Effect of Stereoisomerism on the Structure and Linear Rheology of Poly(Lactic Acid)

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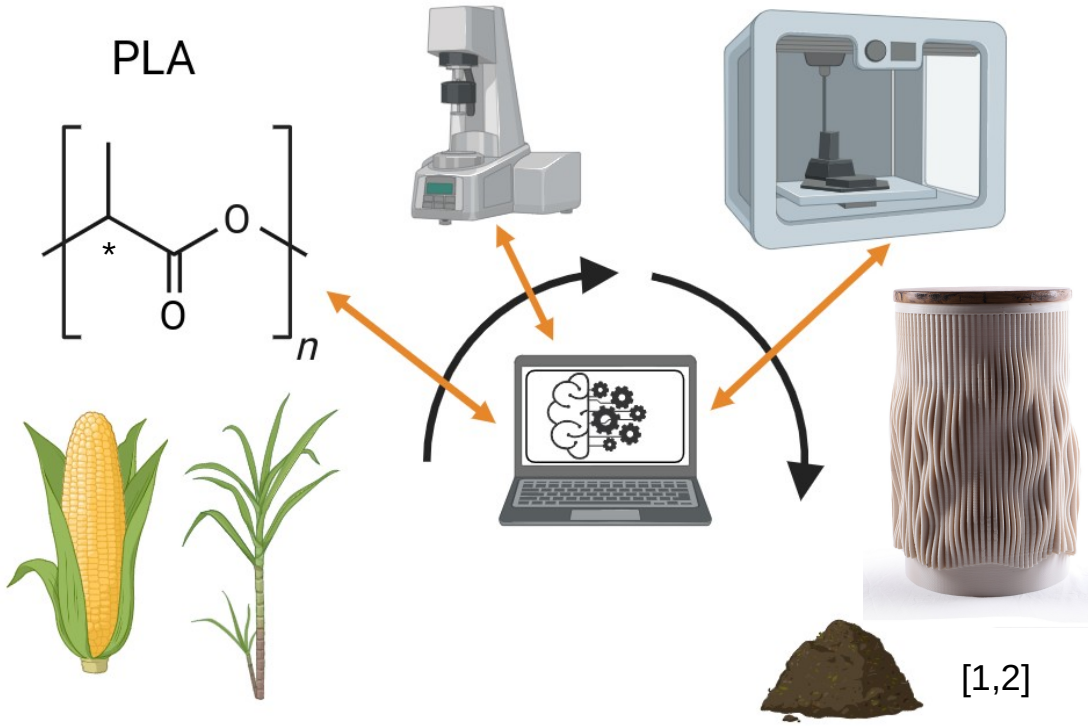
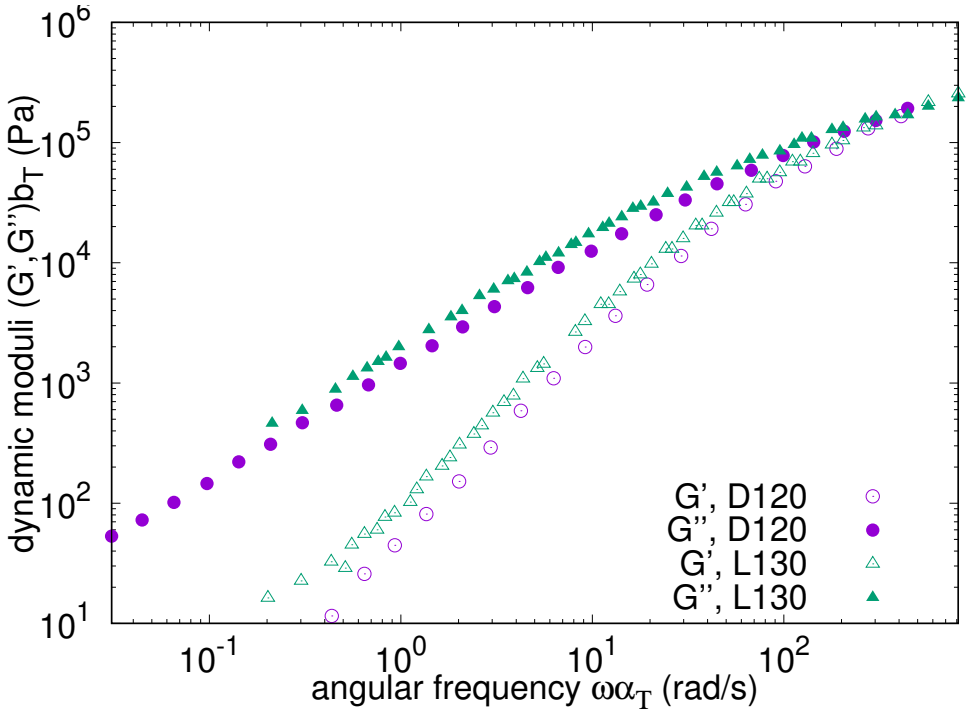
PITS3D Strategy:



