Bottom-up approach for biodegradable polymers used in additive manufacturing: building computational tools to bridge the gaps

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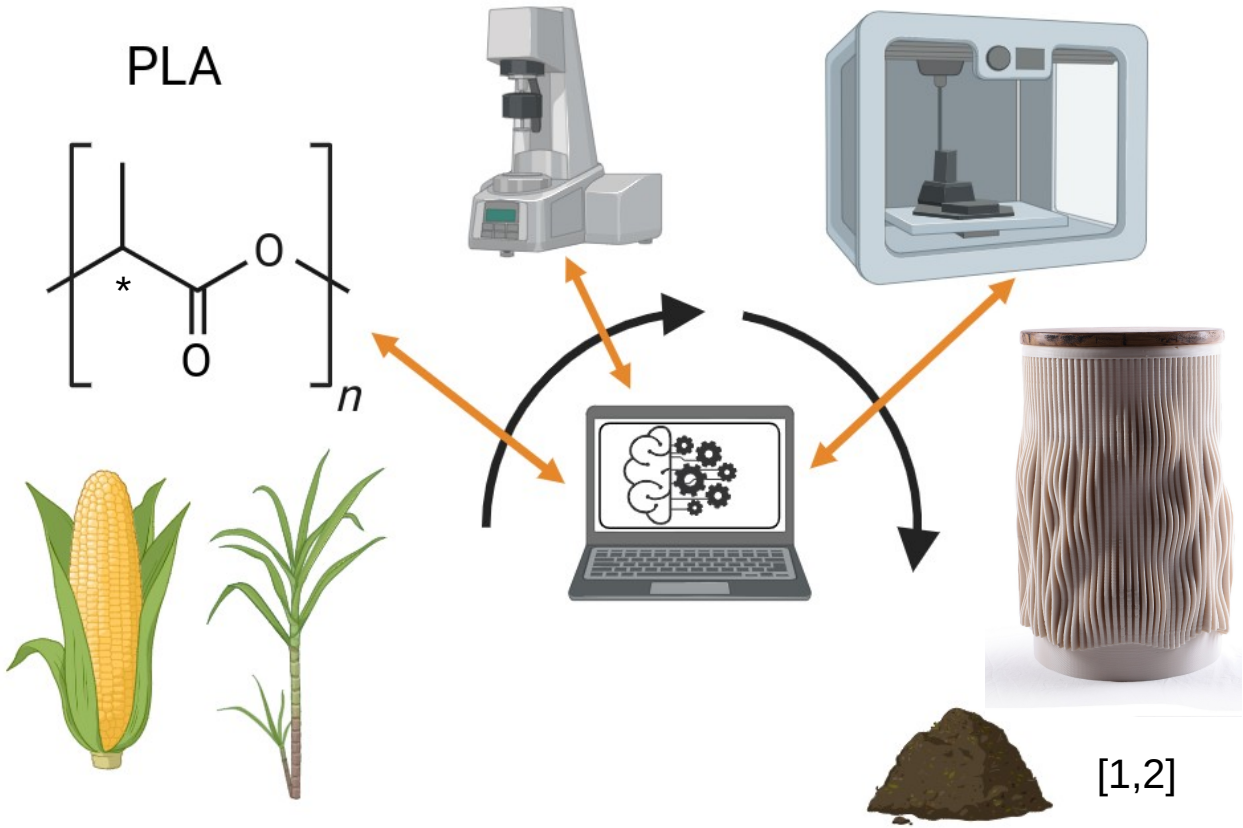

