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Frustrated ABC triblock terpolymer morphologies

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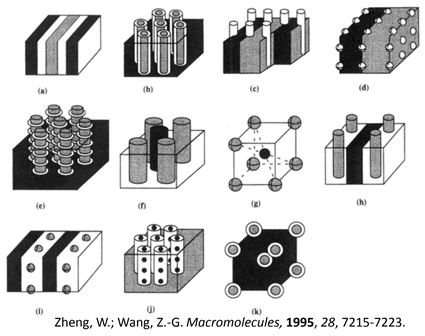
Frustration of multiblock polymers

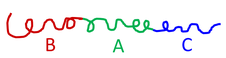
In diblock polymers, composition and molecular weight are the most influential parameters on phase behavior. Adding more blocks makes sequence a powerful influence as well.

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.

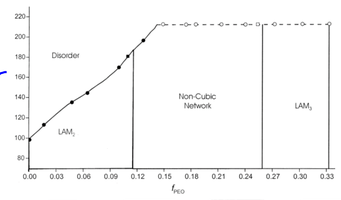


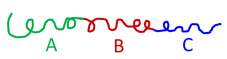
Zheng, W.; Wang, Z.-G. *Macromolecules*, **1995**, *28*, 7215-7223.

An example: PI-PS-PEO versus "frustrated" triblock, PS-PI-PEO

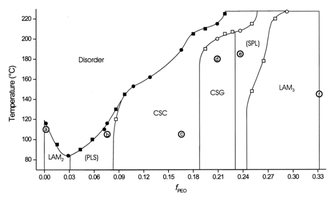


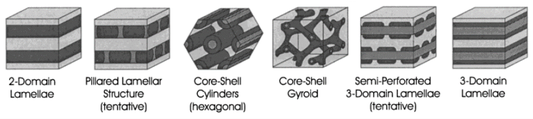
not frustrated





FRUSTRATED



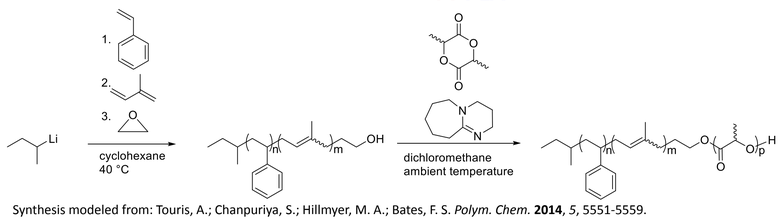


Degree of incompatability: $\chi_{PI\text{-}PEO} > \chi_{PS\text{-}PEO} > \chi_{PS\text{-}PI}$

Bailey, T. S.; Pham, H. D.; Bates F. S. *Macromolecules*, **2001**, *34*, 6994-7008.
Epps, T. H.; Bailey, T. S.; Waletzko, R.; Bates, F. S. *Macromolecules*, **2003**, *36*, 2873-2881.

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

Degree of incompatability: $\chi_{PI\text{-}PLA} > \chi_{PS\text{-}PLA} > \chi_{PS\text{-}PI}$



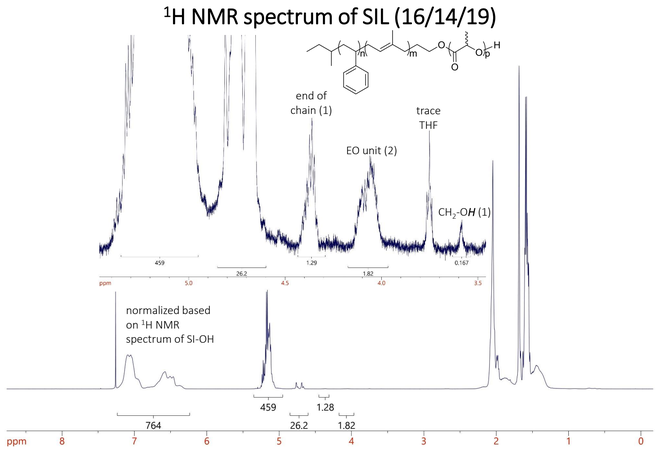
Synthesis modeled from: Touris, A.; Chanpuriya, S.; Hillmyer, M. A.; Bates, F. S. *Polym. Chem.* **2014**, *5*, 5551-5559.

