

8

Macromolecules at interfaces and structured organic films

8.1 MACROMOLECULES AT INTERFACES

The previous chapter introduced us to the importance of soft matter in nanotechnology, focusing on the importance of self-assembly as a parallel, scalable route to creating highly controlled and ordered structures on the nanoscale. In this chapter we pursue the topic of how the properties of organic materials, and in particular polymers, can be exploited to make functional nanoscale devices, focusing now on their use in ultrathin films and single-molecule layers.

This area has its roots in a number of classical areas of materials science and chemical engineering. The exploitation of macromolecules at interfaces has historically been a central concern of colloid science, and already forms the basis of major industries. Examples include:

- (i) the use of interfacially grafted and adsorbed polymers to control colloid stability in industries such as food, pharmaceutical formulations and personal care products;
- (ii) control of interactions between submicron polymer particles to optimise the process of film formation in water-based varnishes and paints;
- (iii) submicron polymer coatings on plastic film to add functionality by controlling surface properties such as adhesion and printability;
- (iv) control of the wetting properties of surfaces by treatment with self-assembled monolayers, such as in the surface treatment of glass fibres for use in composite materials.

As these technologies become refined and our understanding and control of them at the nanoscale becomes more precise, new areas exploiting the properties of

macromolecules at interfaces are becoming important. Areas in which rapid progress is being made include:

- DNA microarrays, more colloquially known as gene chips, are already a big industry. These devices, using an array of different macromolecules tethered to a planar surface, permit the rapid screening of gene expression, and are likely to be the first of a variety of new highly parallel approaches to systems biology and chemical analysis.
- Other approaches to miniaturising techniques in chemistry and biochemistry, including microfluidics, and nanodevices for microreactors and for sorting and separating molecules and biomolecules.
- Plastic electronics, in which the self-assembling properties of polymers in thin films are used to make fully optimised electronic and optoelectronic devices by simple and cheap processing routes.
- The precise control of interactions between synthetic materials and human cells, for tissue engineering and other biomedical purposes.

In the future we anticipate that exploitation of the properties of self-assembly and responsiveness to the environment that are characteristic of macromolecules at interfaces will be used to make wholly new types of functional nanodevices. Some of these will be synthetic devices that mimic some of the operating principles of cell biology, exploiting the principles of conformational change and molecular recognition in nanomachines such as molecular motors and selective valves and pumps. Other areas of application will be found in truly molecular-scale electronic devices, in which much of the nanofabrication of the molecular components of circuits is achieved by self-assembly.

The study of the properties of macromolecules at interfaces represents a fascinating interaction between fundamental surface physics and applied chemistry. In asking why surfaces and interfaces are so important for macromolecular systems, it is worth making a fundamental comparison between the surface of a simple polymer, like polystyrene, and the surface of an elemental material such as silicon.

Silicon has an open diamond structure with each atom separated by 0.54 nm whereas polystyrene has a random coil structure, with a segment length of 0.67 nm. However, when considering the effect of a surface it is perhaps better to consider the size of the polymer chain, which scales as the square root of the number of monomers in the chain. As an example, polystyrene of molecular weight $100\,000\text{ g mol}^{-1}$ has ~ 960 monomers and a chain size of $\sim 8.5\text{ nm}$. To a first approximation, the effect of a surface can be considered relevant over a distance 15 times greater in polystyrene than in silicon. In macroscopic situations this may not always be significant but on length scales of several nanometres, it is particularly important because virtually every chain in a polystyrene nanoparticle will have some contact with the surface. This will not be true of silicon particles of similar size. From this point of view, polymers at surfaces are considerably more influential than small-molecule systems.

The interaction of uncharged materials with each other at the nanoscale is largely controlled by long-range (van der Waals) forces. The forces are long-range because their

extent of interaction covers distances of up to 100 nm. Macroscopically, we consider these van der Waals interactions to be surface forces. Nanoscopically, these surface forces are the size of the materials themselves. Therefore, whatever the material, surfaces are very important in nanotechnology because it is via these surface forces that materials interact with each other.

8.2 THE PRINCIPLES OF INTERFACE SCIENCE

8.2.1 Surface and interface energies

The presence of an interface between a material and the vacuum (i.e., its surface) represents a major perturbation, and the importance of this perturbation necessarily increases as the dimensions of a system approach the nanoscale. The size of the perturbation is measured by the *surface energy*. The surface energy – to be thermodynamically precise, we should talk about a *surface free energy*, which is equivalent to a *surface tension* – tells us how much the system energy increases if new surface is created from bulk material. The equivalence of surface free energy and surface tension is easily demonstrated if one thinks about the energy required to create a new surface from, say, a liquid trapped in a square wire frame of length l . The energy required to extend the frame in any one direction by a distance x will be $2lx\gamma$. This is work done against the surface tension, and so the surface free energy per unit area, γ , must be equal to the surface tension. The factor 2 is a simple statement that there are two surfaces in the liquid film. The magnitude of surface energies varies from around 30 mJ m^{-2} for hydrocarbon-based materials such as polymers, to 70 mJ m^{-2} for water, to nearly 0.5 J m^{-2} for mercury. Most materials have surface energies that are lower than water, which means they will form a coating on water. The ability to coat water is extremely useful in creating thin organic coatings by, for example, the *Langmuir–Blodgett* technique (Section 8.5.2.2).

The origin of the surface energy lies in the cohesive force that binds together condensed matter of any kind, either solid or liquid. A crude but useful way of thinking about surface energy is to imagine the atoms or molecules in a solid or liquid to be held together by bonds of energy ε . If each molecule occupies a volume v_0 , and each molecule has bonds to, on average, z other molecules, then the total cohesive energy per unit volume of the solid or liquid is given by $L = z\varepsilon/2v_0$. To a first approximation we can identify this with the latent heat. If we now create some new surface, we have to ‘cut’ some bonds – at a surface a molecule will interact with fewer molecules than it does in the bulk. If each molecule at the surface on average interacts with z' other molecules, then the surface energy $\gamma = z'\varepsilon/2v_0^{2/3}$. From this we can show that the surface energy is directly proportional to the cohesive energy. Solids or liquids that have strong cohesive forces holding them together have large values of the surface energy.

An interface between two different solids, between two different liquids, or between a solid and a liquid also has an energy associated with it, assuming the pairs of materials are not mutually soluble. The values of these *interfacial energies* are generally up to an order of magnitude or so less than surface energies; to make an interface between two

materials A and B one has to cut A–A bonds and B–B bonds, but at the interface some of this energy cost is recovered by the formation of new A–B bonds. If the energy gained by making new A–B bonds actually exceeds the energy cost of breaking A–A bonds and B–B bonds then the materials must be mutually soluble.

The cohesive forces binding atoms and molecules together can have different origins. The simplest situation to consider is that of two atoms or molecules that are alike. In this case the forces interacting between them are always attractive and are known as van der Waals interactions. These van der Waals interactions have an interaction energy proportional to r^{-6} . At very small r (typically less than 0.5 nm) electron clouds begin to overlap and the Pauli exclusion principle forces electrons into more energetic orbitals. This means there is a repulsive term in the interaction potential between atoms and molecules, which is commonly represented as a potential proportional to r^{-12} (though there is nothing fundamental about this functional form, and many other short-ranged functions have also been proposed): see also Section 1.4.2.5.

If one knows the form of the potential between any two *atoms*, then to find out how two larger *bodies* of material interact, an obvious (though not rigorously correct) approach is to sum the interactions between every pair of atoms in the two bodies. In practice this is done by integration. The simplest case is when we have a single atom or molecule interacting with a surface that is sufficiently thick and sufficiently extensive in area that we can consider the surface to be a *semi-infinite medium*. If the medium has density ρ and the atom is distance D away from its surface, then we consider the interaction between the atom and an annulus of the material of radius x and depth z . We then integrate these interactions throughout the depth of the medium and over all annuli:

$$W(D) = -2\pi C\rho \int_D^\infty dz \int_0^\infty \frac{x dx}{(x^2 + z^2)^{6/2}} = \frac{-\pi C\rho}{6D^3}. \quad (8.1)$$

It is easy to alter this equation for other forms of the attractive potential. If we replace the atom or molecule by a surface of the same material, the energy of interaction of the two surfaces is best given per unit area:

$$W(D) = \frac{-\pi C\rho}{6} \int_D^\infty \frac{\rho dz}{z^3} = \frac{-\pi C\rho^2}{12D^2}. \quad (8.2)$$

This equation represents the energy required to separate to infinity two surfaces that are initially a distance D apart. If the original distance can be thought of as the separation of atoms in a bulk material, we can identify this with the surface energy. In fact, the energy required to separate two surfaces must be 2γ per unit area. This can be equated to the attractive potential between two surfaces derived above:

$$2\gamma = \frac{-\pi C\rho^2}{12D^2}. \quad (8.3)$$

Usually this equation is rewritten

$$\gamma = \frac{A_H}{24\pi D^2}, \quad (8.4)$$

where $A_H = -\pi^2 C \rho^2$ is known as the *Hamaker constant*. For two different materials the Hamaker constant may be rewritten $A_H = -\pi^2 C \rho_1 \rho_2$. This simple result is very important in considering the stability of films on surfaces. It should be noted that such van der Waals forces depend on the nature of any intervening medium, and also that the above calculation neglects any other form of interaction between the components.

It is clear that in any system consisting of a dispersion of nanosized droplets or particles, surface and interfacial energies provide a major driving force for change. The smaller the particle, the larger the proportional importance of the surface or interface energy becomes. There are two particularly important ways in which a system can reduce its overall interfacial energy: aggregation and adsorption.

In the phenomenon of aggregation, nanoscale particles reduce their area of effective interface by joining together. If the particles are liquid, two such particles will lose their identity on coming together and will *coalesce* to create a single, larger particle. Solid particles are unable to deform on contact and instead *flocculate* to produce more or less open networks of joined together particles.

For adsorption to take place, a third material must be present (usually in solution in a liquid phase). Suppose this material, which we call C, has the property that the sum of the energies of the A–C interface and the B–C interface is less than the energy of the A–B interface. Then if a thin layer of this material is interposed between the two materials, it can have the effect of reducing the interfacial energy. The most common way of achieving this is by using a molecule with an *amphiphilic* character. For example, if A is a hydrocarbon (perhaps submicron polymer particles of the kind found in emulsion paint) and B is water, then if the molecule C is of mixed character, with part of the molecule being hydrophobic and part hydrophilic, then it is likely to be effective at reducing the interfacial energy.

The phenomenon of adsorption can, according to circumstances, be beneficial or deleterious in its effects.

8.3 THE ANALYSIS OF WET INTERFACES

Some general methods of analysing surfaces and interfaces have been introduced in Chapter 2. The specific problems of analysing interfaces involving polymers are that they are often wet, in the sense that we are interested in a solid–liquid interface rather than a solid–vacuum interface. This means we need tools that, rather than being surface-specific, interrogate buried interfaces, and we need techniques that do not need to operate in ultra-high vacuum conditions. Some key techniques that fulfil some or all of these condition include:

- *Light reflection techniques*: ellipsometry and surface plasmon resonance can provide sensitive measures of the amounts of material that adsorb at a solid–liquid interface.
- *Neutron reflectometry*: the smaller wavelength of neutrons compared to light allows one to probe the structure of an adsorbed or grafted layer in more detail, with subnanometre resolution. It is necessary to label the species that is being probed with deuterium. This is discussed in more detail in Section 2.8.4
- *Atomic force microscopy*: see Section 2.5.2.

8.4 MODIFYING INTERFACES

Interfaces have an associated energy, and because the surface-to-volume ratio of a particle is much greater when the particle is small, such small particles are always highly unstable unless their interfaces have been modified to prevent aggregation. Classically, this is the province of *colloid science*. When nanoscale particles are dispersed in water, steps are required to prevent the particles aggregating. Such *colloidal stabilisation* is usually achieved by modifying the surfaces of the particles to create an energy barrier which prevents the particles from sticking to each other. This can be done by arranging for the surfaces of the particles to be charged, or by coating them with a molecular layer of material. This molecular layer, often made up of polymers, may be physically or chemically attached to the surface.

Physical attachment has the advantage that it is simple and often requires nothing more complex in processing terms than exposing the surface to be modified to a solution of the modifying agent. Its disadvantages are that the molecules are not firmly attached to the surface, and with a change of conditions it is possible for them to leave the surface once again. Chemical attachment avoids this difficulty, and typically such layers are considerably more robust than physically attached layers, but of course the consequences of this are the more complex processes required to attach the molecules.

8.4.1 Adsorption and surfactancy

It is a general principle that if one has a two-component mixture near a surface, the composition of the mixture near that surface will be altered in a way which lowers the energy of the surface. This is the principle on which surfactants work. In a solution of surfactants in water, surfactant molecules migrate spontaneously to the surface of the water and in the process lower its surface tension, often by a very significant amount. There is a fundamental thermodynamic relation, the *Gibbs adsorption isotherm*, between the excess amount of surfactant at the surface, the degree to which the surface energy is lowered, and the thermodynamics of the surfactant–water interaction.

The most familiar class of surfactants are *amphiphilic* molecules – molecules with two separate parts, one hydrophobic and one hydrophilic. As discussed in the previous chapter, these materials are the basis of soaps and detergents. In addition to lowering the energy of a water surface, they will usually lower the interfacial energy between water and various solids as well. This is the basis of detergency, in which fat or dirt particles are coated by surfactants to be lifted off a substrate.

