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ABCA' Tetrablock Terpolymers: Synthesis and Morphology

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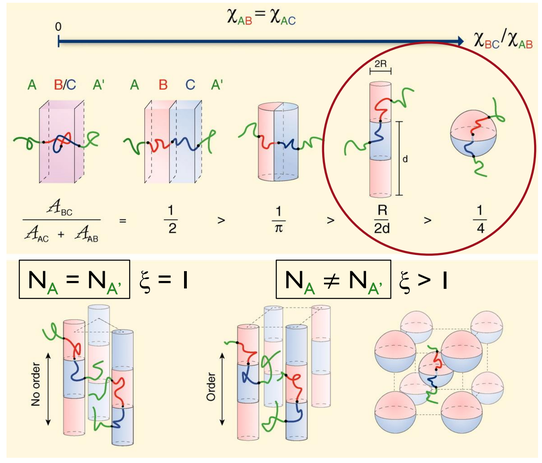
Potential effects of block asymmetry (ξ)



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

Underexplored morphologies of ABCA' polymers

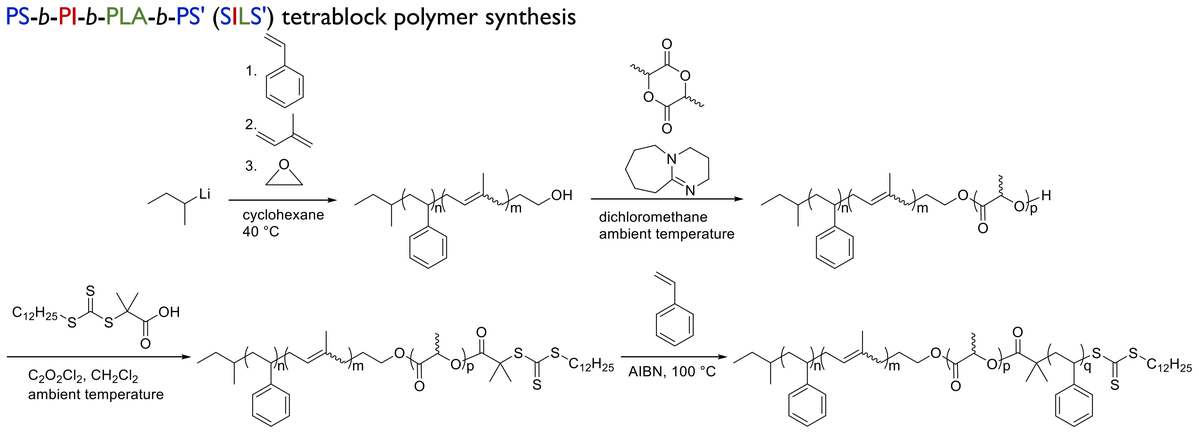
- Synthetically challenging
  - Targeting low Đ, controlled M_n and volume fractions
  - High χ_{BC}: $\chi_{PI-PLA} = \frac{250}{T} - 0.41$
- Potential for unknown structures
  - Hierarchical, non-centrosymmetric
  - Entropically favored packing of small and large chains together
- Computationally driven
  - Model materials for comparison of theory and experiment

ABCA' synthesis via sequential polymerizations

PS-*b*-PI-*b*-PEO-*b*-PS synthesis: Touris, A.; Chanpuriya, S.; Hillmyer, M. A.; Bates, F. S. *Polym. Chem.* **2014**, *5*, 5551–5559.

