Experimental report

23/12/2021

Proposal:	**9-11-2065**	**Council:**	4/2021
Title:	Conformation of cyclic vs linear polylactide in solution		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:
polylactide in d8-THF
polylactide in d6-acetone

Instrument	Requested days	Allocated days	From	To
D11	2	1	16/09/2021	17/09/2021
D22	2	0		
D33	2	0		

Abstract:

Polymers with their end groups joined together are known as cyclic polymers, and this lack of free end groups provides different physical properties to linear polymers. Due to synthetic difficulties up until recently, the physical conformations that these polymers adopt (along with the ways in which they relax stress) are thought to be unique but have yet to be fully defined. There is an array of publications regarding this matter, but many have opposing conclusions and the topic remains quite open. We would like to use SANS experiments to probe the physical nature of cyclic poly(lactide) (cPLA) samples in solution with an emphasis on the physical conformations compared to linear counterparts. We have cPLA samples ranging from 18,000 to over 100,000 g mol-1 in molecular weight, allowing for an in-depth study. PLA is one of the most promising bio-based and biodegradable polymers having seen substantial commercial attention and use in biomedical applications. Experiments on PLA samples would be useful for the advancement of cyclic polymers and of bio-based polymers, given that the unique properties of the former have the potential to aide in the commercialisation of the latter.

Background:

Due to a lack of free end groups, cyclic polymers are known to have lower viscosities, higher melting and glass transition temperatures, greater thermal stability, and faster crystallisation rates than comparable linear polymers. Until recently however studies on cyclic polymers were hampered by difficulties in synthesizing these materials. New catalysts and methods now mean that cyclic polymers can be made at a range of molecular weights, for a greater diversity of polymers, allowing studies to better understand their behaviour. Poly(lactide) (PLA) is a promising bio-based/biodegradable polymer. The linear form of PLA is the most commercially produced at the moment, while the cyclic form is now attracting attention, so a better understanding of the polymer-solvent interactions and the effects of polymer geometry on its conformation in these systems will demonstrate where cyclic PLA may provide improved properties for applications, such as the synthesis of drug delivery particles.

Previous literature:

Gartner et al. compared poly(styrene) samples of low molecular weights at different temperatures (30 – 70 °C) over a q range of 0.01 to 0.4 Å^{-1}.[1] The authors found that the cyclic polystyrene samples were noticeably more affected by temperature variation compared to the linear samples. Their work mostly centered on the effects of solvent quality on chain scaling and sample molecular weights were limited to 14,000 g mol^{-1}. Another paper by Gooßen et al. also experimented with cyclic poly(styrene) only (i.e. no comparisons with linear samples) at lower q.[2]

Experimental details:

As stated in the initial proposal, the solution configuration of cyclic and linear poly(lactide) samples in THF-d^8 (a good solvent for PLA) and acetone-d^6 (a theta solvent for PLA) at 1 wt% polymer in solution, were analysed via Small Angle Neutron Scattering (SANS) across a q range of 0.00254 to 0.54413 Å^{-1} on D11. This q range required 3 different detector distances (28, 8 and 1.7 m) to measure 3 different q regions. Due to the lengthy times required to measure at low q (i.e. ~0.002 – 0.006 Å^{-1}), this range could not be measured for all samples in the time allocated for this experiment. The samples were measured in 2 mm thick 120-QS cylindrical cells. All samples were measured at 15 °C and some were also measured at 40 °C to investigate the temperature dependance of the polymer conformations. The backgrounds (i.e. the solvents) and empty cells were also measured in order to allow background subtraction.

Measurements were made on cyclic and linear PLA samples synthesized from racemic lactide (a mixture of L and D stereoisomers), with molecular weights ranging from 18,000 g mol^{-1} to over 100,000 g mol^{-1} as initially proposed, and also on some newer samples. These include poly(L-lactide) (PLLA) and heterotactic poly(rac-lactide) samples which were measured to compare how tacticity, monomer choice and crystallinity affected neutron scattering results. PLLA is also the commercial form of PLA and the most commonly reported cyclic form of this polymer, hence its inclusion in this experiment. These newer samples were characterized (i.e. cyclic nature proven) using MALDI-TOF mass spectrometry as well as differences in viscosity and glass transition temperature. The molecular weights of these samples ranged from ~15,000 g mol^{-1} to ~250,000 g mol^{-1}.