	M_n PS[a] (kg/mol)	M_n PI[a] (kg/mol)	M_n PLA[a] (kg/mol)	Đ[b]	φ_{PS}[c]	φ_{PI}[c]	φ_{PLA}[c]
SIL (16/14/19)	15.9	14.2	19.0	1.01	0.33	0.34	0.33
SIL (16/14/9)	15.9	14.2	09.2	1.01	0.40	0.41	0.19

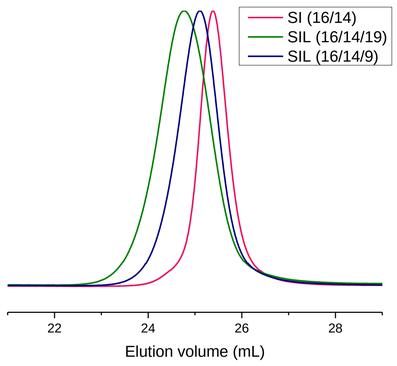
[a]Calculated from relative integrations in the ^{1}H NMR spectra that were normalized based on the end group in the diblock precursor. [b]Dispersity from LS-SEC in THF at 25 °C. [c]Volume fractions determined using 140 °C densities ρ(PS) = 0.969 g/cm^3, ρ(PI) = 0.83 g/cm^3, and ρ(PLA) = 1.154 g/cm^3.

Polystyrene-*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.

^{1}H NMR spectrum of SIL (16/14/19)

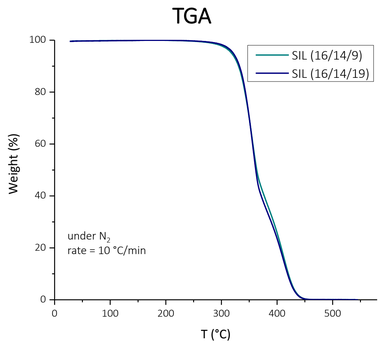


LS-SEC, RI traces



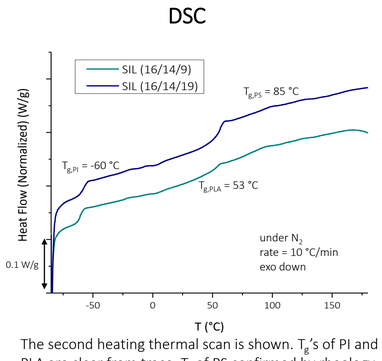
Thermal characterization of the polymers

TGA



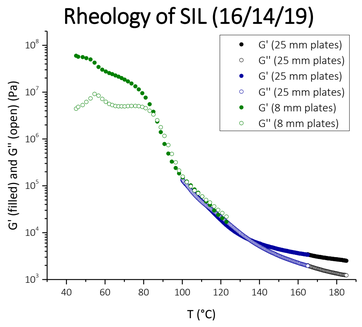
5 % mass loss occurred around 320 °C for both polymers.

DSC



The second heating thermal scan is shown. T_g's of PI and PLA are clear from trace. T_g of PS confirmed by rheology.

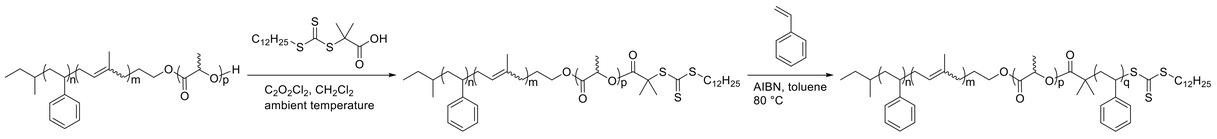
Rheology of SIL (16/14/19)

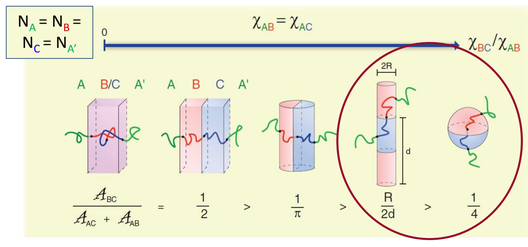


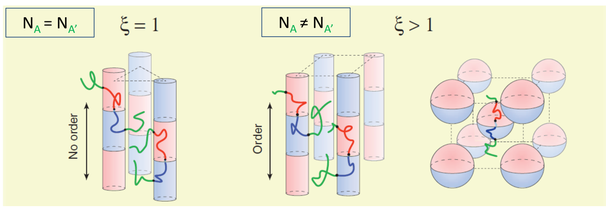
DMA temperature sweep upon heating; rate = 5 °C/min; ω = 3 rad/s (black) and 1 rad/s (green and blue); strain < 10 %. No T_{ODT} observed.