[1] https://adicork.es/index.php/sectores/; [2] Created with BioRender.com

State of the art: experiment, homopolymers

- crystalline
- PLLA mostly with some % of D, pure PDLA not much known
- similar LVE spectra [1]
- comparable T_g [1]



[1] Othman, Norhayani, PhD thesis, 2012

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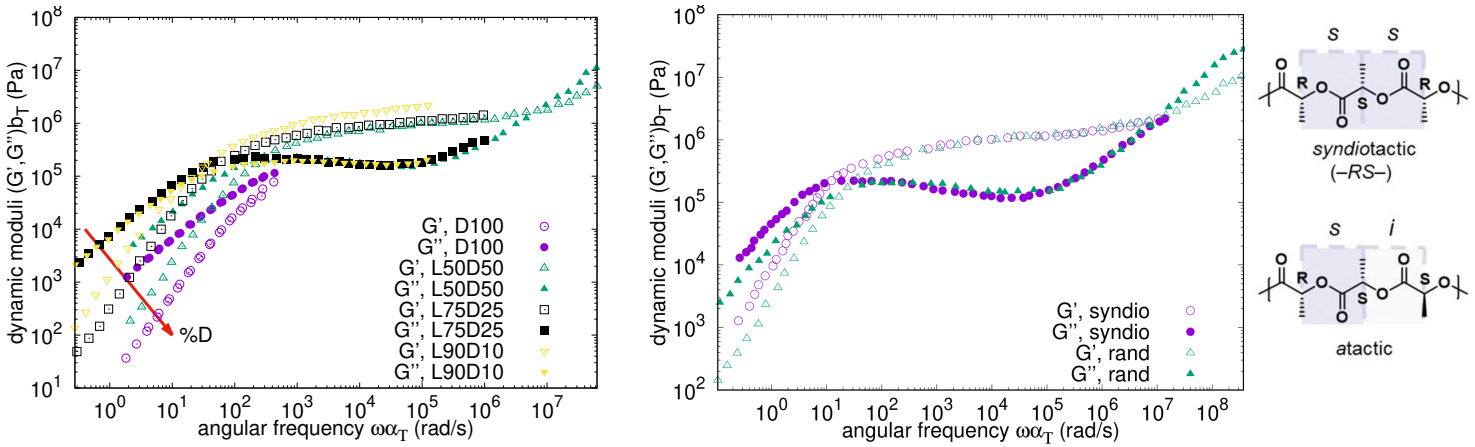
State of the art: experiment, copolymers

- PDLLA-amorphous
- effect of the increasing D-content (X_D) and tacticity
- $$T_g = T_{g,\infty} - \frac{52 + 791 X_D}{M_n}$$



[1] Othman, Norhayani, PhD thesis, 2012, L.-E. Chile, P. Mehrkhodavandi, S. G. Hatzikiriakos, Macromolecules (2016) 49 (3), 909-919

[2] P. A. Klonos et al., Polymer (2024), 305, 127177

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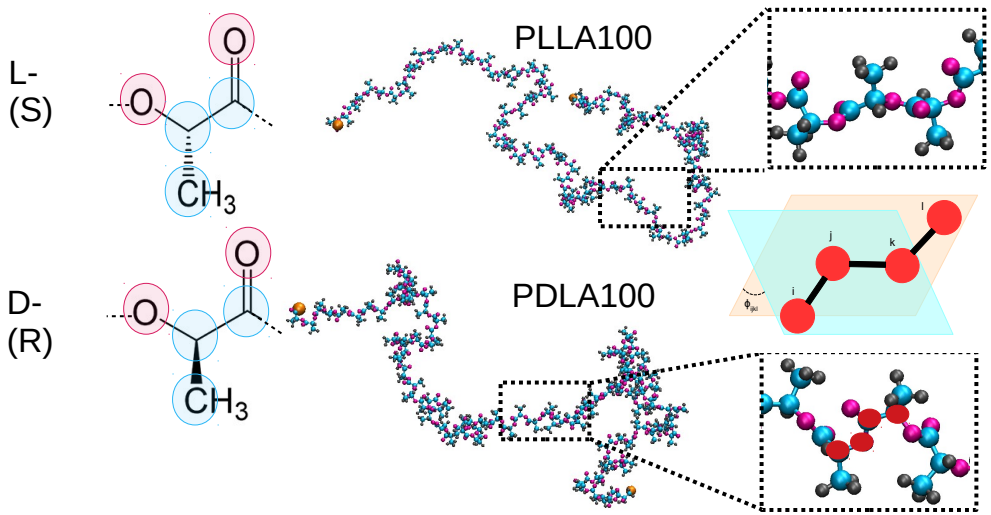
State of the art: simulation