[1] https://adicork.es/index.php/sectores/; [2] Created with BioRender.com

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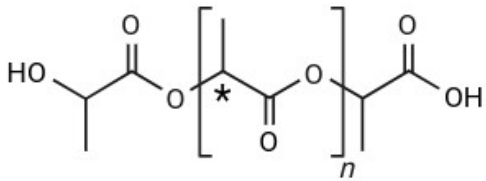
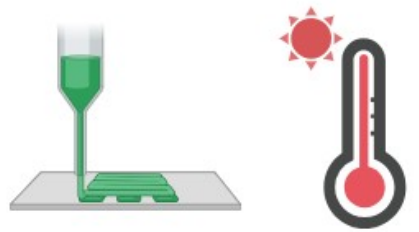
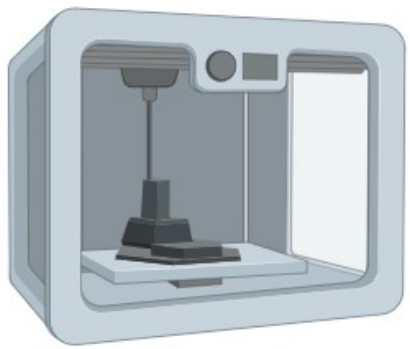
Poly(lactic acid) in additive manufacturing

- ✓ widely popular, easy to print
- ✓ low melting point, no heated tray
- ✘ sensitive to sunlight and high temperatures
- ✘ commercial samples of unknown composition
  - ➔ L- vs. D- stereoisomer
  - ➔ additives, polydisperse samples
  - ➔ empirical approach to nanocomposite design

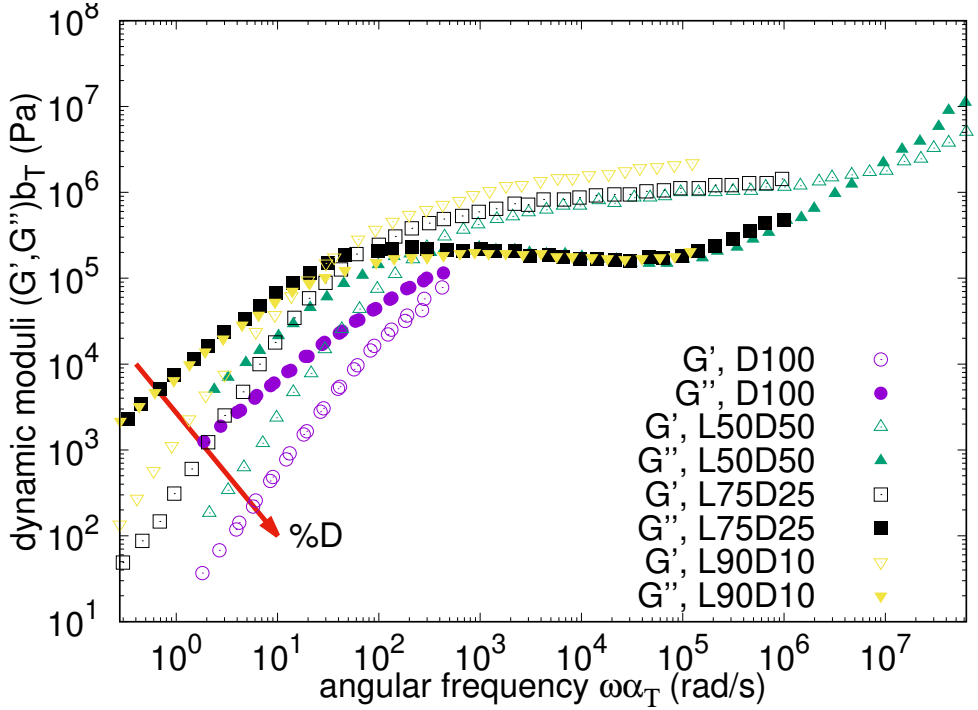






Rheology of poly(lactic acid)

