Grünes Plastik - von der Vision zur Anwendung

Which bio to solve which problem, and how? Setting today's scene.

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Aachen Maastricht Institute for Biobased Materials
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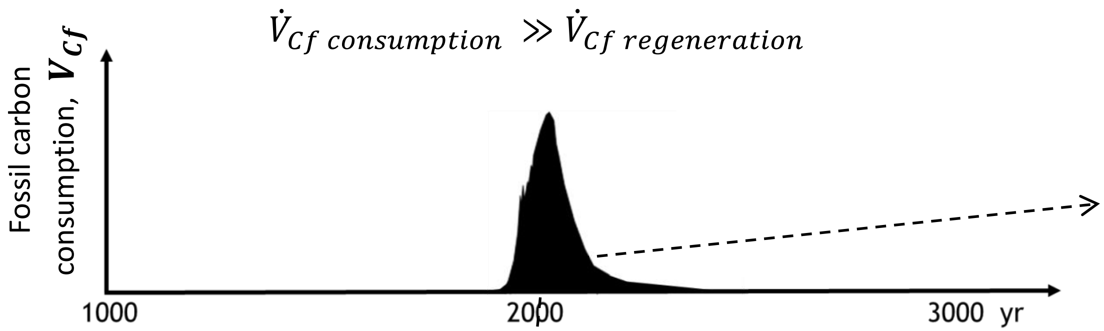
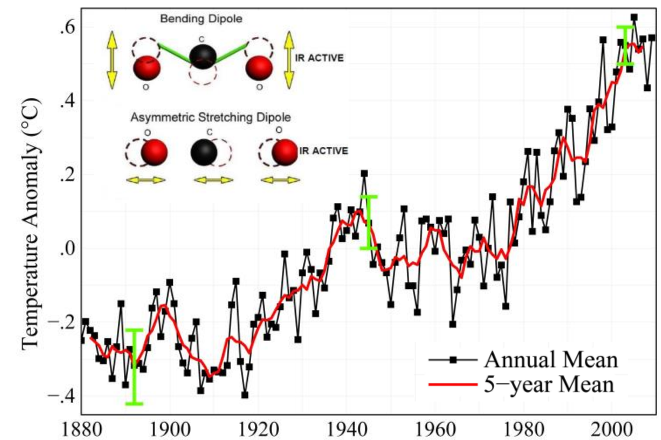
CO_2 accumulation in earth's atmosphere and oceans

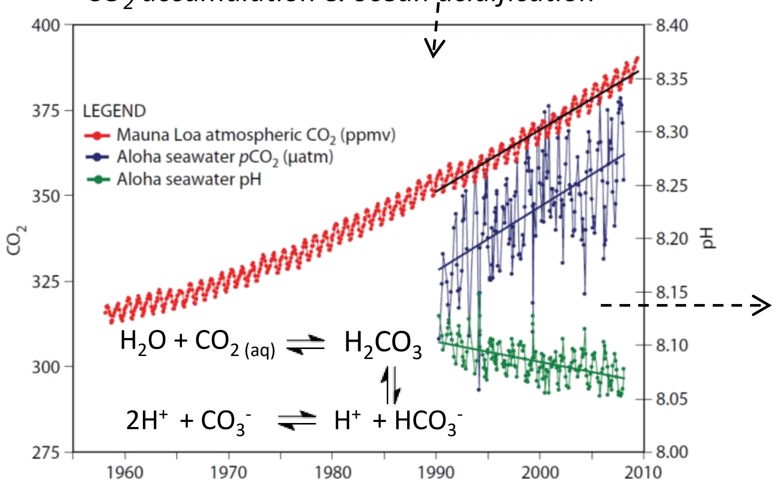


Global land & ocean warming

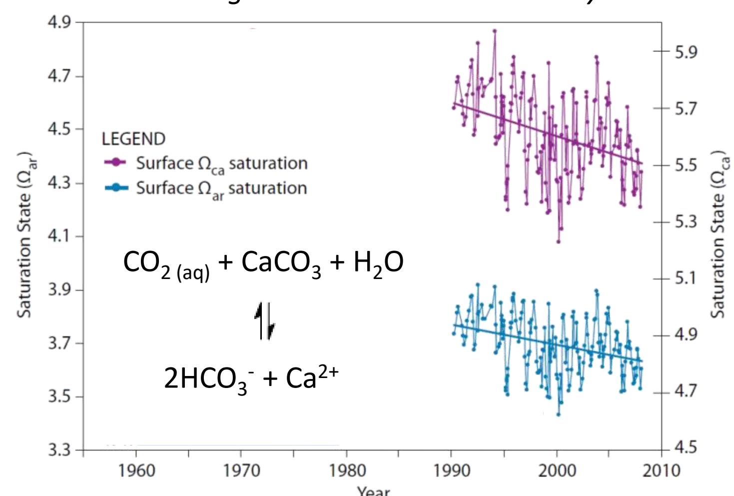


NASA 2009

CO_2 accumulation & ocean acidification



Unbalancing ocean carbonate chemistry



Feely 2009

No past event parallels present and projected rates of disrupting the balance of ocean carbonate chemistry - a consequence of the present ***unprecedented rapidity of CO_2 release****. (Hönisch, 2012)*

CO_2 accumulation in earth's atmosphere and oceans

A threat to marine biodiversity

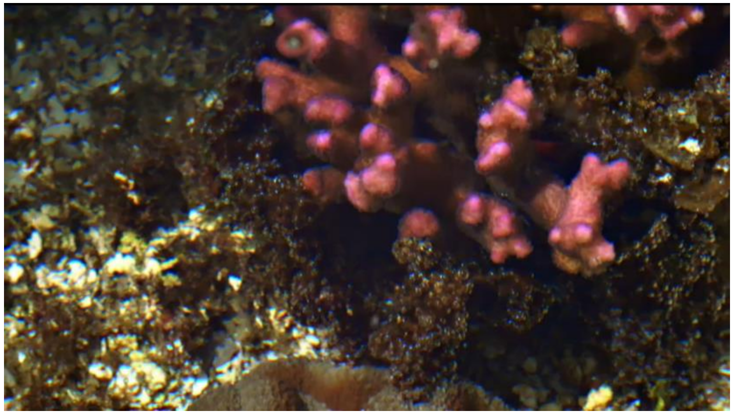
(Van Hooijdonk, 2013)

