Block Copolymer Melts as Nano-Materials

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Introduction

Block copolymers consist of at least two chemically different polymer chains joined together, usually at their ends, by a covalent bond. The simplest molecular architecture is only two blocks (A and B blocks) joined at their ends – linear diblocks. In a melt (many chains, no solvent) the diblocks self-assemble into crystal-like morphologies. For example, the photograph in Fig. 1 is the pattern formed from a triblock copolymer melt and is known as the 'knitting pattern'. It is a periodical pattern, with the repeat period being of the order of nanometres. For the simplest diblock system the morphological patterns that evolve depend on the fraction f, of the minority block (A-block) in the chain and the temperature of the system. These melts self-assemble because the chemically different chains do not want to mix. Instead they would like to phase separate. However, macrophase separation is inhibited because this would mean the polymer chains would be stretched enormously. Polymer chains would then lose their entropy (or randomness). Consequently, the best compromise is for the system to microphase separate and hence we find these nanoscale morphologies. For a diblock melt the various morphologies are shown in Fig. 2. The repeat unit length of these patterns depends on N, the polymerisation index γ, the interfacial tension between A and B blocks b, polymer bond length and T, the temperature of the system.

Although these morphologies form locally, on a global scale the patterns are disrupted by defects, misalignments and grain boundaries (see Fig. 3). How can we obtain a global, regular pattern over a sample of size 1 square mm or larger? The answer is to confine the block copolymer melt between two flat plates and then apply external fields (e.g. shear, electrical, chemical) to iron out the defects. The physics of the system becomes a combination of bulk effects, surface/confinement effects and external fields.
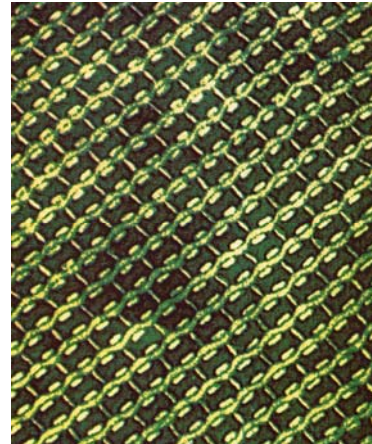

Fig. 1: Knitting pattern from a triblock copolymer melt. (R.Stadler, Germany)

Physics of diblock systems

The various morphologies that form in diblock melts represent a balance between enthalpy and entropy of the chains. The enthalpic interaction between A and B blocks is given by γA, where A is the surface area between A and B domains. The entropy of the chains diminishes as the end-to-end distance R, of the chain increases. Within the Gaussian random flight model, the entropy of the chains is given by $3kR2/Nb2$. Thus, the free energy of the system is a sum of enthalpic and entropic contributions, which is given by $F = \gamma A + 3kTR2/Nb2$. This energy is minimised with respect to R, under the constraint of incompressibility of the melt. This leads to the optimal repeat unit length (e.g. for the lamellar phase) of $R0 \propto N2/3\gamma1/3$.

Confined melts

For confined films, the physics now becomes a compromise between bulk effects (above) and confinement effects. For example, consider the sketch in Fig. 4 where the diblock melt is confined between two plates. There are two possible orientations of the lamellae – parallel to the plates or perpendicular to the plates. In the parallel orientation the lamellae are strained if the film thickness D, is not an integer multiple of $R0$ (since chains must stretch). However, in the perpendicular orientation the lamellae are unstrained as chains lie parallel to the plates. Thus, the perpendicular state should be observed.

On the other hand, if we put external fields on the confined melt, such as a surface chemical field in favour of the A blocks, the parallel orientation will be preferred. By putting electric fields on diblock melts (Fig. 5) one can also enhance the perpendicular orientation if the dielectric permittivity of the A block is greater than the permittivity of the B block.
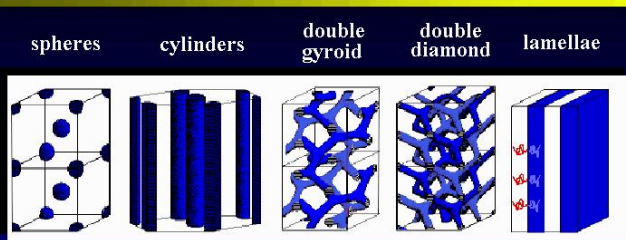
BLOCK COPOLYMER STRUCTURES

