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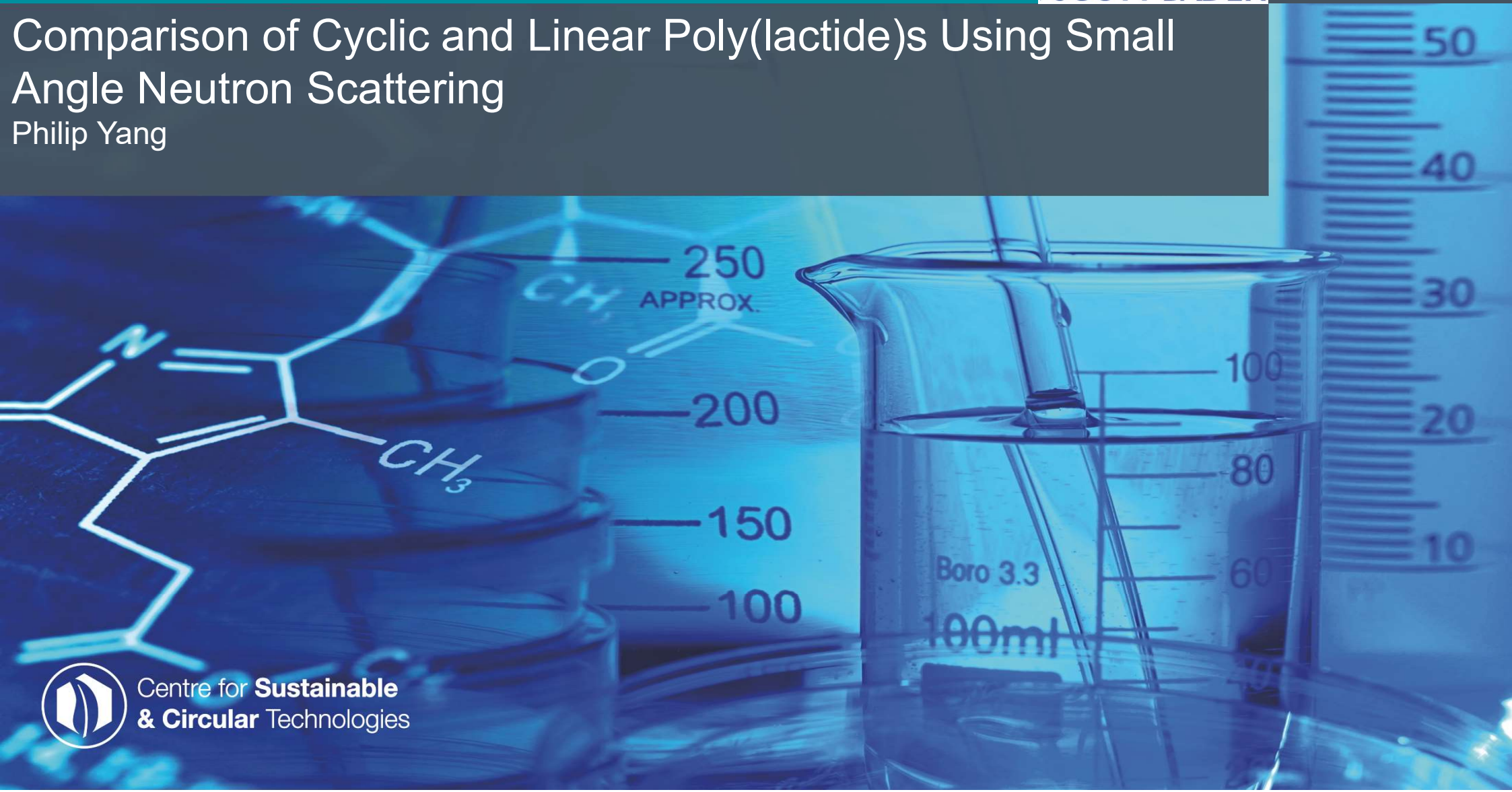
Comparison of Cyclic and Linear Poly(lactide)s Using Small Angle Neutron Scattering