8.4.2 Polymer adsorption

Polymers are more effective at adsorbing at interfaces than chemically similar small molecules, and having adsorbed at such interfaces they are more effective than analogous small molecules at keeping interfaces apart. This makes them extremely valuable for colloidal stabilisation, and they are used to stabilise nanoscale dispersions of liquid and solid particles in a wide variety of existing industrial and domestic processes.

Why are polymers so effective at adsorbing to surfaces? The simplest way of thinking about this is to realise that adsorption describes an equilibrium between molecules attached to the surface and molecules free to move around in the solution. An adsorbing species will lower the energy of the surface by becoming attached there, but the cost of this is a loss of entropy that arises because the molecule is localised there. Compare a small molecule and a chemically identical polymer consisting of N subunits. If we move the small molecule and the polymer from the solution to the surface, we lose the same amount of entropy but we gain a factor of N more energy from the polymer, simply because it has N subunits, each of which lowers the energy of the surface as much as the small molecule.

The shape that a polymer adopts at a surface is conventionally thought of as consisting of three different elements: *trains* of consecutive polymer segments all stuck to the surface, *loops* of polymer segments leaving the surface but anchored to it by trains at each end, and *tails* of polymer segments attached at one end only. Statistical mechanical theories predict the relative amount of loops, trains and tails, as well as their distributions of sizes. We should picture a surface coated with adsorbed polymer as presenting a rather fluffy appearance, with a polymer coating which has rather low density but which protrudes a distance of up to tens of nanometres into the surrounding fluid (Figure 8.1).

The interaction of two nanoparticles coated with such a fluffy layer is rather complicated, though generally it is repulsive. The biggest effect is osmotic pressure; as we bring two polymer-coated surfaces together, the polymer segment concentration between the surfaces rises. This leads to an osmotic force pushing the surfaces apart. However, it is possible, if the density of polymers coating the surfaces is relatively low, for polymers attached to one surface to find free areas on the other surface to stick to as well, leading to the formation of polymer bridges between the two surfaces. This can lead to a net attraction between the two surfaces.

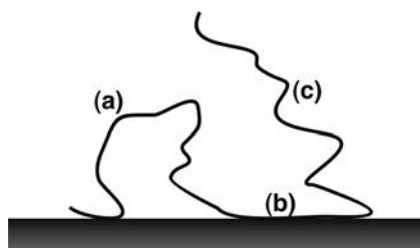


Figure 8.1 An adsorbed polymer may consist of (a) loops, (b) trains and (c) tails

8.4.3 The chemistry of grafting

Adsorption processes, whether of small molecule surfactants or of polymers, are effective ways of modifying a solid surface or a solid–liquid interface, but because the molecules are only physically attached to the surface the process can often be reversed, and with a change of conditions the adsorbed molecules may well become detached. More permanent molecular layers can be created by covalently bonding short to medium-sized organic molecules by one end to the surface. In some cases, such permanently bound layers can be formed with a very complete degree of surface coverage and a high degree of order within the layer; these systems are known as *self-assembled monolayers* (SAMs). Two classes of SAM-forming systems have been particularly important: alkylthiol molecules bound to a gold surface, and alkoxy silane or chlorosilane molecules bound to a surface of silicon oxide.

Self-assembled monolayers have a variety of uses. Broadly speaking, they form a convenient way to modify the wettability of surfaces, they can control the adhesion between a surface and a bulk phase in contact with it, they can control the interaction of a surface with cells (Chapter 9), and they can be used to introduce controlled chemical functionality at a surface. In the latter case, further reactions can be carried out exploiting that functionality; in particular, this route can be used to immobilise macromolecules at the interface. A very important example of this is in DNA chips. A DNA chip, more properly a DNA microarray, consists of an array of different oligonucleotides immobilised on a flat surface; they allow the rapid, parallel detection of specific nucleotide sequences, and as such have revolutionised the study of gene expression and promise major advances in genetic diagnosis in medicine. Although DNA microarrays have so far made the biggest impact, other types of microarrays, involving small molecules, proteins or polysaccharides, are likely to grow in importance in the future, as the power of this type of massively parallel experimentation becomes apparent.

The lateral patterning methods collectively described as *soft lithography* also rely on the facile formation of self-assembled monolayers, and their subsequent modification. Most usually, these methods exploit the reaction between gold surfaces and alkylthiols.

8.4.3.1 Gold/thiol chemistry

Perhaps the most reliable way of making a high-quality self-assembled monolayer uses alkanethiols attached to a gold surface. The required alkanethiol, RSH, is simply applied from solution to the gold surface; it is believed that it binds as a thiolate, RS^- , to a well-defined site in the gold (111) surface. As a result of a fortuitous commensurability between the separation of the binding sites and the effective cross-section of the alkyl chain, the chains form a densely packed array (Figure 8.2).

The dense packing of the chains in an alkylthiol monolayer means that the gold surface is effectively completely screened from the environment. This means that the chemical character of the surface can be easily changed; by using alkylthiols with different terminal functional groups, a wide variety of chemical functionalities can be introduced at the surface. Thus surface properties such as contact angle can be changed over a very wide range of values. The ease with which functional groups can be

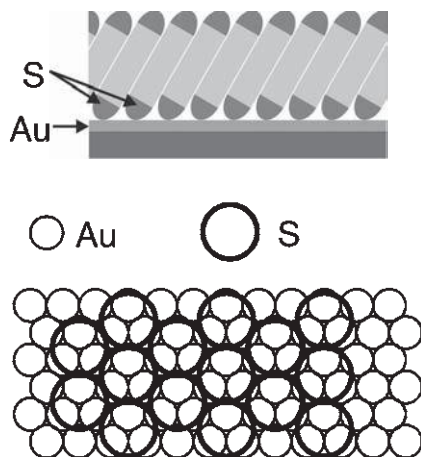


Figure 8.2 The attachment of alkanethiols to gold. Adapted from T. P. Sullivan and W. T. S. Huck, Reactions on monolayers: organic synthesis in two dimensions, *Eur. Journal Org. Chem.* **1** 17–29 (2003)

introduced at the surface also allows one to carry out further chemical reactions, as discussed below. The only disadvantages of gold/thiol self-assembled monolayers are their somewhat limited thermal stability and the need for a gold surface.

8.4.3.2 Silane coupling agents

Possibly the most well-established technique for creating a single molecular layer relies on the use of so-called silane coupling agents to create covalent bonds between the surface of glass, silica or the native oxide of silicon and small organic molecules.

There are two basic starting points. The first uses chlorodimethyl long-chain alkylsilanes or alkyltrichlorosilanes, which readily react with silanol groups (Si–OH) on the surface of silicon, silicon dioxide or glass to yield a robust covalent linkage between that surface and the hydrocarbon group. The second uses trialkoxy(alkyl)silanes, which are somewhat less reactive but which produce the same end result. The use of trialkoxy or trichloro compounds tends to produce more robust monolayers than the corresponding mono compounds, because having made one bond to the surface, each molecule has available two more reactive groups with which it can form bonds to its neighbours, resulting in a tough two-dimensional network. The downside is that in some reaction conditions alkyltrichlorosilanes in particular can begin to react with each other in solution, resulting in large aggregates which subsequently become attached to the surface. The resulting surface layers are much thicker and rougher than true monolayers.

Perhaps the most well-known of the silane coupling agents is aminopropyltriethoxysilane (AMPTES), which is a very widely used route to putting amine groups on a surface. This is the first step in many procedures for attaching proteins, DNA or other molecules to a glass surface.

The alkyl group in AMPTES is probably too short to pack in a well-ordered self-assembled monolayer. Monolayers with a degree of two-dimensional order comparable

to that obtained with gold/thiol SAMS are achievable with molecules such as octadecyltrichlorosilane (OTS). OTS provides a very effective way of rendering a glass, silica or silicon surface strongly hydrophobic.

In this context it is worth mentioning one other approach to making silicon surfaces hydrophobic. In a process widely used in the semiconductor industry for 'priming' silicon wafers prior to coating with photoresist, hexamethyldisilazane (HMDS, $\text{Me}_3\text{SiNHSiMe}_3$), is applied from vapour. The reaction



is different to the reaction that produces the coating of silicon dioxide by trialkoxyalkylsilanes or trichloroalkylsilanes, but the end result is rather similar.

8.4.3.3 Macromolecular layers

In many cases the creation of a self-assembled layer at a surface is simply the first step towards introducing a more sophisticated functionality at that surface. In many applications one needs to graft a layer of macromolecules at that surface. Such a grafted layer is often referred to in polymer and colloid science as a *polymer brush*. This is a process that has been extensively used in colloid science to stabilise particles against aggregation. An application that can possibly be considered as a special case of colloid stabilisation is the use of grafted poly(ethylene oxide) to protect a surface against non-specific protein adsorption. An application that depends on very specific interactions between grafted macromolecules and molecules from the environment is exemplified by DNA microarrays, which rely on the covalent attachment of strands of DNA to surfaces.

We can distinguish between two broad approaches to attaching macromolecules to surfaces. In the grafting-to approach, preformed macromolecules are attached to the surface either chemically or physically. For physical grafting, one needs a polymer with a sticky end-group; for example, in water a block copolymer with a long water-soluble block, such as poly(ethylene oxide), with a shorter hydrophobic block on the end will form a grafted layer on a hydrophobic surface, with the end-block strongly and selectively adsorbing to the surface. Covalent attachment, which has obvious advantages of stability over physical attachment, is achieved by reacting a functional group on the end of the polymer chain to a complementary group on the surface. Surfaces with amine functionality have been extensively exploited in this way.

In the grafting-from approach, on the other hand, polymerisation of a macromolecule is initiated at the surface, growing the grafted chain in situ. Both approaches have advantages and disadvantages. Grafting-to generally allows one to use a much wider variety of synthesis routes, so the range of polymer architectures that can be used is generally much wider. But grafting-from usually produces layers with a considerably greater grafting density. In the original developments of the grafting-from technique, radical polymerisation was carried out from surface-bound initiators, resulting in dense and thick layers of highly polydisperse polymers. More recently, however, controlled radical polymerisations such as atom transfer radical polymerisation have been developed which allow the potential for much greater control of the architecture of the surface-grafted polymers.

8.4.4 Physical properties of grafted polymer layers

The questions that arise about the structure of self-assembled monolayers generally concern the perfection of their two-dimensional packing. In the ideal case, an alkanethiol or alkyltrichlorosilane with an alkyl chain of length between 12 and 20 carbon atoms will form a highly ordered, densely packed two-dimensional layer. In contrast, the disposition of long, flexible, macromolecules grafted to interfaces is determined not by considerations of packing and order, but by entropy. The freedom of grafted polymer molecules to adopt many different conformations, and the fact that in an aqueous medium, a solvent or a melt, chain conformations are constantly changing under the influence of Brownian motion is crucial in determining the properties of the grafted layer. In particular, the remarkable efficiency with which end-grafted chains can stabilise colloids against aggregation and prevent non-specific protein adsorption to surfaces is bound up with the condition that the configurational entropy of the grafted chains must be maximised.

More exotic applications of polymer brushes may rely on reversible behaviour; this is the ability of the polymer brush to change its conformation in response to changes in its environment. Depending on the pH, salt concentration, or temperature of the surrounding medium, a brush layer may swell or collapse. Such switchable behaviour is very useful if, for example, one wishes to control wettability or adhesion by changing these parameters. One brush layer may achieve this goal but sometimes two brush layers (a mixed or binary brush) can also be used. Here two different polymers are attached to the substrate, and their behaviour is complementary; i.e., when one brush polymer collapses, the other swells. This has been demonstrated experimentally by exposing a binary brush layer to different solvent vapours.

To understand the properties of grafted polymer layers, polymer brushes, it is helpful to compare one brush polymer with an untethered chain in a good solvent. The simplest model of a free polymer is the freely jointed chain; i.e., each monomer can move around at any angle compared to the next. This is physically not true, because bond angles are fixed. However, over a certain number of monomers, information about the bond angle is lost; the corresponding distance is known as a *persistence length*, and as a result we can define an effective statistical step length, in terms of which the long-range properties of a real polymer with short-range interactions can be mapped onto an equivalent freely jointed chain. The (end-to-end) length of the chain in a neutral, or *theta*, solvent is given by the random walk result $\langle R^2 \rangle^{1/2} = Na^{1/2}$, where a is the step size. This is exactly the same result as the mean free path traversed before an electron undergoes the spin-flip scattering of Equation (4.30). The random walk enables the polymer chain to maximise its *conformational entropy*. However, the freely jointed chain model, even with an effective step length, does not account for long-range interactions. For a solvent whose interaction with a polymer segment is indistinguishable from the interaction between two polymer segments, an *athermal solvent*, the effect of these long-range interactions is to expand the chain. The fact that two polymer segments cannot physically be in the same place at the same time leads to an effective repulsive interaction, known as the *excluded volume* interaction.

Most solvents are not neutral, and in addition to the excluded volume interaction we need to consider the effect of interactions between solvent molecules and chain segments. In a poor solvent, polymer segment–segment interactions are more favourable than polymer–solvent interactions, and the chain tends to collapse; conversely, in a good solvent the chain will tend to expand to maximise segment–solvent contacts.