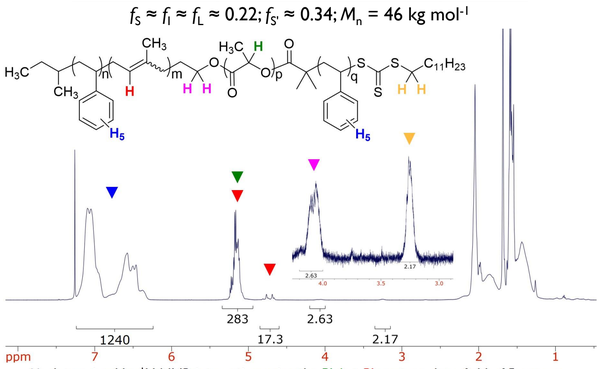
In this strategy, the length of A and A' are completely independent

PS-*b*-PI-*b*-PLA-*b*-PS' (SILS') tetrablock polymer synthesis



¹H NMR spectrum of a SILS' polymer

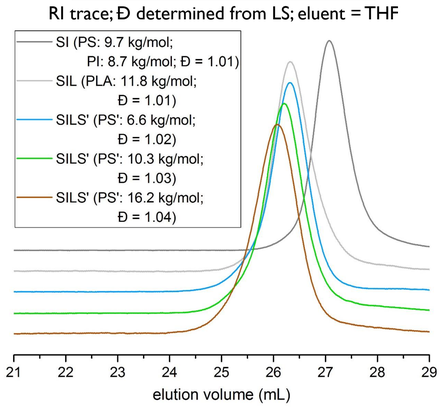
$f_S \approx f_I \approx f_L \approx 0.22$; $f_{S'} \approx 0.34$; M_n = 46 kg mol^{-1}



M_n determined by ¹H NMR integration using the PLA + PI protons downfield of 5 ppm as a reference. Integration of PI protons upfield of 5 ppm remained consistent.

SEC of SILS' polymers

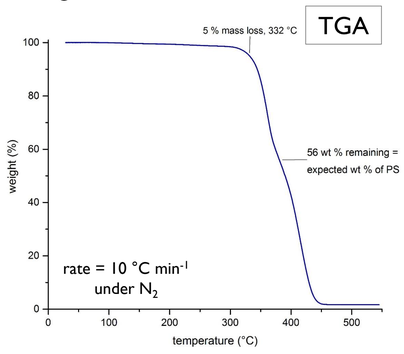
RI trace; Đ determined from LS; eluent = THF



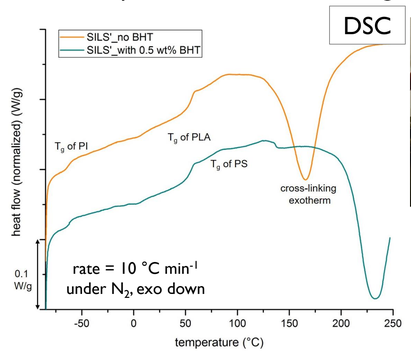
Block polymer stability

- A radical scavenger (BHT) and inert conditions (under argon) were necessary to avoid cross-linking or other degradation reactions over time at elevated temperature or in solution, e.g. during solvent casting

