Toughening of poly(lactic acid) by various poly(caprolactone-co-(D-lactic acid))-copolymers

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Fraunhofer UMSICHT
Bio-Based Plastics

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From laboratory to industrial practice
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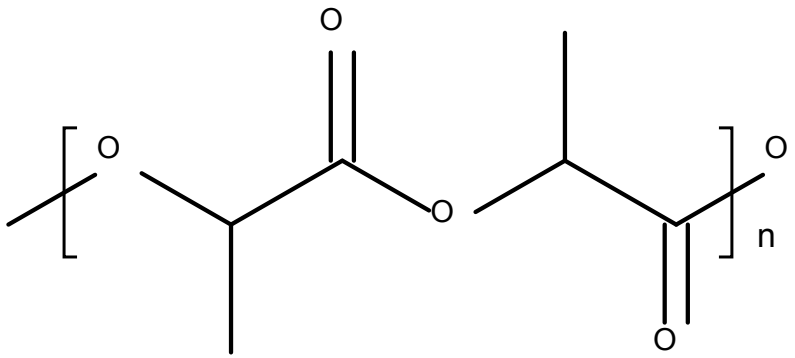
Poly(lactic acid) (PLA)

Biobased polyester

- Monomer unit: lactic acid
  - Asymmetric carbon atom

  → two enantiomers



Major drawbacks of PLLA:

- Low elongation of break
- Low toughness

E-modulus	3550 MPa
Tensile strength	59 MPa
Elongation at break	1,5 %
Charpy-toughness	1,4 kJ/m²

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Plasticizing poly(lactic acid)

- External plasticizers: citrate esters, (poly-)adipates; oligomeric polyethylenglykol (PEG), polycaprolactone (PCL);
- Polymer blends with: PBAT, PBST, Starch

- drawback:
  migration of the plasticizer

Source: Pixabay

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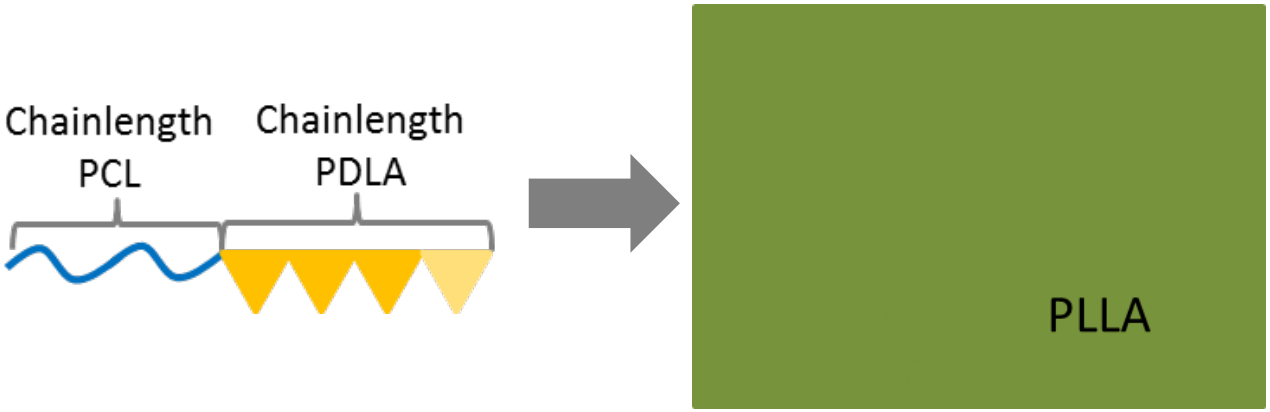
Trapping the plasticizer via stereocomplex crystallization

- Synthesis of various PDLA-b-PCL blockcopolymers with
  - PCL plasticizing segment and
  - PDLA compatibilizing segment
- Optimizing chemical interaction between PDLA-blocks and PLLA-matrix



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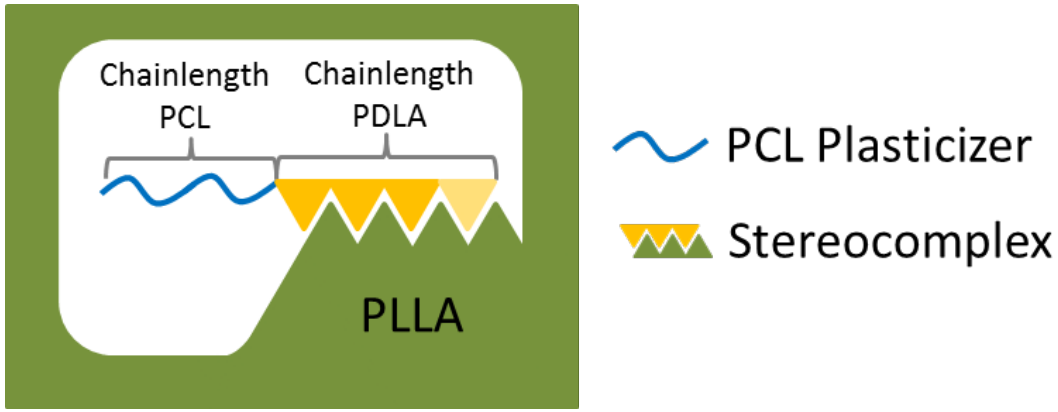

Status quo: Blends of PLLA and PCL

- Blends of 90% w/w PLLA and 10% w/w PCL with various molecular weight were prepared
- Flory-Huggins calculations show a theoretical miscibility of all prepared blends

Fox-Flory equation:

