chains (which may be regarded as the limiting case of a micelle with $p = 1$).

We may write the free energy of a system of micelles of different p as a sum of ideal gases:

$$\beta F = \sum_p n_p ((\log n_p/V - 1) + \beta E_p) \quad (4.4.12)$$

in which there are n_p micelles of aggregation number p , with formation energy E_p , a system of total volume V . The total number of copolymer chains is

$$N = \sum_p p n_p \quad (4.4.13)$$

We determine the number n_p of each size of micelles, by minimizing the free energy with respect to the set of $\{n_p\}$ values, subject to the constraint of fixed total number N of copolymer chains. We enforce the constraint by means of a Lagrange multiplier μ :

$$0 = \frac{\partial(F - \mu N)}{\partial n_p} = kT \log n_p/V + E_p - \mu p \quad (4.4.14)$$

Solving for n_p , we have

$$c_p = n_p/V = e^{-\beta(E_p - \mu p)} \quad (4.4.15)$$

Effectively, μ is the chemical potential for chains, which must be equal for each species of micelles, each of which may be regarded approximately as a separate phase. The value of μ is determined by the normalization requirement above. Alternatively, we may replace μ in terms of c_1 , the concentration of single chains, as

$$c_p = c_1^p e^{-\beta(E_p - pE_1)} \quad (4.4.16)$$

Now we consider the case of spherical micelles, for which the optimal aggregation number is very well defined, so that we can simplify the sum over micelles to only two terms, $p = 1$ and $p = p^*$. Intuitively, when the system is very dilute, the translational entropy favors the dissolution of micelles into single chains. As the concentration increases, a rapidly increasing fraction of chains are found in micelles, which are energetically favorable compared to single chains.

We may define the ‘‘critical micelle concentration’’ (CMC) c^* as the chain concentration at which half the chains are in micelles. Above c^* , essentially all new chains added go into micelles, leaving the concentration c_1 of isolated chains approximately constant. To compute c^* , we may set $c_1 = c^*/2$ and $p c_p = c^*/2$, which leads to

$$c^* = 2e^{\beta(E_p - pE_1)/(p-1)} / p^{1/(p-1)} \approx e^{\beta(E_p/p - E_1)} \quad (4.4.17)$$

Thus the CMC is exponentially small if the micelle formation energy is large.

Cylindrical micelles

The equilibrium among micelles of different aggregation number takes a very different form for cylindrical micelles, because of the form of the micelle energy E_p :

$$E_p = p\epsilon - \alpha \quad (4.4.18)$$

The energy E_p takes this form because the micelle formation energy per unit length is constant, except for a correction at each end for the endcaps, which are by assumption less favorably assembled.

Applying this energy with the result of the previous section for the concentrations of the different species, we have

$$c_p = c_1^p e^{\beta(p-1)\alpha} = (c_1 e^{\beta\alpha})^p e^{-\beta\alpha} \quad (4.4.19)$$

Now enforce the normalization,

$$c = \sum_p p c_p = \sum_p p x^p e^{-\beta\alpha} \quad (4.4.20)$$

with x defined as $c_1 e^{\beta\alpha}$. The sum is a geometric series that can be performed, with the result

$$c = e^{-\beta\alpha} x / (1 - x)^2 = c_1 / (1 - c_1 e^{\beta\alpha})^2 \quad (4.4.21)$$

As long as c_1 is much smaller than $e^{-\beta\alpha}$, the denominator is essentially unity, and c is approximately c_1 . That is, almost all the chains are in spherical micelles — endcaps with no cylindrical midsection. The CMC is again defined so that $c_1 = c^*/2$; using this in the above gives, after a bit of algebra,

$$c^* = e^{-\beta\alpha} (2 - \sqrt{2}) \quad (4.4.22)$$

Unlike the case of spherical micelles, for which the micelle size is very well defined, cylindrical micelles are polydisperse. We are interested in the probability $P(p)$ that a randomly chosen micelle has length (mass) p . We have

$$P(p) = c_p / \sum_p c_p = x^p / \sum_p x^p = x^p (1 - x) = (1 - x) e^{p \ln x} \quad (4.4.23)$$

with $x = c_1 e^{\beta\alpha}$ as above. We would like to have this relation in terms of the overall concentration c instead of c_1 .