CO_2 accumulation in earth's atmosphere and oceans

A threat to marine biodiversity

12 months reference: *healthy condition*

12 months acidified: *slow calcification, "osteoporosis"*



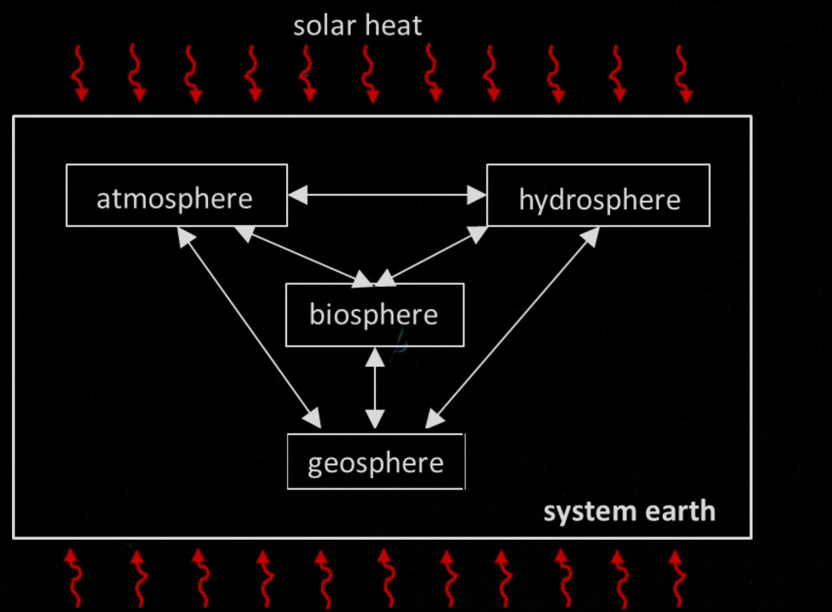
12 months ΔT = 4°C: *high mortality, bacterial slime*

12 months acidified and ΔT = 4°C: *dead and dissolving*

(Van Hooijdonk, 2013)

CO_2 accumulation in earth's atmosphere and oceans

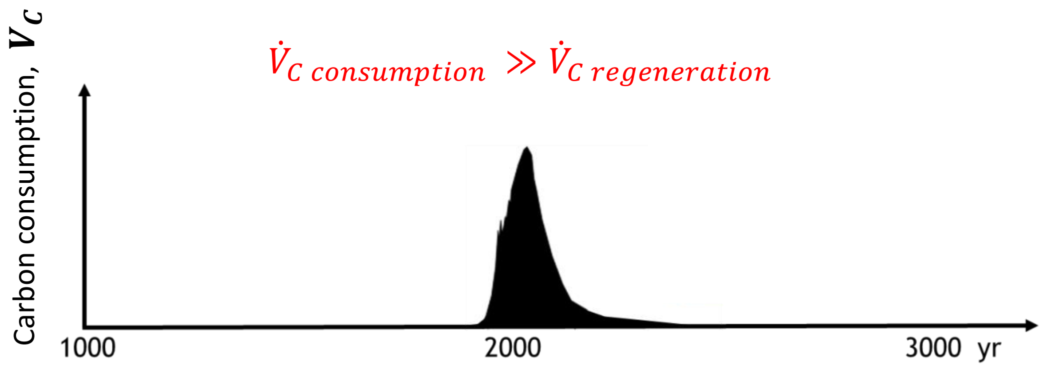
*Global change & **symbiosis with system earth***

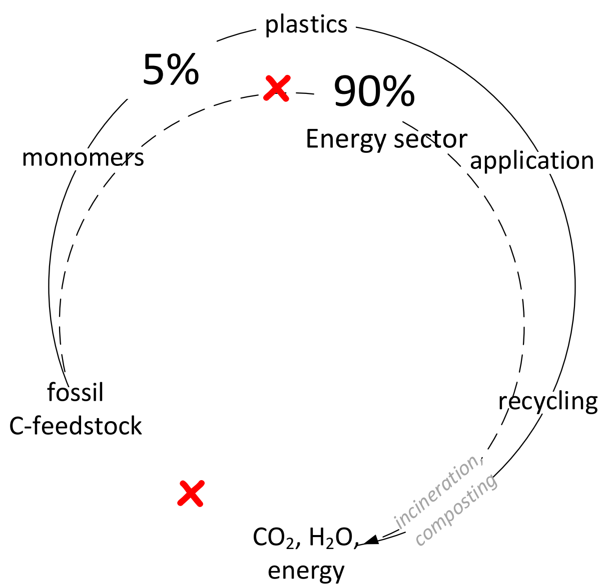


(P. Westbroek)

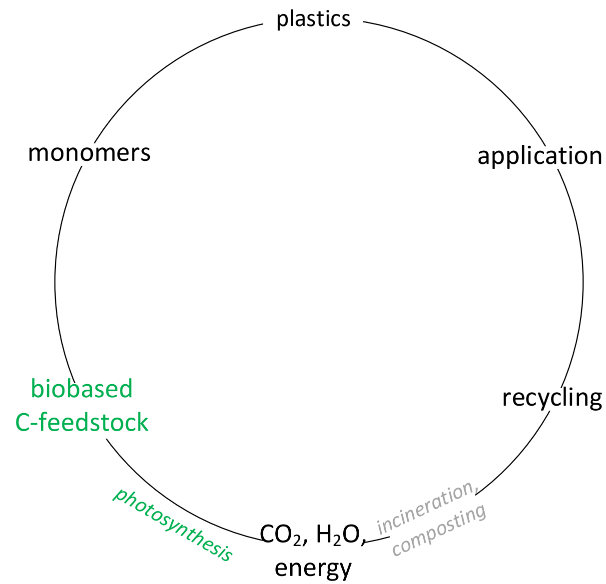
(Earth rise, NASA 1968)

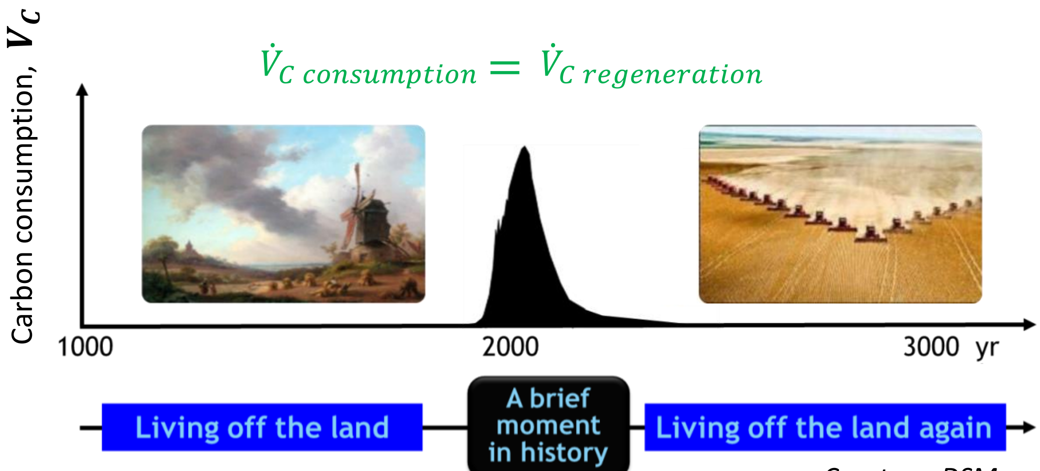
CO2 accumulation in earth's atmosphere and oceans