- Shift of T_g from 58°C to 42°C

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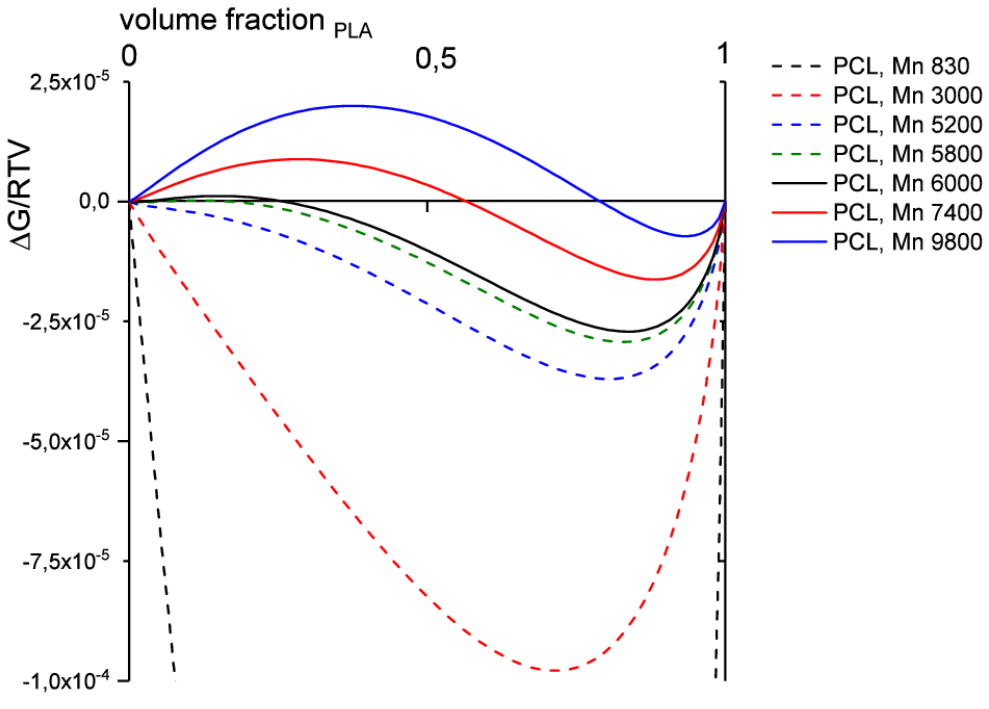

Fox-Flory equation:

- Shift of T_g from 58°C to 42°C

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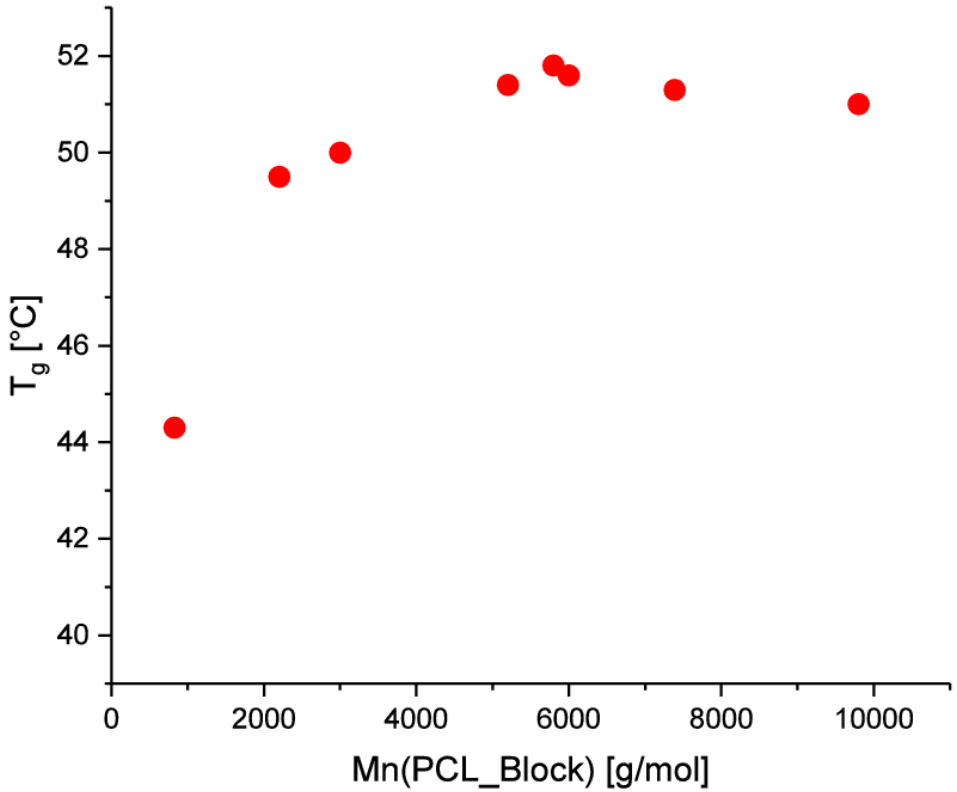
Status Quo: Blends of PLLA and PCL

- Observed shift of T_g is smaller than in theory
  - Low molecular weight oligomers lead to lower T_g
- Crystallization peak of PCL
  - Phase separation



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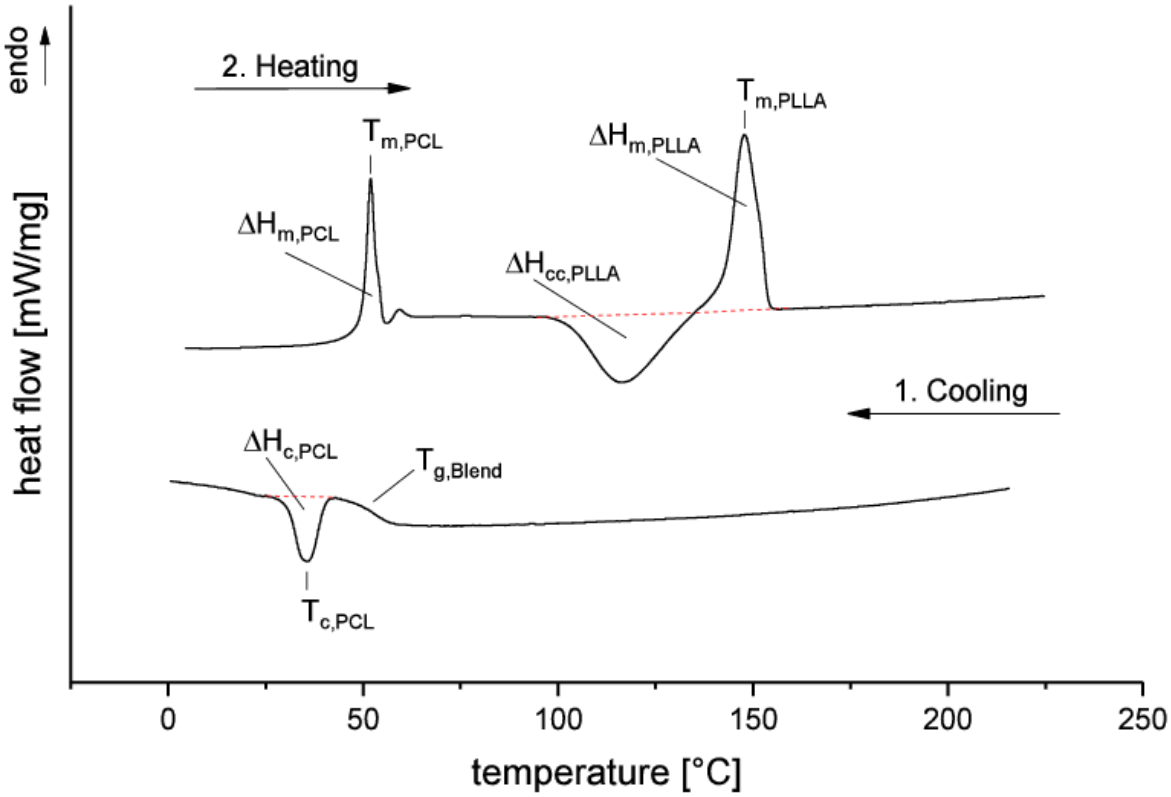

