



# Poly(ethylene furandicarboxylate) (PEF): A bio-based alternative to PET

## Amorphous chain mobility in relation to crystallization

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One of the most utilized thermoplastic polyesters is the fossil-based poly(ethylene terephthalate) (PET)

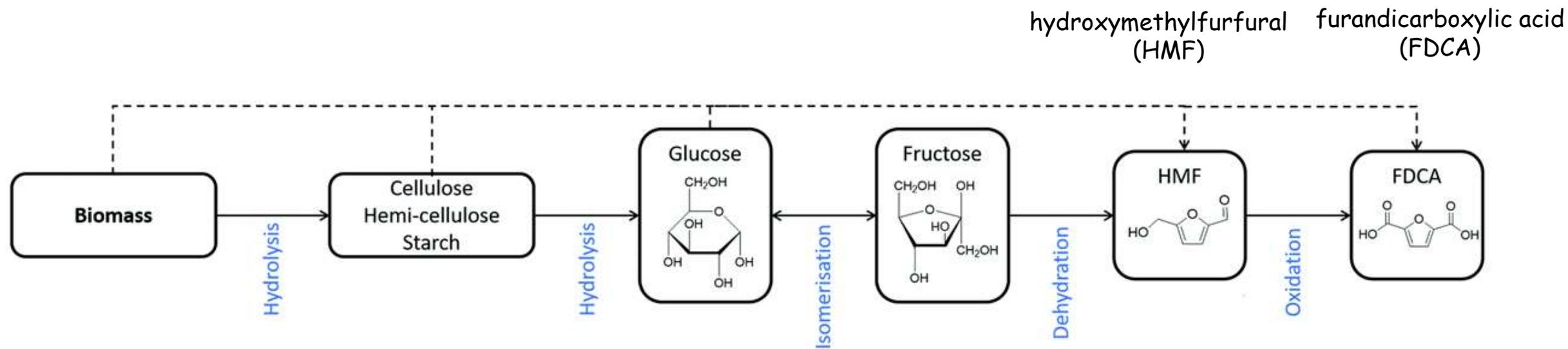
Furan-based polyesters, as poly(ethylene furandicarboxylate) (PEF), have proven to be excellent PET substitutes

The **glass transition temperature** of PEF is higher than that of PET (85 °C vs. 75°C),  
which is useful for heat resistant packaging

The **melting temperature** is lower than that of PET (210 °C vs. 250 °C),  
which facilitates extrusion and blow molding processes

The PEF **elastic modulus** is higher than that of PET (amorphous: 3.5 GPa vs. 2.5 GPa)

But the most interesting property of PEF with respect to PET is its lower **gas permeability**  
The strongly enhanced CO<sub>2</sub> barrier properties make PEF very interesting for packaging of carbonated drinks.  
Permeability is strongly reduced also for O<sub>2</sub> and H<sub>2</sub>O.



PEF: polycondensation (FDCA + ethylene glycol)

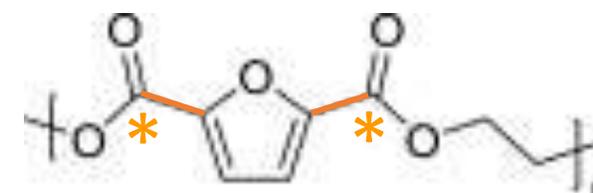
catalysts

- metals (Sb, Ti, Ge, Sn) to be removed
- eco-friendly ionic liquids
- enzymes

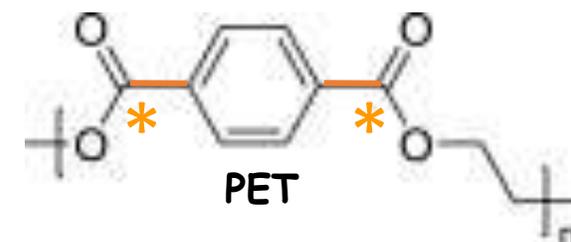
## CHEMICAL STRUCTURE

Differences in ring size, chain linearity and polarity result in significantly different properties

	distance between the carboxylic acid groups (* )	angle between the C-C bonds (— )
PEF	4.83 Å	129 °
PET	5.73 Å	180 °