Rebalancing CO_2 emissions; a must for BioBased resources



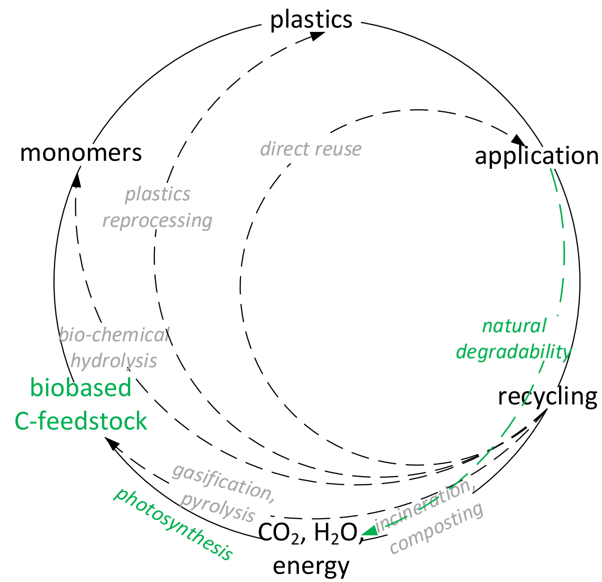


Courtesy: DSM

Perturbed CO_2 formation rates without recycling; plastic pollution

If recycled, plastics are:

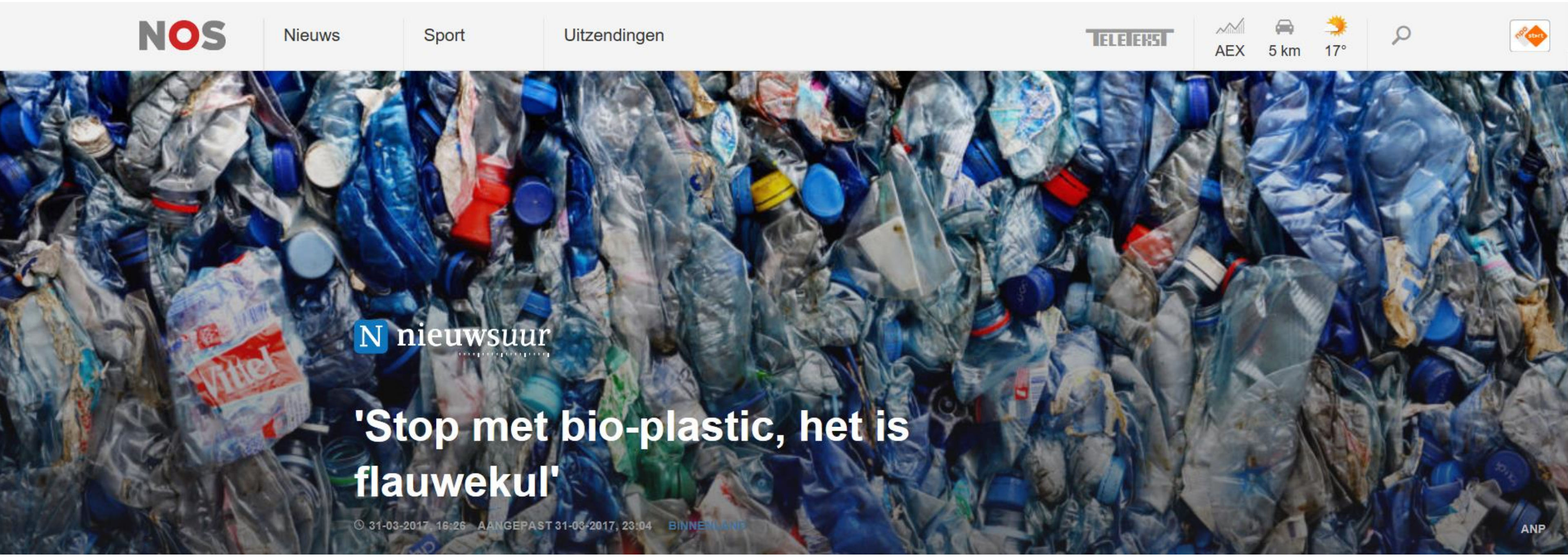
- made via energy efficient manufacturing
- found in sustainable, energy saving solutions like light-weight transportation, insulation, easy communication
- easily recyclable, preserving its carbon nutrients and caloric value



Without recycling, plastics are:

- a threat to marine biota and health via entering food chain
- clogging water drainage and purification systems, causing floods and spreading of diseases like malaria and Zika

BioBased vs. Biodegradables – lost in definitions



"Bio-plastics do not dissolve once left in the bushes. Neither in the sea."

(plastic soup foundation)

"Too many non-compostable plastics end up in our organic waste streams."

(Attero)

BioBased vs. Biodegradables – lost in definitions

Compostable
EN13432:2000

Industrial composting: 70°C, not solving plastic pollution.

BioBased vs. Biodegradables – lost in definitions

Industrial composting: 70°C, not solving plastic pollution.