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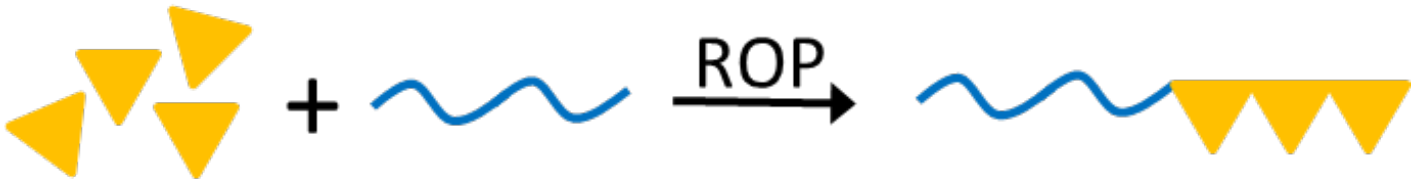
Linear PDLA-b-PCL blockcopolymers

- Synthesis of linear PDLA-b-PCL blockcopolymers via ring-opening polymerization of D-Lactide



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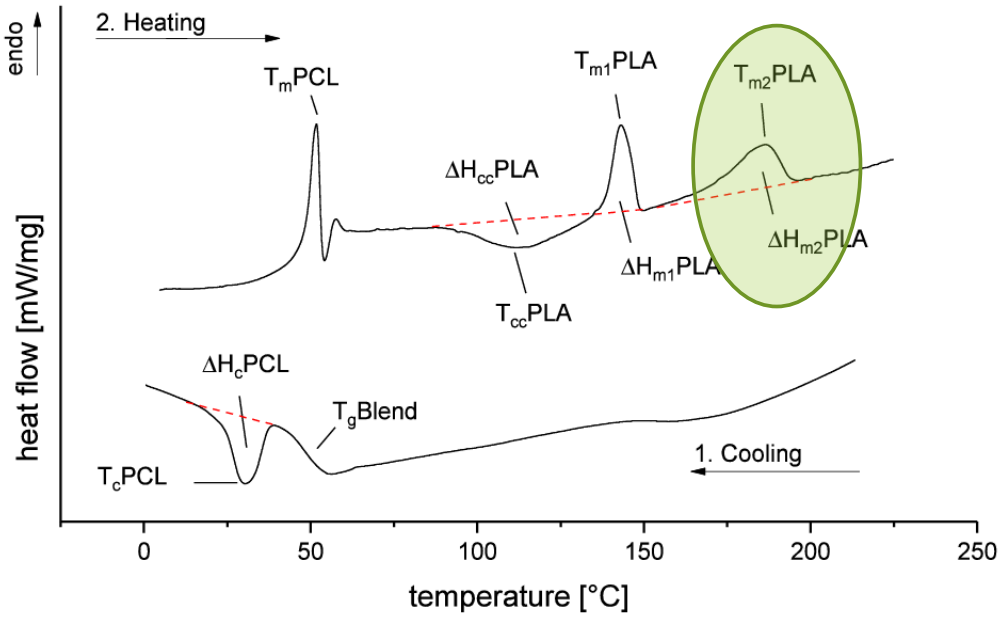
Linear PDLA-b-PCL blockcopolymers

Effects on thermal behaviour

- Blends of PLA and a constant PCL content of 10 % w/w
- Second melting peak:
  → stereocomplex
- Stereocomplex formation leads to lower crystallinity of PCL phase
- Lower crystallinity of PCL phase increases its plasticizing effect



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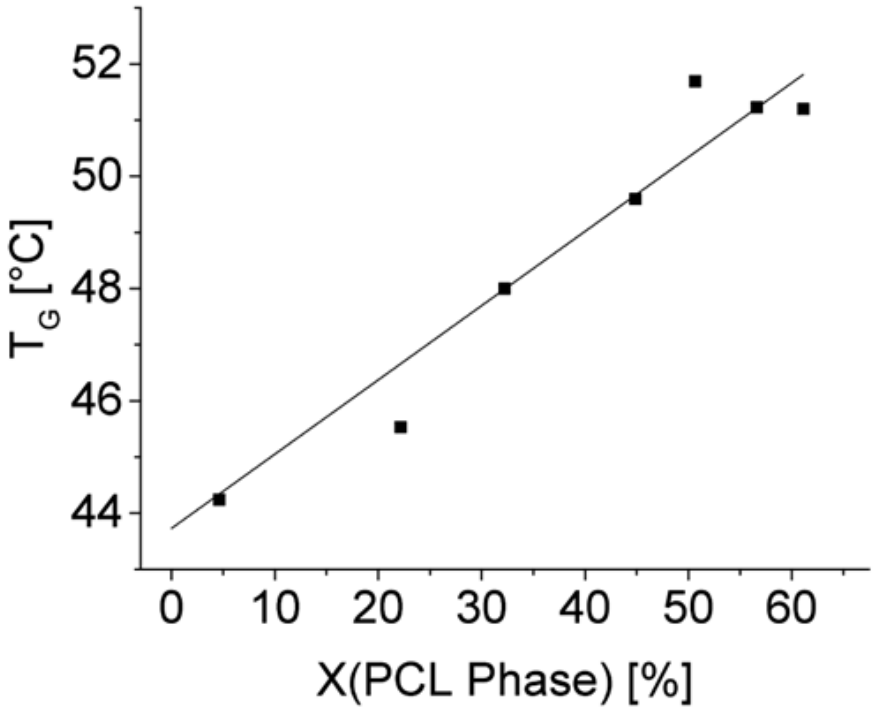