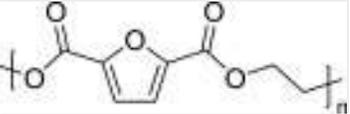
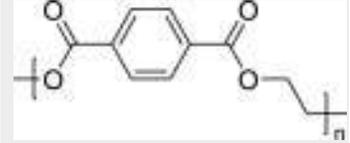


PEF



PET

PEF : smaller ring size, non-linear chain, strong permanent dipole (two doublets of non-binding electrons)

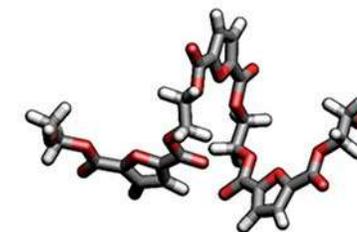
amorphous		$\rho$ (g/cm <sup>3</sup> )	$V_{sp}$ (cm <sup>3</sup> /g)	$V_o$ (cm <sup>3</sup> /g)	$V_f$
PEF		1.37	0.73	0.59	0.19
PET		1.33	0.75	0.65	0.13

$V_o$  = specific volume at 0 K (occupied volume), calculated from groups contributions [1]

$V_f$  = fractional free volume =  $(V_{sp} - V_o) / V_{sp}$

Non-linear chain and coiled-helix conformation in the amorphous phase

→ poor chain packing [2]



*anti*<sup>FDCA</sup>*gauche*<sup>EG</sup>

[1] S.K. Burgess et al, *Macromolecules* 2014, 47, 1383

[2] C.F. Araujo et al, *Macromolecules* 2018, 51, 3515



## AMORPHOUS PEF Barrier properties

	Permeability O <sub>2</sub> (barrer)	Permeability CO <sub>2</sub> (barrer)	Permeability H <sub>2</sub> O (barrer)
PEF (35 °C)	0.011	0.03	11
PET (35 °C)	0.114	0.49	38

$$1 \text{ barrer} = 10^{-10} \text{ cm}^3_{\text{STP}} \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$$

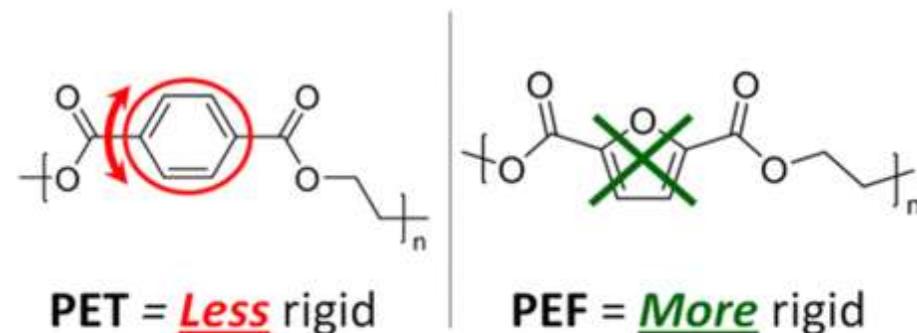
PEF exhibits a **significantly reduced permeability to O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O**

The improved barrier properties of PEF compared to PET appear **unexpected**  
in relation to the higher fractional free volume of PEF vs PET

Another PEF property influences the barrier properties: **CHAIN RIGIDITY**

S.K. Burgess et al, Macromolecules 2014, 47, 1383

The significantly smaller gas permeability in PEF is the result of reduced diffusion coefficient due to lower chain mobility and hindered local motions (furan ring-flipping) (small angle oscillations of the rings through rotations around the external C–C bonds)



After the gas molecules has dissolved in the polymer, the rotatable benzene ring and the more mobile molecular segments of PET can allow the gas molecules to diffuse easily. Conversely, the hindered furan ring-flipping and the poor segment mobility of PEF make difficult for the gas to pass through, slowing down and inhibiting the diffusion.