Philip Yang



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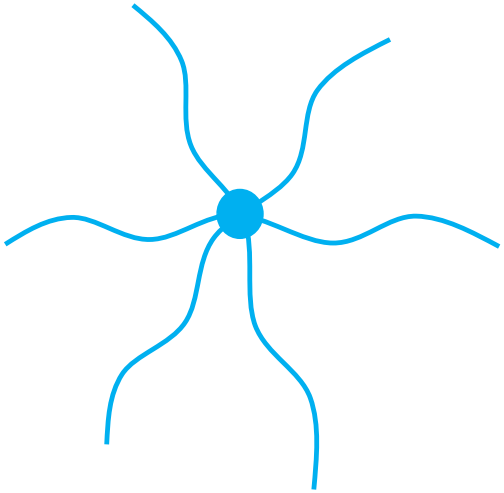
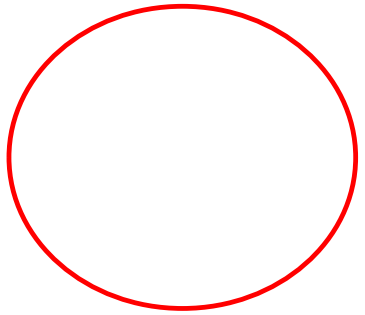
Introduction – Polymer topology

Linear

Branched



Star



Cyclic

Compared to linear polymers, cyclic polymers possess:

- Lower viscosities
- Higher glass transition temperatures
- Greater thermal stability
- Faster crystallisation rates

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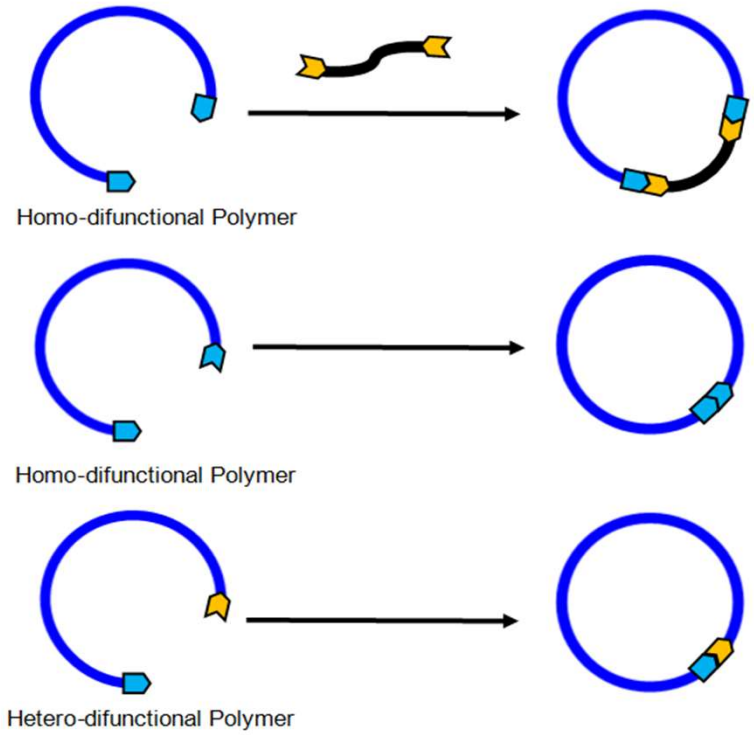
Yang, P. B., Davidson, M. G., Edler, K. J., Brown, S., Biomacromolecules, 2021, 22, 3649–3667

