Frustrated ABC triblock terpolymers morphologies

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Frustration of multiblock polymers

In diblock polymers, composition and molecular weight are the most influential parameters on phase behavior. Adding more blocks makes sequence a powerful influence as well.

An ABC triblock polymer can access a variety of morphologies that cannot be accessed in a diblock polymer. These morphologies are

driven, in part, by the incompatibility of the covalently linked blocks.

An example: PI-PS-PEO versus “frustrated” triblock, PS-PI-PEO

not frustrated

Degree of incompatibility: X_{PI-PEO} > X_{PS-PEO} > X_{PI}

PS-b-PI-b-PLA synthesis and molecular characterization

Degree of incompatibility: X_{PS-b-PLA} > X_{PS-PLA} > X_{PS}\n
Polyethylene-b-polyisoprene-b-polylactide (SIL) triblock polymers present a highly frustrated system that can be used to access interesting morphologies in the bulk and in thin films. SIL polymers with equal volume fractions of the styrene and isoprene blocks have not been previously studied. We aimed to characterize these materials and compare the morphological consequences of frustration in the bulk and thin film.

LS-SEC, IR traces

[Diagram showing SEC traces for different samples]

Thermal characterization of the polymers

TGA

DSC

Rheology of SIL (16/4/19)

°C

The second heating thermal scan is shown. Left in graph: A and B are clear from trace of PS confirmed by rheology.

DSC temperature scans upon heating: rate = 5°C/min, α = 3

Future work

• Electron tomography and AFM imaging of the surface of a bulk sample will be utilized to link the bulk and thin film morphologies.

• Bulk morphologies of asymmetric ABCA\' tetrablocks are unexplored. A multitude of molecular variables in ABCA\' polymers can be systematically tuned. To that end we are targeting ABCA\' tetra block terpolymers: polyethylene-b-polyisoprene-b-polylactide-b-polyethylene (SIL\'). We will focus on highly frustrated systems (circled in red) and vary the asymmetry (g) of the A and A\' blocks.

[Diagram showing various morphologies and compositions]

Probing bulk morphology by SAXS and TEM

SAXS consistent with hexagonal symmetry

Room temperature SAXS 2D patterns. Samples were solvent cast for 1 week at ambient temperature and thermally annealed for 30 min at 110°C. Peaks expected for hexagonal symmetry are indicated relative to the measured principle scattering peak of polyethylene (PEO)

SIL (16/4/19)

D_{ax} = \frac{2a}{q^*} = 54 nm

SIL (16/4/19)

D_{ax} = \frac{2a}{q^*} = 42 nm

TEM reveals core-shell cylinders with non-constant mean curvature

Room temperature TEM images. Samples were solvent cast for 1 week at ambient temperature and thermally annealed for 30 min at 110°C. Samples were stained with NaOH and/or phospholipids before imaging with ultrathin gold or silver. Inset: SAXS, G' & G'' (25 mm plates) and G' & G'' (8 mm plates) of SIL (16/4/9)

Comparison with other frustrated ABC triblock polymers at equal composition

Solubility parameters (cal/cm^3)^1/2 illustrate frustration and suggest origin of morphology:

PLA, 11.4 > P2VP, 10.4 > PEO, 9.9 > PS, 9.1 > PI, 8.1

Comparison of PS-b-PI-b-PLA (16/4/19) (left) and PS-b-PI-b-PLA (16/4/9) (right) post thermal annealing

Block assignment and thin film morphology from AFM

AFM confirms cylindrical core is PLA and reveals spheres-on-cylinders

AFM images of PS-b-PLA (16/4/19) post thermal annealing and post PLA etching

Diameter of cylindrical core is PLA

Spheres-on-cylinders favorability arises from trading IL contacts for SL contacts

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