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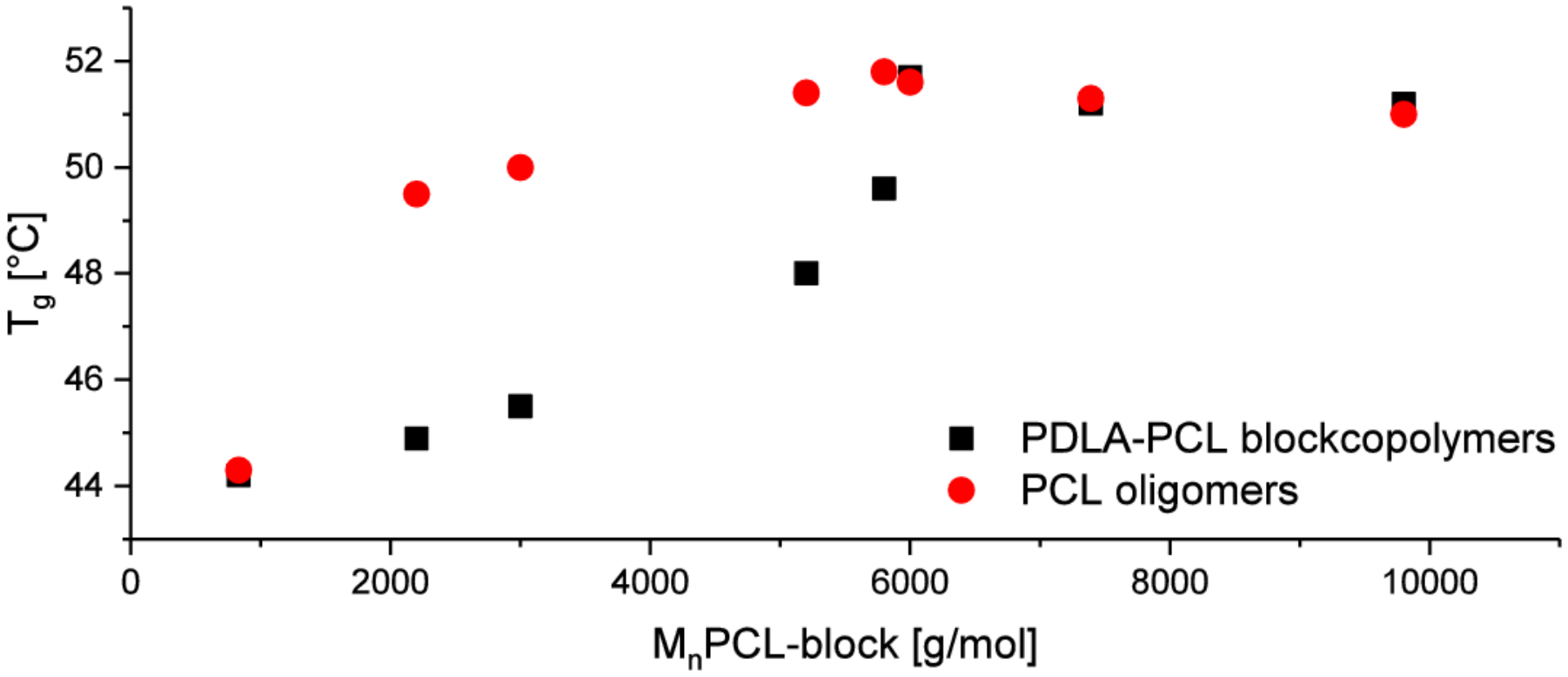

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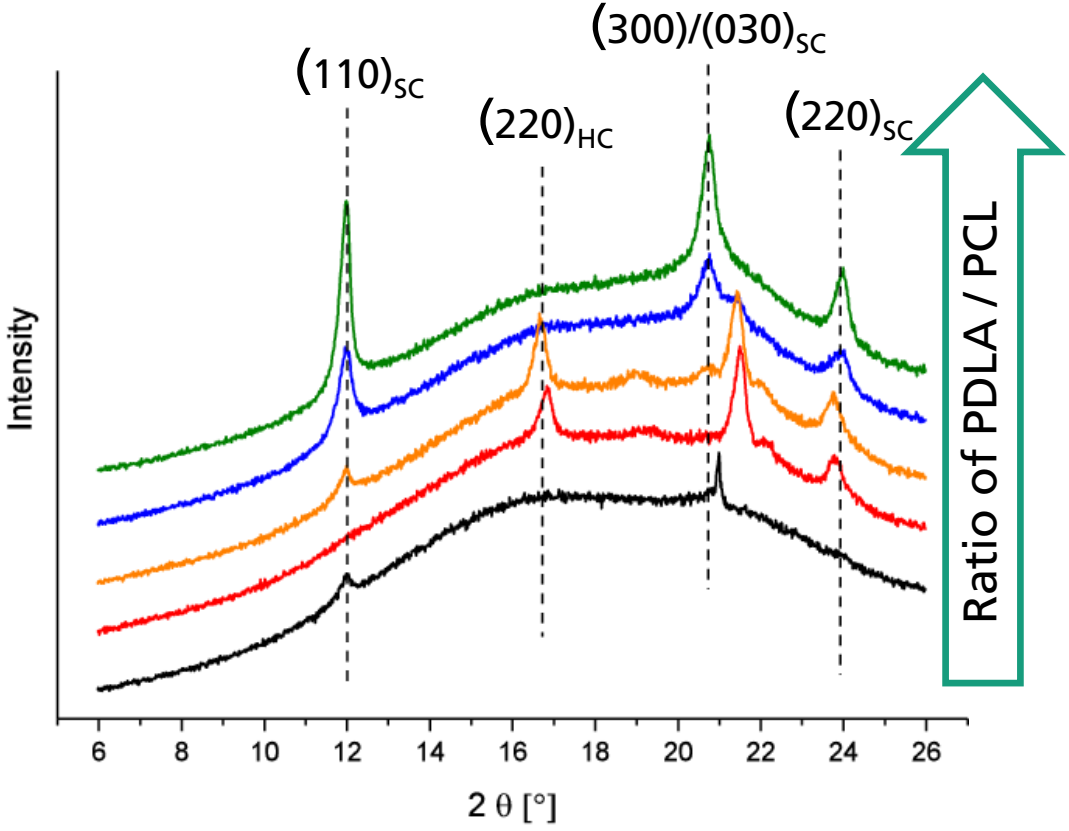
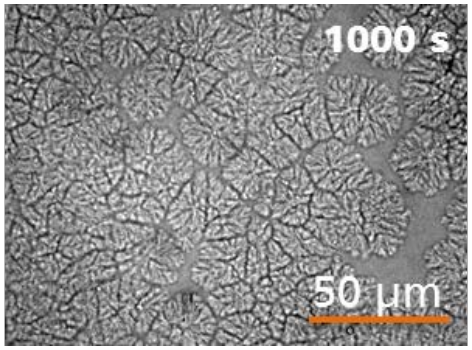
Linear PDLA-b-PCL blockcopolymers