- PLLA and PDLA should have the same force field, PDLLA not much data
- similar to proteins: slow structural rearrangements (slow equilibration and properties such as T_g sensitive to the dihedral functions)
- H-bonds: atomistic detail



Simulations: systems

Label	Mw [g/mol]	Microstructure	
		L	*D*
PLLA10	0.7 k	100%	0%
PLLA30	2.2 k	100%	0%
PLLA100	7.2 k	100%	0%
PLLA125	9.0 k	100%	0%
PLLA150	10.8 k	100%	0%
PLLA175	12.6 k	100%	0%
PDLA30	2.2 k	0%	100%
PDLA100	7.2 k	0%	100%
Copo55D	7.2 k	45%	55%
Copo16D	7.2 k	84%	16%

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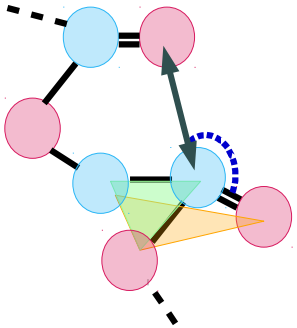
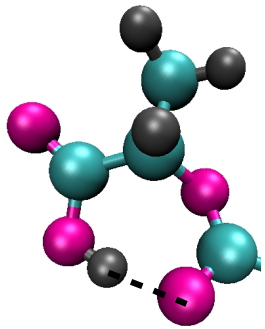
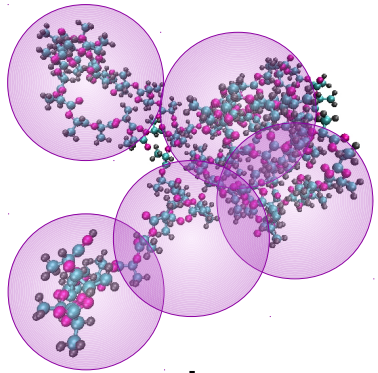
Simulations: structural properties



n-π*



H-bond



shape

- ✓ form factor
- ✓ packing length
- ✓ domain analysis
- ✓ characteristic ratio

- PDLA slighly more flexible than PLLA
- clear diferences in n-π* parameters between homopolymers
- PDLLA: more spherical, more flexible, more compact, more intramolecular H-bonds
- more D content=more flexibility
- Gaussian character for chain longer than 100 monomers

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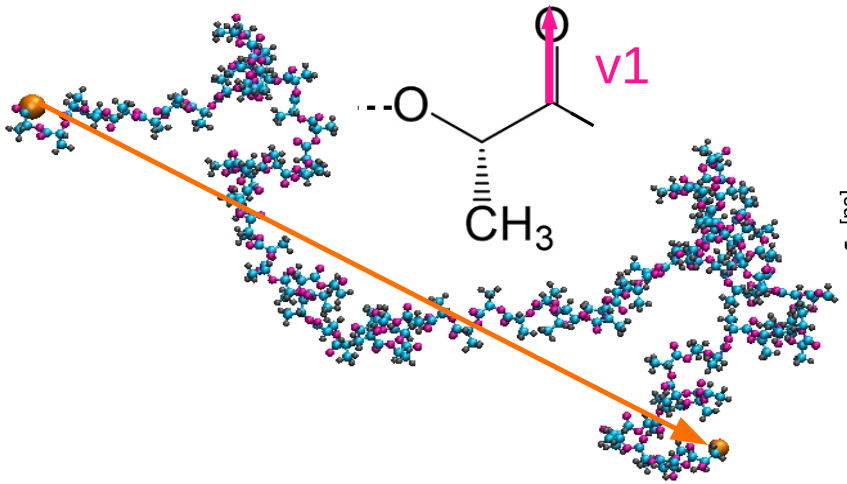
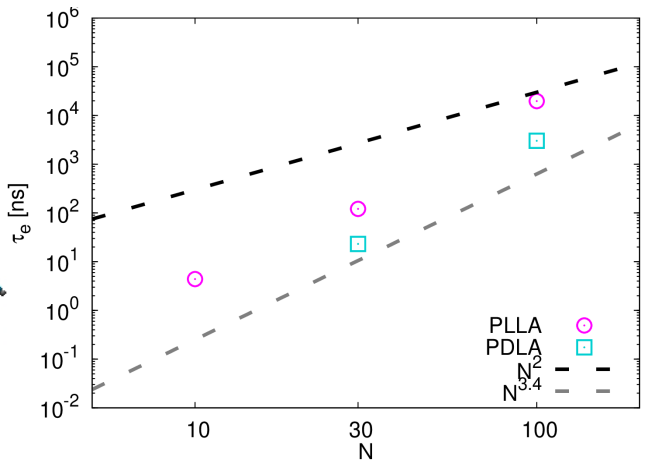
Simulations: dynamical properties





