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3. 063 Polymer Physics
Spring 2007
Problem Set #4
Due Wednesday April 25, 2007

4.1 Chain Grafting Density

The area per chain on a surface, Σ, is an important quantity that influences the thickness of the polymer layer. We have encountered several situations that all related to what are termed "*polymer brushes*:"

(i). The corona region of a diblock copolymer micelle
(ii). Ligand chains tethered to a nanoparticle
(iii). Blocks tethered to the IMDS between microdomains
(iv). Noncrystalline blocks of a semicrystalline block copolymer lamella.

(a). Draw schematics of each of the situations described in i - iv above and label the key features.

(b). Derive an expression to calculate the area per chain Σ of a lamellar diblock from the individual block molecular weights, the lamellar repeat distance.

(c). Derive an expression to calculate the area per chain Σ for a chain folded lamellar crystal knowing the molecular weight of each block, the lamellar crystalline core thickness, the c axis repeat distance of the crystalline block, the density of each component.

4.2 Shape Memory Polymers

Materials are said to show a shape-memory effect if they can be deformed and fixed into a temporary shape, and then later, recover their original, permanent shape by an exposure to an external stimulus.

Consult the paper by Bob Langer in Science, Vol 296, Issue 5573, 1673-1676, 31 May 2002

"Biodegradable, Elastic Shape-Memory Polymers for Potential Biomedical Applications"

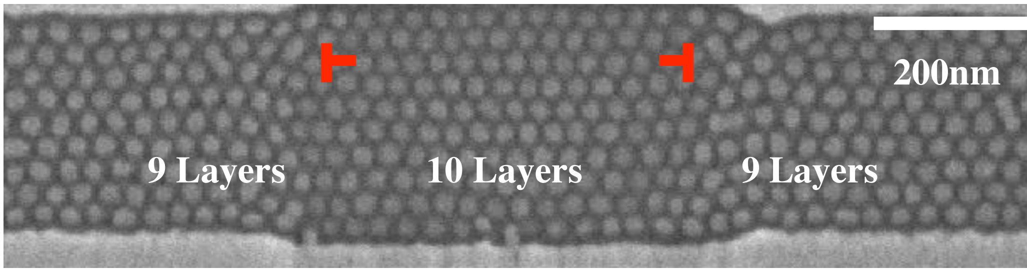
(a). Explain why it may be advantageous to use shape memory polymers in biomedical devices and provide an example of a useful shape change device.

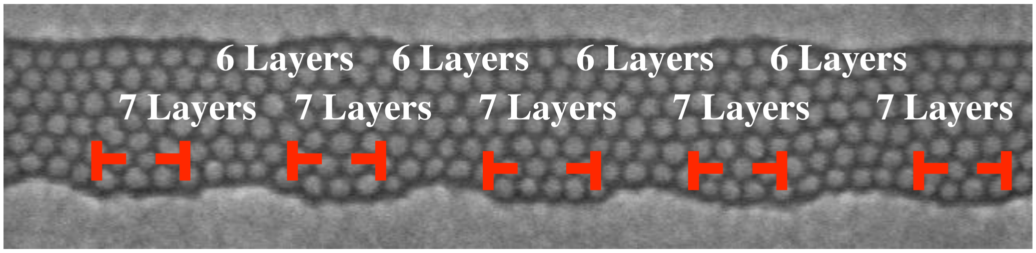
(b). Explain Langer's choice of polymer and the key material and processing parameters needed to create the shape memory polymer.

(c). High paid MIT Consultant: You've been tasked by management to come up with a multiple step shape memory polymer (SMP) device that can execute two successive and distinctive shape changes in orthogonal directions for a new application. Having read about SMPs you decide to use a semicrystalline block copolymer that has one noncrystalline block with a T_g of 40C and one crystallizable block with a T_m of 60C and a T_g of -30C in order to attempt to realize two separate thermally triggered events. Describe how you might prepare a suitable device out of this block copolymer that would exhibit the required shape changes. Hint: consider triggers in series and triggers in parallel.

4.3 Templated Self Assembly

Use of a template to pattern block copolymers can enable excellent long range ordering of the domains due to the constraint of the template on the alignment and spacing of the microdomains. Below are SEM images of a monolayer of PFS spherical domains confined between SiO_2 walls after RIE processing of the PS/PFS diblock. (PS = polystyrene, PFS = poly(ferrocenyldimethylsilane). Purposeful introduction of defects can also be obtained using a patterned substrate. The figure below shows how the variation of the separation of a pair of confining walls induces periodic arrays of point dislocations (red "perpendicular" symbols). The environment around dislocation defects in 2D (line defects in 3d become point defects in 2d) is alternatively 5 nearest neighbors or 7 nearest neighbors. Normally the p6mm packing gives 6 nearest neighbors. Such defects will localize light within the photonic crystal and depending on the symmetry and geometry of the defect environment, various interactions will occur.





Demonstration of control of ordering and introduction of defects within confined block-copolymers. SEM image by Dr. Joy Cheng, MIT.

(a). In the PS/PFS diblock system, the PFS block prefers to wet the silica surface of the substrate, while the majority PS block prefers to segregate to the upper (air) interface. Draw a schematic of the expected sample cross section delineating the IMDS for the PFS spherical domains. Also note all locations of the block junctions.

(b). Suggest a reason for why the outer most rows of spheres are, on average, somewhat smaller than the spheres in the interior of the channels.

4.4 SemiCrystalline Flexible Chain Polymer Morphologies

Indicate the type of structural crystalline organization that would result from the following growth conditions. Include in your answer a description and a labeled schematic of both the molecular and supramolecular morphology.

(a) Crystallization from very dilute solution.

(b) Crystallization from the polymer melt.

(c) Crystallization from melts subject to elongational velocity gradients such as fiber spinning.