Introduction – Cyclic Polymer Synthesis



Ring closure polymerisation

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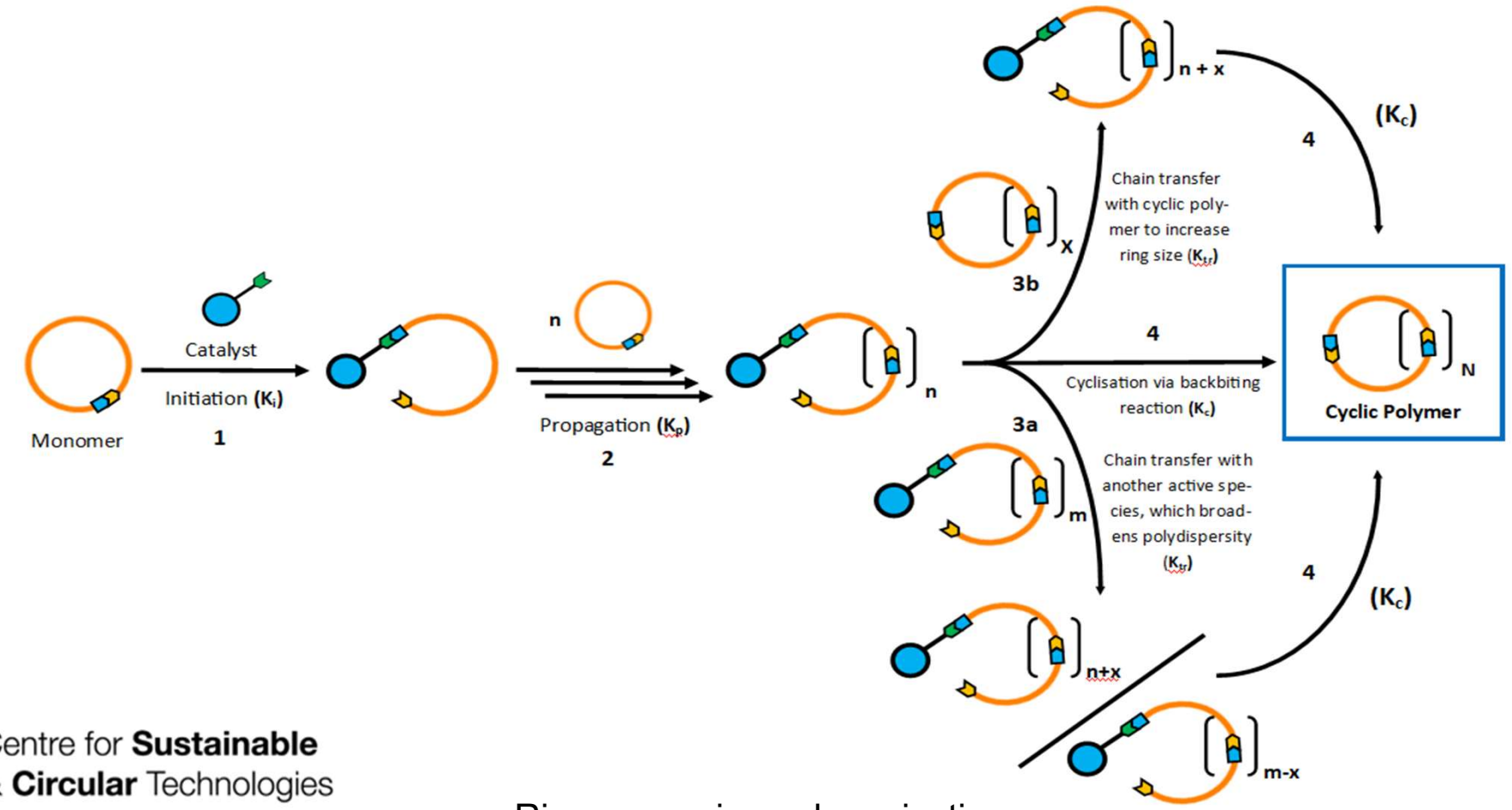
Introduction – Cyclic Polymer Synthesis