- the segmental and terminal dynamics of PDLA slighly faster than that of PLLA, T_g of PDLA lower than that of PLLA
- PDLLA: combination of slower and faster segments, environmental effects
- terminal dynamics: between Rouse and entanglement scaling

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Experiments: samples

Label	Mw [g/mol]	Microstructure	
		L	*D*
PLLA10K	10 k	100%	0%
PDLLA10K	10 k	50%	50%
PLLA25K	25 k	100%	0%
PDLA25K	25 k	0%	100%
PDLLA25K	25 k	50%	50%
PLLA50K	50 k	100%	0%
PDLA50K	50 k	0%	100%
PDLLA50K	50 k	50%	50%

two commercial samples for 3D printing: PLA3D850, and recycled PLA (Smartfil, Smart Materials 3D)

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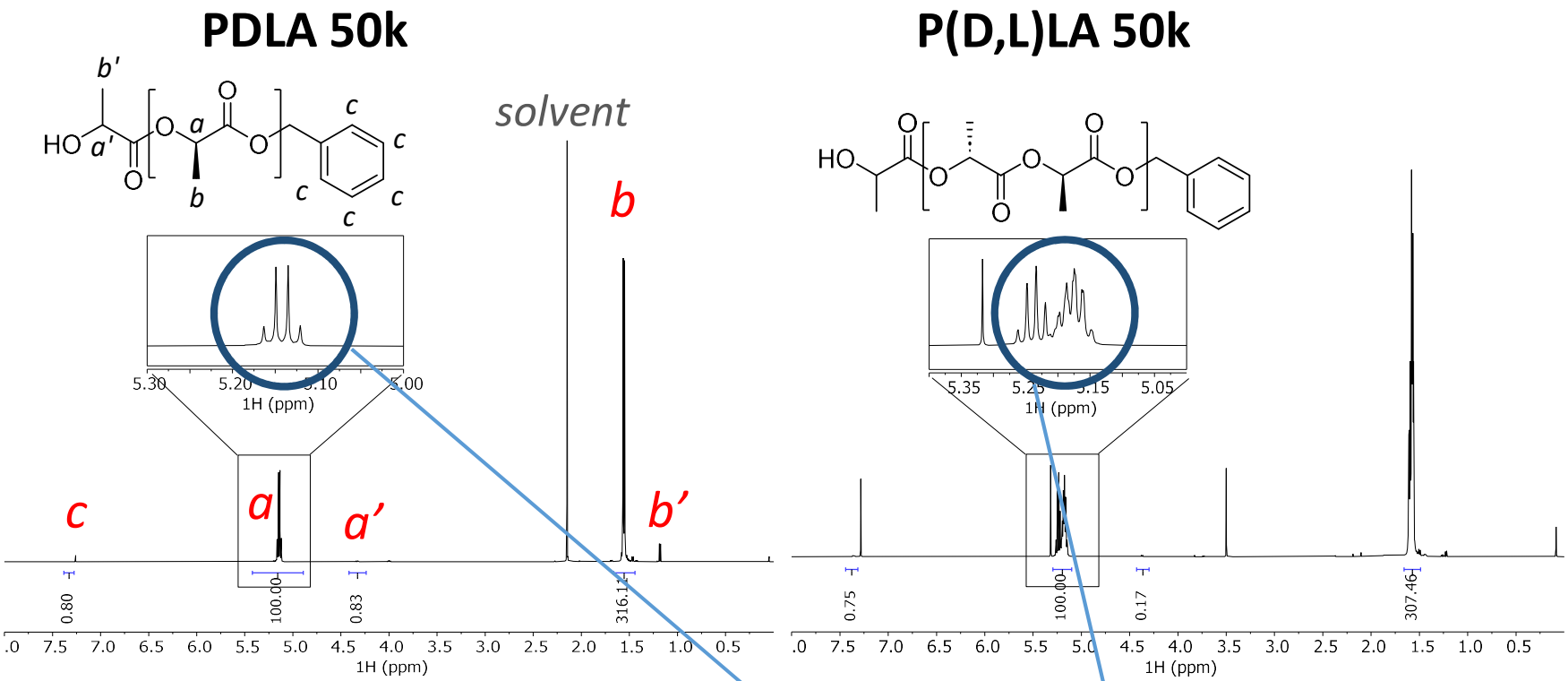
Experiments: NMR



$$M_n = 72 \cdot \frac{a}{\frac{c}{5}} = 45.0\ kDa$$

Fully isotactic vs no stereocontrol
(all possible tetrads formed)