If c far exceeds c^* , then c is much greater than c_1 , which implies that c_1 must become essentially equal to $e^{-\beta\alpha}$. Then we can approximate

$$c \approx e^{-\beta\alpha} / (1 - c_1 e^{\beta\alpha})^2 \quad (4.4.24)$$

This can be inverted for x , as

$$\begin{aligned} x &\approx 1 - 1/\sqrt{c \exp \beta\alpha} \\ \ln x &\approx -1/\sqrt{c \exp \beta\alpha} \end{aligned} \quad (4.4.25)$$

Using this result in $P(p)$ above gives

$$\begin{aligned} P(p) &\approx e^{-p/\bar{p}}/\bar{p} \\ \bar{p} &= \sqrt{c \exp(\beta\alpha)} \end{aligned} \quad (4.4.26)$$

That is, the length distribution is exponential, with a characteristic length \bar{p} that scales with the square root of concentration.

4.5 Copolymer asymmetry and micellar structure

For the case of copolymer mesophases without solvent, we found that the asymmetry of the copolymer (fraction of A monomers, say) controlled the geometry of the domains, whether spherical, cylindrical, bicontinuous, or lamellar. Intuitively, we expect a similar progression for copolymers in selective solvents. However, the details of the progression are different, and in a way more complex, because the environments of the two blocks are very different (grafted layer in melt versus solution).

Just as for melt mesophases, we anticipate three contributions to the free energy per chain for micellar structures in solution: chain entropy (whether stretching or compression) in the core, interfacial tension of the core in contact with nonsolvent, and chain entropy (stretching) in the corona. Unlike melt mesophases, we shall find that the chain entropy terms in core and corona scale rather differently on the overall molecular weight of the diblock. For melt mesophases, at a given diblock asymmetry the two stretching terms scaled in the same way with overall chain length, which meant that the optimum mesophase length scale (i.e., the sphere or cylinder radius, or lamellar period) was determined by a balance of two terms, interfacial tension and chain stretching.

In contrast, for diblock micelles in solution, we have a free energy that is the sum of three terms, all of which scale differently with the lengths of the A and B blocks. The interfacial tension term of course always favors micellar structures of larger dimension, while either core or corona stretching favors smaller dimensions. As a result, the balance of terms that determines the micellar size given a geometry will generically be struck either between the interfacial tension and corona stretching, or between interfacial tension and core stretching, with a crossover in behavior at the point at which core and corona stretching contributions are comparable in magnitude.

To analyze this situation, we begin with a rather asymmetric diblock, with a short core (A) block and long corona (B) block, such that chain stretching in the core is negligible compared to the interfacial tension and corona stretching. As long as the only two important terms in the free energy are interfacial tension and corona stretching, it is clear that the spherical micelle will have the lowest free energy.

To see this, compare spherical, cylindrical, and lamellar structures at the same “coverage” (chains per interfacial area) σ . Because the spherical structure is more outwardly curved than the cylinder, which in turn is more outwardly curved than the lamella, there is more room at a given distance from the interface for B blocks to avoid each other in the sphere than in the cylinder or lamella. Hence at any given σ the corona free energy will be lower for the spherical micelle than for the other two competing structures. (The optimal value of σ will be found by balancing the tension and corona stretch terms.)

For the cylindrical and lamellar structures to become competitive, chain stretching of the core blocks must therefore become important. As we increase the length of the A blocks, the optimized radius of the spherical micelle will grow. For spherical micelles of aggregation number p and radius a , we have

$$\begin{aligned} A &= 4\pi a^2 = p/\sigma \\ V &= 4\pi/3 a^3 = pN_A\Omega_0 \end{aligned} \tag{4.5.1}$$

which leads to

$$V/A = a/3 = N_A\Omega_0\sigma \tag{4.5.2}$$

Thus at fixed area per chain, the radius grows linearly with the A block length. Since the radius of gyration of the A block only grows as $N_A^{1/2}$, the core block eventually becomes stretched. When this occurs, the virtue of the spherical geometry (that it most effectively relieves the stretch of the

corona) becomes a vice, relative to the cylindrical and lamellar structures. To see this, we write the geometrical constraints for cylinders and lamellae analogous to the above.

