

**Experiment title:**

STRUCTURATION IN SOLUTIONS OF ABC TRIBLOCK COPOLYMERS

Experiment number:

SC-667

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Report:

The structure and the dynamics of block copolymers are of great current interest. To date, many studies have dealt with melts or solutions of AB diblock copolymers and ABA triblock copolymers. In these systems, the organisation is not very different from that existing in lyotropic liquids. In ABC triblock copolymers, the presence of block C which is incompatible both with A and B brings a higher degree of complexity. For instance, it has been found that ABC copolymers in melts exhibit a wealth of different morphologies. By contrast solutions and especially concentrated solutions have remained largely unexplored in spite of their importance in many fundamental and practical issues.

Very recently, we have performed systematic small angle X-ray scattering on the ID02 beamline at the ESRF facility in order to investigate the equilibrium structure of poly(styrene)-poly(butadiene)-poly(methyl methacrylate) copolymers in solution. Presently, even if the quantitative interpretation of the data is not achieved, we are able to summarise some of the major results.

Disorder-order transition

The analysis of the static structure factor at different concentrations show that solutions of SBM copolymers exhibit a disorder-order transition at low polymer concentration. Solutions above the disorder-order are ordered materials.

Structure of ordered solutions (pure triblock copolymers)

The organisation of the copolymers in solutions depends on the molecular composition and on the solvent. We have focused on $S_{11}B_{19}M_{70}$ and $S_{22}B_{22}M_{56}$ ($M_n \cong 125000$ g/mol and 145000g/mol) in toluene and

chloroform. Toluene has a slight preferential affinity for the poly(butadiene) and poly(styrene) blocks while chloroform has roughly the same affinity for the three blocks. Since $S_{11}B_{19}M_{70}$ and $S_{22}B_{22}M_{56}$ are strongly asymmetric due to the presence of a large poly(methylmethacrylate) block, strong curvature effects are expected. Indeed, $S_{11}B_{19}M_{70}$ and $S_{22}B_{22}M_{56}$ in chloroform form core-shell spheres and cylinders in a continuous poly(methylmethacrylate) matrix. The surprise is that this tendency to curvature disappears in toluene which is slightly selective of the poly(butadiene) and poly(styrene) blocks, even if the difference of affinity is quite small. In toluene, both copolymers arrange into lamellae. In conclusion, the morphology of triblock copolymers in solutions can be tuned accurately by changing the solvent quality. We are developing a quantitative interpretation and modelling of this result.

Role of defects and impurities

The presence of diblock copolymers is another important parameter which greatly affect the organisation of SBM copolymers in solutions. From now on, we have discovered two important phenomena :

- (i) the presence of SB diblock can act to stabilize a micro-structure which would not be formed otherwise. For instance, the structure of solutions of $S_{11}B_{19}M_{70}$ in chloroform shifts from core-shell spheres to core-shell cylinders and finally lamellae when the amount of $S_{40}B_{60}$ diblocks is increased.
- (ii) SB diblocks generate specific defects which can be controlled accurately. We have identified two kinds of defects : microphase separation and formation of super-structures.