The effect of both excluded volume and polymer–segment interactions can be expressed by monomer repulsion energy with the following form:

$$E_{\text{repulsive}} \approx k_{\text{B}}T\nu(T)c^2R^3 = k_{\text{B}}T\nu(T)N^2/R^3 \quad (8.5)$$

where T is the absolute temperature, $\nu(T)$ is a temperature-dependent constant and c is a concentration. The concentration can be replaced by $1/R^3$, which simplifies the equation. Note that we ignore numerical prefactors because they contain no important physical information; this is known as a *scaling theory*. A chain cannot extend indefinitely, and so there must be an attractive energy countering this repulsion. This attractive energy may be obtained by considering the chain to be a spring obeying Hooke's law. This elastic term is then given by

$$E_{\text{elastic}} \approx k_{\text{B}}T \frac{R^2}{Na^2}, \quad (8.6)$$

where Na^2 is the chain's unstretched (random walk) length. The length of a polymer chain in a good solvent is thus a compromise between these two results, which may be added and minimised with respect to R . The final result gives the *Flory radius*, $R_{\text{F}} \propto N^{3/5}$. The constant ν is known as *excluded volume*. This result is valid for dilute and semi-dilute polymer solutions. In molten polymers (i.e., without solvent), the chain has a random walk conformation ($R \propto N^{1/2}$) because there a monomer cannot differentiate between monomers of its own chain and monomers of other chains.

The conformation of polymer brushes is dependent upon two parameters: the number of monomers in the chain, N , and the distance between polymer chains, d . The distance between brushes can be replaced by a *grafting density*, $\sigma = a^2/d^2$, where a is the polymer segment size. On length scales smaller than d , chains may be treated as if they were in a good solvent. We then suggest that the brush can be made up of n blobs, each containing $N_{\text{b}} = N/n$ monomers (Figure 8.3). The better the solvent, the more extended the brush but this does not affect the arguments that we shall describe below. In poor solvents, brushes tend to collapse to exclude solvent. The worse the solvent, the more collapsed the brush until the equivalent of a dry polymer brush is obtained. In a poor solvent, the height of a brush is proportional to the number of monomers in the brush and some function of grafting density, which depends on solvent quality.

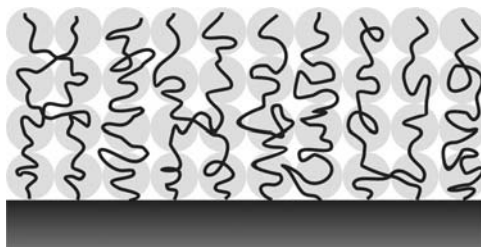


Figure 8.3 Brushes can be thought of as several blobs, where the number of monomers N_{b} in each of the n blobs is related to the number of monomers N in the polymer brush by $N = N_{\text{b}}n$; $n = 4$ in this sketch

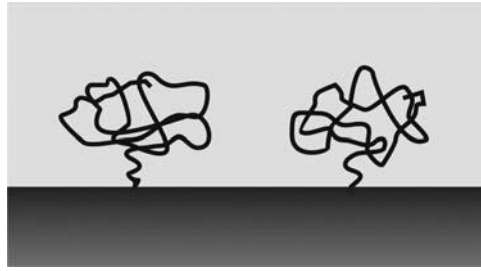


Figure 8.4 In dilute solution the chains are not close enough to interact with each other. They can then adopt a ‘mushroom’ conformation

We shall only consider brushes in good solvents. We divide our consideration of polymer brushes into three sections: semi-dilute solutions, concentrated solutions and molten brushes. The case of the isolated brush (dilute solutions) is less interesting because the brush may be treated as a single chain in a good solvent. For this reason, such a brush is commonly known as a mushroom (Figure 8.4).

8.4.4.1 Semi-dilute solutions

In a semi-dilute solution we can use a scaling model to understand the physical properties of polymer chains. We know that $\sigma = a^2/d^2$ and $d = aN_b^{3/5}$, and can use these equations to calculate the height of the brush, which must be given by $h = Nd/N_b$. From substitution we obtain

$$h = Na\sigma^{1/3}. \quad (8.7)$$

In semi-dilute solutions, the brush height is directly proportional to the number of monomers in the brush.

8.4.4.2 Concentrated solutions

A concentrated solution may be considered to be one in which the brush chains overlap and strongly interact. This strong interaction occurs when $\sigma > a^2/\langle R^2 \rangle$, which means that the projected area of a tethered chain on the substrate is smaller than the cross-sectional area of an untethered chain in the solvent. We need to include this interaction in a model for the brush height. We achieve this by considering excluded volume, which is a means of describing the affinity of a chain for a solvent rather than itself or other chains of the same species. In this respect, we apply exactly the same argument for a concentrated brush layer as for a single chain in a good solvent:

$$E_{\text{conc}} \approx k_B T \left(\frac{h^2}{Na^2} + \frac{v(T)N^2\sigma}{ha^2} \right). \quad (8.8)$$

In this case we have replaced the $1/R^3$ term in the repulsive component of Equation (8.5) by σ/ha^2 , which may be understood if one writes $\sigma/ha^2 = 1/hd^2$, which may be taken as a concentration; i.e., $1/R^3$. If we minimise the above equation with respect to h and equate the result to zero, we obtain $h \propto N(v(T)\sigma)^{1/3}$, which is the same grafting density and chain length dependence as in the semi-dilute regime. This does not mean that the physics is the same: in this concentrated regime the origin of the extension of the brush is the osmotic pressure difference between brush and solvent.

8.4.4.3 Molten brushes

A molten brush in this case is one where the solvent is replaced by a melt of the same polymer. Unfortunately, it is not one that can be considered by using simple arguments. We have mentioned that a polymer in the molten state has a random walk configuration, which would imply that $h \propto aN^{1/2}$ with no dependence on grafting density. This cannot be true, because it is not possible to indefinitely graft chains into ever smaller areas. Another objection is that by the nature of the random walk result, the brush layer would be very well defined. This cannot be true, because such a well-defined layer would have a very large entropic penalty in the free energy of the system (sharp interfaces have a large energy penalty). The interface between the brush and molten polymer must be diffuse, and it is calculated by using self-consistent mean field theory. This is a much more complex calculation and involves starting with a suitable test chain that interacts with other chains via a spatially varying free energy (or chemical potential). An iterative process of guessing the energy associated with a given test chain as a function of the total mean field interaction takes place before the best (self-consistent) result is achieved. Readers familiar with atomic physics will recognise these ideas from the Hartree–Fock method for determining the electronic orbitals for many-electron atoms.

8.4.5 Nanostructured organic coatings by soft lithography and other techniques

The utility of the above methods of coating surfaces is greatly increased if we have the power to apply the chemistry only to specific regions of the surface. To achieve this we require certain lithographic or patterning techniques. We shall address the ideas behind creating patterns on surfaces using self-assembly in Section 8.7 and here we shall consider lithographic methods. The standard lithographic method involves the use of self-assembled monolayers and a poly(dimethyl siloxane) (PDMS) mask. We can assume that the PDMS mask already contains the information on the required structure. This mask is coated with a self-assembled monolayer (SAM), which is imprinted on the surface of interest. The SAM can then be used as a template for further chemistry. This form of lithography (microcontact printing) is discussed in Section 1.4.1.2. Another important form of lithography is photolithography, also discussed in Chapter 1. Here UV radiation illuminates a mask. The mask is a glass slide covered with a chrome pattern. The UV radiation passes through the unpatterned part of the glass onto a photoresist. A negative photoresist is produced when the UV photopolymerises or cross-links the exposed

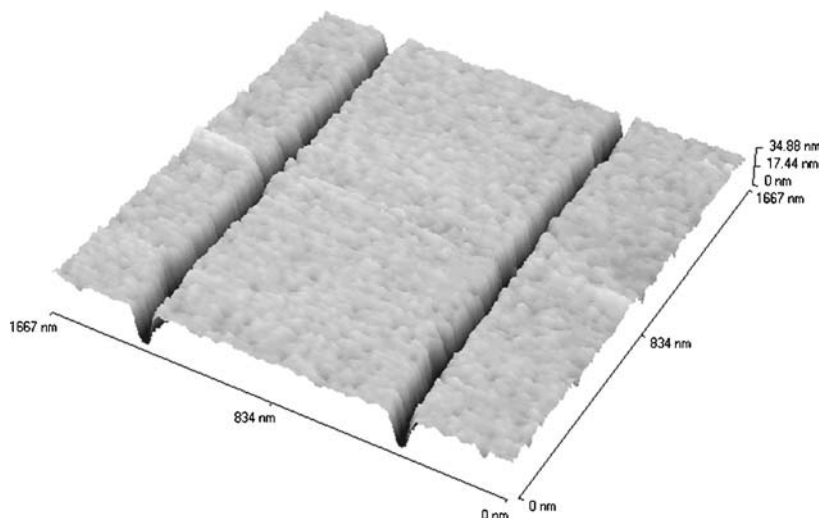


Figure 8.5 Scanning near-field photolithography has been used to create these nanometre-scale trenches in a gold layer. UV light has been passed through a SNOM tip to oxidise an alkanethiolate self-assembled monolayer. The exposed region and the underlying gold were removed by a wet chemical etch. This image was taken using atomic force microscopy. Image reproduced courtesy of Dr Shuqing Sun and Professor Graham Leggett

region. The remainder of the (unexposed) film can be dissolved away. A positive resist is created when the UV radiation destroys the exposed region.

One limitation of these techniques of lithography is the length scale of the pattern that may be achieved. The mask for microcontact printing contains patterns of several microns in size (hence microcontact); smaller sizes are difficult to achieve in PDMS (PDMS is an excellent material because it is deformable and easily cross-linked from a mould to give it its elastic qualities). Photolithography is also generally limited to micron-scale structures because of the wavelength of light; the technique is *diffraction limited*. However, as mentioned in Chapter 2, the diffraction limitation can be circumvented by using a SNOM. In the case of photolithography the UV light is passed through the SNOM tip, enabling the creation of structures of some 50 nm or even smaller; an example is shown in Figure 8.5. Again, the structure created can be used as a template for the chemistry described above.

Another interesting use of the scanning probe techniques in this area is the dip pen nanolithography method in which an AFM tip can be coated with a material, and then moved around a surface depositing this material (Section 7.4). A great advantage of this technique compared to many other forms of lithography is that an array of AFM tips may be used to produce the same pattern simultaneously.

8.5 MAKING THIN ORGANIC FILMS

One of the easiest ways to make a nanoscale structure involves making thin polymer coatings. Coatings of submicron thickness are routine even on the cheapest commodity

polymers, and the process of spin-coating, an important part of fabricating semiconductor nanostructures, can be effectively carried out using equipment costing only a few dollars. Making *structured* films on nanometre length scales is a little more difficult, but nonetheless a number of fairly straightforward methods exist for making *layered* films; that is, films with structure at nanometre length scales in the direction perpendicular to the film surface. It is more difficult to pattern films laterally and we discuss this in the next section.

What all these methods have in common, and what sets them apart from the methods used to make magnetic multilayers and semiconductor heterostructures, is that they are processes that are carried out in *ambient conditions*, rather than in high or ultra-high vacuum. This means that the capital cost of the plant needed to make these structures is usually very low, and one can countenance high-volume, low-cost, applications.

8.5.1 Spin-coating of polymers and colloids

An extremely good way of making a solid film is to start with a liquid film. Liquids have the remarkable property of being *self-levelling*; the action of surface tension keeps a liquid surface smooth and flat. If the liquid is a polymer solution, then if we can remove the solvent in a way that maintains the flatness of the original liquid film, we end up with a polymer film whose thickness can be closely controlled and which in favourable circumstances is smooth down to the nanometre scale.

A relatively thick layer of a polymer solution can be made by simply coating a surface with the liquid, then scraping off the excess with a blade held at a controlled distance from the substrate. This process, known for historical reasons as *doctor-blading*, can produce smooth and uniform films with thicknesses in the range of tens of microns. But to obtain uniform films with thicknesses less than one micron, the technique of choice is *spin-coating*.

In spin-coating, a sample is flooded with a polymer solution and then rapidly spun round (a spin speed of 2000 revolutions per minute is typical). The hydrodynamics of the situation leads to a rather uniform thickness of solution being left on the substrate, the thickness of which depends on the viscosity of the polymer solution and the spin speed. This film then thins as the solvent evaporates.

The ideal outcome of a spin-coating process is a film that is uniform in thickness to within a few percent over an area of many square centimetres, with a root mean square surface roughness of around 1 nm, and a thickness that can be precisely controlled within the range 10–1000 nm. To achieve this, one needs a solvent with the following properties. It should be not too volatile; if significant evaporation occurs during the initial film thinning phase then hydrodynamic instabilities can lead to non-uniformities in the final film. It should remain a good solvent for the polymer in question at all concentrations, to avoid problems that arise from premature precipitation of the polymer before the spinning process is complete. Finally, the solution should wet the substrate well, to avoid film break-up during spinning.

The use of this kind of solution-based coating process is not restricted to simple solutions of polymers; it can also be used to apply materials that are in an essentially colloidal form, or materials that are soluble precursors which react to form an insoluble final product. Photonic crystals are an example of colloidal system (Section 7.4.3).