For cylinders of radius a , length L , and λ chains per unit length, we have

$$\begin{aligned} A &= 2\pi aL = \lambda L/\sigma \\ V &= \pi a^2 L = \lambda L N_A \Omega_0 \\ V/A &= a/2 = N_A \Omega_0 \sigma \end{aligned} \quad (4.5.3)$$

And for lamellae of area A , thickness $2a$ (half-thickness a is the “radius” of the lamella) and σ chains per unit area on each side of the lamella, we have simply

$$\begin{aligned} V &= 2aA = 2\sigma A N_A \Omega_0 \\ V/2A &= a = N_A \Omega_0 \sigma \end{aligned} \quad (4.5.4)$$

Evidently, we can write

$$a = d N_A \Omega_0 \sigma \quad (4.5.5)$$

in which $d = 3, 2, 1$ corresponds to spheres, cylinders, and lamellae.

Thus we see that for fixed coverage σ and A block length N_A , the spherical micelle has the largest radius, followed by the cylinder and then the lamella. This leads to greater stretching of the core block in the spherical micelle, which eventually favors the other two structures as the A block length increases.

To analyze this crossover, it is useful to write expressions for the stretching free energy per chain of core and corona blocks in each geometry, in terms of the coverage σ . In the core, we estimate the stretch energy per chain as

$$\beta F_A/\text{chain} = \frac{a^2}{N_A b^2} = \frac{d^2 N_A \Omega_0^2 \sigma^2}{b^2} \quad (4.5.6)$$

in which $d = 3, 2, 1$ for the spherical, cylindrical, and lamellar structures respectively. (The second equality follows from using the expressions for R in the respective structures.)

We also require expressions for the corona block dimensions and stretching for cylindrical and lamellar structures. These are obtained in the same way as for spherical micelles.

To summarize the results: for spheres we have

$$\begin{aligned} 4\pi r^2 &= p\xi^2 \\ p &= 4\pi a^2 \sigma \\ R &= \left(a^{5/3} + (5/3)(N_B/n_s)(a^2\sigma)^{1/3} l_s^{5/3} \right)^{3/5} \\ \beta F_B/\text{chain} &= (a^2\sigma)^{1/2} \log R/a \end{aligned} \quad (4.5.7)$$

The corresponding results for cylinders are

$$\begin{aligned} 2\pi rL &= \lambda L \xi^2 \\ \lambda &= 2\pi a\sigma \\ R &= \left(a^{4/3} + (4/3)(N_B/n_s)(a\sigma)^{1/3} l_s^{5/3} \right)^{3/4} \\ \beta F_B/\text{chain} &= 2(a^2\sigma)^{1/2} \left((R/a)^{1/2} - 1 \right) \end{aligned} \quad (4.5.8)$$

and for lamellae

$$\begin{aligned} 1 &= \xi^2 \sigma \\ R &= (N_B/n_s) l_s^{5/3} \sigma^{1/3} \\ \beta F/\text{chain} &= (N_B/n_s) l_s^{5/3} \sigma^{5/6} = (a^2 \sigma)^{1/2} R/a \end{aligned} \quad (4.5.9)$$

Now it turns out to be helpful to consider micellization from the opposite limit, in which the core stretching dominates the corona stretching, and the area per chain is determined in each structure by a balance between corona stretch and interfacial tension. Neglecting for the moment corona stretch, we can write the free energy per chain as

$$\beta F/\text{chain} = \frac{\beta \gamma}{\sigma} + \frac{d^2 N_A \Omega_0^2 \sigma^2}{b^2} \quad (4.5.10)$$