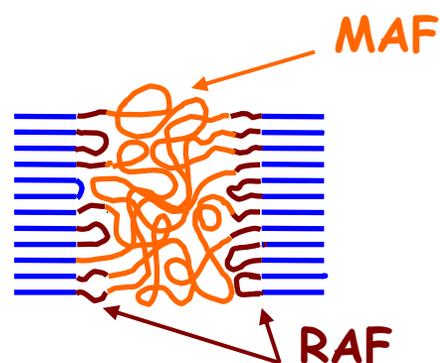
## semi-crystalline polymer

## 3-phase model

crystalline fraction (CF)

rigid amorphous fraction (RAF) - nanophase

mobile amorphous fraction (MAF)



The rigid amorphous fraction is located at the amorphous/crystal interface amorphous polymer segments covalently connected to the crystals, with mobility hindered by the near rigid crystalline structures

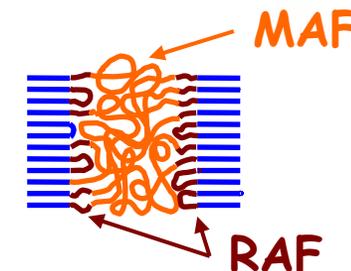
The mobile amorphous fraction vitrifies/devitrifies at  $T_g$

The rigid amorphous fraction vitrifies/devitrifies at temperatures higher than  $T_g$

Many macroscopic properties of polymeric materials are defined not only by the crystallinity degree, but also by the RAF percentage (present up to about 20-30 wt%)

## MECHANICAL PROPERTIES

At temperatures higher than the glass transition,  
 an increase in crystallinity produces an increase in the elastic modulus  
 an increase in rigid amorphous fraction produces an increase in the elastic modulus [1,2]



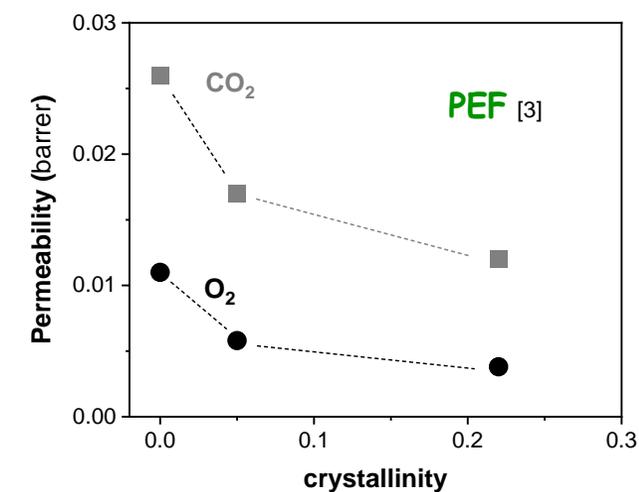
$$E_{MAF} < E_{RAF} < E_C$$

## PERMEABILITY PROPERTIES

An increase in crystallinity produces a decrease in gas permeability  
 no linear correlation between gas permeability and crystallinity

$$P_{RAF} < P_{MAF} < P_C \quad [1]$$

An increase in rigid amorphous fraction produces an increase in gas permeability  
 (higher free volume of the RAF with respect to the MAF)