The most common polymer-based colloidal suspensions are the water-borne latexes that are the basis of emulsion paint. Such colloidal suspensions when applied in a thin film will in some circumstances form a uniform thin coating. This process has a number of stages; as the water evaporates, the colloidal particles pack together in a dense array (if the colloidal particles are spheres with a narrow size distribution, the most efficient packing will be a colloidal crystal). If their physical state permits it, the particles will then deform, and diffusion of polymer molecules will take place at their interface, until the integrity of the individual particles is completely effaced and a smooth film is obtained. In industrial systems the last stages are often helped by the inclusion of a volatile plasticiser which helps the polymers in the particles to flow and interdiffuse. Some chemical cross-linking will generally take place in order to increase the robustness of the final films.

Polymer latexes are generally in the size range 100 nm to 1 μm , and as such cannot be used to make nanoscale polymer films. Smaller colloidal particles include so-called *microgels*, in which one or a few chains are internally cross-linked to make polymer particles on the length scale of 10 nm or less. A polymer colloid of growing commercial and technological importance is formed when the conducting polymer poly(3,4-ethylene dioxythiophene) PEDOT is synthesised in the presence of polystyrene sulfonate (PSS). It seems that this material forms, in aqueous solution, a colloidal dispersion with some similarity to a microgel, in which small clusters of PEDOT and PSS chains are linked by physical cross-links. This material is important because it provides a practical route for spin-coating a conducting layer, opening up the possibility of low-cost all-polymer optoelectronic devices (Chapter 6).

Inorganic thin films can also be made by spin-coating, using the sol-gel chemistry described in Section 1.4.2.6. These systems, sometime known as *spin-on* glasses, are based on solutions of silicon and metal alkoxides which slowly hydrolyse to form first polymers, and then networks of inorganic oxides. The resulting films are composed of a swollen gel, which can be baked to form a dense, sintered inorganic glass.

8.5.2 Making organic multilayers

Nanostructured polymer multilayers are not quite as easy to make as single thin films, but a number of effective approaches exist which exploit the idea of self-assembly in more or less pure forms to make multilayers using relatively simple apparatus.

In some circumstances, spin-coating can be adapted to making multilayer coatings by simply successively spin-coating multiple layers on the same substrate. The requirement for this is that, having laid down one polymer, the solvent used to deposit the next polymer is not a solvent for the first one. Even in cases where the solvent for the second polymer is a non-solvent for the first polymer, so that the first polymer is not physically removed, one should still expect some intermixing of the polymers at the interface due to the solvent-induced swelling of the first polymer near its surface. In practice the range of polymers that can be made into multilayers by this route is relatively restricted.

More powerful routes to making multilayers rely on the phenomenon of *adsorption*. A polymer molecule adsorbed from a dilute polymer solution at an interface generally forms a rather loose layer about one molecule thick; if the interface is removed from the solution, this adsorbed layer will stay on the substrate and collapse to form a thin, dense

layer whose precise thickness is controlled by the nature of the polymer–substrate interaction and the thermodynamics of the polymer solution. If the final substrate is dipped sequentially into a series of different polymer solutions, we have the technique of *layer-by-layer deposition*. If, on the other hand, the monomolecular layer is created at an air–water interface, and such layers are picked up sequentially onto a solid substrate, we have the classical *Langmuir–Blodgett* (LB) technique.

8.5.2.1 Layer-by-layer deposition

In layer-by-layer adsorption, one needs to ensure that if polymer A is deposited first on the substrate, the next polymer to be deposited will adsorb at the polymer A – water interface. The original way of ensuring that this is so relies on making multilayers in which each layer is an alternately charged polyelectrolyte. So, starting with a substrate that has an overall positive charge in water, one would dip this into a solution of a polymer with a net negative charge. On removing the substrate, we would have a monomolecular layer with a negative charge, which can then be dipped into a solution of a positively charged polymer. Attracted by the opposite charge, this polymer layer will strongly adsorb on top of the previously deposited layer. This cycle of deposition of alternately charged polymer layers can be continued to build up a multilayer (Figure 8.6).

Using a typical pair of polyelectrolytes such as sodium poly(styrene sulfonate) and poly(allylamine hydrochloride), it is possible by this method to build up multilayers consisting of as many as 60 pairs of layers, with each pair of layers having a thickness of a few nanometres. This layer thickness can be controlled by variables such as the concentration of polyelectrolytes and salts in the adsorbing solutions. X-ray and

[Image not available in this electronic edition.]

Figure 8.6 Layer-by-layer deposition of charged polymer films. In the first instance, a positively charged substrate is dipped into a polyanion solution (1) and then washed (2). Only one negatively charged layer is deposited on the substrate because of the Coulombic repulsion between like charges. This process can then be repeated with a polycation solution (3) followed by further washing (4). The process can be repeated until numerous layers have been deposited. Counterions are not shown in the figure. Adapted with permission from G. Decher, *Science* **277** 1232–1237 (1997). Copyright 1997 AAAS

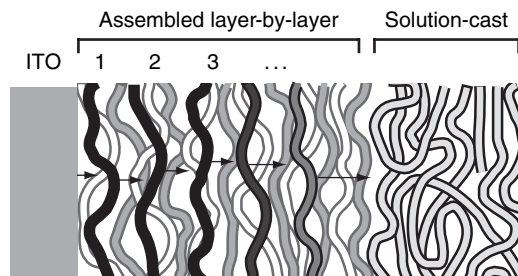


Figure 8.7 The layer-by-layer deposition method has been demonstrated in a light-emitting diode. Layer-by-layer deposition is used to deposit the anionic complex of PEDOT (darkest chains) and PSS (light chains) on an indium tin oxide (ITO) electrode. A cationic poly (*p*-xylylene- α -tetrahydrothiophenium) layer (grey chains) is then deposited. The doping density of the PEDOT is reduced in each subsequent layer (the chains are shown less dark). A light-emitting polymer layer can then be spin cast onto the graded interface. Reproduced with permission from P. K. H. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli and R. H. Friend, *Nature* **404**, 481–484 (2000). Copyright 2000 Nature Publishing Group

neutron reflectivity studies of the structure of the multilayers reveals that the interfaces between each layer are rather broad; in fact the interface width is comparable to the overall layer thickness. These films should be thought of as *fuzzy multilayers*.

A strength of the layer-by-layer approach is that it can be extended to incorporate many other species besides simple polyelectrolytes. Examples of such species include colloidal particles such as gold colloids and clay platelets, biological macromolecules such as proteins and DNA, dendrimers and C₆₀, and nanoparticles such as cadmium telluride.

The layer-by-layer approach has been demonstrated in practical devices. We recall the blend of PEDOT and PSS, which has applications as a hole injection layer in semiconducting polymer devices. The interface between the active layer and the PEDOT/PSS injection layer is sharp (because the layers are deposited separately) and the associated energy is likely to hinder carrier motion. By depositing PEDOT/PSS complexes in a layer-by-layer approach, a graded interface can be created (Figure 8.7). This gradient is achieved by chemically reducing the doping density in the PEDOT/PSS complex in each subsequent layer. The reduction of the doping density causes an increase of the ionisation potential of the PEDOT and should be modified to ensure a match to the active layer (in this case a light-emitting diode), which is deposited onto the graded interface. Of course, the doping may be varied to allow different active layers to be used. We return to the theme of hole injection layers from PEDOT/PSS blends in Section 8.8.1.

8.5.2.2 Langmuir–Blodgett techniques

The Langmuir–Blodgett technique is another means of layer-by-layer adsorption, but it does not rely on electrostatic attraction to provide a stable, well-defined layer. Another practical difference between the LB technique and the layer-by-layer adsorption method is that multilayers produced by the LB technique are not fuzzy but rather have an interface which can be on the subnanometre length scale. The deposited layers must

fulfil certain requirements, which will be discussed below; the technique is not general, but neither is it limited to polymers, and small-molecule multilayers may equally well be deposited.

The first layer is deposited by simply spreading a few drops of solution onto a liquid surface (usually water because of its low vapour pressure and high surface tension). The solvent evaporates, leaving a monolayer of the solute on the fluid surface. Here it is best to use a solvent with a high vapour pressure. The resultant surface is usually not completely covered, and barriers are used to move the molecules together to form a monolayer. These barriers are used to reduce the total surface area of liquid until it is equal to that of the coating layer (Figure 8.8). The surface pressure of the monolayer can be measured and this gives a measure of the interaction of the molecules on the surface. As such, they can be treated as if they are the different phases of matter as the barriers push the molecules together, beginning with a gas of non-interacting particles, through forming a liquid-like layer of interacting molecules, before, at high pressures, the strength of interaction is great enough that the molecules form a 'solid' ordered surface phase. This solid phase can have highly crystalline properties over very large length scales, depending on the material deposited. Fatty acids are a class of material that in general provide very high quality monolayers with long-range order.

The trick to forming multilayered structures via LB deposition is to use a molecule with ends that respond differently to the solvent. For example, a monolayer can be achieved by pushing the substrate into the LB film, and allowing it to adsorb (Figure 8.9(a)). In this case the adsorbed side of the film will be hydrophobic because it is the hydrophobic component that is at the air surface before introducing the substrate. We denote the hydrophobic end by A and the hydrophilic end by B. Bringing the substrate up again will allow the other end (B) to be deposited first on the substrate. In this way multilayers can be deposited. Whether the structure is (substrate upwards) AB–BA–AB as in repeating this procedure, or otherwise, depends on the deposition method used. For example, continually using downward movement of the substrate for the deposition would result in a multilayer with a structure AB–AB–AB, and so on; permutations are illustrated in Figure 8.9(b).

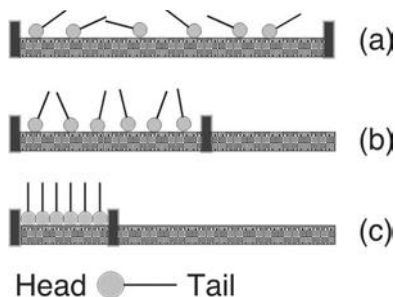


Figure 8.8 During Langmuir–Blodgett film deposition the coating layer orients itself such that the hydrophilic head group of the coating molecule is in contact with the water surface. The tail is hydrophobic. After solvent evaporation the molecules are dispersed on the surface; this is the gas phase (a). By moving the barriers, the molecules interact to form a liquid-like layer (b). Eventually the molecules cannot be moved any closer, and a solid, often highly crystalline layer emerges (c). Reproduced with permission from L. T. Jones, PhD thesis, University of Sheffield, 2003

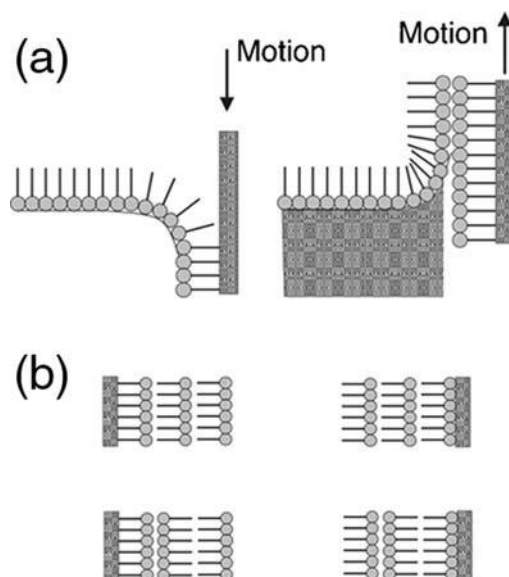


Figure 8.9 LB deposition can be used to create multilayers. (a) The nature of the multilayer can often be varied by controlling whether the substrate is pulled from or dipped onto the monolayer film. (b) Using this method, four different forms of multilayer can be created with head groups opposing each other or in contact with each other. Reproduced with permission from L. T. Jones, PhD thesis, University of Sheffield, 2003

Although LB film deposition is a cumbersome technique, it provides excellent control over film thickness and over macroscopic length scales. Although the technique is perhaps best known for producing multilayers of controlled properties (e.g., thickness, refractive index and polarisation), it is also very often useful simply to have a discrete number of layers in a uniform film, which is not possible using more rapid means of film creation such as spin-casting.

8.6 SURFACE EFFECTS ON PHASE SEPARATION

Here we shall consider how the surface can be used to trigger specific patterns in polymers. This patterning may occur laterally or perpendicularly, with both possibilities being useful in their own right. We first consider order forming perpendicular to the surface, giving rise to lamellar structures.

8.6.1 Polymer blends

Many materials are used in laminate form, which gives them a rigidity and strength that might not be very easily achieved otherwise. A difficulty with creating such structures is that the preparation of multilayers is usually a multi-step process involving different stages such as coextrusion, high-pressure or high-temperature treatment.

Phase separation is an extremely good example of how bulk behaviour is modified by the presence of a surface. Before we consider the effect of the surface, it is necessary to grasp a broad understanding of the mechanism in the bulk. One form of bulk phase separation was covered in Chapter 7 during the discussion of the hydrophobic effect. In the hydrophobic effect, the phase separation is a competition between different entropic effects; there might be ordering around a hydrophobic aggregate but this has a smaller energy cost as ordering around many individual molecules. A more general view ignores the precise nature of what makes a mixture immiscible; hydrophobicity might cause individual molecules to avoid contact in a mixture, but there might be other reasons, such as packing considerations. To consider a very simple formulation, we consider the Gibbs free energy to consist of an entropic term (favouring the mixing of the two components) and an enthalpic term (favouring phase separation). The physics behind the enthalpic component need not be understood, and in polymer mixtures it is represented by a term called the Flory–Huggins interaction parameter.