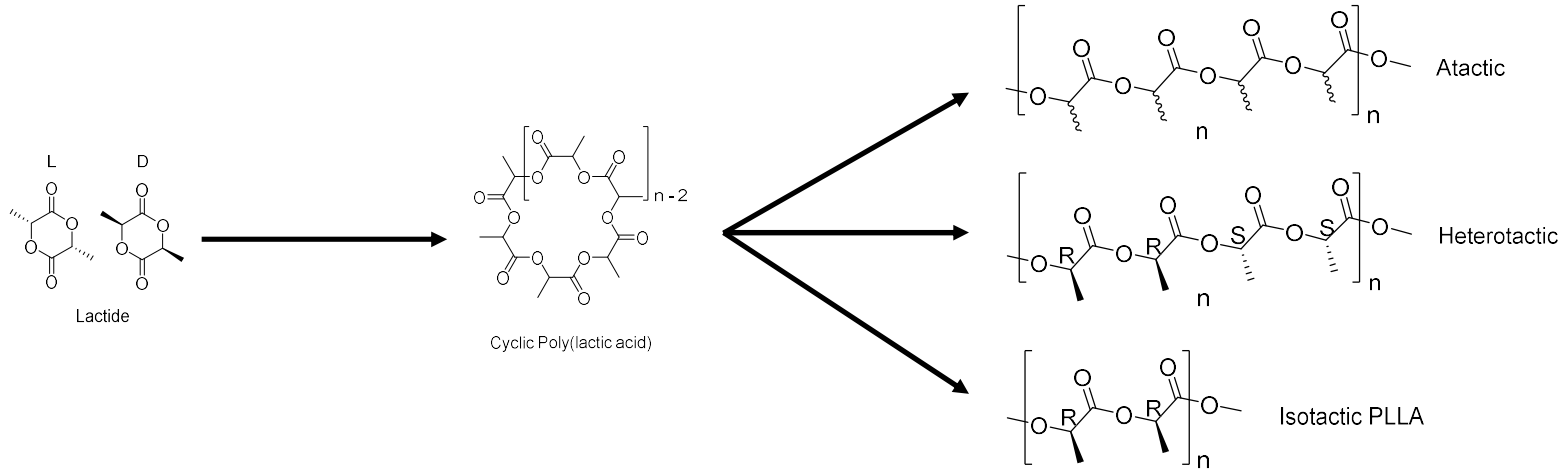


Ring expansion polymerisation

Yang, P. B., Davidson, M. G., Edler, K. J., Brown, S., Biomacromolecules, 2021, 22, 3649–3667

Introduction – Our work on cyclic polymers

- Our work explores the use of the cyclic topology and its varied properties as a way to improve the versatility and commercial viability of bio-based and biodegradable polymers:



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Introduction – Our work on cyclic polymers

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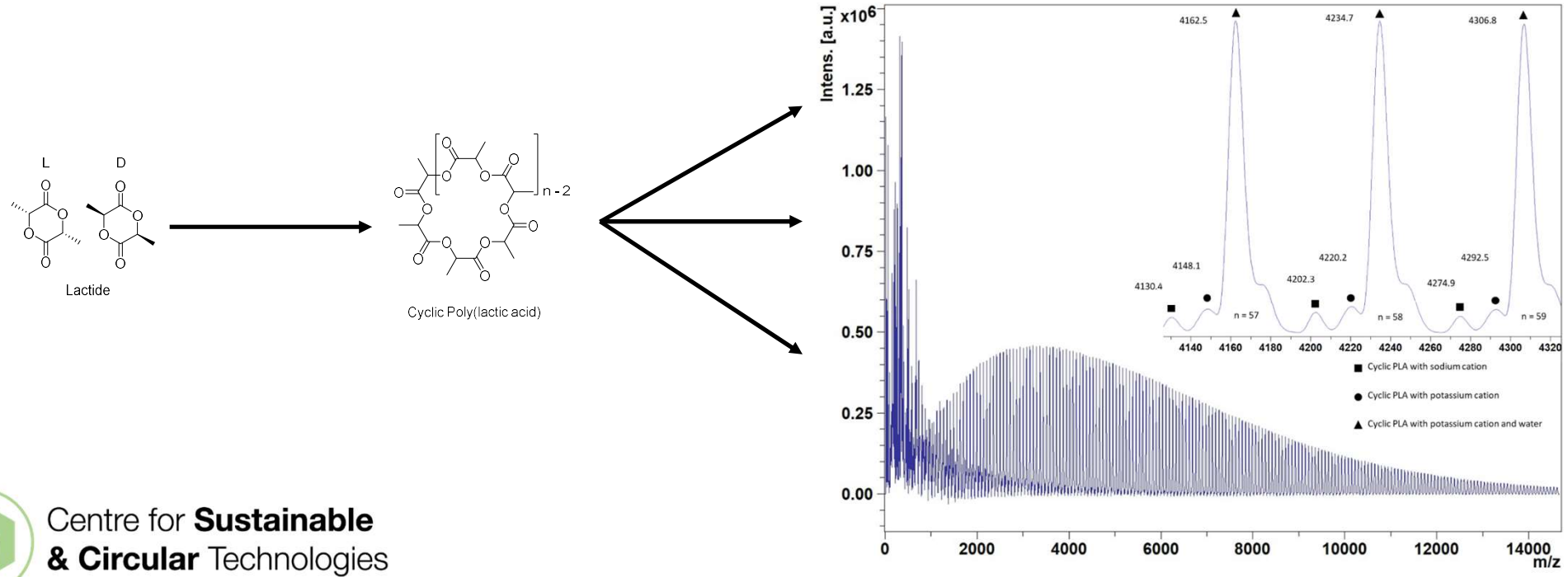