Effect on crystallization

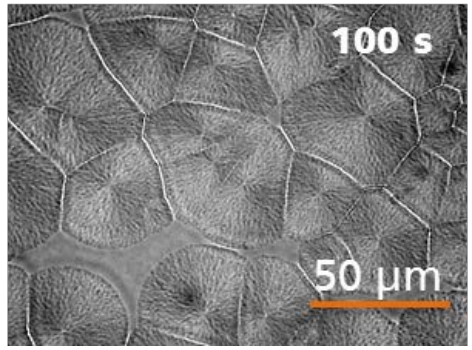
- XRD analysis



- Thermo optical analysis



PLA + PDLA-b-PCL



PLA + PDLA

- Slower crystallization kinetics compared to PLA stereocomplex crystals

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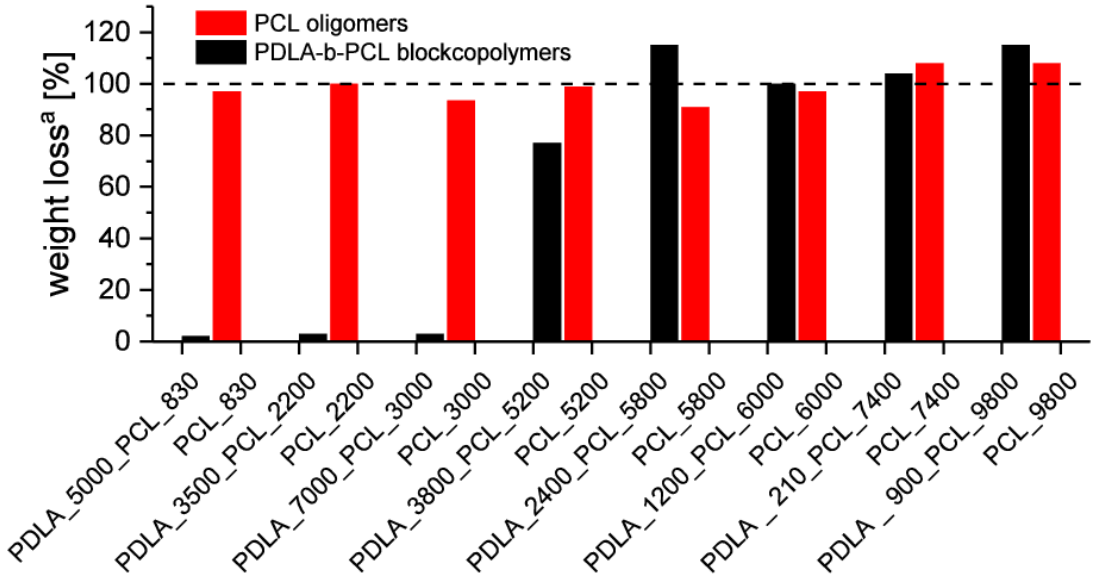
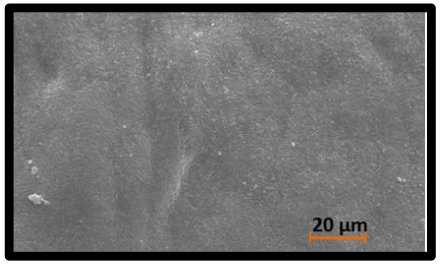
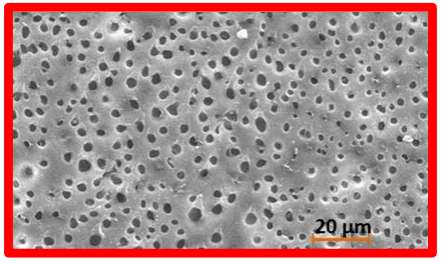
Linear PDLA-b-PCL blockcopolymers

Effects on elongation and migration

Blockcopolymer	Young`s-modulus [Mpa]	Tensile strength [Mpa]	Elongation at break [%]
-	1590 ± 492	58,2 ± 6,1	2,1 ± 0,2
PDLA_5000_PCL_830	3980 ± 502	120,0 ± 24,3	2,7 ± 0,6
PDLA_7000_PCL_3000	2130 ± 618	68,6 ± 2,5	2,6 ± 0,3
PDLA_3800_PCL_5200	2060 ± 70	57,2 ± 2,3	4,9 ± 3,0