The corresponding optimal coverage scales as

$$\sigma^* \sim \left(\frac{\beta \gamma b^2}{d^2 N_A \Omega_0^2} \right)^{1/3} \quad (4.5.11)$$

which determines the optimal core radius $a^* = d N_A \Omega_0 \sigma^*$. The optimal free energy scales as

$$\beta F^*/\text{chain} \sim (\beta \gamma)^{2/3} (d^2 N_A \Omega_0^2)^{1/3} \quad (4.5.12)$$

Evidently the lamellar phase ($d = 1$) has the lowest core stretching energy at fixed σ , and is therefore preferred when the core stretching dominates the corona stretching. (In all three structures, the coverage is determined in this limit by minimizing the above free energy; different optimal values ensue, because of the differing values of d above.)

Now we progressively increase the length of the corona block. At first, the corona is short compared to the core radius; we have a “crewcut micelle” (in which the length of the “hair” is short compared to the radius of the “head”). In this limit, the free energy per chain in the corona is the same function of N_B and σ in all three structures, because the corona brush is approximately flat in all three cases.

As we increase the length of the corona block, the corona free energy per chain increases, at first without much perturbing the optimal coverage. Eventually, the corona free energy per chain becomes comparable to the core free energy per chain, beyond which point the corona begins to dominate in the balance that determines the coverage (and hence the micellar dimension).

We now estimate the block length N_B^* at which this occurs, and whether the corona brush is still a crewcut at this crossover. Assuming first that the corona brush is approximately planar, we equate our estimate of the optimal core plus tension free energy per chain to the free energy per chain of a planar brush:

$$(\beta \gamma)^{2/3} (d^2 N_A \Omega_0^2)^{1/3} \sim (N_B^*/n_s) l_s^{5/3} \sigma^{*-5/6} \quad (4.5.13)$$

with σ^* given as above.

After a bit of algebra we have a crossover condition

$$N_B^* \sim N_A^{11/18} \quad (4.5.14)$$

In the above, we have suppressed factors of d , and made these simplifying assumptions: 1) the thermal blob size l_s is comparable to the size of a monomer $\Omega_0^{1/3}$; 2) the number of monomers

n_s in a thermal blob is of order unity; 3) the interfacial tension γ is of order kT per monomeric dimension.

Now we verify that chains of this length result in a corona that is still short compared to the micelle radius. We form the ratio h/R , where h is the corona height and R the micelle radius; using our scaling results above, we have

$$h/R \sim \frac{N_B^* \sigma^{*1/3}}{N_A \sigma^*} \sim N_B^*/N_A^{7/9} \sim (N_B^*/N_A^{11/18}) N_A^{-1/6} \quad (4.5.15)$$

Thus we see that for N_A large (polymeric), the ratio h/R is still small when we reach the crossover point at which the corona begins to matter (at which $N_B^*/N_A^{11/18}$ is of order unity).

As we continue to increase the corona block length beyond this crossover, the coverage in each micellar structure is determined by a balance of the interfacial tension and corona stretching terms, still in the crewcut limit. The optimal coverage begins to decrease as N_B increases. Eventually, we reach a value of N_B at which the corona thickness becomes comparable to the core radius.

To find out when this occurs, we examine our results for the corona dimension R for spheres and cylinders. In each case, we see that the expressions involve a comparison of the core radius a to a term proportional to N_B . When the two terms are comparable, we are at the limit of the crewcut micelle regime.

In fact, it turns out we can write the corona radius expressions for all three geometries as a function of a single scaling parameter, as follows:

$$x = \frac{N_B l_s^{5/3} \sigma^{-2/3}}{n_s N_A \Omega_0} \sim (N_B/N_A) \sigma^{-2/3} \quad (4.5.16)$$

$$R/a = f_d(x) = \begin{cases} (1 + 5x/3d)^{3/5} & \text{spheres} \\ (1 + 4x/3d)^{3/4} & \text{cylinders} \\ x & \text{lamellae} \end{cases} \quad (4.5.17)$$

(Likewise, we see that the corona free energy per chain in all three structures is a function only of R/a times the same prefactor.)

