

Hierarchy in Block Copolymer Morphology

(Web report)

By

MANGESH CHAMPHEKAR
(Materials Science and Engg.)

ABSTRACT

In the recent years, the study of block copolymers has received special attention from polymer scientists, as it has proved to be of a great importance in a variety of fields like life-sciences, tissue engineering, drug delivery, and nanotechnology and material sciences. This has led to a thorough investigation of the “hierarchy of the block copolymer morphology” i.e. the microscopic level changes taking place during the actual formation of the polymer. Complexation of oligomeric amphiphiles to polymers using ionic interactions, coordination, or hydrogen bonding leads to polymeric comb-shaped supramolecules (complexes), which self-assemble at a length scale larger than a few nm¹. Self-assembly at an order of magnitude larger than the nanometer length scale is provided by block copolymers, and combination of the latter two concepts leads to structural hierarchies¹. Although, extensive research has been conducted on this topic; an attempt is made here to explain the morphology of block copolymers in the various forms.

INTRODUCTION:

In biological systems, various complicated models for functional and responsive materials are formed due to self-assembly using competing hydrophilic/hydrophobic interactions and complementary physical interactions, also leading to structural hierarchies¹. This has encouraged scientists to consider structural hierarchies in synthetic materials in order to improve their properties or to achieve switching and responsive properties¹. An example of this is provided by block copolymers consisting of covalently connected flexible blocks of individual polymers. Here, we restrict our discussion to di-block copolymers only. In di-block copolymers, where two polymers A and B are covalently connected to each other in a linear fashion, form self-assembled stable morphologies (spherical, cylindrical, gyroid, and lamellar structures).

The self-assembly of polymer-amphiphile complexes can be combined with di-block copolymers, which leads to hierarchy of structures, i.e. structure-*within*-structure, with one block that has an attraction with the amphiphile and the other block has not⁵. The self-assembly now takes place at two length scales, where the long periods of the block copolymer and the polymer-amphiphile complex are 20–100 nm and 2–6 nm, respectively⁵. The morphology depends on several parameters: the volume fraction of domains, the degree of complexation, the alkyl tail lengths of the amphiphiles, and temperature⁵. The figure shown below is a schematic representation of a hierarchical self-assembly. Also, block copolymers can make self-assembled nanostructures both in bulk and in solutions and mixtures.

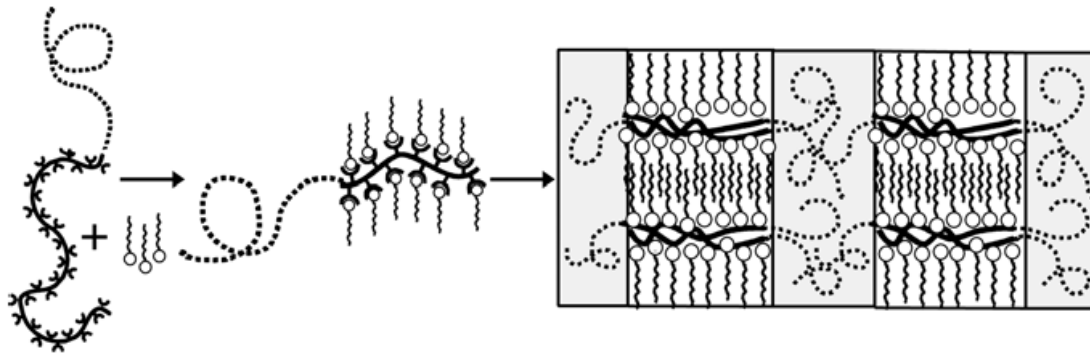


Figure-1 – Comb shaped supramolecular structures of block copolymers ⁵

Nowadays it is a known fact that, crystallization can radically change the mesophase diagram of the di-block copolymers: when crystallization occurs from a single-phase melt, a lamellar morphology results for a wide range of compositions ⁶. Various characterization techniques such as SAXS/WAXS/DSC demonstrate that the structure in these materials extends hierarchically from angstroms to microns, develops rapidly and simultaneously on all length scales ⁶. Finally, these di-blocks freely co-crystallize with the homopolymer of the crystallizable block polymer blends ⁶. The figure below shows the morphological hierarchy exhibited by block copolymers crystallizing from single-phase melts. From left to right: spherulites; block copolymer micro domains; lamellar crystals; crystalline block unit cell.