Results and discussion:

The intensity vs. q plots from this experiment agree with the previous literature in terms of plot shape and trends. Figure 1 shows comparisons of atactic cyclic and linear polymers of racemic lactide (PLA) which showed a strong incline at low q, similar to that seen in the paper by Gooßen et al.[2] As implied in the paper by Gartner et al.[1], there is a steeper slope at low q for the cyclic sample compared to the linear suggesting a larger R_g for the cyclic polymer.

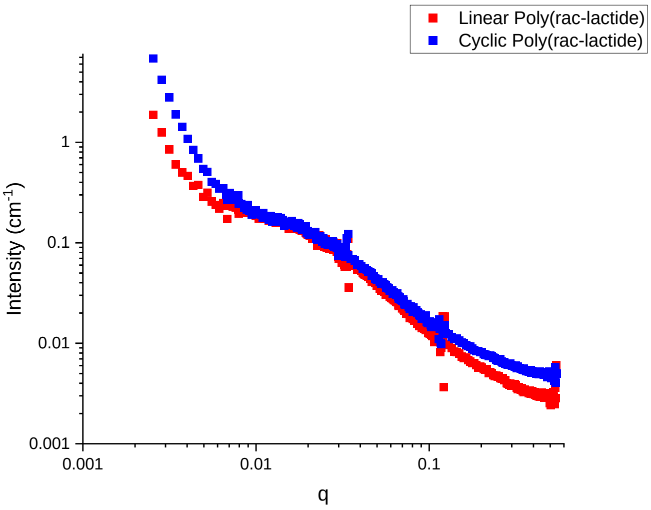

Figure 1: Intensity vs. q plot comparing cyclic and linear Poly(rac-lactide) samples at the same molecular weight.

As expected, the cyclic samples were much more affected by a change in temperature compared to their linear counterparts, although in our case the effect was mainly seen at the higher end of the q range. This was particularly evident in the samples dissolved in THF-d^8 (see Figure 2). The same trend was seen in the theta solvent for PLA, acetone-d^6. These results are in good agreement with the paper by Gartner et al. as the cyclic sample is more affected by temperature at all areas of the q range. The strong variation at high q may be due to the glass transition temperature for these samples (which are around 45 – 50°C) which may be causing a unique effect in the cyclic sample only.

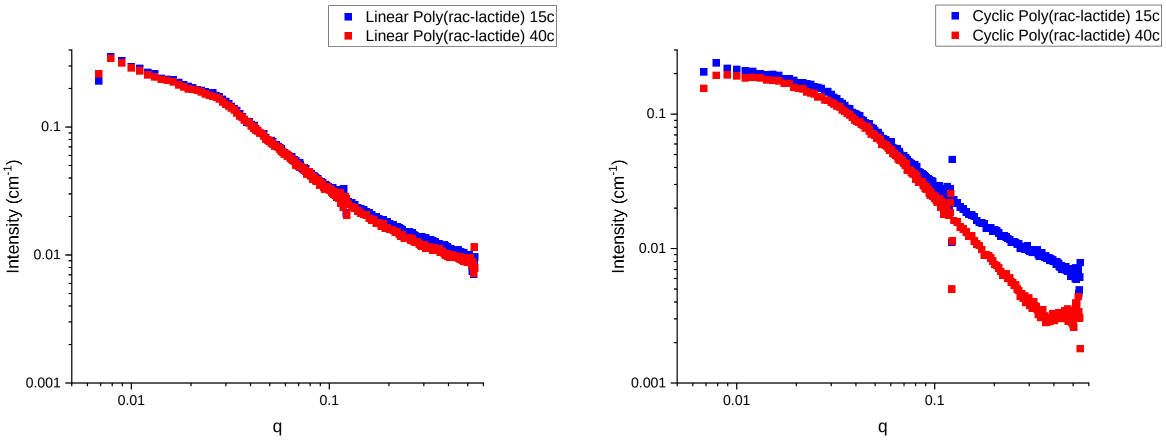

Figure 2: Comparison of temperature dependance of linear (left) and cyclic (right) Poly(rac-lactide) samples at 15 and 40 °C, in THF-d^8

In addition, there were noticeable differences between samples of poly(L-lactide) and poly(rac-lactide) of similar molecular weights (see Figure 3). These differences varied between cyclic and linear samples. Atactic and heterotactic poly(rac-lactide) samples were also compared.