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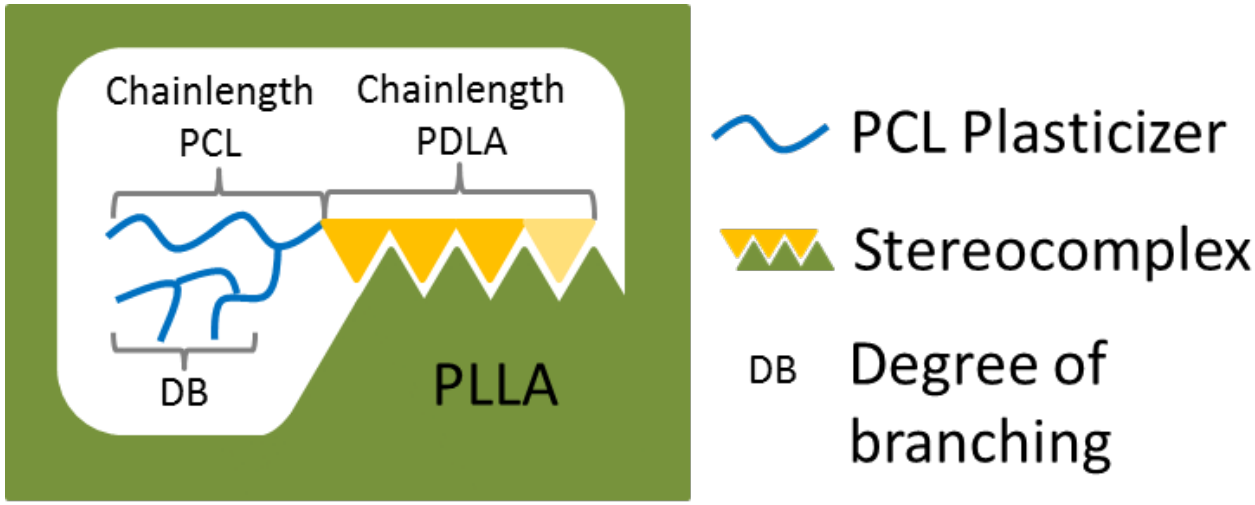
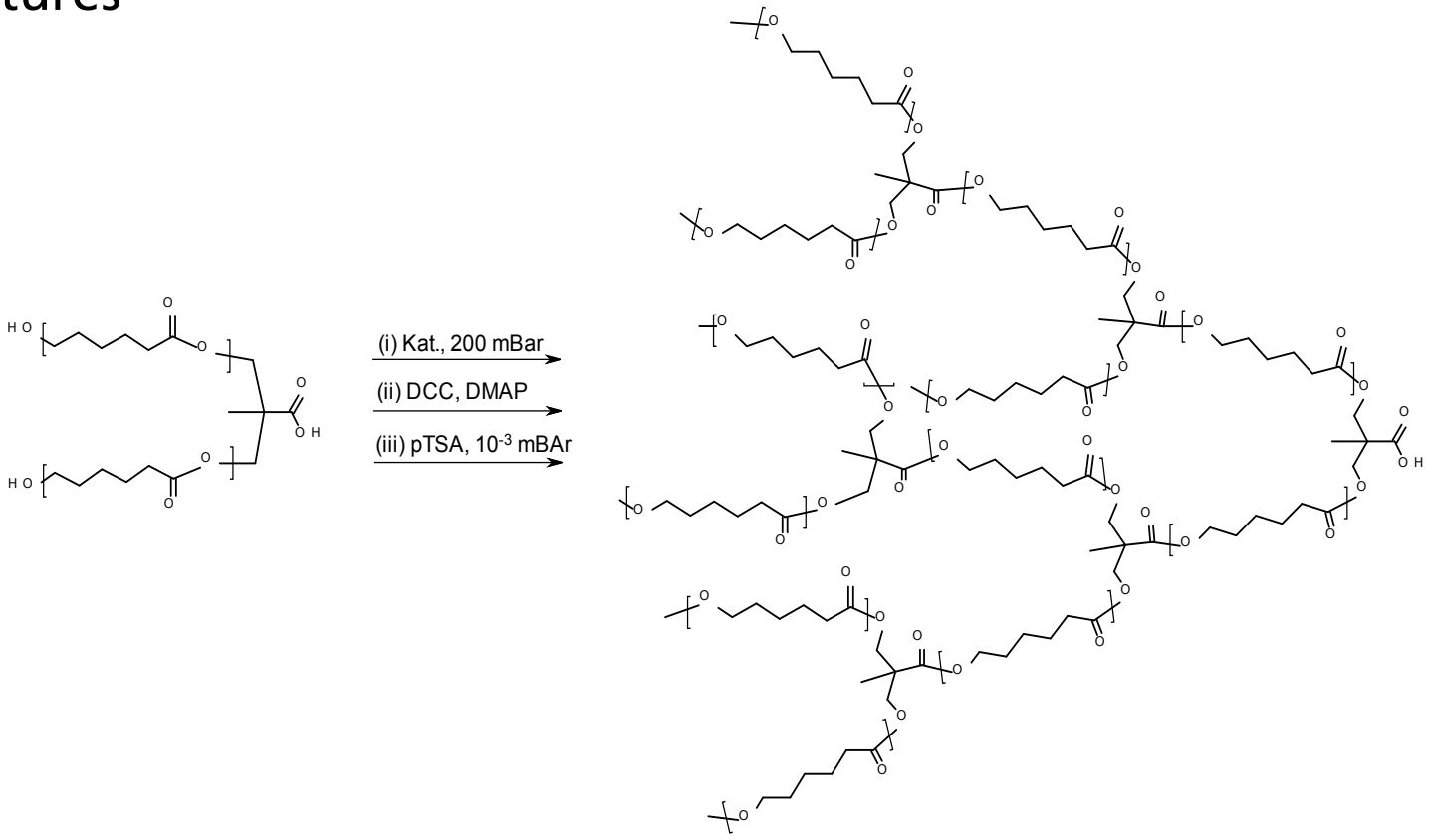
Branched PDLA-b-PCL blockcopolymers

- Modulation of PCL crystallinity via incorporation of branching points



Branched PDLA-b-PCL blockcopolymers

- Synthesis of AB_2 macromonomers and further esterification to branched structures



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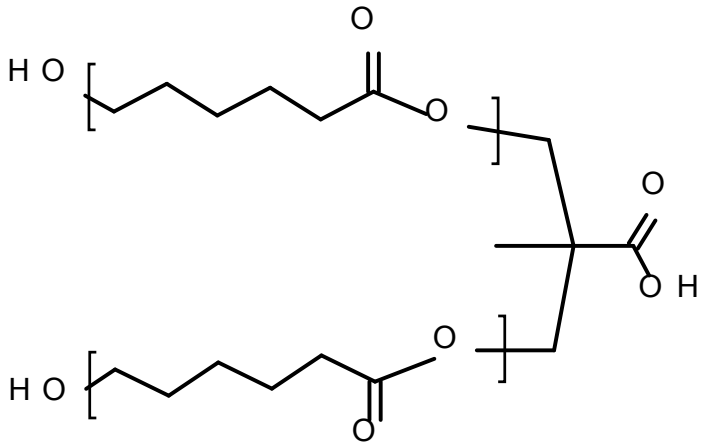
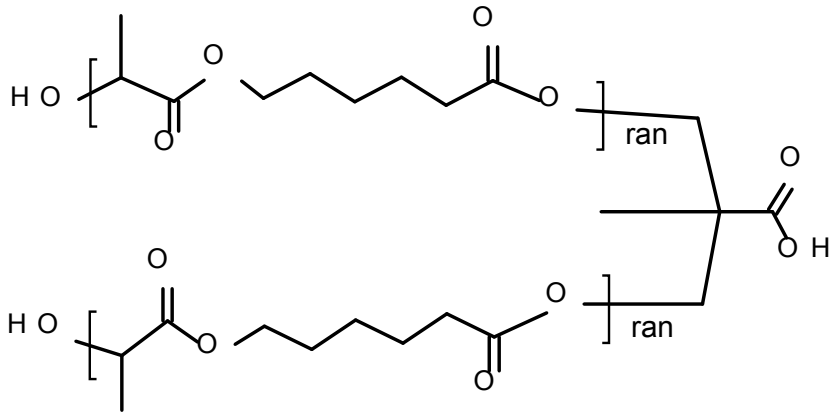
Branched PDLA-b-PCL blockcopolymers