- effect of the increasing D-content
- 100k, 423K, 10%, 25%, 50%, 100%



Othman, Norhayani, PhD thesis, 2012

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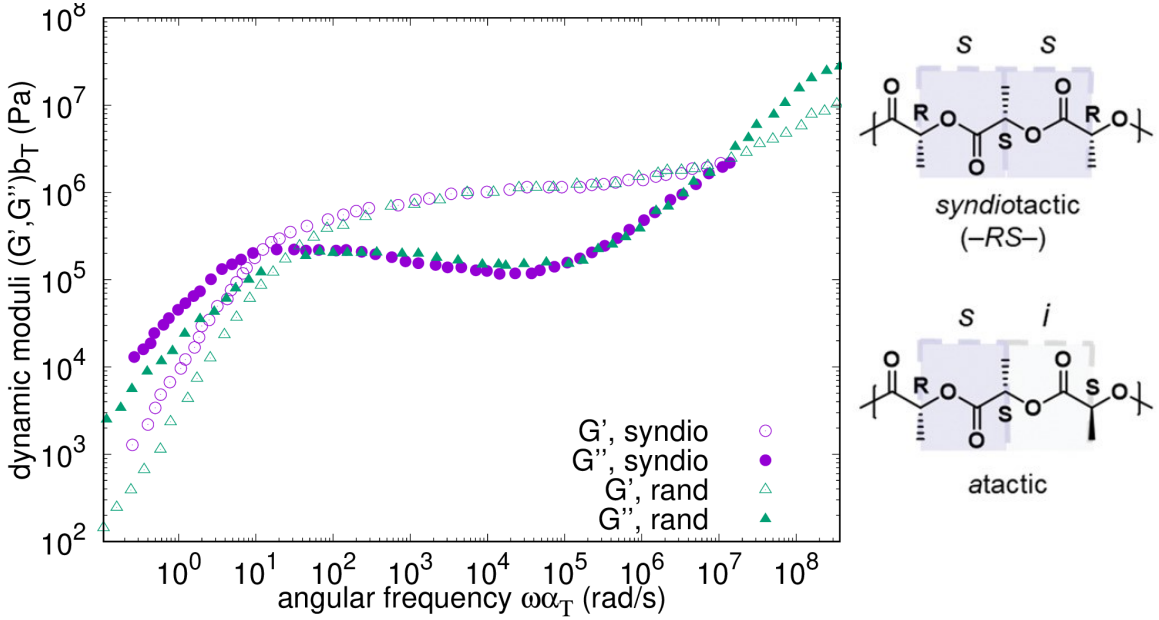
Rheology of poly(lactic acid)

- effect of tacticity
- ≈150k, 50% D, syndiotactic vs. atactic



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Systematic bottom-up simulation approach

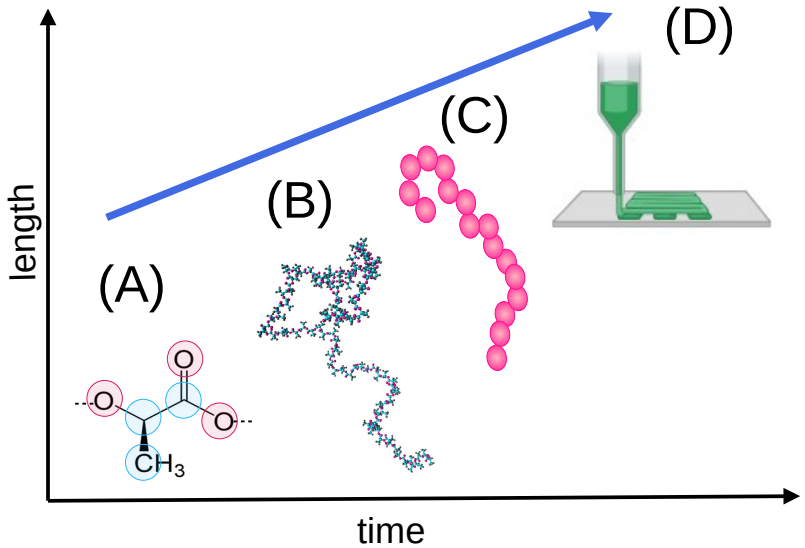
Computational methods:

(A) quantum: force field

(B) atomistic: chemistry-specific interactions

(C) coarse-grained: trends at mesoscale

(D) continuum



Multiscale:

✓ quantitative predictions of macroscopic properties

✘ time and resourse intensive

[1] Guseva, D. V.; Glagolev, M. K.; Lazutin, A. A.; Vasilevskaya, V. V.; Polym. Rev. 2023, 0, 1–39