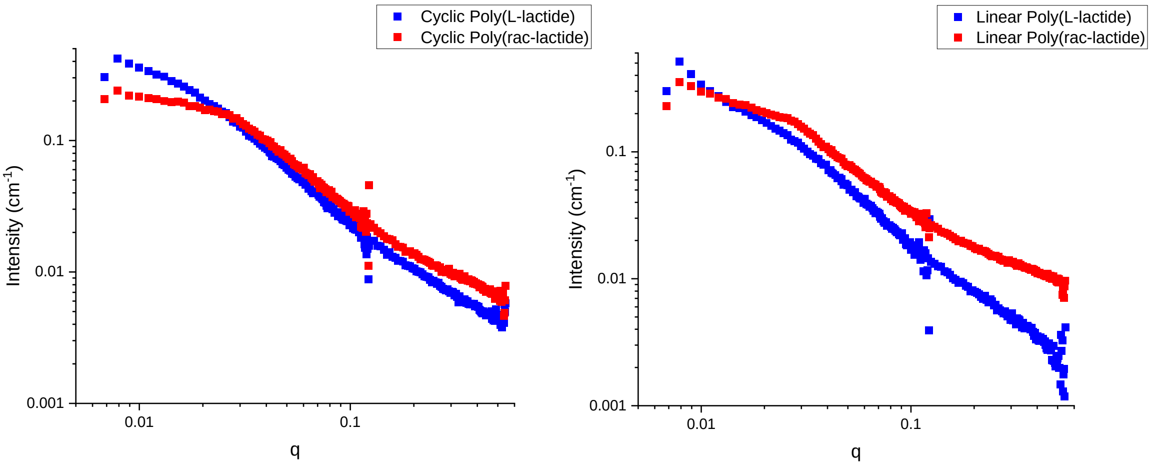

Figure 3: Comparison of intensity vs. q plots of PLLA and atactic Poly(rac-lactide) samples of cyclic (left) and linear (right) topologies

Following these experiments and initial results, we will calculate Porod slopes and the radius of gyration for the various datasets to compare the shapes of cyclic and linear polymers in acetone and THF so that any trends with molecular weight, polymer structure and solvent type can be ascertained. The datasets will also be cleaned up to remove any anomalous results around the areas where the low, medium and high q regions have been stitched together.

Then, the data will be fitted using the RPA model in SASView for linear or cyclic polymers developed by Gartner et al.[1], and the data for PLA will be compared with their results on cyclic and linear polystyrenes, to give information on the solution nanostructures of the cyclic and linear polylactide samples. These results will be combined with our other data on T_g, melting point and the viscosity of these polymers in solution which will shed more light on the physical nature of the cyclic polymers and how they could best be utilised in applications as research begins to turn towards their commercial potential.

References:

(1) Gartner, T. E.; Haque, F. M.; Gomi, A. M.; Grayson, S. M.; Hore, M. J. A.; Jayaraman, A. Scaling Exponent and Effective Interactions in Linear and Cyclic Polymer Solutions: Theory, Simulations, and Experiments. *Macromolecules* **2019**. https://doi.org/10.1021/acs.macromol.9b00600.

(2) Gooßen, S.; Brás, A. R.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D.; Rubinstein, M.; Roovers, J.; Lutz, P. J.; Jeong, Y.; Chang, T.; Vlassopoulos, D. Influence of the Solvent Quality on Ring Polymer Dimensions. *Macromolecules* **2015**, *48* (5), 1598–1605. https://doi.org/10.1021/ma502518p.