The competition between entropy and enthalpy leads to a dominant wavelength (called a spinodal wavelength) during the early stages of the phase separation. The energy cost of having separate phases is contained within the free energy. More interfaces means that the enthalpic component of the free energy is dominant over the entropic component. Fewer interfaces (i.e., larger phases) means that entropy still plays an important role in the final structure. Given that the number of phase-separated domains of each phase per unit volume must be constant (because the free energy per unit volume must be constant), there will be a constant distance between these interfaces or between the different phases. The consequence of this behaviour is that the phenomenon of spinodal decomposition results in ordered structures in three dimensions. These structures may be either bicontinuous (two continuous phases) or one phase dissolved in another.

In the event of a surface being present, the phase separation will be modified. Because the lower-energy phase of the phase-separated mixture will preferentially segregate to a surface, the phase-separated morphology must be altered by the presence of a surface. In practice the surface triggers the direction of the phase separation because the symmetry of the mixture has been broken by the presence of a surface. This can give rise to a lamellar structure (Figure 8.10(a)). Although multilayered structures are possible, experimentally it is very difficult to realise more than two or three layers close to the surface because deeper in the film, thermal noise will force the lamellar structure to break up. Figure 8.10(b) and (c) show examples of multilayered structures in polymer films. The formation of stratified films in this fashion is known as *surface-directed spinodal decomposition* and has been studied in various polymer blends. Strictly, spinodal decomposition is an initial growth process; although the formation of the structure shown in Figure 8.10(b) and (c) would have been initiated by spinodal decomposition, late-stage coarsening effects will have been significant. The principles will still apply to other mixtures but polymers have shown the most striking behaviour, mainly because it is easier to achieve larger length scales with polymers, due to their greater size.

We know from the above discussion that phase separation in the bulk has a constant length scale. In polymer blend films, the length scale of this layering is close to that in bulk mixtures. However, in thin films (typically ~ 100 nm or less) this spinodal length scale will be reduced with decreasing film thickness. For films as thin as, or slightly

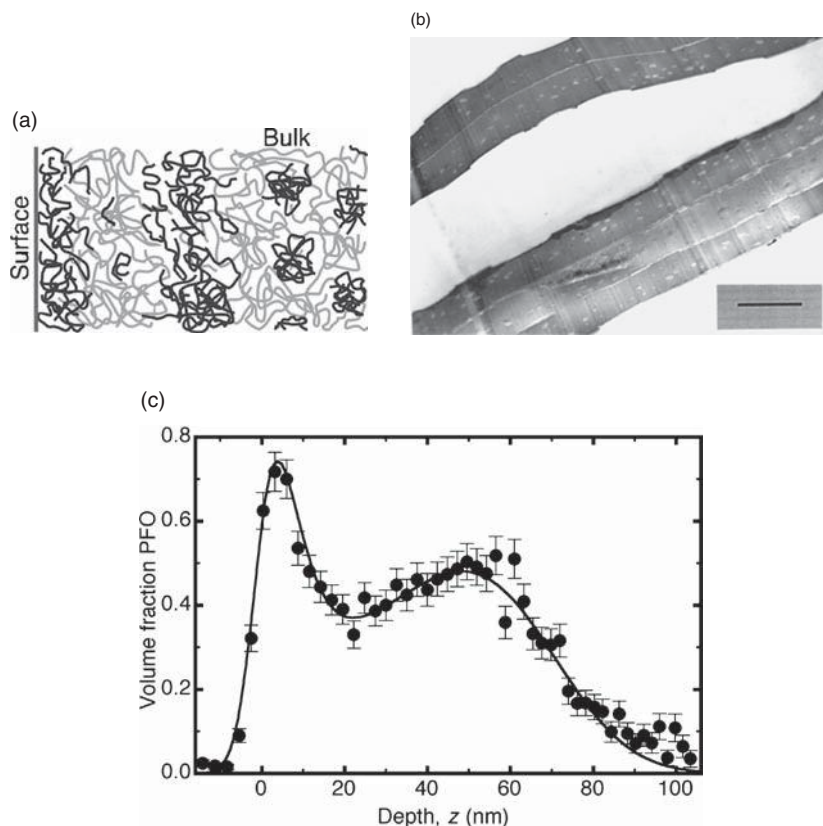


Figure 8.10 (a) Surface-directed spinodal decomposition is shown schematically. The dark chains segregate preferentially to the surface due to their lower surface energy. The phase separation is directed parallel to the surface and results in a layered structure. Deeper into the film, thermal noise breaks up the layered structure to leave an isotropic phase-separated structure. (b) An electron micrograph of two cross sections of a film of polystyrene and polybutadiene embedded in a resin (white matrix). Note the different layers in this film. Darker regions are polybutadiene-rich (the polybutadiene had been stained with OsO_4 to provide contrast with the polystyrene). The craters at the surface of these sections contained polystyrene that dissolved in the resin. The scale bar is $1\ \mu\text{m}$. (c) These ion beam data show the structure perpendicular to the surface in a blend of poly(9,9-dioctyl fluorene) (PFO) and poly(9,9-dioctyl fluorene-*alt*-benzothiadiazole) (F8BT); their chemical structures are shown in Chapter 6. The ordinates represent the fractional volume occupied by PFO. In this case there is a surface layer, rich in PFO, followed by a depletion layer, rich in F8BT, before bulk structure exists. Note that ion beam experiments have a finite resolution of $\sim 10\ \text{nm}$, so the exact volume fraction at the surface ($z = 0$) is washed out. Part (b) is reproduced from M. Geoghegan, R. A. L. Jones, R. S. Payne, P. Sakellariou, A. S. Clough and J. Penfold, *Polymer* **35**, 2019–2027 (1994). Part (c) is adapted from J. Chappell, D. G. Lidzey, P. C. Jukes, A. M. Higgins, R. L. Thompson, S. O'Connor, I. Grizzi, R. Fletcher, J. O'Brien, M. Geoghegan and R. A. L. Jones, *Nature Materials* **2**, 616–621 (2003). Copyright 2003 Nature Publishing Group

thinner than, the bulk spinodal length, the length scale of the phase separation will decrease, but for very thin films, the lamellar structure will not be stable at all, and the film will break up laterally. Of course the length scale where this becomes significant will depend on parameters such as temperature and polymer molecular weight, but as a rule of thumb one can say that films thinner than 100 nm are not likely to be stratified. When very thin films phase separate, therefore, larger length scales are likely to be observed as lateral domains (in the plane of the film).

8.6.2 Block copolymers

We know from the previous chapter how block copolymers pack in the bulk. We have also seen how curvature and interfaces are important parameters in this packing. However, in a film the surface inhibits some bulk conformations, because the surface tends to prefer orientations with one component preferentially adsorbed. An example of a morphology that would be stable on a surface is a lamellar A–B diblock copolymer structure. However, such a film would not necessarily be self-levelling, as we have mentioned to be the case for liquid films. We assume that the copolymer is symmetric, and has lamellar spacing l . If the surface and substrate favour the A block, then the film will have a stable uniform lamellar structure provided its thickness is an integer multiple of $2l$. However, if the two surfaces favour different components then the film has a uniform lamellar structure if its thickness is given by $2(n + \frac{1}{2})l$, where n is an integer. For any other thickness, the film has to orient itself into steps of different thicknesses so that the relevant criterion is satisfied. We might want to create a structure of lamellae lying perpendicular to the surface, and this is somewhat more challenging. One way to achieve this is to produce an energetically neutral surface. A random copolymer-coated surface of the appropriate composition of A and B monomers is one way to achieve such a surface, because the net copolymer–surface interaction will be the same for both of the blocks. Figure 8.11 illustrates the various ways that block copolymers may be oriented when in contact with a surface. Another way to recreate a lamellar block copolymer pattern perpendicular to the substrate is via an epitaxial route (Section 8.7.1). Rough substrates can also inhibit ordering parallel to the substrate because of the amount of bend required in the copolymer layer. In this case it is energetically favourable for the polymers to order perpendicularly to the surface.

An effective route to the creation of perpendicular lamellae on a given surface is to use external fields to align the block copolymer. Even copolymers consisting of polymers with a very small polarisability can be aligned using electric fields. Although enormous electric fields ($\sim 10^7 \text{ V m}^{-1}$) are needed to cause rearrangement in materials with small polarisabilities, this is easily manageable with very thin films. In the first experiments, utilizing diblock copolymers of polystyrene and poly(methyl methacrylate) (PMMA), films of $\sim 20 \mu\text{m}$ thickness were aligned in this way.

Block copolymer structures can be used as a template for nanocontact printing, for example. To achieve such structures one component of the block copolymer needs to be fixed before being etched in plasma. The etch selectively removes the unfixed part of the copolymer film, whereas the fixed part will remain; this is known as reactive ion etching,

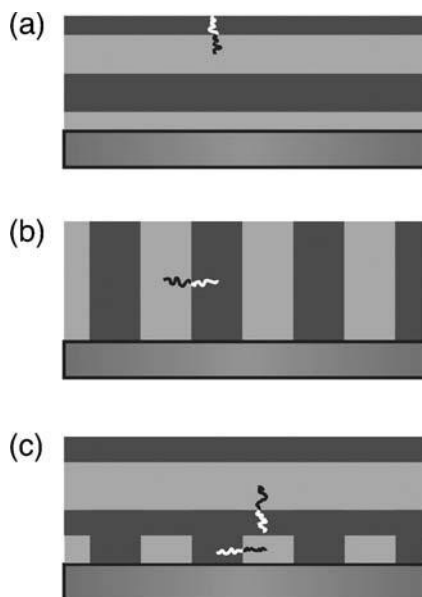


Figure 8.11 Orientation of symmetric diblock copolymers on a surface. (a) Generally symmetric diblock copolymers will form lamellae parallel to the surface. (b) Lamellae perpendicular to the surface is a higher energy state and normally requires a surface neutral to both blocks (other possibilities are discussed in the text). (c) Both possibilities may coexist, with lamellae both perpendicular and parallel to the surface. This combined geometry has the advantage that the film thickness requirements in the text need not be met

and can be used to create both positive and negative masks (Figure 8.12). This might be by cross-linking, or by using a stain. Staining is common in electron microscopy to create contrast where no heavy elements exist (Figure 8.10(b) contains an example of a stained polymer). Oxides of metals such as ruthenium or osmium react with double bonds present in the material and create a cross-link containing the heavy metal. Such a structure would be stable under plasma etching. Instead of plasma etching, UV radiation may be used. For example, in the case of the polystyrene–PMMA diblock copolymers discussed in the previous paragraph, UV radiation destroys the PMMA but fixes (cross-links) the PS. The PMMA can then be dissolved away. An application of this for creating magnetic nanowires is discussed in the next section.

We have described how to make lamellar blocks perpendicular to a substrate surface, but lamellae parallel to the substrate are also useful. We know that this is readily achievable with symmetric diblock copolymers, but such structures can also be achieved using asymmetric block copolymers by the addition of a suitable homopolymer. Figure 8.13 shows how a diblock copolymer, which forms spheres in the bulk, can be made to orient itself into lamellae by the addition of a homopolymer that is miscible with the shorter of the two blocks.

Pattern formation in block copolymers has many parallels in crystallinity; indeed block copolymers form crystal structures, and like small-molecule crystals, block

[Image not available in this electronic edition.]

Figure 8.12 Reactive ion etching (RIE) creates positive and negative masks from thin films of block copolymers of polystyrene and polybutadiene which form polybutadiene spheres in the bulk. Here the polybutadiene is the darker component and wets both interfaces. By exposing the film to ozone, the polybutadiene can be degraded and removed, but by staining the polybutadiene with osmium, it becomes fixed and more resistant to an ion etch than polystyrene. Depending on the preparation route, the RIE will remove more or less polymer where the spheres initially were located, leaving holes or columns in the substrate. Adapted with permission from M. Park, C. Harrison, P. M. Chaikin, R. A. Register and D. H. Adamson, *Science* **276**, 1401–1404 (1997). Copyright 1997, AAAS

copolymer ordering is only perfect over small length scales. Part of the problem lies with preparation techniques, any impurities in the polymer can give rise to defects. The issue of polydispersity (spread in molecular weight distribution) is also relevant here, but relatively monodisperse block copolymers can order despite the effects of polydispersity because the chains in each block still have random conformations. A different major problem comes from ordering initiating at different points, which gives rise to grain boundaries. As a general rule, ordering in block copolymers is at best of order a few hundred nanometres. There are efforts to overcome the length-scale difficulty using, for example, solvent vapours to plasticise the copolymers, which enables them to order. A more practical disadvantage of using block copolymers is that they are expensive to synthesise, which may outweigh the cost benefits of using a self-assembly process.