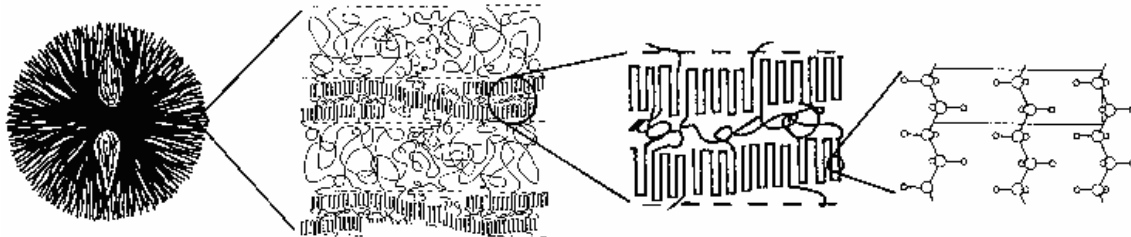


Figure-2 - Morphological hierarchy exhibited by block copolymers crystallizing from single-phase melts. left to right: spherulites; block copolymer microdomains; lamellar crystals; crystalline block unit cell ⁶

Now, after a brief introduction about the morphology of block copolymers, we will discuss their hierarchical morphology in some specific cases as stated below.

DISCUSSION:

1) Hierarchical self-assembly in block copolymer/ amphiphile complexes-

It has been known that various self-assembled structures are possible by physically bonding oligomeric repulsive side chains to homopolymers¹. Often the self-assembled structures are lamellar, yet cylindrical¹. But, the more complex phases have been studied as well. Hydrogen bonding allows non-charged self-assembled structures, as has been shown using the examples of poly(4-vinylpyridine)/alkylphenols and poly(ethylene oxide)/dodecylbenzene sulfonic acid¹. Due to its weakness, hydrogen bonding allows additional freedom to control the strength of bonding¹. Also, coordination is beneficial for self-assembly as it allows the tuning of the self-assembly using both the ligands and the counter-ions¹. Here, four alkyl chains bond to each repeat unit of poly(4-vinylpyridine), i.e. P4VP, where two octyl chains are due to the ligands, and one dodecyl tail in each of the dodecylsulfonate counter-ions. The side chain crowding leads to cylindrical self assembly¹.



Figure -3 - Coordinated comb shaped polymeric supramolecules and their cylindrical self-assembly (left)¹
Structure of poly(styrene)-*b*-poly(4-vinylpyridine) (right)¹

Typical example of the hierarchical self-assembly of the di-block copolymer/amphiphile complexes is poly(styrene)-*b*-poly(4-vinylpyridine) i.e. (PS-*b*-P4VP) where normally one pentadecylphenol (PDP) or nonadecylphenol (NDP) molecule is hydrogen bonded vs. each pyridine group.

2) Self-organization of block copolymers in melts-

Simple A-*block*-B copolymers self-organize into various morphologies in the melt, i.e., without a solvent. At low volume fractions of block-A, f_A , the system is initially disordered, i.e., the small A-block dissolves in the B-block. Above $f_A = 0.12$, small spheres of A are formed in a matrix of block-B. Upon further increasing the length of the A-block, the system undergoes a change from a spherical to a cylindrical morphology and then finally to a lamellar micro-phase near $f_A = 0.32$. More complex morphologies, such as the bicontinuous gyroid phase, perforated lamellae and the (metastable) modulated lamellae, are found in the close vicinity of compositions between lamellae and cylindrical

morphologies for sufficiently small values of the Flory-Huggins parameter $\chi \propto 1/T$ ². This parameter describes the strength of the enthalpic interaction between A and B. This transition between two micro-phases is called an order-order transition (OOT)². This generally requires a change in the lengths of the two blocks. Upon heating, the system undergoes an order-disorder transition (ODT) to a disordered state². For di-block copolymers, this usually occurs at very high temperatures as both, the repulsion between the two blocks and the block lengths are generally very large². The ODT may be accessible only at low or moderate molecular weights, e.g. at 164 °C for a PS(10k)-*block*-PI(10k) copolymer².