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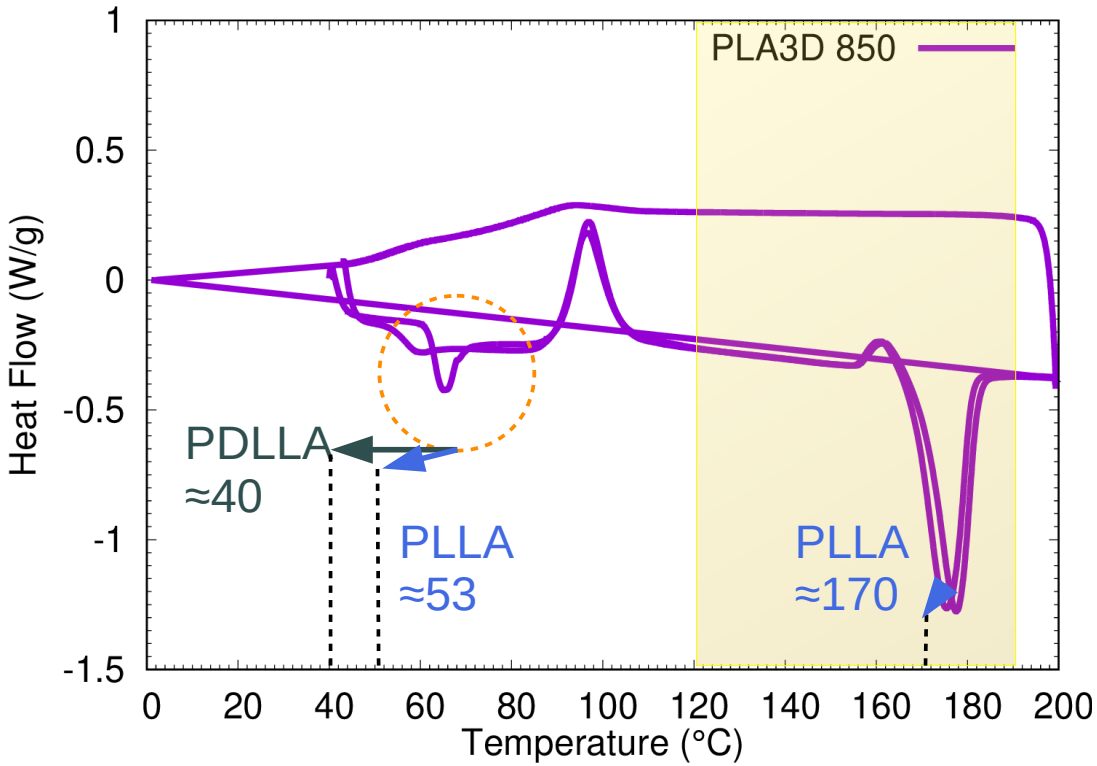
Experiments: NMR

- two types of solvent, consistent results

Polymer	Target MW (kDa)	MW In $CDCl_3$ (kDa)	MW in DMF-d_7 (kDa)
P(D,L)LA	10	10.7 ± 1.6	10.5 ± 1.6
	25	24.3 ± 3.6	26.1 ± 3.9
	50	48.0 ± 7.2	51.4 ± 7.7
P(L)LA	10	9.7 ± 1.5	12.0 ± 1.8
	25	25.5 ± 3.8	25.0 ± 3.8
	50	50.7 ± 7.6	48.0 ± 7.2
P(D)LA	25	28.1 ± 4.2	24.0 ± 3.6
	50	45.0 ± 6.8	49.3 ± 7.4

Experiments: DSC



- $X_c = \frac{\delta H_m - \delta H_c}{H_m^*}.100$
- $X_c(\mathrm{PLLA10}) = 31\%$
- $X_c(\mathrm{PLLA25}) = 30\%$
- $X_c(\mathrm{PLLA50}) = 24\%$