Fig. 2: Diblock copolymer morphologies: Lamellae 0.35<f<0.5, double gyroid f ~ 0.34, HCP cylinders 0.12<f<0.33, BCC spheres f<0.12.
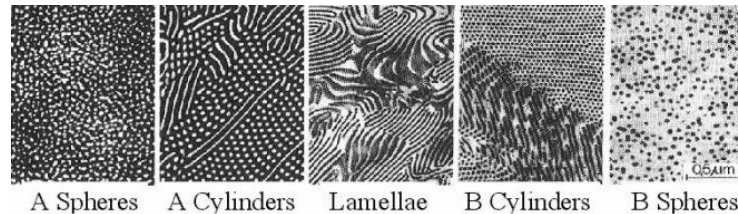

Fig. 3: Experimental block copolymer global structures. Note, that a regular pattern does not form over the entire sample. It is disrupted by grain boundaries, misalignments and defects.
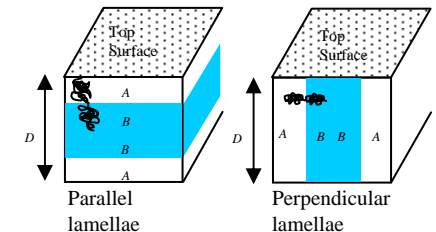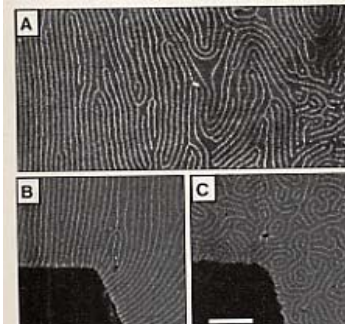

Fig. 4: Confined thin film melts of block copolymers. In the left sketch the lamellae are oriented parallel to confining plates and the chains are stretched. In the right sketch lamellae are oriented perpendicular to plates and the chains are not stretched.

Fig. 5: External electric field alignment. E-field is vertical.
(A) In middle of gap b/w plates (B) Adjacent to plates and
(C) Adjacent to plates, but no E-field. (T. Russell, Amherst)

Applications of block copolymer systems

Block copolymers have now been recognised as an avenue to reduce size scales for important technological applications such as for integrated circuit boards or magnetic data storage media from the order of microns to nanometres – a 1000 fold decrease in size. If such a decrease can be achieved, the increase in speed and capacity of these materials will be dramatic. Once a required morphology or pattern has formed, one can transfer this to a suitable substrate (usually by plasma etching techniques) and then this will form a template for cheap and easy replication. The lamellar phase has also been predicted to be used as a tuneable 1D photonic band gap material.

Other applications of these block copolymer melts include the formation of lithographic masks or nanoporous membranes. To achieve this, we could begin with the cylindrical phase and orient the cylinders perpendicular to the confining surfaces. The pattern at the surfaces would be that of HCP circular dots, which would form the holes in our membrane. The same phase and technique could be used to form ultra-thin nanowires. Once the perpendicular cylinders have formed, one dissolves away the inner component of the cylinders by using a suitable solvent. Then the void space is filled with a suitable metal such as cobalt. One can further reduce the diameter of these cylinders by using the BCC spherical phase as the starting point and confining this phase between two plates. Due to the strain in the system, the BCC phase will transform to the HCP cylindrical phase, but with much smaller diameter cylinders.

Conclusions and future developments

We have shown that block copolymers can be used to reduce size scale in important technological applications from the order of microns to nanometres. To do this we exploit the natural, self-assembling property of block copolymer melts. However, we must iron out the defects in the morphological patterns to obtain a global (of the order of mm2), regular, well oriented pattern. To do this we must confine the block copolymer melt to a thin film and then apply external fields. If this is done appropriately, one can obtain long range patterns (see Figs. 1, 5a and 5b).

The future of this field is extremely bright. In this poster we have only considered the simplest molecular architecture of the polymer chains – linear diblocks. In fact, if we increase the complexity of the molecular architecture (to triblock or multiblocks) or to architectures such as stars or hetero-branched copolymers, the number of morphological patterns explodes into the hundreds and thousands. The aim of this work would be to design the molecular architecture of the polymer chains so that the melt would self-assemble into any desired pattern.

References: GG Pereira, Phys. Rev. E, **63**, 061809, (2001); Eur. Phys. J. E, **7**, 273 (2002); J. Chem. Phys., **117**, 1878, (2002).