- AB_2 macroinitiators with PCL and with poly(CL-co-LA) „arms“:

PCL:



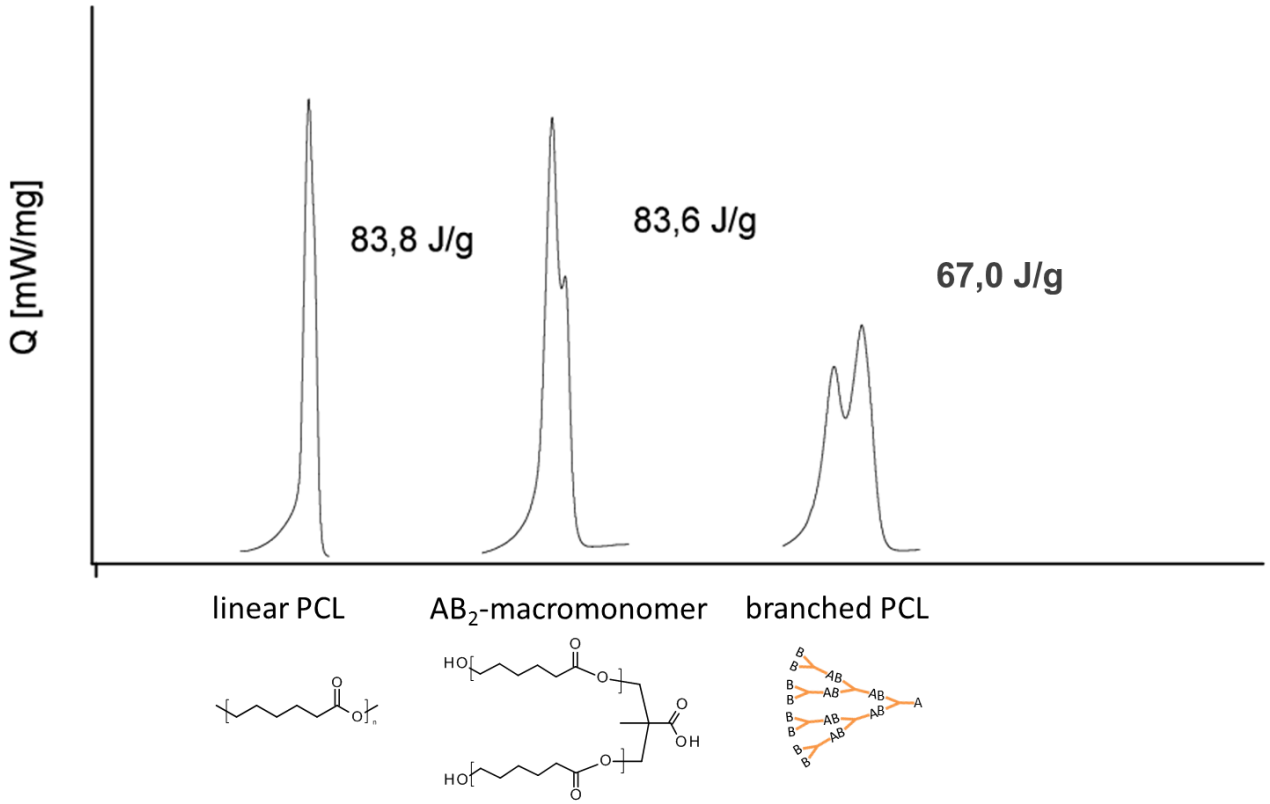
PCL-co-LA:



- Crystallization occurs like in linear PCL
- LA units decrease crystallinity of the macromonomers

Branched PDLA-b-PCL blockcopolymers

- After esterification of the macromonomers its crystallinity decreases



- In case of PCL-co-LA macromonomers no crystallization was observed

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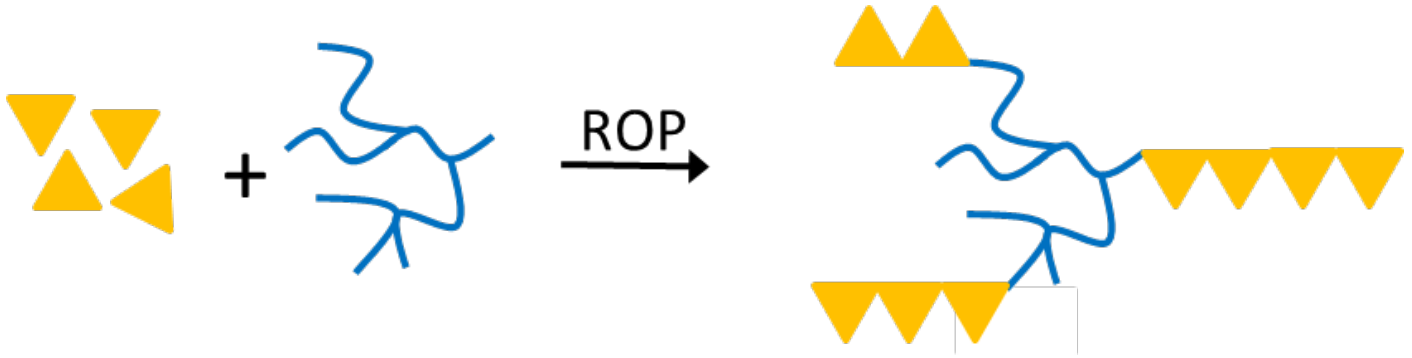
Branched PDLA-b-PCL blockcopolymers