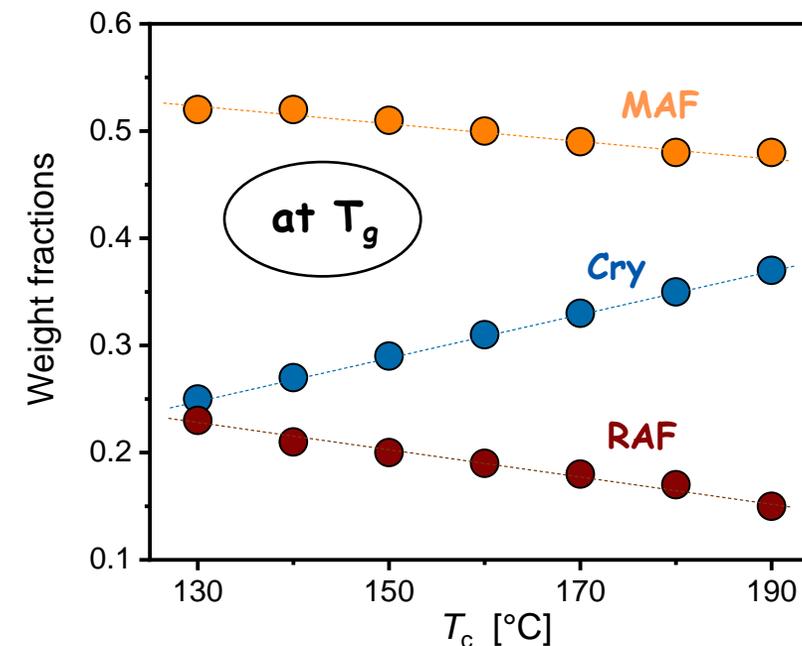
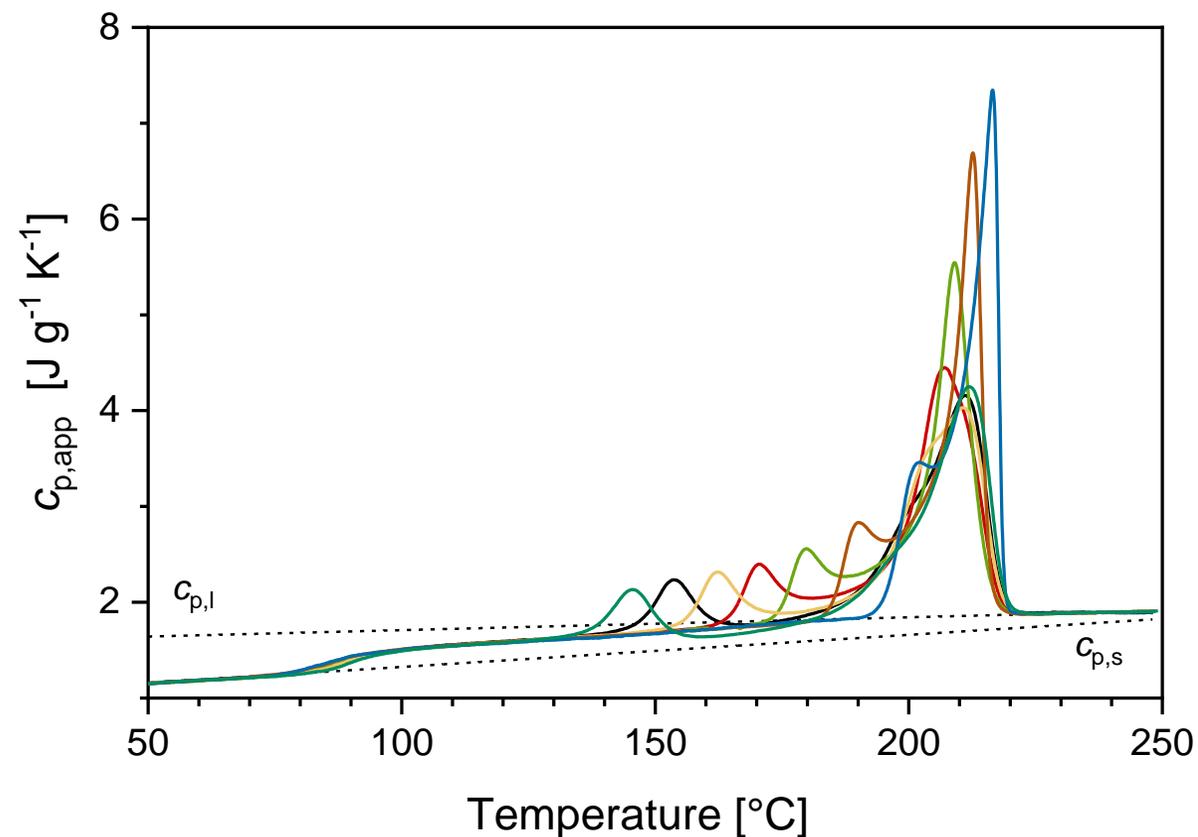