Boyan Slat: 7,250,000,000 kg per gyre in 5 years

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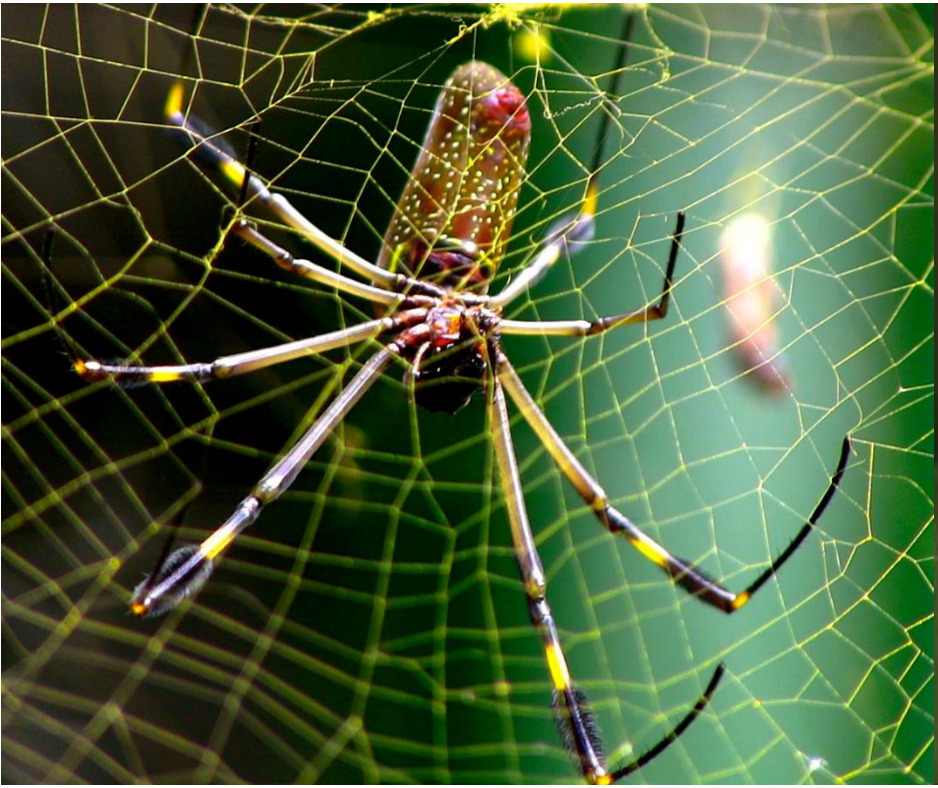
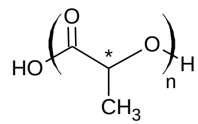
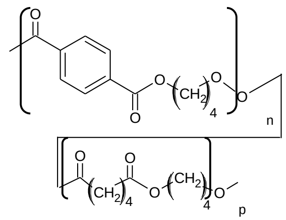
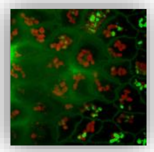
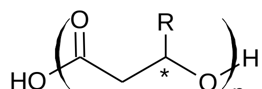
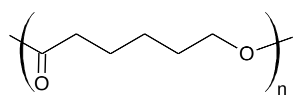
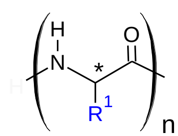
*“Prosperity and adequate recycling are globally unbalanced.
Fate of plastics (products) is responsibility of its creators!”*

Timed vs. naturally actuated biodegradation



Trends: Biomimetics in biodegradation, nano-dietary supplements, often first biomedical

BioBased vs. Biodegradables – consensus of definitions

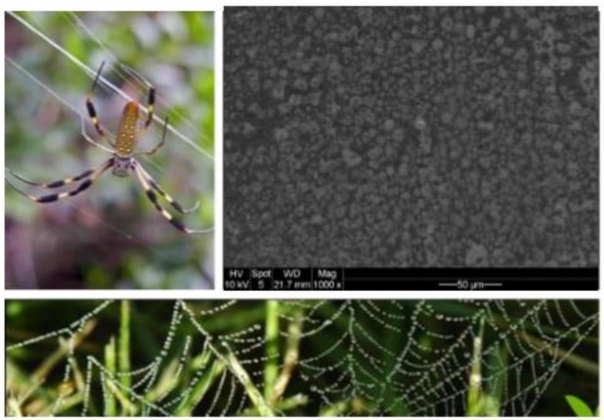
source	polymer	structure	T_g (°C)	T_m (°C)	biodegradable	conclusion
	poly(lactide)		57	175	yes, in industrial composting (**T>70°C**)	**recycling**
	poly(butylene adipate-co-terephthalate)		61	120	yes, in industrial composting (**T>70°C**)	**recycling**
	poly(hydroxy alkanoate)	 with R = CH_3, CH_2CH_3	**< 5**	< 180	yes, even in nature	**uncontrolled** natural permanent degradability
	poly-ε-caprolacton		**-60**	60	sometimes, even in nature	**uncontrolled** natural permanent degradability
	silks		**< 5 -180**	$T_m > T_d$	yes, even in nature	**controlled** naturally actuated degradability

Molecular mobility, indicated by T_g, is key for enzyme operations.

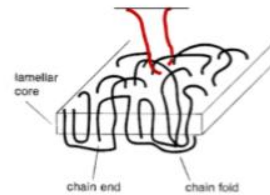
BioBased vs. Biodegradables – what is biodegradability?

$$C_{pol.material} + O_2 \xrightarrow{aerobic} CO_2 + H_2O + C_{residual} + C_{biomass}$$

water as actuator

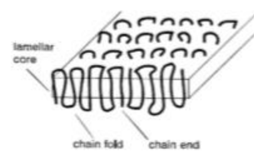


but there is more



PHB fast crystallized:

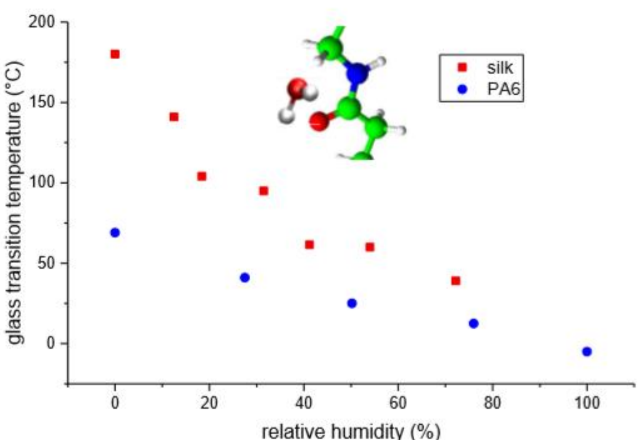
- Switch board, entangled
- Non or poorly biodegradable

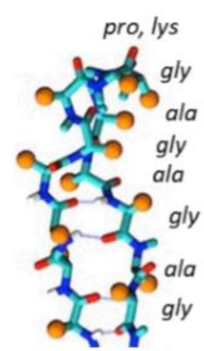


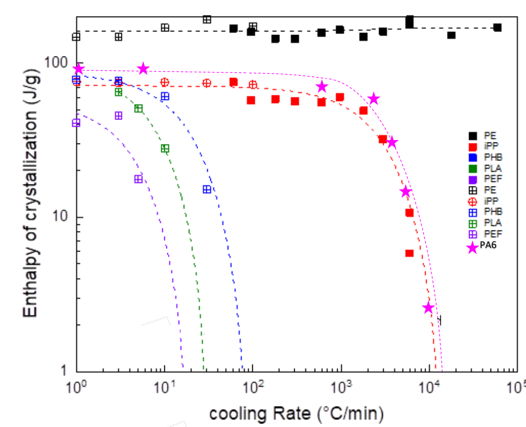
PHB slowly crystallized:

- Adjacent re-entry, disentangled
- Biodegradable!