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' tetrablock terpolymers: polystyrene-*b*-polyisoprene-*b*-polylactide-*b*-polystyrene (SILS'). We will focus on highly frustrated systems (circled in red) and vary the asymmetry (ξ) of the A and A' blocks.



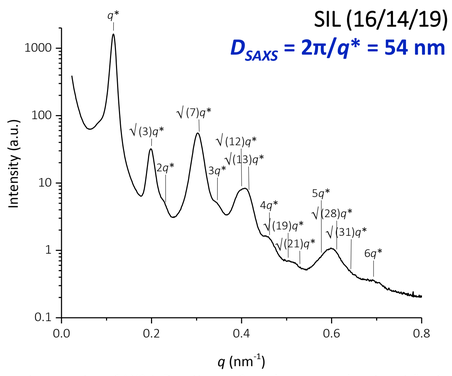


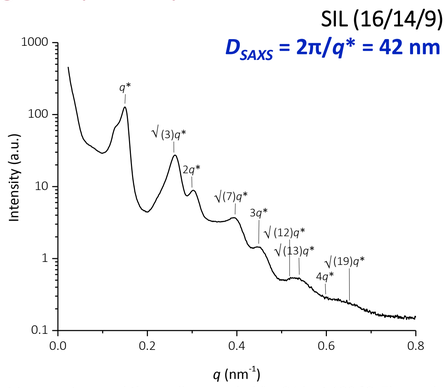


Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science*, **2012**, *336*, 434-440.

Probing bulk morphology by SAXS and TEM

SAXS consistent with hexagonal symmetry

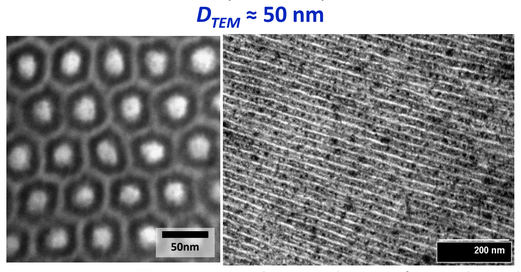




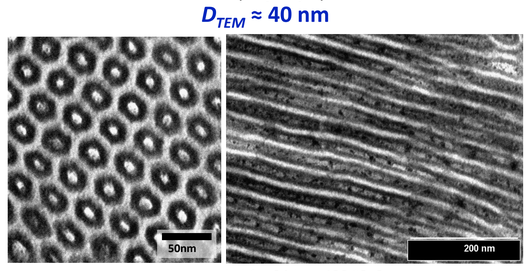
Room temperature SAXS 1-D patterns. Samples were solvent cast for 1 week at ambient temperature and thermally annealed for 24 h at 120 °C. The peaks expected for hexagonal symmetry are labeled relative to the measured principle scattering peak, q^*.

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

SIL (16/14/19) $D_{TEM} \approx 50$ nm



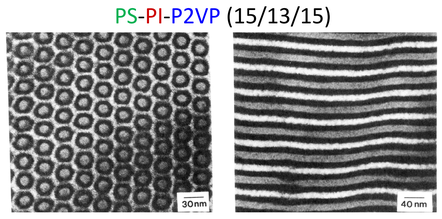
SIL (16/14/9) $D_{TEM} \approx 40$ nm



Room temperature TEM images. Samples were solvent cast for 1 week at ambient temperature and thermally annealed for 24 h at 120 °C. Samples were stained with OsO_4 and I_2. Assignments based on staining and an etching experiment with AFM (below): matrix = PS, cylinder shell = PI, and cylinder core = PLA.

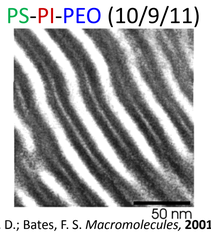
Comparison with other frustrated ABC triblock polymers at equal composition

PS-PI-P2VP (15/13/15)



Gido, S.P.; Schwark, D. W.; Thomas, E. L.; Goncalves, M. C. *Macromolecules*, **1993**, *26*, 2636-2640.

PS-PI-PEO (10/9/11)



Bailey, T. S.; Pham, H. D.; Bates, F. S. *Macromolecules*, **2001**, *34*, 6994-7008.