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Challenges and motivation

- ✘ biodegradable polymers similar to proteins: slow structural rearrangements
- ✘ H-bonds: atomistic detail
- ✘ chirality: random L- and D- content
- ✘ lack of open-access data for data-driven approaches
- ✓ extensive atomistic data set which can be used for systematic bottom-up and/or data-driven approaches
- ✘ lack of experimental reference, monodisperse and well-defined systems
- ✓ theoretical and experimental rheological data on reference systems to determine printability

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Systems under investigation

- molecular dynamics simulations: atomistic and coarse-grained
- non-entangled melts
- 500K, 1 atm

Label	Mw [g/mol]	Microstructure	
		PLLA	*PDLA*
PLLA100	7.2 k	100%	0%
PDLA100	7.2 k	0%	100%
Copo100	7.2 k	45%	55%
PLLA30	2.2 k	100%	0%
PDLA30	2.2 k	0%	100%
Copo30	2.2 k	84%	16%

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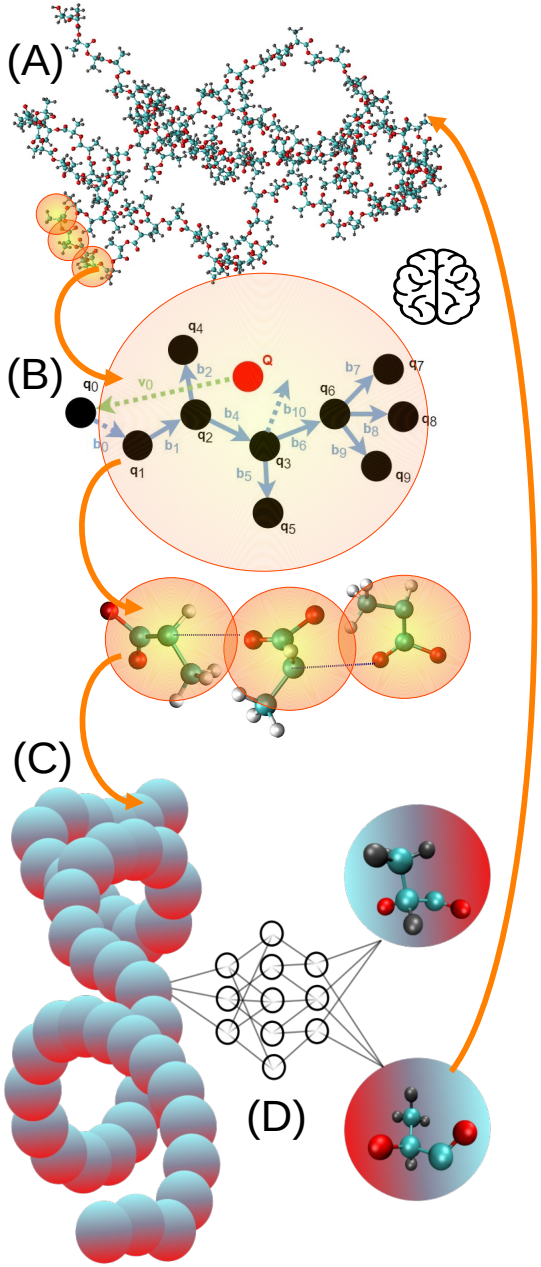
Backmapping procedure

(A) atomistic dataset, 5000 frames per system, training set: PLLA100, PDLA100 and Copo100

(B) encoding and learning
- convolutional neural network
- versatile: bond vectors and lengths
- local: no intermonomeric and intermolecular information