Hocking P.J. *Macromolecules* **1996**. 29(7): p. 2472-2478







BioBased: Biological monomers, man-made polymerization

source	monomer	polymer
	lactide	poly(lactide) (PLA)
	succinic acid	poly(buthylene-succinate) (PBS)
	11-amino-undecanoic acid 1,10-dodecane-dioic acid	polyamide 11 polyamide 4,10
	5-amino valeric acid	polyamide 5

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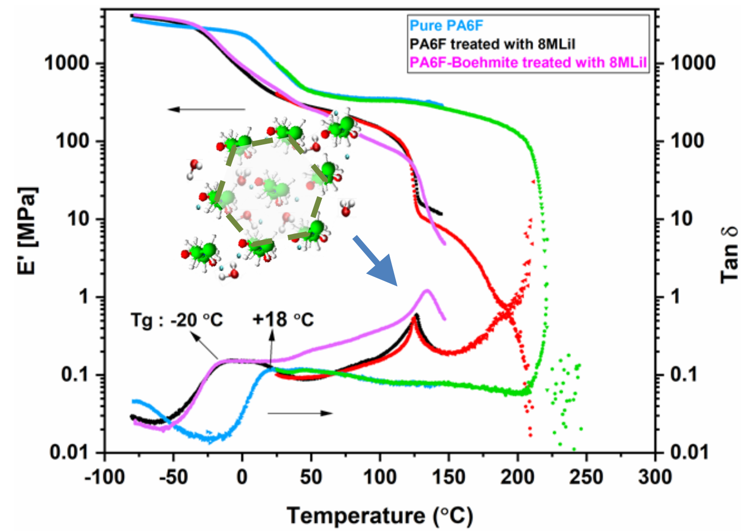
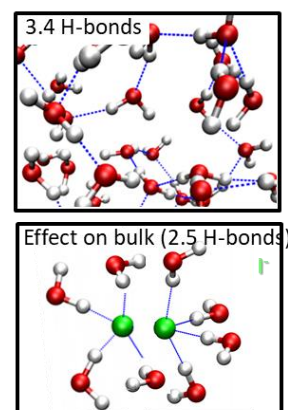
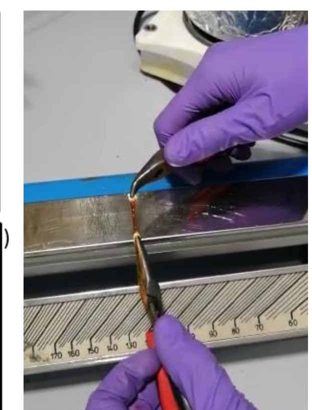
Polarity/hydrophilicity

Hydrophilicity: Water and ion assisted processing into unique, conventionally not attainable orientation.







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	furandi-carboxylic acid	poly(ethylene-furanoate) (PEF)

Towards engineering plastics on the expense of biodegradability!

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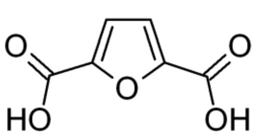
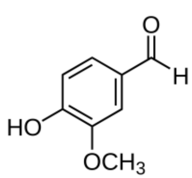
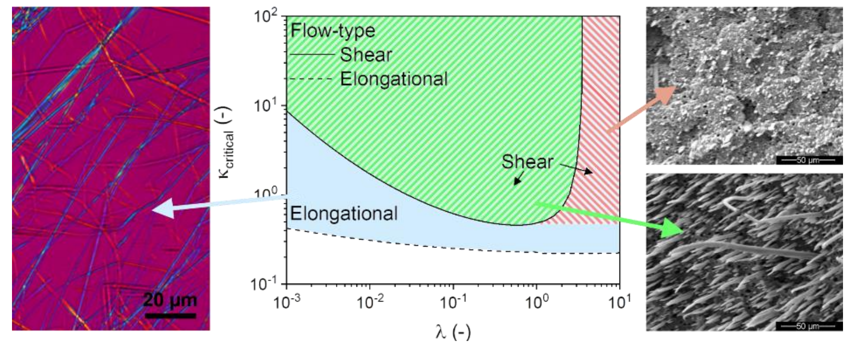


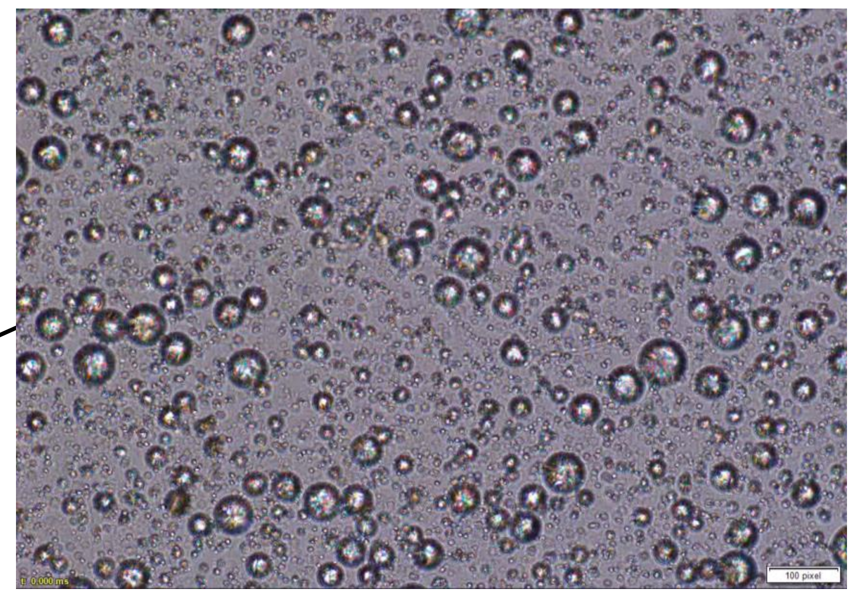


aromaticity/rigidity

+ vanillic acid
+ hydroxy-benzoic acid

Circularity: Melt re-processable self-reinforced biobased liquid crystalline polyester – PLA blends





Courtesy: Gijs De Kort (AMIBM)