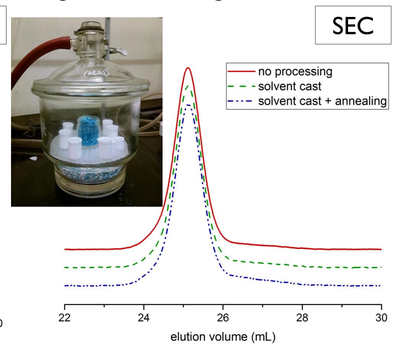
TGA



DSC



SEC



Acknowledgements

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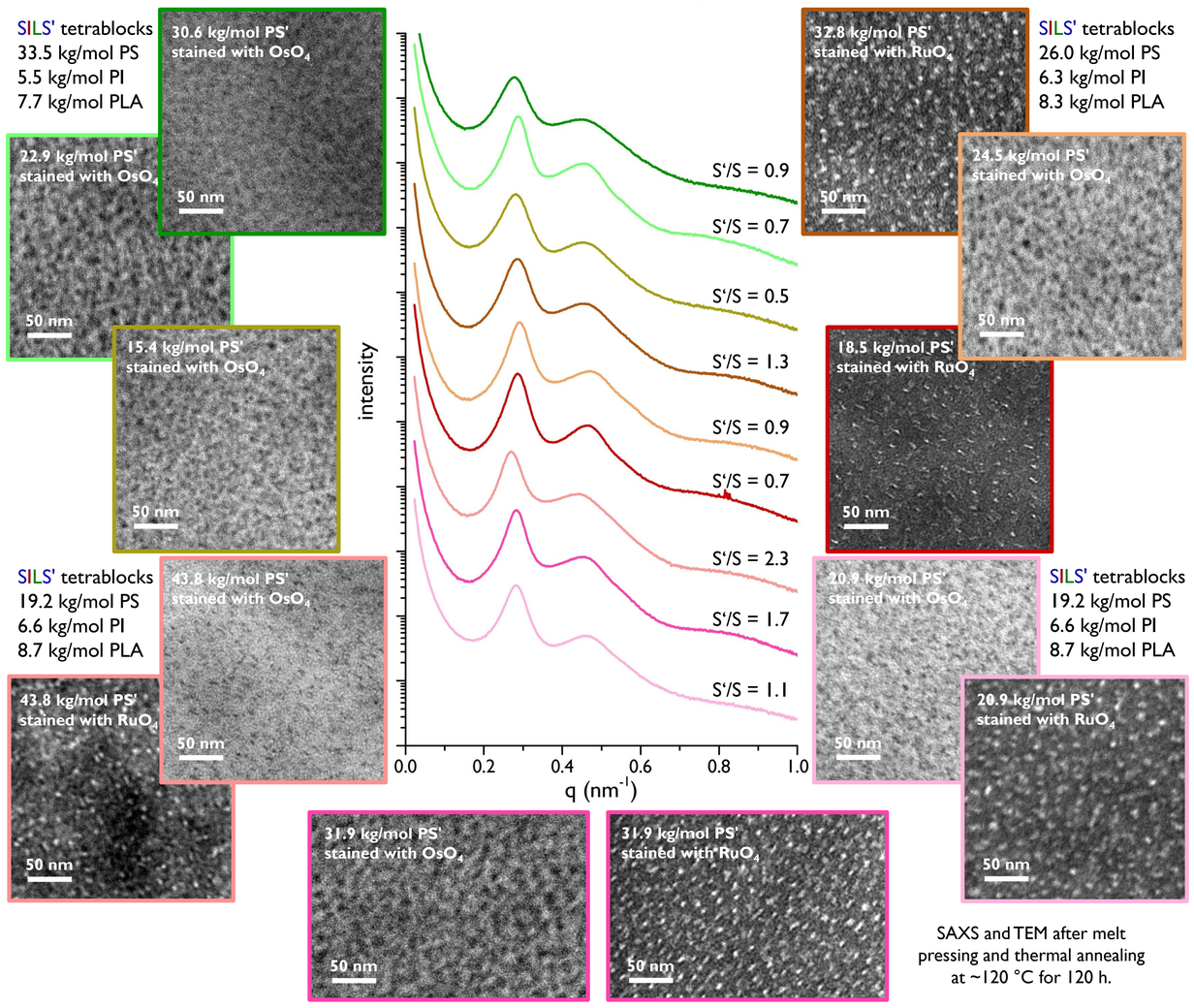
Characterization Facility

Polymers with $f_{PS} > f_{PI} \approx f_{PLA}$

- When $f_{PI} \approx f_{PLA} < 0.15$, discrete particle-like domains of PI and PLA were observed
- Long-range order was not achieved, even after long thermal annealing times (>100 h)
- Changing ξ did not significantly affect the morphology by SAXS or electron microscopy

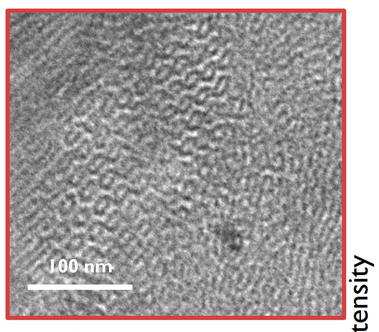


SAXS and TEM after melt pressing and thermal annealing at ~120 °C for 120 h.