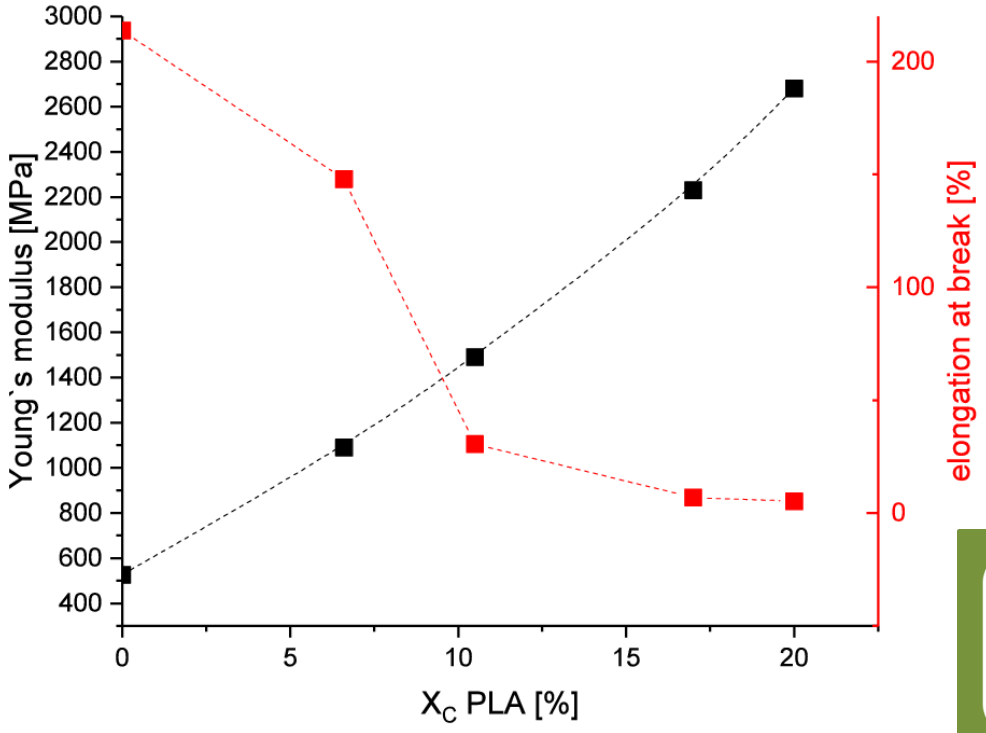
- Synthesis of blockcopolymers with branched soft block via ring opening polymerization of D-Lactide

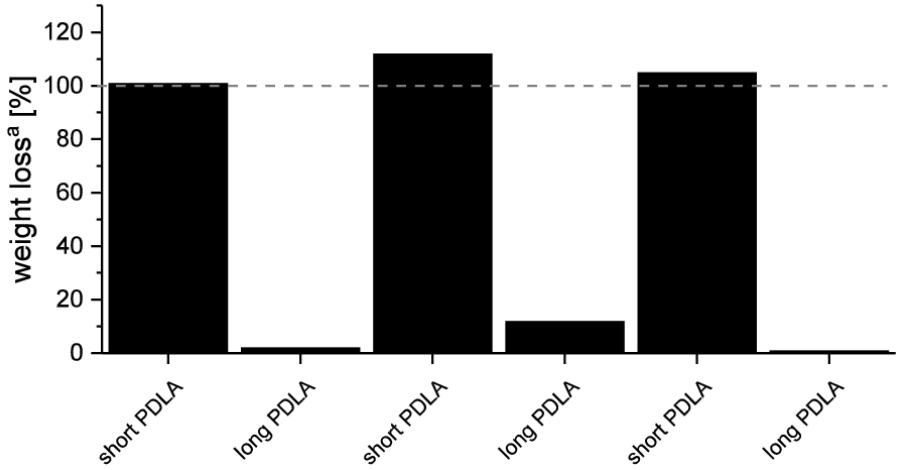


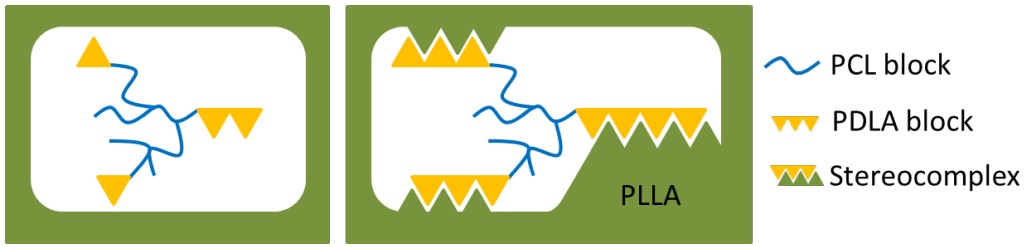
- Blends were prepared containing 10 % w/w of soft block

Branched PDLA-b-PCL blockcopolymers

- Correlation between PDLA-chain length, mechanical properties and migration tendency







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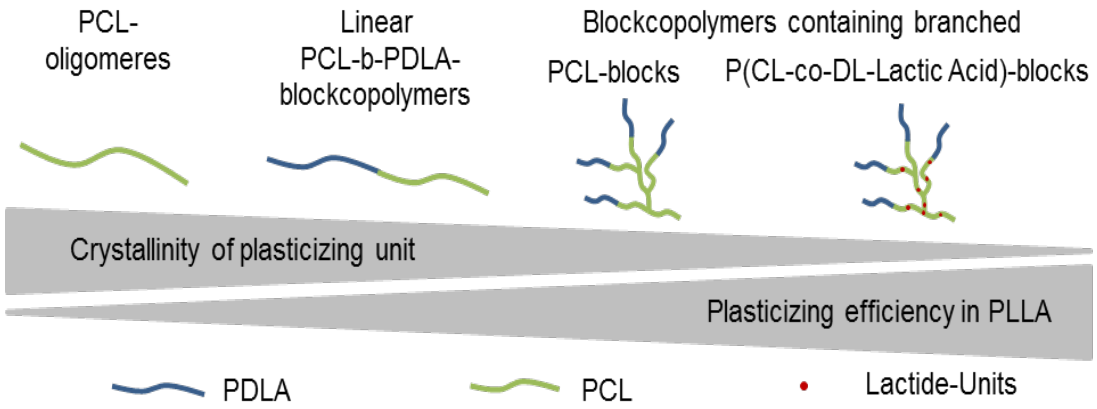
Conclusion

- PDLA-b-PCL blockcopolymers form a stereocomplex with PLLA
- Stereocomplex formation leads to:
  - modulation of PCL crystallinity
  - decrease of migration



- Further modulation of PCL crystallinity by incorporation of branching points increases the plasticizing efficiency of the copolymers

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Thank you for your attention

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