(C) coarse-graining, monomer-like representation

(D) backmapping
- verify the model
- testing the transferability



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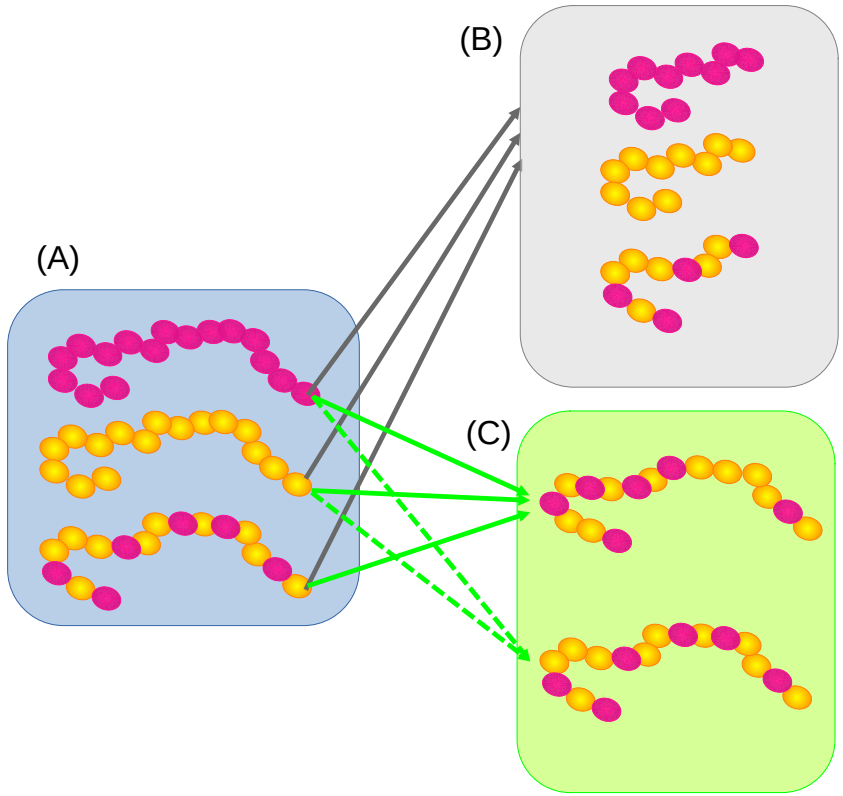
Backmapping procedure: transferability

(A) training set: PLLA100, PDLA100 and Copo100

(B) transferability across Mw
- ➔ PLLA30, PDLA30, Copo30

(C) chemical transferability
- ➔ copolymer with a different copolymer sequence
- ➔ copolymer trained solely on homopolymers



✓ possible extension to any molecular weight: industrially relevant Mw

✓ capability of creating any composition: mimicking conditions during synthesis

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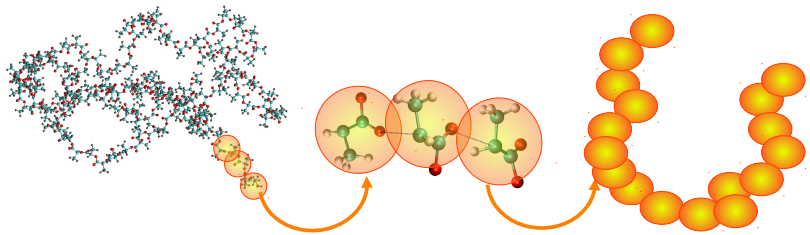
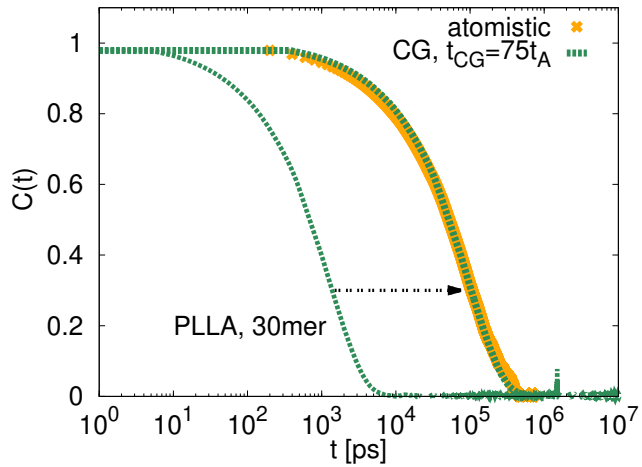
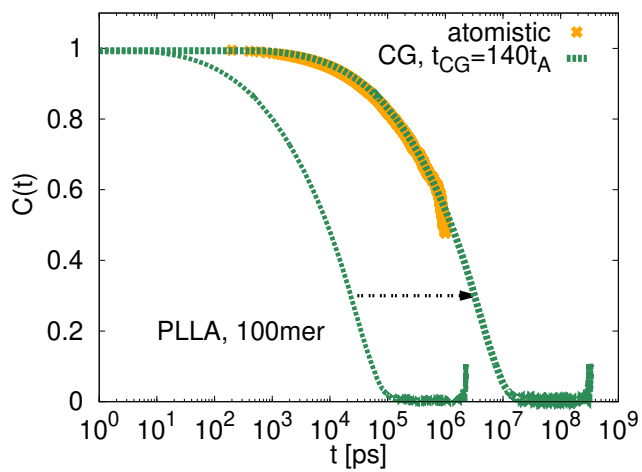
Coarse-graining procedure