[1] M.C. Righetti, L. Aliotta, N. Mallegni, M. Gazzano, E. Passaglia, P. Cinelli, A. Lazzeri, Front. Chem. 2019, 7, 790 (PHBV)

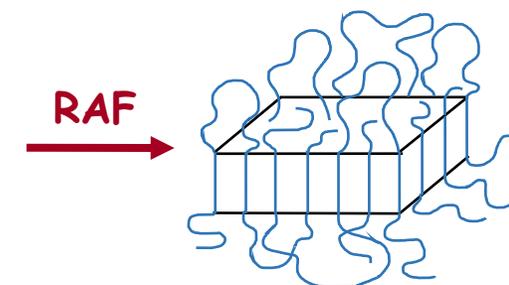
[2] L. Aliotta, M. Gazzano, A. Lazzeri, M.C. Righetti, ACS Omega 2020, 5, 20890 (PLLA)

[3] S.K. Burgess et al, Polymer 2016, 98, 305

## PEF: rigid amorphous fraction (RAF) at $T_g$ as a function of $T_c$

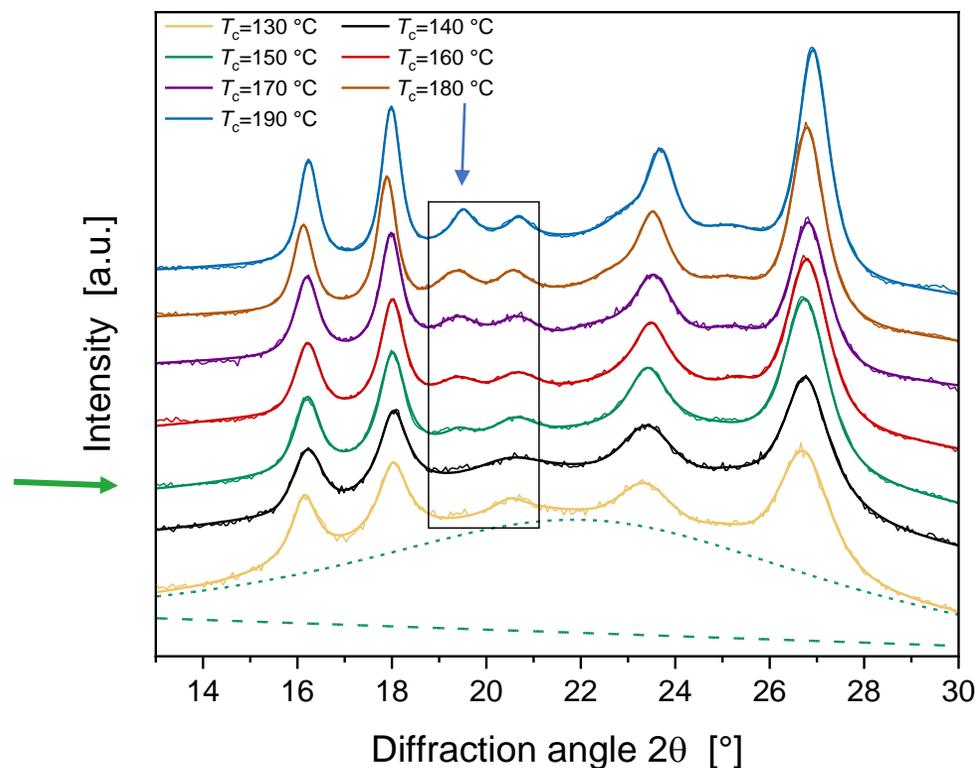
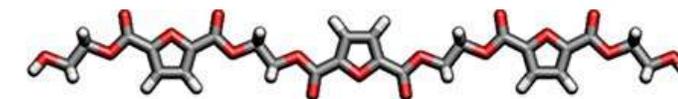