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

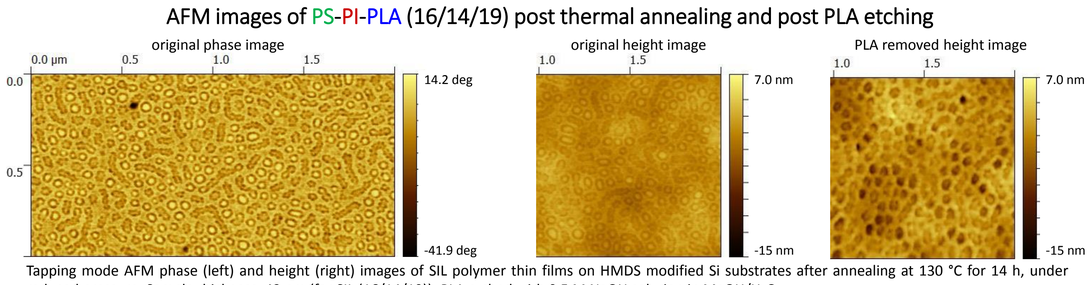
PLA, 11.4 > P2VP, 10.4 > PEO, 9.9 > PS, 9.1 > PI, 8.1

Legrand, P; Lesieur, S.; Bochot, A.; Gref, R.; Raatjes, W.; Barratt, G.; Vauthier, C. *Int. J. Pharm.* **2007**, *344*, 33–43. Arichi, S.; Matsuura, H.; Tanimoto, Y.; Murata, H. Bull. Chem. Soc. Jpn. **1966**, *39*, 434-439. Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Ed.; CRC Press: Boca Raton, 2007.

Block assignment and thin film morphology from AFM

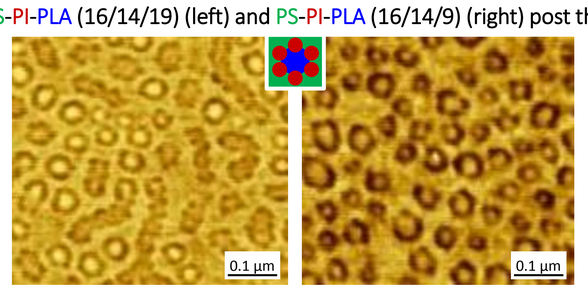
AFM confirms cylindrical core is PLA and reveals spheres-on-cylinders

AFM images of PS-PI-PLA (16/14/19) post thermal annealing and post PLA etching

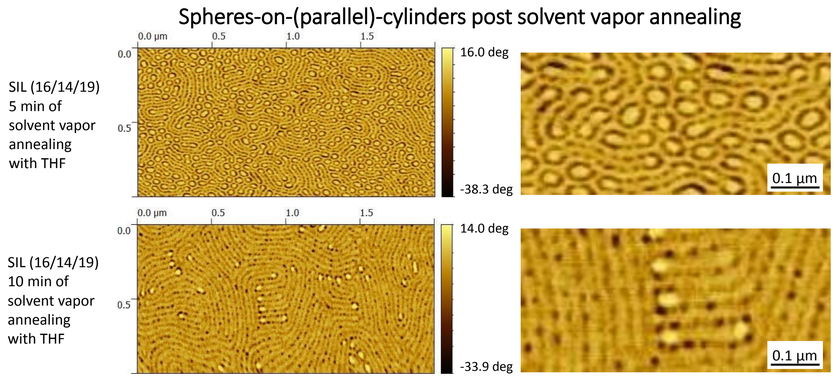


Tapping mode AFM phase (left) and height (right) images of SIL polymer thin films on HMDS modified Si substrates after annealing at 130 °C for 14 h, under reduced pressure. Sample thickness: 43 nm (for SIL (16/14/19)). PLA etched with 0.5 M NaOH solution in MeOH/H_2O.

Comparison of PS-PI-PLA (16/14/19) (left) and PS-PI-PLA (16/14/9) (right) post thermal annealing



Spheres-on-(parallel)-cylinders post solvent vapor annealing



Tapping mode AFM phase images of SIL polymer thin films on unmodified Si substrates after solvent vapor annealing with THF for 5 (top) or 10 (bottom) minutes. Sample thickness: 28 nm.

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

Acknowledgements

Advanced Photon Source
DND-CAT
Data collected by Sam Dalsin

University of Minnesota
and the U of M
Characterization Facility