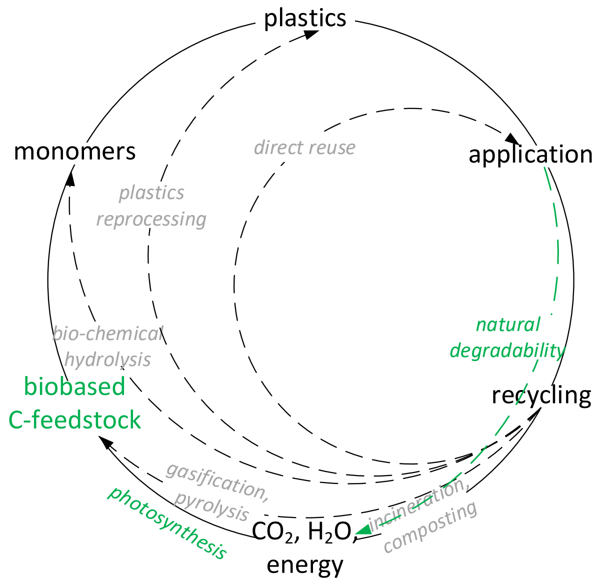
Which bio to solve which problem

Biodegradables in tackling pollution:

- Controlled degradation **V**, demands correct information and discipline **X.**
- Naturally actuated biodegradation **X**, we're learning.

BioBased polymeric materials:

- Processing, additives, performance **V**
- **Biomedical applications as catalyst in the fossil-to-biobased transition; <u>from plant to implant</u>**



To value bio:

- Identify which bio first
- New, circular value chains
- New parameters
- Your motivation

Green plastics; following the Green Chemistry Principles

Green Chemistry Principles enable scientists and engineers to protect and benefit the economy, people and the planet by finding creative and innovative ways to reduce waste, conserve energy, and discover replacements for hazardous substances.

1. Better prevent waste than treat or clean up waste.
2. Maximize incorporation of all materials used into the final product.
3. Use and generate substances with little or no toxicity to human health and the environment.
4. Preserve efficacy of function while reducing toxicity.
5. Prevent or minimize use of auxiliary substances.
6. Minimize energy requirements, recognized for environmental and economic impact.
7. Feedstock should be renewable rather than depleting.
8. Minimize unnecessary derivatization to minimize reagents and waste.
9. Catalytic reagents are superior to stoichiometric reagents.
10. Design for degradation into innocuous products, not persisting in nature.
11. Real-time analysis for pollution prevention.
12. Inherently Safer Chemistry for Accident Prevention.

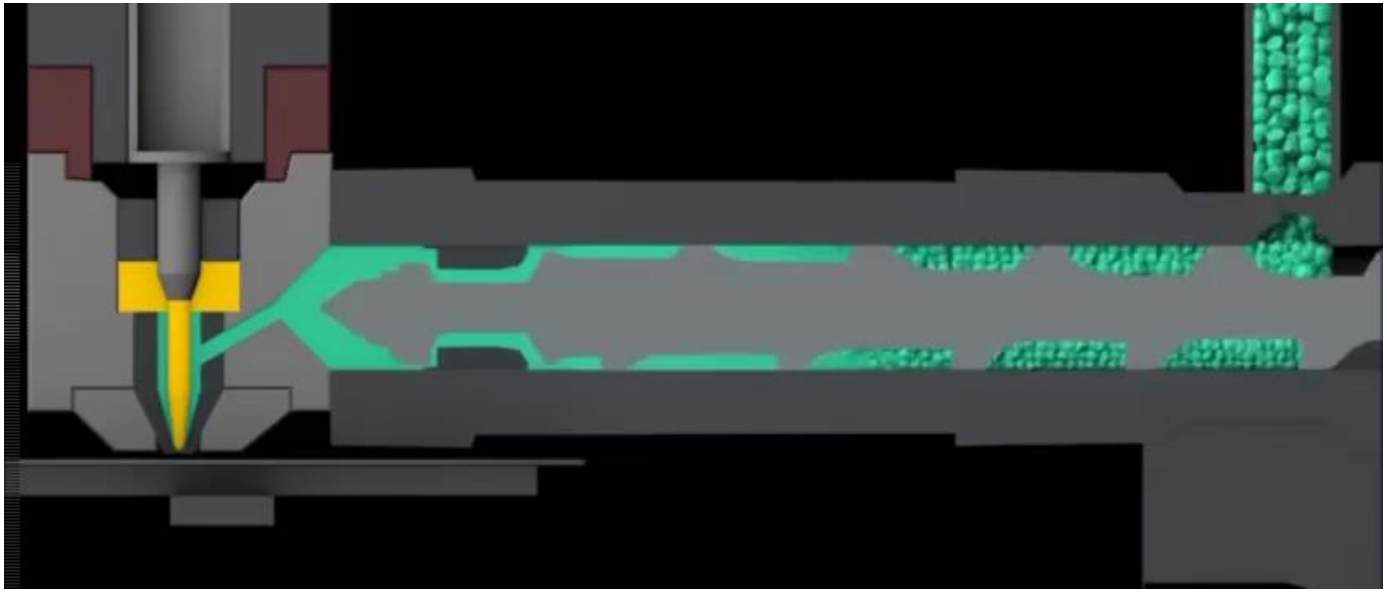
www.acs.org

“No drop-in, but biologically induced material functionalities with added value, justification of higher costs.”

"Only if one understands polymeric material functionalities down to morphological, structural and ultimately molecular length-scales, the added technical functionality of biobased molecules is recognised."

Example, defining bio-induced functionality and value

Evergreen in 3D Printing of thermoplastics: break the compromise between in molecular diffusion and crystallization rates to gain strength in *z* direction.