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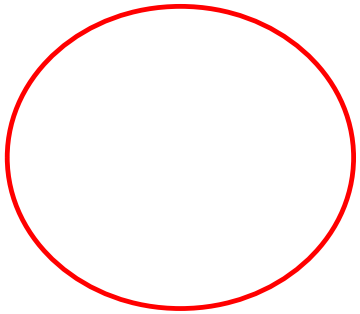
Introduction – Unanswered rheological questions



Cyclic

- How do polymers without free end groups relax stress?
- What conformations do cyclic polymers adopt?
- SANS experiments lacking for cyclic polymers currently

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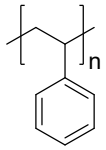
Previous literature:



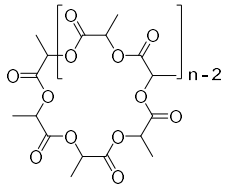
Poly(styrene)

χ_{eff} (cyclic) < χ_{eff} (linear)

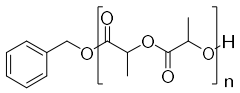
ν (cyclic) > ν (linear)

χ_{eff} = Polymer-solvent interaction parameter
ν = Flory exponent

This work:



Cyclic



Linear

Poly(lactide)

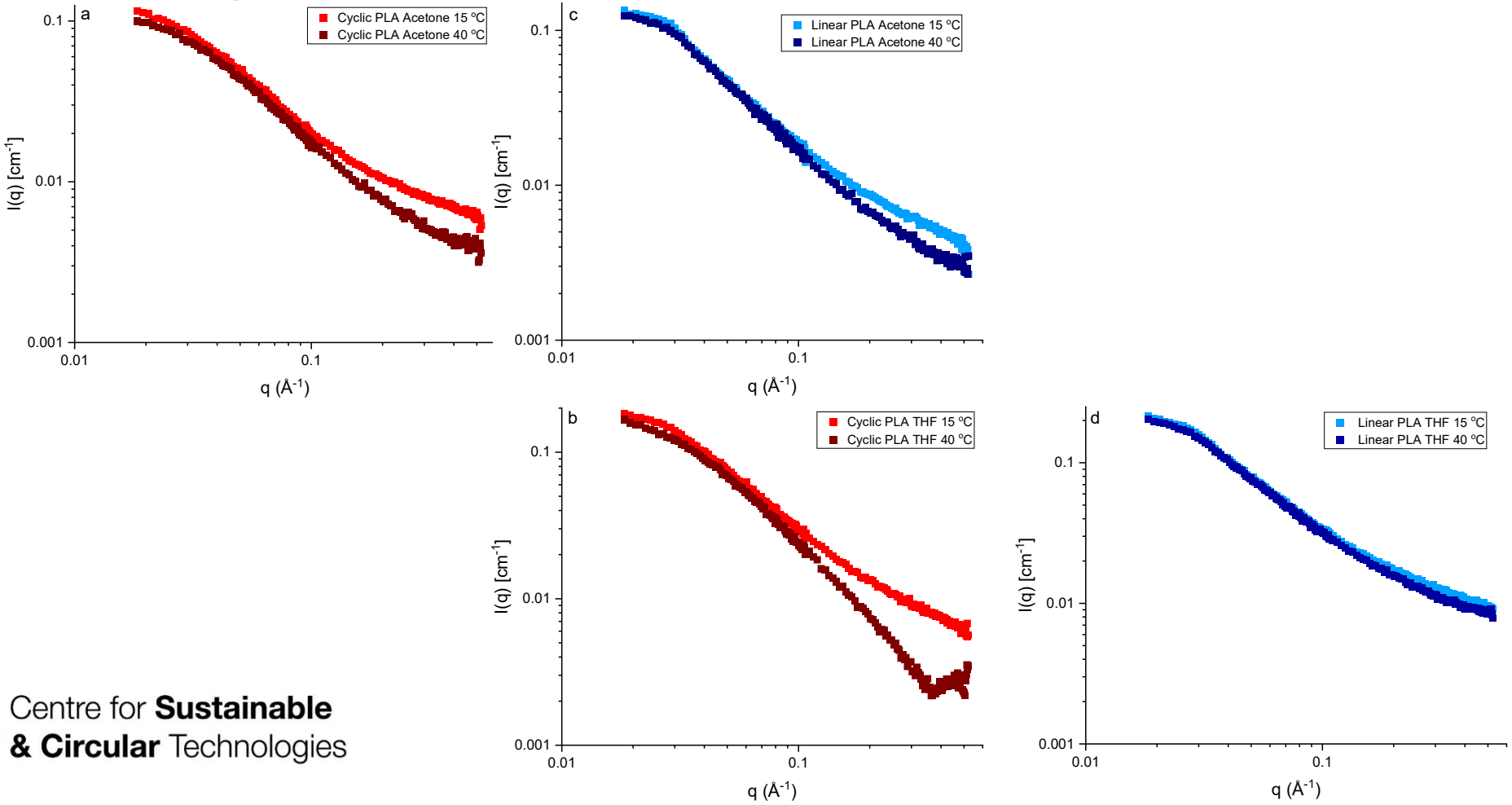
M_n = 18,330 - 74,440 g mol^{-1}

T = 15, 40 °C

Solvent = acetone-d^6, THF-d^8

Gartner, T. E. et al., Macromolecules, 2019, 52 (12), 4579-4589

Results – Temperature Effects



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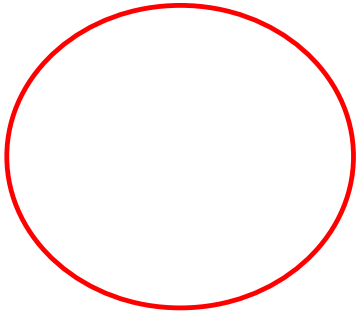
Results – Data Fitting

- The SANS data was fitted using RPA models in SASview 5.04 with χ_{eff} and v as floating variables.
- Two different models were required to account for the differences in excluded volume between the two topologies.
- Custom RPA models were kindly provided by Professor Michael J. A. Hore.
- Error in χ_{eff} and v values was tested by setting the starting values of χ_{eff} and v to 0.25, 0.5 and 0.75 before fitting the data. This resulted in zero variation in the final values after fitting.