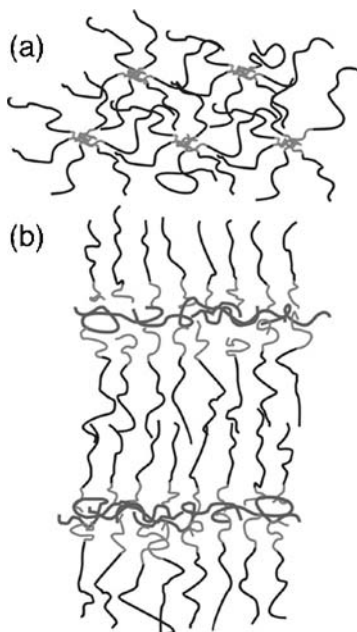


Figure 8.13 (a) A block copolymer A–B in which the B block is shorter than the A block will form spheres of the B block in the bulk. (b) A lamellar structure can be formed by the addition of a homopolymer that is miscible with the B block. This homopolymer may be the same as the B block, but the only criterion is that it be miscible with the B block

8.7 NANOPATTERNING SURFACES BY SELF-ASSEMBLY

Although there are many different methods of creating patterns on surfaces, most of those discussed so far are periodic. The goal for patterning will be achieved when methods of producing non-repeating or more complex structures are achieved. A good example of the need for such structures is in the creation of integrated circuits. Other examples of the need for complex structure on a substrate include micro- and nano-fluidics. However, uniform patterning could also play a role, such as in structures relating to data storage, where complex pathways are much less important than compressing very many bits in a single structure. Similarly, protein and DNA arrays, which might be used for gene sequencing, and chemical sensing devices require only ordered structures as the basic templates.

Sections 1.4 and 8.4 briefly explain how lithographic means can be used to create templates. The use of stamps is a well-accepted route to creating a pattern on a surface. However, such soft lithography does have some disadvantages. There may well be only one master stamp. This stamp will be used to create perhaps a hundred production stamps, which in turn will be used for the lithography. Clearly such a serial process is inefficient, and possibly quite expensive for large-scale production. Any refinement of the stamp, such as the addition of chemical heterogeneity, will also add time and cost to

the process, which could well be prohibitive. Finally, the creation of the smallest structures for the stamp will be diffraction limited at some point.

There are a variety of non-lithographic means towards pattern formation, which have inherent advantages. The major disadvantage of non-lithographic processes is that they tend to be rather specific and we have rather limited control over the parameters influencing the desired structure. In one example, we shall show how dewetting can be used to create long-range patterns. However, not all films will dewet and specific substrate preparation may be necessary in order to tune the polymer–substrate interaction to create the desired structure. This is a general truth about self-assembly; the physics gives us a choice of results over which we have limited control. Therefore, to gain the widest possible choice about the use of non-lithographic printing, we shall need to know all of the many possible routes to creating the structures. The future for soft lithography will probably require a marriage of top-down approaches and self-assembly.

The self-assembly of block copolymers in an electric field has been used to create a series of upright block copolymer cylinders which could be treated with UV radiation. The radiation could be used to destroy the cylinders (PMMA) but fix (by cross-linking) the matrix (polystyrene). Electrodeposition could then be used to inject cobalt into the cylindrical voids. The end result is cobalt nanowires in a polystyrene matrix. The success of such an experiment is due to self-assembly and provides an excellent example of the sort of technologies that could develop from these ideas. However, the nanowires created in this way are not flexible and bends and turns are not built into the system. There is only one length scale involved, hence incorporating the structure into any workable device would require considerable engineering of the other components so this technology would be successfully assimilated into the final structure. It is quite possible that an integration of nanowires and a lithographic template (as described above) could produce more useful structures, as well as perhaps having even better block copolymer ordering.

Another interesting example of the use of both lithography and self-assembly concerns inkjet printing as the starting point for creating a thin film transistor circuit. This experiment, more than most, illustrates how microcontact printing and self-assembly can be used together to make usable devices. It is possible to use inkjet printing to spread a conducting polymer onto a surface, but unfortunately the droplets tend to spread with accidental short circuits as a consequence. A photolithographed film can be used to stop this spreading by providing regions of different wettability across the surface. Blends of PSS and PEDOT can be used as source and drain electrodes of a transistor, which can then be inkjet printed onto the substrate; shorting will be prevented by the repulsion provided by a polyimide line on the otherwise hydrophilic substrate. A film of semiconducting polymer, F8T2 (Chapter 6), is then spin-coated onto the resultant structure, providing broad and complete coverage. A dielectric layer is spin-coated onto the F8T2 before a PSS/PEDOT gate is deposited on top by inkjet printing. This describes a perfectly workable device, but the device quality is actually improved by self-assembly in the F8T2 layer. Annealing the F8T2 at high temperature (in its nematic liquid crystalline phase) enables it to align parallel to the polyimide structure. The alignment remains after the structure is quenched down to room temperature. The major benefit of this alignment is greater current flow due to fast intrachain charge transport.

8.7.1 Patterns produced on heterogeneous substrates

A rather obvious way to produce patterned structures is to have a pattern to begin with. The film will simply replicate that pattern. This is, after all, the basis of lithography. However, there are subtleties that should be understood in these processes. We begin our discussion of heterogeneous substrates with the simplest example of the use of self-assembled monolayers to provide a basis for pattern replication. Experiments using block copolymer templates are useful to show why pattern replication does not always occur, and we shall then close this section by discussing the importance of topography.

Earlier in this chapter we discussed how to produce a lamellar surface structure using surface-directed spinodal decomposition. In thin films (i.e., films significantly thinner than the bulk spinodal wavelength) a lamellar structure is unstable and patterning takes place in the plane of the film. There is likely to be preferential segregation of one component to the surface or substrate (or both) but the dominant effect will be lateral phase separation, where again the dominant length scale involved is related to the spinodal wavelength. Suppose we now attempt to deposit such a structure on a micro- or nanopatterned surface by spin-coating. Figure 8.14 shows how a polymer blend

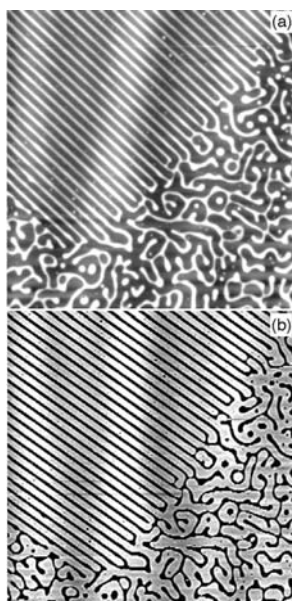


Figure 8.14 A polymer blend phase separates to replicate the structure of a self-assembled monolayer. An immiscible blend of polystyrene and poly(vinyl pyridine) is shown on a substrate patterned with stripes of gold and the SAM; the image was taken using atomic force microscopy and the periodicity of the pattern is 2.4 μm . (a) The poly(vinyl pyridine) adsorbs onto the gold and the polystyrene adsorbs onto the SAM. Away from the pattern, the phase separation proceeds as expected on a pure substrate. (b) The poly(vinyl pyridine) has been removed by dissolution of the sample in ethanol (a non-solvent for polystyrene). The removal of the poly(vinyl pyridine) demonstrates that the polystyrene segregates to the SAM. Reproduced with permission from M. Böltau, S. Walheim, J. Mlynek, G. Krausch and U. Steiner, *Nature* **391**, 877–879 (1998). Copyright 1998 Nature Publishing Group

structure is modified by spin-coating onto a lateral gold pattern, which has been created by microcontact printing of a SAM onto a silicon substrate. Notice how the blend phase separation follows the SAM structure, replicating its wavelength. Outside the SAM structure, the pattern replication fails and the structure takes on its own somewhat larger wavelength. This means that the phase-separated morphology will take on a shorter wavelength than would be expected on a neutral unpatterned substrate because the energy cost associated with having a greater areal density of interface is paid for by the energy gain due to the preferential attraction of one of the components (here polystyrene) to the gold pattern.

The use of block copolymers to reproduce nanoscale patterns is also useful as a means to control the behaviour of other polymer mixtures. Phase separation in polymer blends takes place over rather large length scales, given initially by the bulk spinodal wavelength and more practically by various coarsening processes. However, if the polymer blend is on a (patterned or ordered) copolymer surface, spatial variations in the surface energy will control the final morphology, reducing the length scale of the phase separation. The use of ordered block copolymers as a substrate is slightly different from using random copolymers because a random copolymer-coated surface will essentially result in a surface with a particular value of the surface energy, whereas a block copolymer can provide a spatial variation in the surface energy. The use of an A–B copolymer template for an A/B polymer blend would probably be the most useful variation on this theme, but the copolymer can still be effective in changing the behaviour of other blends provided there are sufficient variations in surface energy. Figure 8.15 shows an example of the use of block copolymer patterns to control the length scale of phase separation.

Suppose we can create a self-assembled monolayer that is an exact match for a block copolymer lamellar length scale. In this case we can align a lamellar block copolymer structure perpendicular to a substrate rather than parallel. This substrate replication (epitaxy) has the advantage of ensuring long-range order with the block copolymer films; there are fewer dislocations (Figure 8.16). We know that dislocations and grain boundaries can occur in block copolymers but the energy cost of a dislocation is not great, because block copolymers can easily reorient themselves around dislocations. Grain boundaries occur because nucleation of lamellae starts at different points. Self-replication of a self-assembled monolayer by a block copolymer eliminates grain boundaries because *translational order* is inherent in the structure due to the SAM underlayer. The number of dislocations are minimised because the energy cost of their presence is increased; a dislocation will force part of the polymer to lie on an unfavourable part of the substrate pattern.

8.7.2 Topographically patterned surfaces

Any topographical variations of the surface of a substrate have so far been ignored (e.g., surfaces with a chemical topography) or treated as boundaries (e.g., certain examples utilizing lithography). However, in the case of slight variations of substrate topography there are important and significant changes that need to be considered and understood. Wetting of a rough surface is a relatively new subject, and relatively few experiments have

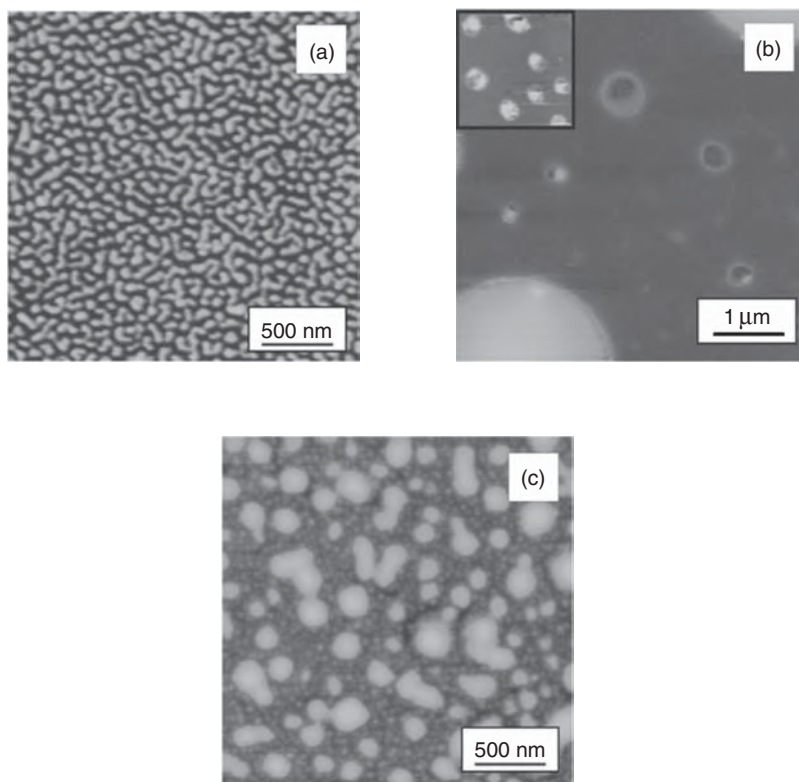


Figure 8.15 Block copolymers can alter the phase separation behaviour of polymer blends by providing a substrate with a spatial surface energy variation. (a) AFM image of a triblock copolymer film on a silicon wafer. The triblock copolymer contains blocks of polystyrene, poly(vinyl pyridine), and poly(*tert*-butyl methacrylate). (b) AFM image of an immiscible blend of polystyrene and poly(*tert*-butyl methacrylate) on silicon. (c) The same blend on the triblock copolymer. Note the much smaller length scale exhibited in (c) than in (b). Reproduced with permission from K. Fukunaga, H. Elbs and G. Krausch, *Langmuir* **16**, 3474–3477 (2000) Copyright 2000 American Chemical Society

been reported. However, the ability to control the contact angle of a fluid by varying substrate topography would be beneficial in producing water (or other) repellent surfaces, as well as micro- and nanofluidic applications. Experiments and theory have shown that a sharp pattern on a surface exaggerates the contact angle, making wettable surfaces even more wettable and non-wettable surfaces even more repellent. The exaggeration of contact angle to make, say, hydrophobic surfaces even more hydrophobic is largely due to the droplet not being able to conform to its equilibrium contact angle on a microscopic scale, forcing the droplet to an even greater contact angle (Figure 8.17).