Now the combination $(N_B/N_A) \sigma^{-2/3}$ can be written as

$$x \sim (N_B/N_A) \sigma^{-2/3} \sim N_A^{-1/6} (N_B/N_B^*) (\sigma/\sigma^*)^{-2/3} \quad (4.5.18)$$

which makes clear that at the crossover to corona-dominated stretching ($N_B = N_B^*$ and $\sigma = \sigma^*$), the corrections due to a finite corona thickness are small (because N_A is large and so $N_A^{-1/6}$ is smallish).

For N_B above N_B^* , the corona stretching balances the interfacial tension to determine the optimal coverage. We may write a scaling form for the free energy per chain as

$$\beta F/\text{chain} = \beta \gamma / \sigma + (N_B/n_s) l_s^{5/3} \sigma^{5/6} \quad (4.5.19)$$

(the second term is a scaling form for the free energy per chain of a flat brush).

Optimizing with respect to σ results in

$$\sigma \sim (\beta \gamma / N_B)^{6/11} \quad (4.5.20)$$

At the crossover to corona-dominated stretching, this coverage should also equal σ^* , which scales as $N_A^{-1/3}$. Equating the two results yields $N_B/N_A^{11/18} \sim 1$, i.e., we recover the crossover condition as we must.

If we use the above result for the optimal σ in the corona-dominated regime to evaluate the parameter x governing the corrections due to finite corona thickness, we have

$$x \sim N_B/N_A^{11/15} \quad (4.5.21)$$

When x is of order unity, we cross over to the regime in which the corona is thick compared to the core, which defines a second crossover length for the B block,

$$N_B^{**}/N_A^{11/15} \sim 1 \quad (4.5.22)$$

We are finally in a position to write an expression for the free energy per chain in a micellar structure that includes all three contributions (interfacial tension, core and corona stretch), as

$$\beta F/\text{chain} = \beta\gamma/\sigma + d^2 N_A \sigma^2 + d N_A \sigma^{3/2} g_d(x) \quad (4.5.23)$$

with dimensionless functions $g_d(x)$ defined for spheres, cylinders, and lamellae as

$$g_d(x) = \begin{cases} (3/5) \log(1 + 5x/3d) & \text{spheres} \\ 2((1 + 4x/3d)^{3/8} - 1) & \text{cylinders} \\ x & \text{lamellae} \end{cases} \quad (4.5.24)$$

In the above, we have suppressed all factors of length (i.e., assumed that l_s equals $\Omega_0^{1/3}$, and taken this length as our scale for measuring area per chain).

We can recast this by putting σ in units of $N_A^{-1/3}$, resulting in

$$\begin{aligned} \beta F/\text{chain} &= N_A^{1/3} \left(\sigma^{-1} + d^2 \sigma^2 + d \sigma^{3/2} N_A^{1/6} g_d(x) \right) \\ x &= N_A^{-1/6} (N_B/N_B^*) \sigma^{-2/3} \end{aligned} \quad (4.5.25)$$

(We note that all three functions $g_d(x)$ are linear for small x , so that all three terms in $\beta F/\text{chain}$ are of the same order at the corona crossover point, for which N_B/N_B^* and σ are both of order unity.)

So — finally — we can compare the free energies of the three different micellar structures on an equal footing, optimizing each structure with respect to coverage σ , and systematically varying N_B . The lowest free energy for a given value of N_B is the preferred structure among the three. We see that the free energy in each phase is proportional to $N_A^{1/3}$, a factor which we may therefore omit from our comparison.

Plotting the three free energy curves in as a function of N_B/N_B^* , we find that in a finite range of values of about 4–11 (centered on the transition from spheres to lamellae at about 5.5), the cylindrical micellar structure is stable with respect to spheres and lamellae. Thus we find that while there is not an entire scaling regime over which cylinders are stable, there is a narrow band of parameter values where cylinders are expected. This calculation therefore illustrates both the utility and limitations of scaling arguments, and the need to complement such arguments with more precise calculations in which the “crossover dependence” with respect to parameters (here, such as coverage and N_B) is accounted for.