Polymers with $f_{PS} \approx f_{PI} \approx f_{PLA}$

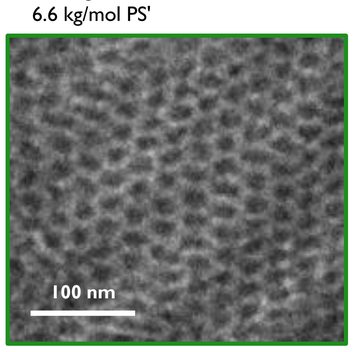
- Ordered triblock polymers ≠ ordered tetrablock polymers
- Larger polymers boosted χ*N* to give ordered structures
- Long-range order difficult to achieve if N is increased further

SIL triblock
4.7 kg/mol PS
3.9 kg/mol PI
5.2 kg/mol PLA

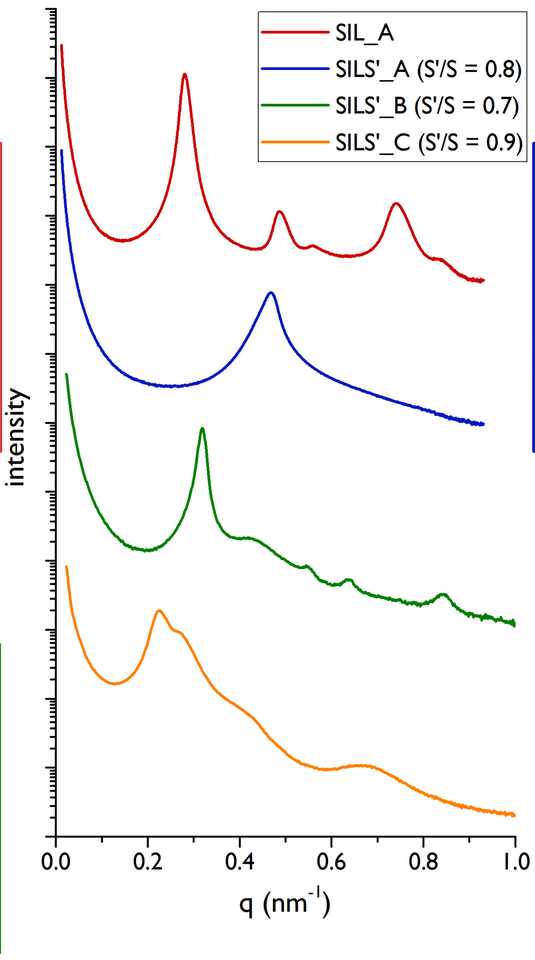


SAXS and TEM after solvent casting.

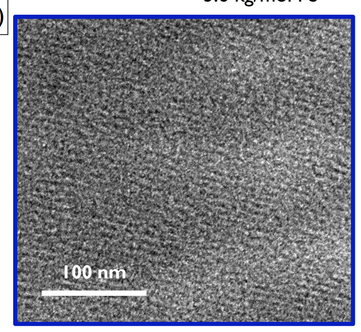
SILS' tetrablock
9.6 kg/mol PS
8.7 kg/mol PI
11.8 kg/mol PLA
6.6 kg/mol PS'



SAXS and TEM after solvent casting and thermal annealing at ~120 °C for 24 h.

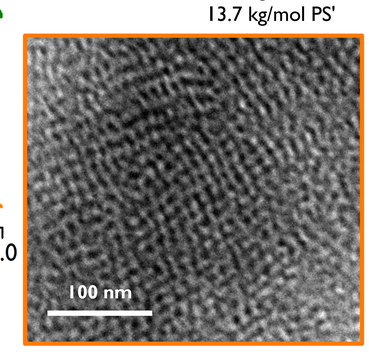


SILS' tetrablock
4.7 kg/mol PS
3.9 kg/mol PI
5.2 kg/mol PLA
3.6 kg/mol PS'



SAXS and TEM after solvent casting.

SILS' tetrablock
15.9 kg/mol PS
14.2 kg/mol PI
16.6 kg/mol PLA
13.7 kg/mol PS'



SAXS and TEM after solvent casting and thermal annealing at ~120 °C for 112 h.