A film coated on a substrate by some solvent evaporation technique will usually have a relatively flat surface, with the only contribution towards surface roughness being thermally induced capillary waves. However, in thin films (a few nanometres thick) the film's surface will convey some aspects of the substrate topography, so if

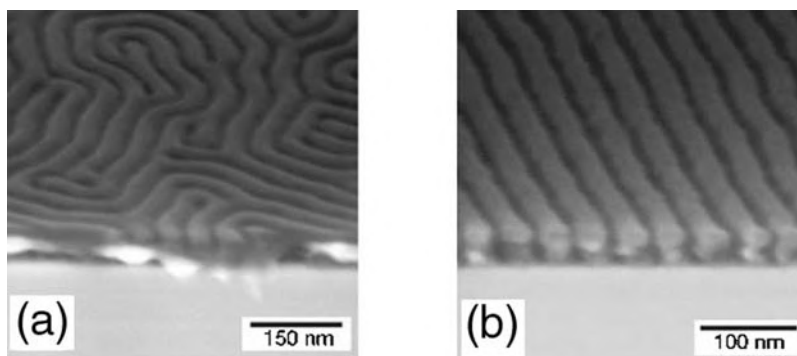


Figure 8.16 Cross-sectional scanning electron microscopy images of a diblock copolymer of polystyrene and PMMA on (a) an unpatterned substrate and (b) a nanoscopically patterned substrate whose pattern replicates the length scale of the copolymer microphase separation. In (b) the polystyrene and PMMA wet different parts of the pattern, causing perpendicular lamellae with impressive long-range order. Reproduced with permission from S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo and P. F. Nealey, *Nature* **424**, 411–414 (2003) Copyright 2003 Nature Publishing Group

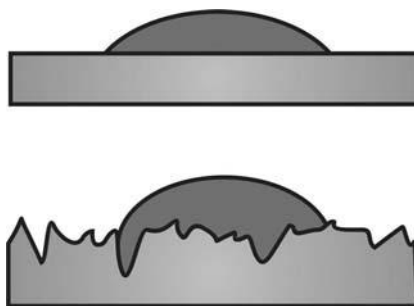


Figure 8.17 A droplet on a rough surface cannot adopt its true contact angle on the microscopic scale, which forces a greater contact angle than it would have on a flat surface of the same material

the substrate is not perfectly flat then it is possible that some imperfections will be replicated in the film surface. Such imperfections can have undesirable effects because it has been shown that ultrathin polymer films can dewet wettable surfaces. This may be because, in films thinner than the polymer chain size, a polymer may be able to adopt its ideal Gaussian (random walk) conformation only if it dewets; i.e., if it forms droplets of a size thicker than the polymer chain. It is nevertheless possible that this dewetting can be used as a means for pattern formation. Figure 8.18 shows a model topography imposed on a silicon substrate. Here the silicon surface is of a sawtooth structure and a polystyrene film, somewhat thinner than the size of a polymer chain in the bulk, is spin-coated onto it. The height of the sawtooth is only a few nanometres, comparable to the size of the polymer film, which forms nanochannels

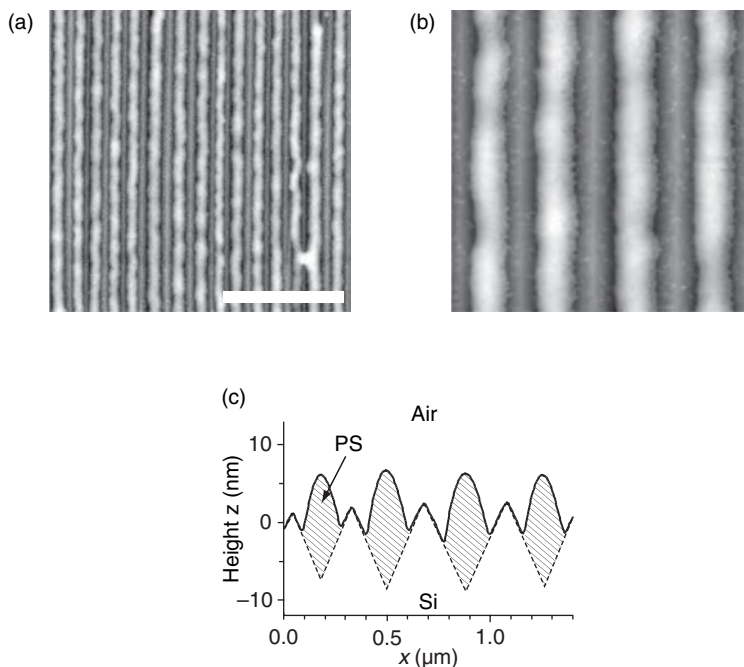


Figure 8.18 A thin (~ 5 nm) polystyrene film is spin coated onto a corrugated silicon substrate and heated to 150°C . Despite the small height and large width of the sawtooth structure on the silicon, the polymer dewets to the troughs in the structure, forming channels. (a) AFM image of the structure. The scale bar is $2\ \mu\text{m}$. (b) Smaller area ($1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$) scan. (c) Line average scan of the data in (b). The position of the silicon substrate underneath the polymer is obtained by interpolation. Note that these AFM images have an exaggerated aspect ratio. Reproduced with permission from N. Rehse, C. Wang, M. Hund, M. Geoghegan, R. Magerle and G. Krausch, *Eur. Phys. J. E* **4**, 69–76 (2001) Copyright 2001 EDP Sciences

when heated above the glass transition (so the polymer can flow). This phenomenon may be exploited to much greater effect if surface chemistry is utilized. Glancing angle evaporation of gold onto the silicon sawtooth structure will result in gold on the peaks with pure (untouched) silicon troughs. The gold may then be used as the basis for thiol chemistry, giving a functional polymer surface (Section 8.4).

8.7.3 Patterns produced by thin film dewetting

Dewetting of films from a surface can have a variety of origins, but the most common of these are for metastable and unstable films in which surface energies and long-range forces play the major role. Metastable films will break up by the thermal nucleation of holes in the film or by the presence of impurities, which will nucleate a hole. Dewetting in metastable films is a random process, so ordered structures will not be possible by this mechanism. However, most unstable films can be used to create a dominant length scale because a spinodal mechanism is responsible for film rupture. If a film is thermodynamically unstable on its substrate,

it will break up. Many small droplets will create a large surface area, whereas few large droplets will not satisfy the thermodynamic driving force for dewetting. The result is that the compromise between limiting the amount of interface created, while enabling dewetting to proceed yields a wavelength, the *spinodal wavelength*, characteristic of the dewetting process. For more unstable films, this spinodal wavelength decreases, reflecting the increased role of the immiscibility between substrate and film. The thermodynamic quantity responsible for the dewetting is usually long-range (van der Waals) forces. The strength of these forces is characterised by the Hamaker constant; Figure 8.19 illustrates the dewetting process. As an example, remember from Section 8.2 that the attractive energy between two planar surfaces separated by a distance x is given by

$$W_{\text{vdW}} = -\frac{A_{\text{H}}}{12\pi x^2}. \quad (8.9)$$

If a film of thickness x separates a substrate from the top surface then it is likely that the thinner the film, the stronger the attractive forces acting across it and the greater the driving force for dewetting.

We discussed earlier in this chapter how spinodal decomposition could be perturbed by a surface, creating a lamellar structure. Similarly, our understanding of dewetting is not limited to creating uniform two-dimensional patterns, because we can also perturb the structure to create a series of lines. This anisotropic dewetting can be achieved by simply rubbing a substrate in a particular direction. This simple act imposes a direction on the dewetting. The dewetting still has a dominant wavelength that is governed by the compromise between the creation of surface area and thermodynamic repulsion (Figure 8.20). In other words, we can control the direction but the physics controls the wavelength. Our ability to alter the size of the structure is limited to our freedom over how far we can control the thickness of the film.

The long-range dispersion forces responsible for spinodal dewetting have also been shown to create ordered structures in free-standing polymer films capped at the top and bottom with an evaporated layer of silicon oxide. The film buckles on heating the

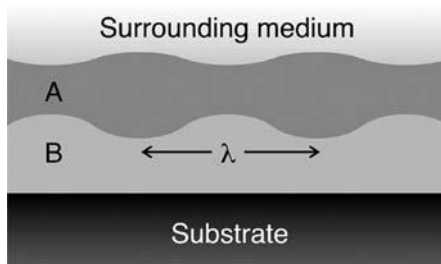


Figure 8.19 If long-range forces between a fluid B and the surrounding medium are greater than those between the surrounding medium and another fluid A, which initially lies on top of B, then the film will break up (film A will dewet film B). There will be a dominating isotropic wavelength governing the dewetting, known as the spinodal wavelength, λ . The amplitude of the fluctuations at each interface is a complicated function of parameters such as viscosities of the components

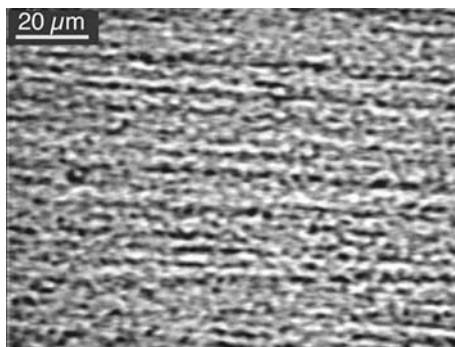


Figure 8.20 A film of PMMA dewetting an underlayer film of polystyrene. The PMMA has been prepared on a glass substrate which had been rubbed preferentially in a particular direction. The direction of rubbing imposes directionality on the dewetting. Apart from the anisotropy of the dewetting, the mechanism is expected to be the same as for Figure 8.19. Reproduced with permission from A. M. Higgins and R. A. L. Jones, *Nature* **404**, 476–478 (2000) Copyright 2000 Nature Publishing Group

trilayer structure to a temperature high enough to melt the polymer, and to leave it very mobile (but not so high as to degrade the polymer or to melt the solid capping layers). The size of the deformation is again a compromise between different physical effects. The bending of the capping layers will oppose the dispersion forces acting across the film. The patterns created by using anisotropic spinodal dewetting or in capped free-standing films are unlikely to be perfect, and so they would be unsuitable for micro- or nanofluidic devices. We therefore need to consider different means to create micro- and nanochannels. We consider two experiments that show ways of achieving reliable channels, one on the micron scale and one on the nanometre scale.

8.8 PRACTICAL NANOSCALE DEVICES EXPLOITING MACROMOLECULES AT INTERFACES

8.8.1 Molecular and macromolecular electronics

8.8.1.1 Polymer electronics

In Section 6.2 the principles of organic LEDs, FETs and photovoltaic devices were explained. Many of the challenges facing their creation concern optimising the structure of polymer films. Devices require more than simply a working medium, they must be connected together. The interconnections necessary for circuitry cannot be produced by self-assembly, and so some top-down method such as inkjet printing must be used. The combination between top-down and bottom-up technologies is not the only marriage of opposites in this area; molecular electronics also requires nanoscale solutions that extend beyond soft matter; the field is a fine example of the *soft–hard interface*. Electron beam lithography may be used to produce circuits instead of inkjet printing and

transistors may be created using carbon nanotubes connected via metallic (gold) interconnects. Although much of what is described below is in terms of soft matter, many of the methodologies discussed in this area may be replaced by a suitable hard alternative. Future work will declare which method is the more viable, but it is likely that a mixture of the two will be appropriate in many devices.

For example, Section 6.2.4.1 considered simple photovoltaic devices such as solar cells. Electron–hole pairs (excitons) created by a source of light need to be collected as a current if they are to be of any use. However, with an exciton diffusion length typically of the order of a few nanometres, there are two main challenges. To improve the efficiency of polymeric/organic photovoltaic devices, we need to be able to create an active region that contains a large amount of interface to ensure that an exciton is likely to recombine before some other decay process removes it without contributing to the current. Secondly, having created a region with a large interface-to-volume ratio, we need to ensure that the electrons and holes created at these interfaces have a clear pathway to the electrodes. Figure 8.21 shows an example of how a polymer blend structure might be designed to achieve these goals. One way of producing such a structure may be to exploit the idea of using electric fields to orient polymers in a blend in the same way as for block copolymers (Section 8.6.2).

The problem in fabricating efficient LED structures is rather like the photovoltaic problem, but in reverse. In this case the challenge is to inject holes and electrons into an active region, where they can combine to form an exciton. Here the ITO electrode is often coated with the PSS/PEDOT complex to provide a high work function coating (Section 6.2.1.2). It is known that the PSS dopant segregates preferentially to a free interface, so it is likely that, assuming the same effect occurs at the ITO interface, there is a gradual increase in work function to the bulk value, which may improve hole injection efficiency. This method may indeed work in parallel with the interface engineering of PEDOT/PSS hole injection layers (Section 8.5.2.1).

In FETs the structure of polymer interfaces is also a critical issue. Here the charge carriers move under forward bias in a polymeric *active layer* from the source to the drain within the first few nanometres of the active layer–dielectric interface. This imposes a requirement that the interface be of a high quality; a roughness (or interfacial width) of

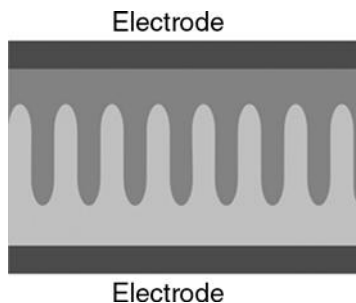


Figure 8.21 A polymer blend photovoltaic device should benefit from phase separation on a small scale such that an exciton formed is never less than ~ 10 nm from an interface at which it can dissociate. The resulting holes and electrons should then have a clear path to the two electrodes so that a current may be created. The diagram shows a morphology satisfying these criteria

several nanometres can seriously inhibit carrier efficiency. It is therefore worth optimising the structure of this interface. This may involve possible solvent treatment for any of the polymers involved. Heat treatment has been shown to change the interfacial width between poly(dioctyl fluorene) (PFO) and PMMA; the correlation between the shape of the interface and performance of devices is presently the subject of research. Similarly, the FET preparation method may also affect the final interface; solvent deposition methods may broaden the interface if the solvent for the active layer even slightly interacts with the dielectric layer (or vice versa if the active layer is deposited first).