Cyclic

Linear

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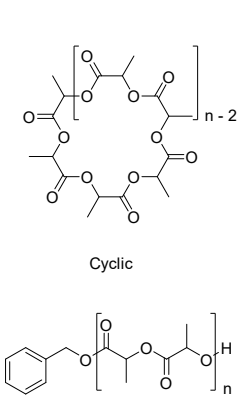
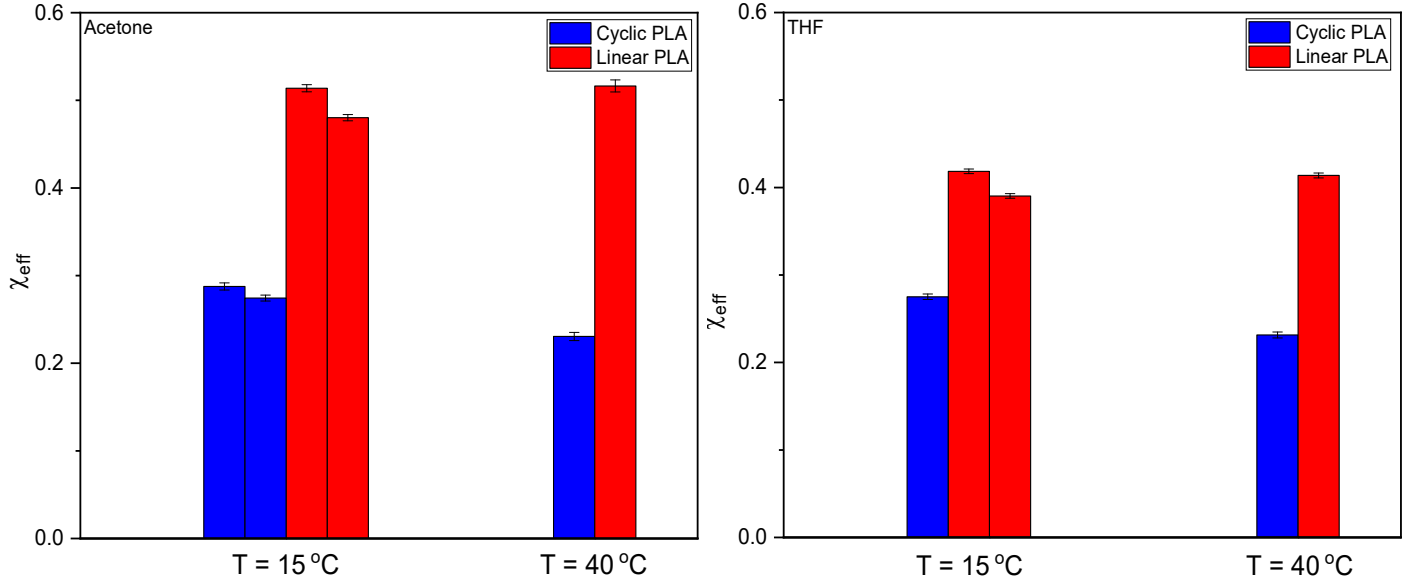
Results – χ_{eff} from Fitted Data of Atactic PLA





- Much greater differences in χ_{eff} compared to previous literature, likely due to smaller form factor of PLA compared to poly(styrene) and presence of hydrogen bonding.