- low MW: modulated DSC

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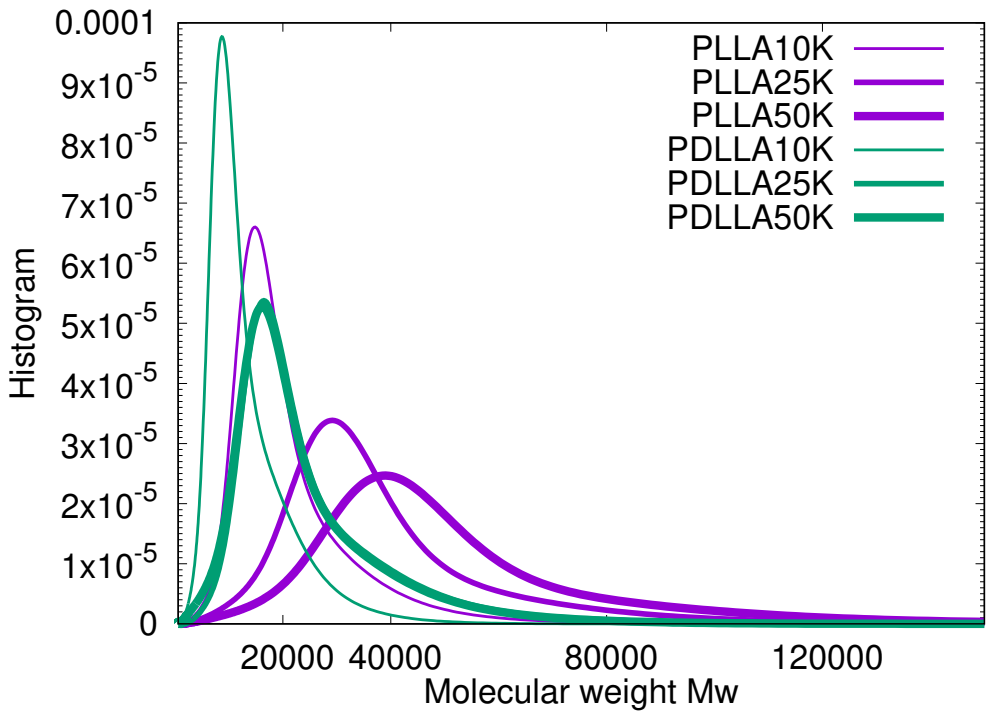
Experiments: GPC-SEC

- THF-acids retention in the column
- DMF-the refractive index increment (dn/dc) unknown
- PDLLA: PI≈1.3-1.5, PLLA: PI≈1.25-1.45



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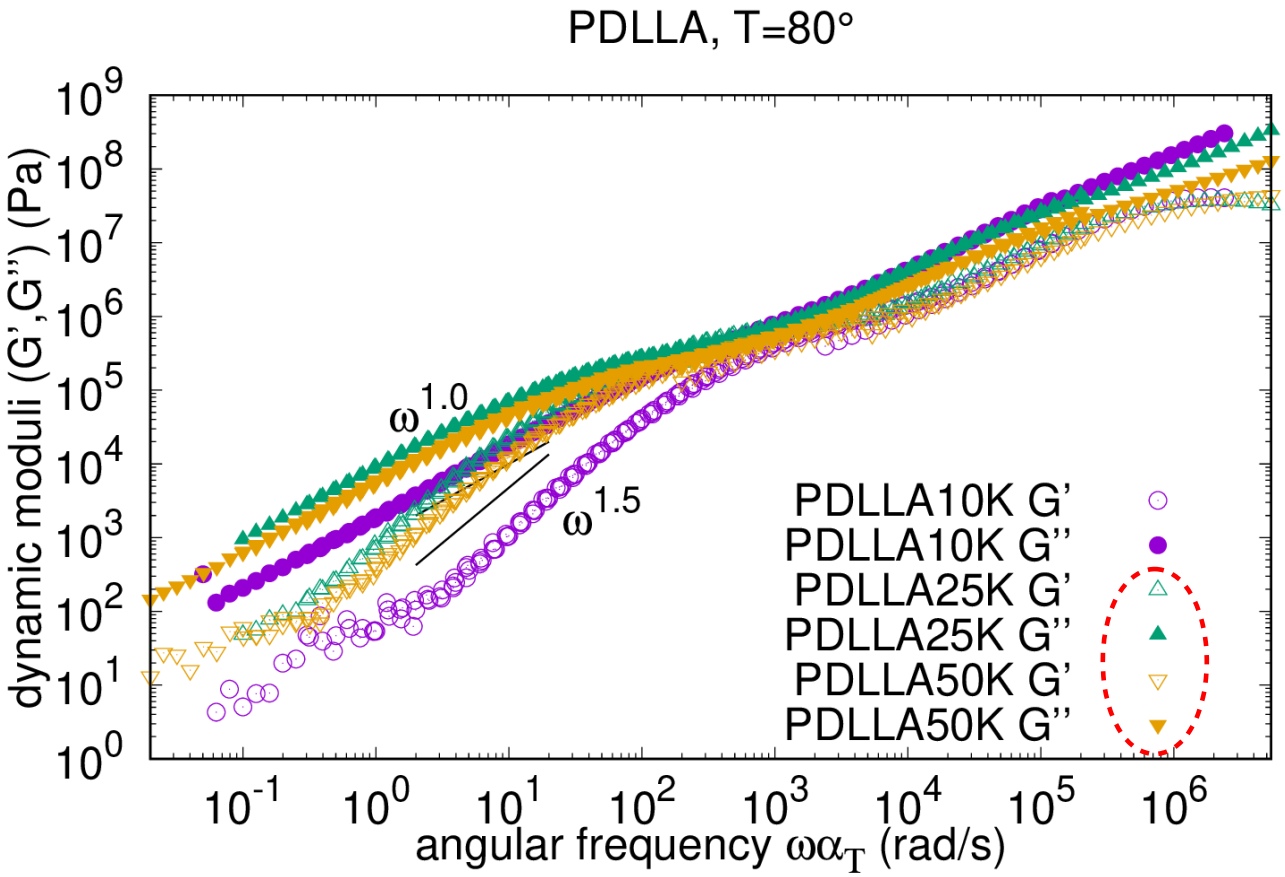
Experiment: linear viscoelastic spectra PDLLA