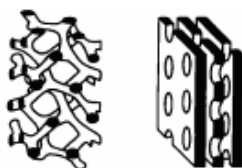
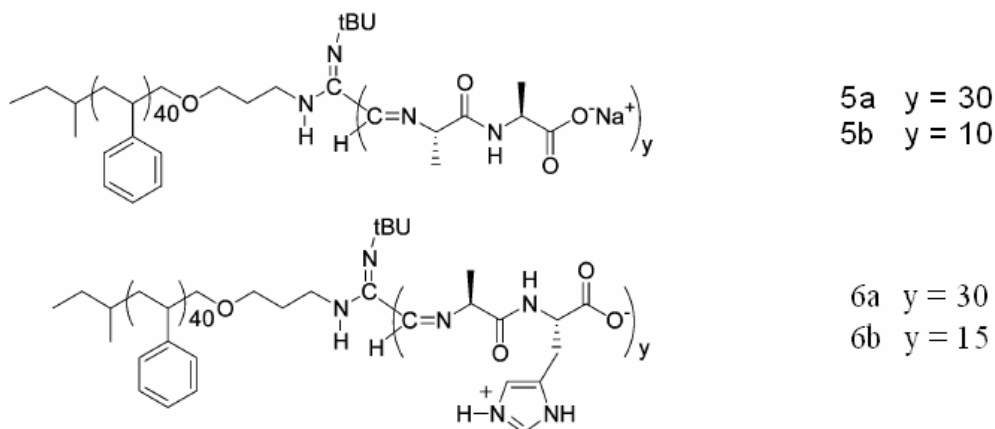


Figure-4 – Complex morphologies of A-block-B di-block copolymers²

3) Transferral hierarchy in block copolymers-

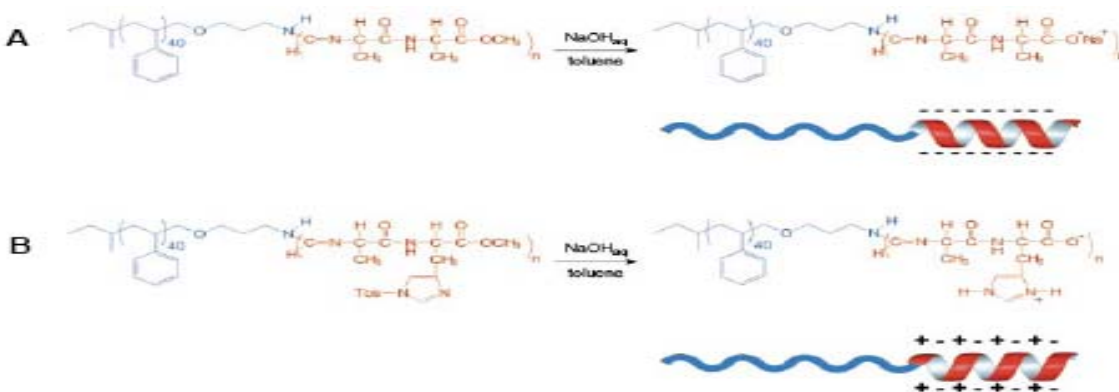
When we go up one level in the organizational hierarchy of block copolymers, i.e., to the transferal level, the study of block copolymers containing a polyisocyanopeptide segment is useful. These types of block copolymers are synthesized by using macromolecular initiators, (amine-derived carbosilane dendrimers and amine-terminated polystyrene) in the Ni(II)-catalyzed polymerization reaction. Such block copolymers display interesting properties due to the large differences in the two component blocks, i.e., the dendrimer has a convex architecture and is flexible, whereas the polyisocyanopeptide part is rod-like and rigid³. These block copolymers appeared to selectively bind metal ions, like silver ions, which were complexed to the polyisocyanide segment, thus resulting into formation of aggregates with dimensions ranging from hundreds of nanometers to over one micron³. Removal of the methyl ester functionalities in block copolymers resulted in chiral superamphiphiles consisting of a charged, helical polyisocyanopeptide head-group and a hydrophobic polystyrene tail³. Under optimized conditions, the macromolecules of negatively charged **5a** self-assembled in aqueous solution to yield micellar rods having lengths up to several micrometers³. Block copolymer **5b** displayed a similar behavior. Compounds **5b** and **6b** in addition to forming bi-layer type assemblies like plates and vesicles also formed helical assemblies³. Thus, the observed differences in the supramolecular structures generated by the negatively charged and zwitterionic copolymers indicate that the helices are formed by a complex assembly mechanism, involving the hierarchical transfer of 'chirality' from the monomeric building blocks to the final chiral superstructures³.