- monomer-like coarse-graining, iterative Boltzmann inversion
- mapping of the time scales to correct the monomeric friction





Alireza F. Behbahani et al., Macromolecules (2021) 54 (6), 2740-2762

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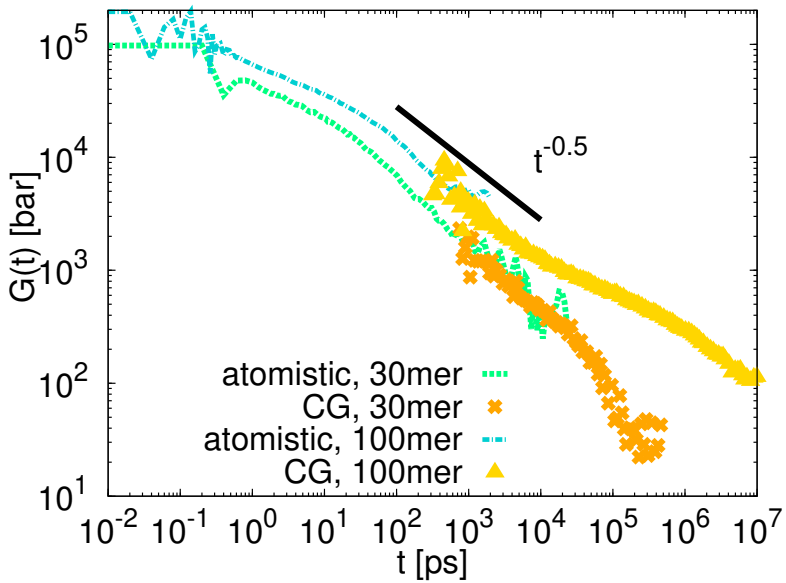
Stress relaxation modulus G(t)

- equilibrium simulations:

$$G(t) = \frac{V}{k_B T} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle$$

- connecting atomistic and mesoscale models to achieve the full relaxation spectrum



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Take-home message

- atomistic database for PLA of various molecular weights, stereochemistry and copolymer composition
- open-access backmapping tool employing convolutional neural networks, extensible for any chiral polymer
- systematic coarse-graining extending the time and length scale
- reference rheology data (to be continued)

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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
- ✏ Eleftherios Christofi, Petra Bačová, and Vagelis A. Harmandaris, Journal of Chemical Information and Modeling 2024 64 (6), 1853-1867: https://pubs.acs.org/doi/10.1021/acs.jcim.3c01870

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- *Gareth H. McKinley*, Massachusetts Institute of Technology, USA
- *Doros Theodorou*, National Technical University of Athens, GREECE
- *Dimitris Vlassopoulos*, University of Crete, GREECE

Key dates

- Abstract submission: **March 12th, 2024 - April 20th, 2024** -- Notification of acceptance: April 25th, 2024
- Early registration: May 31st, 2024 -- Late registration: June 30th, 2024