- LVE confirm GPC data, disagreement with NMR

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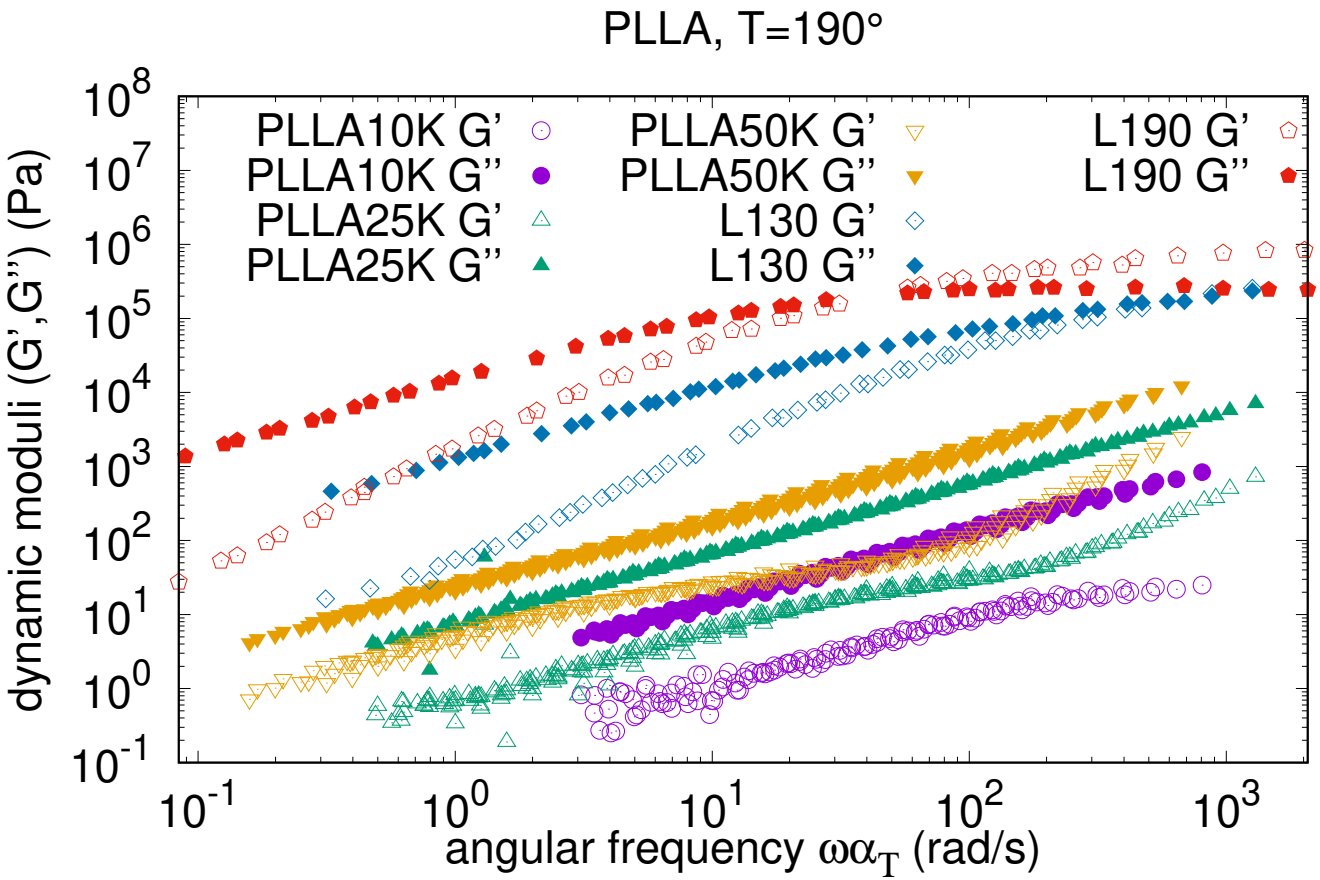
Experiment: linear viscoelastic spectra PLLA