Figures 5 & 6 represent block copolymers of isocyanopeptides and styrene ³

4) Helical Superstructures from block copolymers-

Amphiphilic di-block copolymers in an aqueous environment can assemble into various nano-sized morphologies depending upon the structure of copolymer ⁴. To illustrate this, an example of a block copolymer of styrene and optically active isocyanodipeptide can be considered. The helical poly(isocyanide) head group upon dispersal in water, self-assemble to form superhelices ⁴. The sense of the helix is opposite to that of the constituent polymers, (L or R) ⁴. A series of poly(styrene)-*block*-poly(isocyanide- L-alanine-L-alanine) (PSx-*b*-PIAAy) L-alanine-L-alanine) (PSx-*b*-PIAAy) L-histidine) (PSx-*b*-PIAHy) block copolymers were prepared by the use of a poly-(styrene) derivative of well-defined length, end-capped with an amino group, as the initiator of the Ni(II)-catalyzed polymerization reaction. Removal of the ester functions of PS-*b*-PIAA by treatment with a 1 M aqueous NaOH-toluene (1:1, volume/volume) mixture gave rise to a superamphiphile with a negatively charged helical head group (reaction A); PS-*b*-PIAH gave a superamphiphile with a 'zwitterionic' head group (reaction B) ⁴.



Figures- 7a - Deprotection of the block copolymer of PS-*b*-PIAA to negatively charged superamphiphiles ⁴
 7b – Formation of positively charged zwitterionic superamphiphiles PS-*b*-PIAH block copolymers ⁴

CONCLUSIONS:

We have described how amphiphilic complexes can be bonded to block copolymers to give rise to self-assembly and hierarchy. This is beneficial for obtaining tunable optical properties. Also, block copolymers give rise to various morphologies in the melt form. Hence, by a careful and detailed study, block copolymers in the melt form can prove to be useful in various fields of engineering and technology. The transferal hierarchy shown by block copolymers can be a useful tool for efficient performance of complex tasks such as the ones being performed in nature (e.g. catalysis, transportation, information storage). Charged structures can also be formed by block copolymers in an aqueous environment. This can prove to be very useful for the development of materials with liquid-crystalline or nonlinear optical properties.

Thus, block copolymers are exciting new materials exhibiting varying morphological properties in different environments which can prove to be of great use in a wide range of areas in the coming future.

REFERENCES:

- 1) Olli Ikkala and Gerrit ten Brinke, Hierarchical self-assembly in polymeric complexes: Towards Functional materials, *Chem. Commun.* (Cambridge). 2004 Oct. 7; (19):2131-37.
- 2) Moel, Catharina Hillegonda Maria de, Self-organized supramolecular comb-shaped copolymers, Ph.D dissertation, University of Groningen 2001.
- 3) Jeroen J. L. M. Cornelissen, Hierarchical transfer of stereochemical information in synthetic Macromolecule's, *Pure Appl. Chem.*, 2002; (74), No.11: 2021–30.
- 4) Jeroen J. L. M. Cornelissen, Matthias Fischer, Nico A. J. M. Sommerdijk, Roeland J. M. Nolte, Helical Superstructures from Charged Poly(styrene)-Poly(isocyanodipeptide) Block Copolymers, *sciencemag*, 1998 May 29; (280): 1427-30.
- 5) Harri Kosonen, Functionalization of polymers with self-assembled nanostructures, Doctor of Science dissertation, Helsinki University of Technology, 2004.
- 6) www.princeton.edu/~polymer/crystalbc.html, Polymer Research Laboratory, 2006 Mar 6.