8.8.1.2 Single-molecule devices

One basic requirement of a single-molecule device is that it moves charge from an electron donor molecule to an electron acceptor, or vice versa. To carry this charge along even small distances is something of a challenge because of the very rapid exponential decay in charge transport rate constant. Any molecule that joins a donor and acceptor, a *bridge* or *spacer* molecule, should have its energy matched to the donor and acceptor. This has been shown to be possible for distances of up to 4 nm with molecular wires of oligomeric *p*-phenylene vinylene.

A single-molecule FET requires a polymer to be connected in some way to a source and a drain in order for a potential to be applied across the FET. One part of the molecule must also be in contact with an insulating dielectric material to form the gate voltage. With such a device, a voltage applied across the gate will change the electrical resistance of the molecule, because charge carriers will have their motion impeded or accelerated.

8.8.2 Nanofluidics

The prospect of both automating and miniaturising chemical operations such as analysis or even synthesis is a tremendously attractive one, and the field of *microfluidics*, in which chemical operations are carried out in channels and reactors etched by processes analogous to those used for the planar process of silicon, has experienced tremendous recent growth. The aim is often summed up in the phrase 'laboratory on a chip'. But the business of miniaturising operations that involve fluid flow raises some interesting scale issues, and an understanding of this scaling and the limitations they impose will be particularly important as the size of these devices is shrunk towards the nanoscale.

To see why scale is so important in these devices, let us review the fluid mechanics that controls the simple case of fluid flow in a pipe or channel. The flow of fluid next to a solid wall can generally be taken as zero (though there are important exceptions to this so-called no-slip boundary condition, particularly for polymer and other non-Newtonian fluids), so in order for any fluid to flow, neighbouring regions of the fluid must flow at different rates. The character of the flow depends on a single dimensionless number, the *Reynolds number*, Re . This depends on two material properties of the fluid, its density ρ and viscosity η , and two characteristics of the flow, a typical velocity v and a characteristic size l . (For fluid flow in a pipe this size would be the pipe diameter.) The Reynolds number is the dimensionless combination of these four quantities, $Re = \nu\rho l/\eta$.

The physical significance of this number is that it expresses the relative importance of *viscosity* and *inertia* in fluid flow. At low Reynolds numbers, resistance to flow arises predominantly from viscosity, whereas at high Reynolds numbers inertia dominates. From the definition of the Reynolds number, one sees that for a given fluid, flow at smaller and smaller length scales is increasingly dominated by viscosity. Alternatively, the flow of water through a 1 μm channel will have the same character as the flow of a fluid one million times as viscous as water through a macroscopic, 1 m channel. Water, on the micro- and nanoscales, does not behave as the free-flowing liquid we are used to on the macroscale; rather its properties are as dominated by viscosity as much as treacle or molasses are on the macroscale.

At low Reynolds number, fluid flow through pipes or channels is *laminar*; there is a smooth gradient of velocity from the walls, where the fluid is stationary, to the centre. For a pipe of circular cross section, the rate of flow is given by the *Poiseuille equation*; the flow rate is proportional to the pressure gradient, inversely proportional to the viscosity, and proportional to the *fourth power* of the radius of the pipe. This very strong dependence of flow rate on the dimensions of the pipe or channel poses problems for nanofluidics and microfluidics, in that it makes the simple application of pressure a much less attractive driving force for fluid motion.

One attractive alternative to pressure-driven flows exploits the *electro-osmotic effect*. For aqueous systems containing free ions, one can use an electric field to move the fluid around. This effect relies on the fact that if an ion-containing solution is in proximity to a charged surface, near that surface there is a layer enriched in ions of the opposite charge to the surface. This is the so-called *electric double layer*. If an electric field is applied in the direction of the channel, then this will exert a force on the electric double layer, dragging the fluid along with it. The attractiveness of this method for moving fluids at the micro- and nanoscales comes from the fact that the force is applied to the fluid at the wall, leading to a velocity profile across the channel that is much flatter than it would be for Poiseuille flow. The flow can also be modulated by changing the surface charge.

Another distinctive feature of flows at low Reynolds numbers is that *turbulence* is always absent. The turbulence that is a feature of flow at high Reynolds numbers (see Figure 8.22 for a comparison between lamellar and turbulent flow) leads to an increase in resistance to flow, but it is also of immense value in chemical engineering operations as it provides a very efficient way of mixing fluids. The absence of turbulence at low Reynolds numbers makes operations that rely on mixing fluids rather problematic – in these cases mixing only takes place due to the much slower process of molecular diffusion.

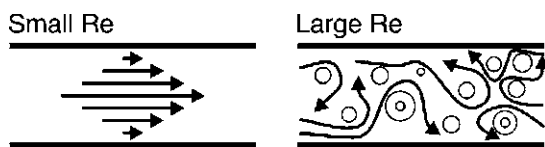


Figure 8.22 Laminar flow occurs at small values of the Reynolds number (Re). This occurs in high-viscosity fluids at low velocities in small dimensions. Turbulent flow occurs at large values of Re , when a low-viscosity fluid is travelling rapidly in a large container

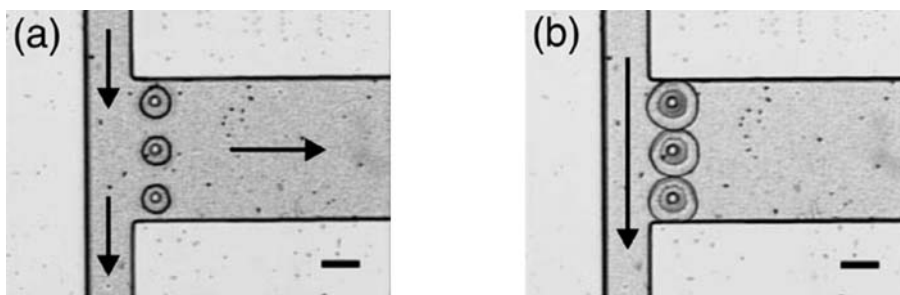


Figure 8.23 A hydrogel is attached to posts at the junction of a microchannel. (a) In poor solvent conditions the gel is collapsed, allowing fluid flow in all channels. (b) In good solvent conditions the gel expands and blocks the flow in one channel. The scale bar is 300 μm . Reproduced with permission from D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss and B.-H. Jo, *Nature* **404**, 588–590 (2000). Copyright 2000 Nature Publishing Group

The absence of turbulent mixing in laminar flows has actually been exploited to make nanostructures. If two capillaries containing different reactants can be brought into contact, then a chemical reaction can be localised to this interface, creating a thin pattern, avoiding the need for conventional lithography. On the other hand, it is more often going to be necessary to promote mixing. One way of doing this is to pattern the walls of the channel with obstacles perpendicular to the flow direction, which even in the absence of turbulence break up the smooth laminar flow and allow mixing to take place more efficiently.

Having created submicron-sized channels, it may well be desirable to control the flow of liquids in these channels. The miniaturisation of valves that are used in macroscopic pipes is not going to be a practical solution, so new ideas are necessary. Polymeric gels are a useful starting point for the control of fluids because they can be expanded and contracted to a given size in response to their environment. Figure 8.23 shows optical microscopy images of such a system. A hydrogel composed of a weak polyacid swells at high pH, impeding the motion of a fluid from travelling through its channel. Of course, the effectiveness of such a barrier will be dependent on the hydrogel and the liquid medium, because some material will often be capable of passing through the mesh of a gel. Although this mechanism has been demonstrated using a pH-responsive gel, the temperature-dependent volume transition in the poly(*N*-isopropyl acrylamide) (PNIPAM), mentioned in Section 7.3.4, could also be used for such a purpose.

8.8.3 Filtration and sorting

Many of the tools of modern science require very pure, calibrated materials and the task of separating, filtrating and sorting materials is not a trivial task if it needs to be performed with a high degree of accuracy. This may well be exacerbated by a lack of material to begin with; if one works with very few molecules or if one *needs* to work with very few molecules, then the sizes of typical devices or vessels is inappropriate. Working with small amounts of material is a necessity in chemical micro- or nanoreactors,

where the smaller length scale *increases* reaction rates because the likelihood of molecules meeting each other can be controlled more efficiently in systems where the length scales are small and the molecular motion is controlled by directed diffusion rather than turbidity. The task therefore is to find a means of moving the required molecule from A to B.

Entropy is an important thermodynamic tool to sort molecular behaviour by the use of *entropic traps*. Macromolecules trapped in materials or devices will try to find locations whereby they can maximise their *configurational entropy*. If it is allowed to do so, a polymer will leave a channel in which it is forced to be stretched in order to find a region where it can exhibit a random structure appropriate to its chemical environment. As an example, a cross-linked polymer (network) will normally contain cross-links randomly distributed throughout the material. Uncross-linked polymers that are mobile within the polymer network will generally seek out regions of material where they can experience the most conformations; these are less cross-linked regions, since cross-links will impede the polymer from having a random walk configuration. Therefore polymer networks can also be expected to act as a form of molecular sieve. Entropy may well also play a role of attracting polymers to surfaces; in a mixture of polymers of different lengths, the longer polymers would be expected to segregate to the surface. This is because the number of configurations of a polymer increases more slowly as a function of chain length than the polymer radius of gyration; therefore, per unit surface, there is a smaller entropy cost in having larger molecules present at the surface. However, in practice smaller polymers tend to segregate to surfaces because of the effect of chain ends.

Molecular sorting devices have been demonstrated using entropy through *confinement*. To move a molecule requires some form of gradient to drive the molecular motion. An electric field is an obvious candidate for such a gradient, although others can be envisaged (e.g., pressure, temperature, chemical potential, and magnetic field). Electric fields are most effective with charged polymers, but as we have seen, they should be of general use in confined spaces because the polarisability of many molecules will ensure that their motion can be controlled. A second requirement is a means of sorting the molecules so that their diffusional behaviour is different. The coupling of confinement and electric fields has been achieved with DNA. By allowing DNA to diffuse in a bath, separated from another bath by a slit of width smaller than 100 nm, an applied electric field can be used to force the DNA through the slit. Eventually the DNA will arrive in the second bath, with the arrival time being dependent on the size of the molecule. Perhaps surprisingly, the longer molecules diffused more rapidly. This is because, when inside the confining slit, the longer DNA can explore more of the slit, and so find the exit more easily; the rest of the molecule is dragged out efficiently (Figure 8.24). A related idea consists of the diffusion of DNA through a membrane pore. As the DNA passes through the pore, the pore is blocked and no current is measured at the electrodes (Figure 8.25). In such an experiment the diffusion coefficients of the DNA can be measured. The size of the DNA molecule can be correlated with the time the electrodes are blocked, creating a means of measuring DNA size, for example.

Responsive polymer brushes can also be used as a means for collecting and rejecting molecules. We have discussed how brush height varies as a function of chain length, grafting density and solvent quality. If these quantities can be varied then the brush

[Image not available in this electronic edition.]

Figure 8.24 DNA will stretch in narrow pores (< 100 nm); the larger the DNA molecule, the more stretched it will be and the faster it will find the exit to another reservoir (a few microns in size). The DNA is forced to diffuse by an electrical potential difference. Adapted with permission from J. Han and H. G. Craighead, *Science* **288**, 1026–1029 (2000). Copyright 2000, AAAS

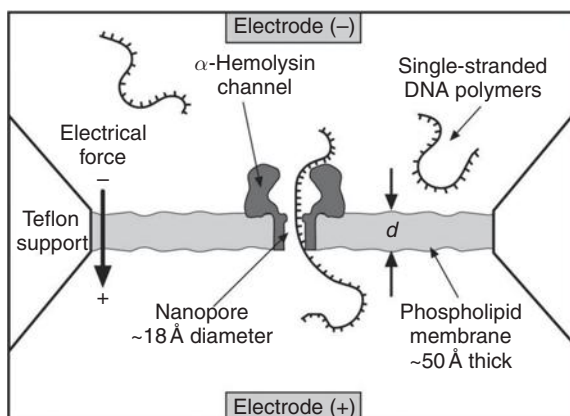


Figure 8.25 DNA can diffuse through narrow pores under the effect of an electrical potential difference. As DNA passes through the pores, it blocks a current from flowing. The time during which there is no current is a measure of DNA size and diffusion coefficient. Reproduced with permission from A. Meller, L. Nivon and D. Branton, *Phys. Rev. Lett.* **86**, 3435 (2001) Copyright 2001 by the American Physical Society

height (and consequently properties) will change accordingly. Any polyelectrolyte brush should exhibit this behaviour, but a particularly interesting example works with brushes of the thermally responsive polymer PNIPAM. PNIPAM is a particularly useful material for a responsive surface because its volume phase transition occurs in response to heat at an accessible temperature. The thermally responsive nature of the polymer is useful because the substrate can be coated with an array of heaters that will cause the brush to collapse *locally*. Experiments have been performed to show that the collapsed brush provided a suitable surface for protein adsorption. The expanded brush is considerably less amenable to protein adsorption and proteins are rejected into the bulk solution. There are many possible uses for such a device; one could, for example, envisage that the trap could be used as a means to concentrate proteins from a dilute flow before releasing them, enriched, into another bath. The method may also have benefits related to molecular weight filtration because larger proteins are more likely to adsorb onto the surface, probably because their larger size means that they have more sticking points.

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Texts on soft condensed matter in general will provide important background material. Two such books are particularly recommended:

R. A. L. Jones, *Soft Condensed Matter*, Oxford University Press, Oxford, 2002.

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For a broad coverage of surface forces, only one book need be consulted:

J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd edn, Academic Press, London, 2003.

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