L130, L190: Othman, Norhayani, PhD thesis, 2012

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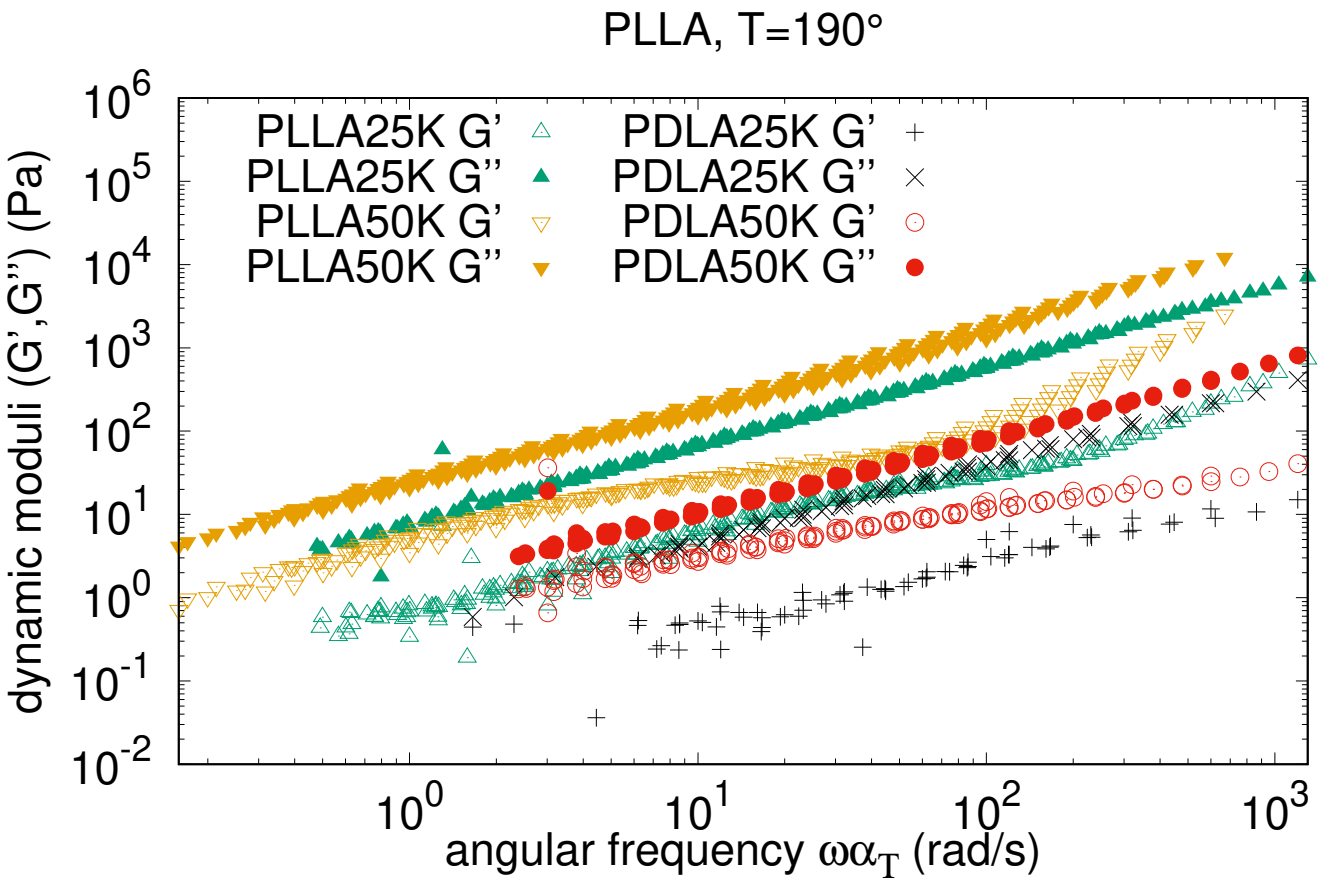
Experiment: linear viscoelastic spectra homopolymers



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Summary

- combination of computational and experimental methods to understand structure-property relation in PLA
- linear viscoelastic spectra complement the results from NMR and confirm GPC
- low Mw homopolymers: PDLA slower dynamics than PLLA, indications of different internal packing at monomeric level (CG potentials)
- copolymers more compact and spherical with internal H-bonds, dynamics intercorrelated

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To do

- quantitative Mw distributions (THF vs. DMF)
- modulated DSC for PDLA
- analysis with the Reptate software
- connecting Mw distributions with LVE spectra
- remove cummulative error in G(t) data from simulation

Keep calm and stay tuned!

- ✉ petra.bacova@uca.es

- ☞ https://polysim.eu/
- ☞ PITS3D project (Grant agreement ID: 101105208): https://cordis.europa.eu/project/id/101105208
- ✏ Petra Bačová, Vagelis A. Harmandaris, Sergio I. Molina, Computational investigation of structural properties of poly(lactic acid) and its stereoisomers: shape, size and flexibility, Macromolecules, in revision

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