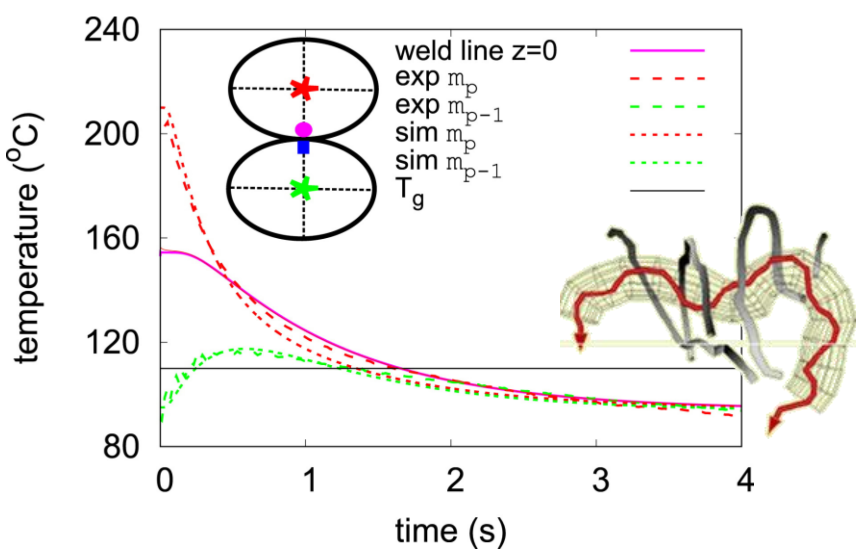


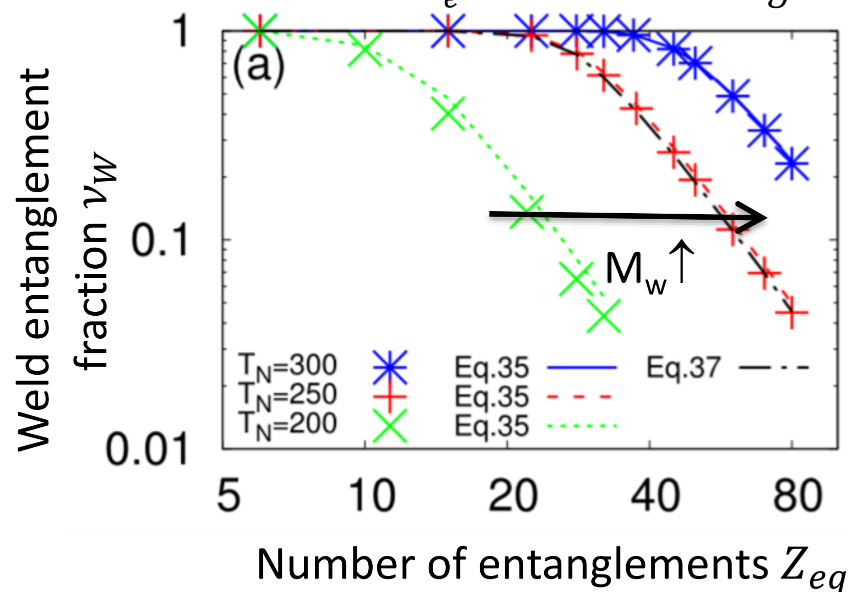
Arburg Freeformer

Example, defining bio-induced functionality and value

Evergreen in 3D Printing of thermoplastics: break the compromise between in molecular diffusion and crystallization rates to gain strength in *z* direction.

$$M_e = 1200 - 1400\ g \cdot mol^{-1}$$





$$\frac{\chi}{R_g} = \left(36 \int_{t_w}^{t_g{}^W} \frac{1}{\tau_d\left(T(t),\dot{\gamma}(t)\right)} dt'\right)^{1/4}$$

χ interpenetration depth
R_g radius of gyration

Typically: 50% of bulk entanglement density

$$M_e^W = \frac{M_e}{\nu_W} \qquad G_c^W \sim \left(1 - \frac{M_e^W}{qM_w}\right)^2 \sim \left(1 - \frac{1}{q\nu_W Z_{eq}}\right)^2$$

Q: correction factor 0.6 for PC

McIlroy, C.; Olmsted, P.D., *Polymer* ***2017****, 123, 376-391*

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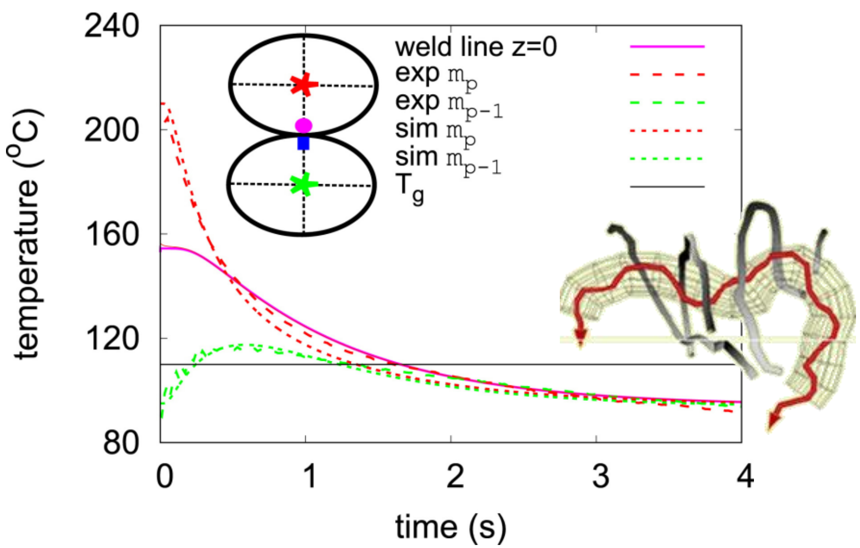

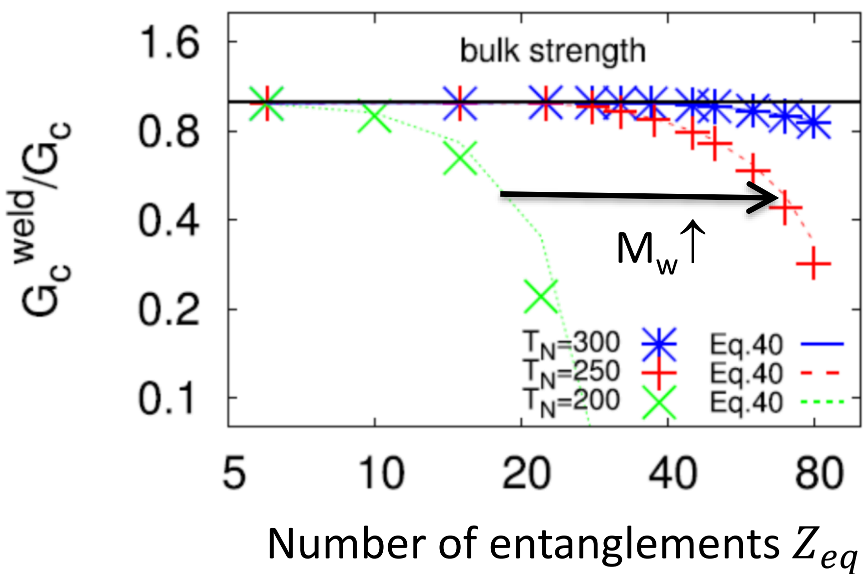

$$\frac{\chi}{R_g} = \left(36 \int_{t_w}^{t_g{}^W} \frac{1}{\tau_d\big(T(t), \dot{\gamma}(t)\big)} dt' \right)^{1/4}$$