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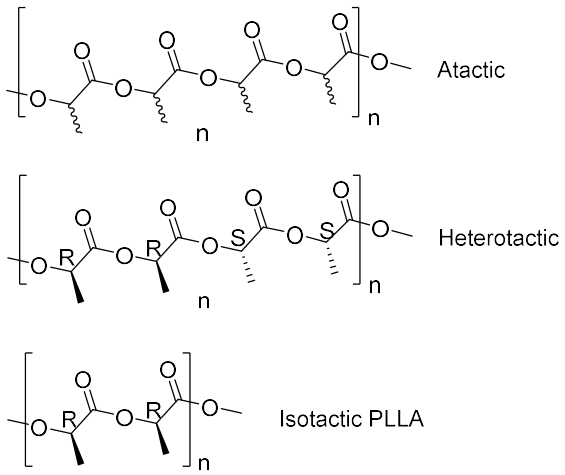
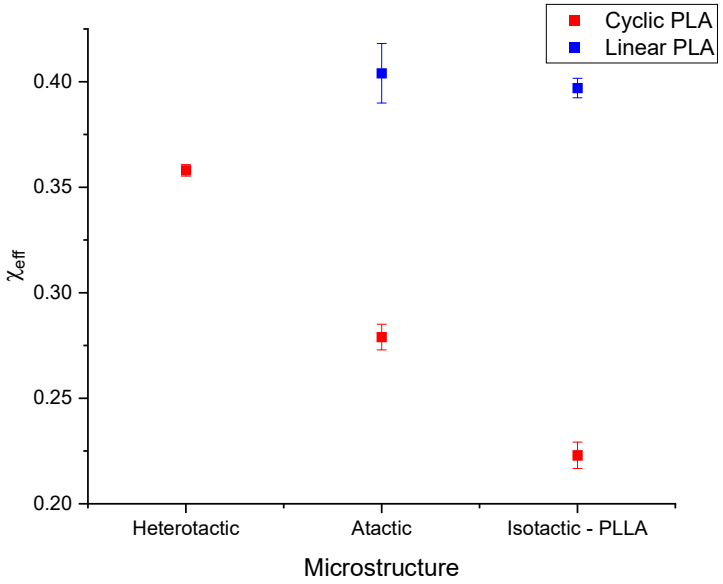
Results – Influence of Polymer Microstructure on χ_{eff}





- Substantial effect on χ_{eff} when polymer microstructure is altered in cyclic case specifically.
- Microstructure has big impacts on polymer properties, crystallinity etc. for PLA

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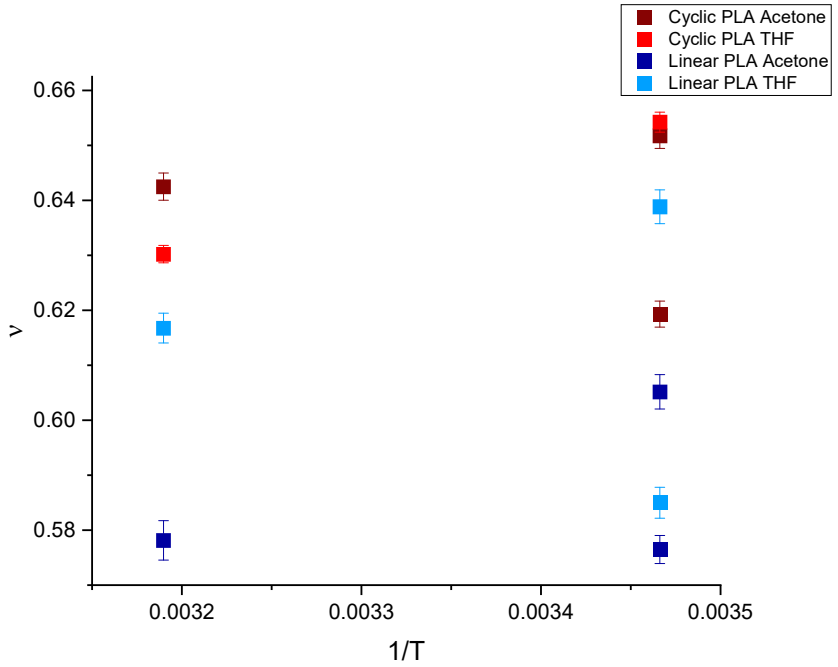
Results - Flory Exponent from Fitted Data of Atactic PLA



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Conclusions and acknowledgements

- Polymer choice, microstructure, solvent choice, temperature found to have substantial effects on scattering behaviour and polymer-solvent interaction parameter.
- These results highlight the importance of further SANS experiments on cyclic polymers and the potential of SANS in identification and characterisation of cyclic topology

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- We would like to thank ILL for the award of beamtime for these experiments, as well as Olga Matsarskaia, Niamh Leaman and Elly Bathke for their assistance with SANS experiments.
- EPSRC, CSCT and Scott Bader for their support of my PhD project
- Karen Edler, Matthew Davidson and group
- Professor Michael J. A. Hore.