χ *interpenetration depth*
R_g *radius of gyration*

Typically: 50% of bulk entanglement density
$\rightarrow$ poor *z*-mechanics

<u>The need for crystallinity in anchoring chains!</u>

McIlroy, C.; Olmsted, P.D., *Polymer* ***2017****, 123, 376-391*

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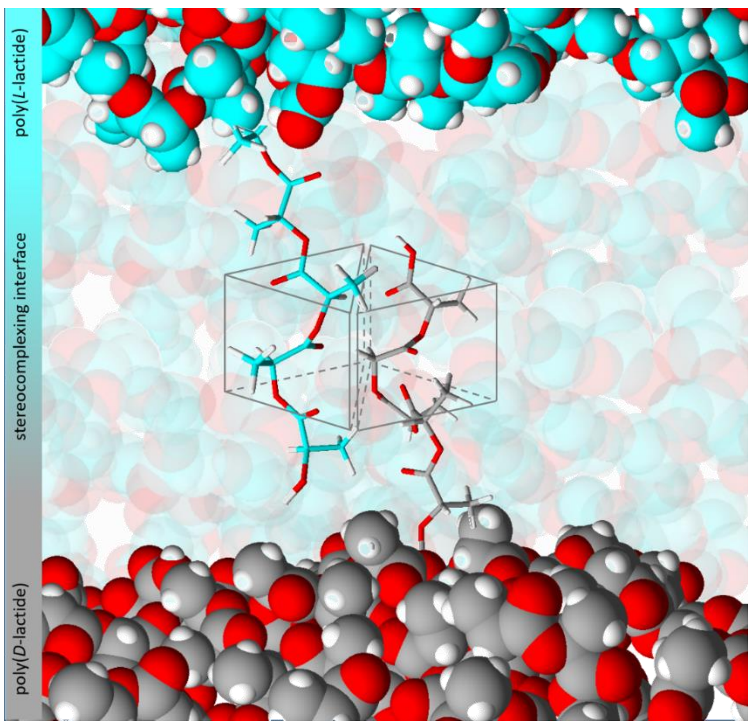
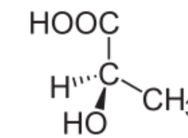
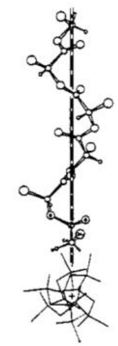


T_m ~ 170°C

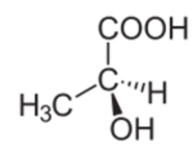


L-LA



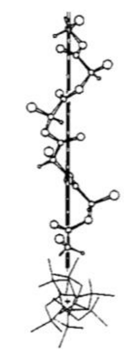
poly(L-lactide)

T_m ~ 230°C



D-LA

T_m ~ 170°C



poly(D-lactide)

Srinivas, V. et al. *ACS Appl. Polym. Mater.* **2019***, 1,* 2131-2139.
Srinivas, V. et al *Additive Manufacturing* **2020**, accepted)

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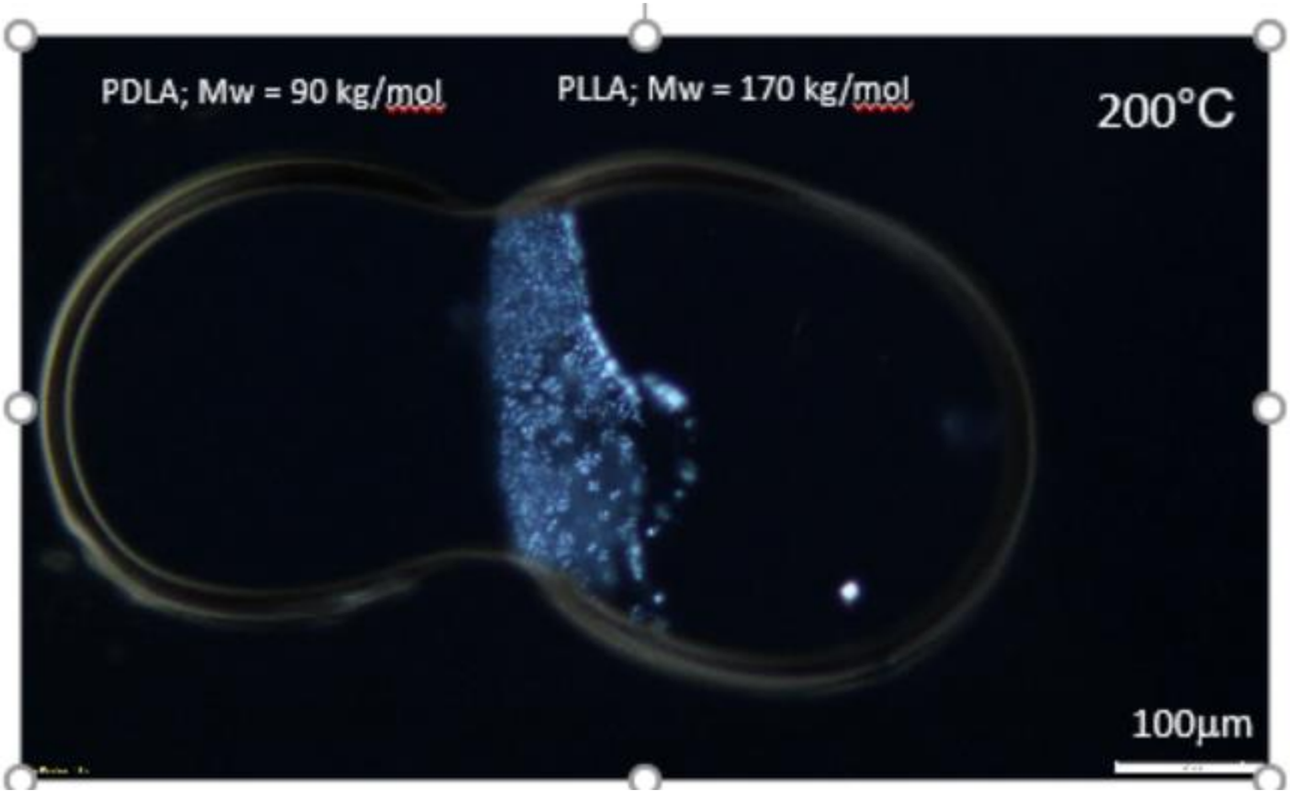

Chirality, naturally occurring in many building blocks/monomers.

Which bio to secure quality of life