The RAF at  $T_g$  increases linearly with decreasing the crystallization temperature



M.C. Righetti, M. Vannini, A. Celli, D. Cangialosi, C. Marega, *Polymer* 2022, 247, 124771

## PEF polymorphism



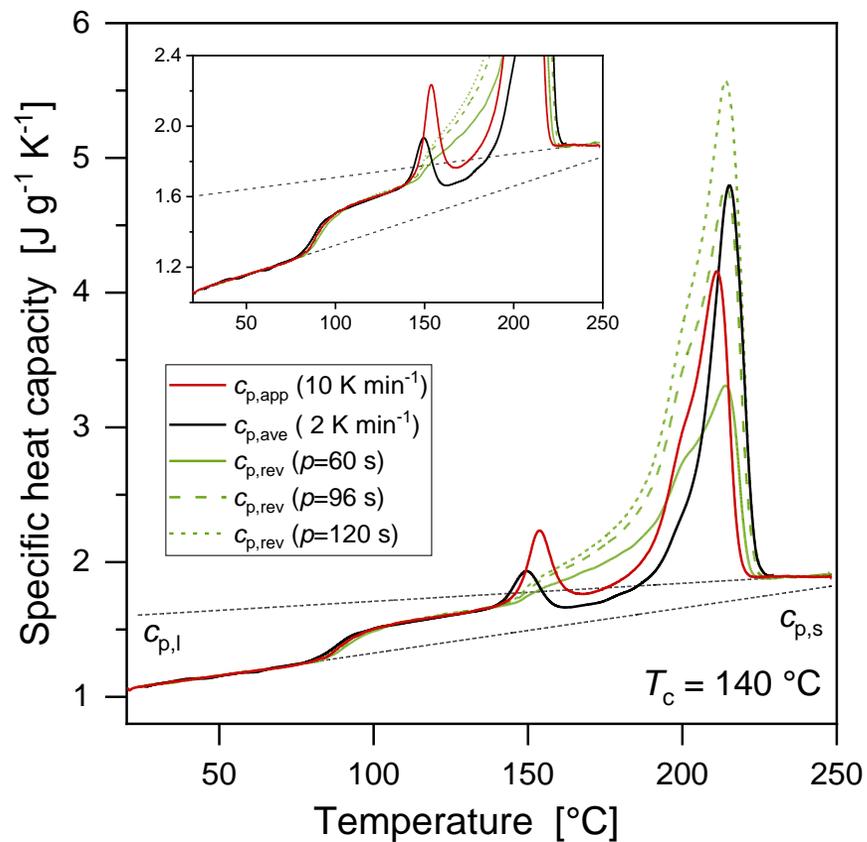
- $\alpha'$ -crystals grow at  $T_c \leq 140 \text{ }^\circ\text{C}$
- $\alpha$ -crystals grow at  $T_c \geq 170 \text{ }^\circ\text{C}$
- a mixture of  $\alpha'$ - and  $\alpha$ -crystals develops at  $150 \leq T_c \leq 160 \text{ }^\circ\text{C}$

$\alpha$ -crystals start to grow: **150 °C**

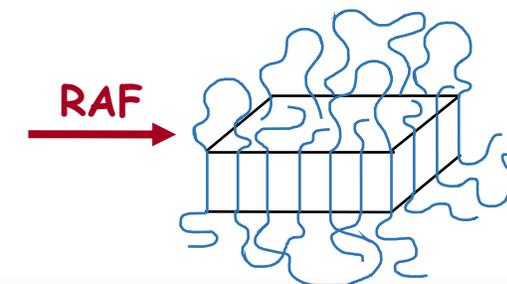
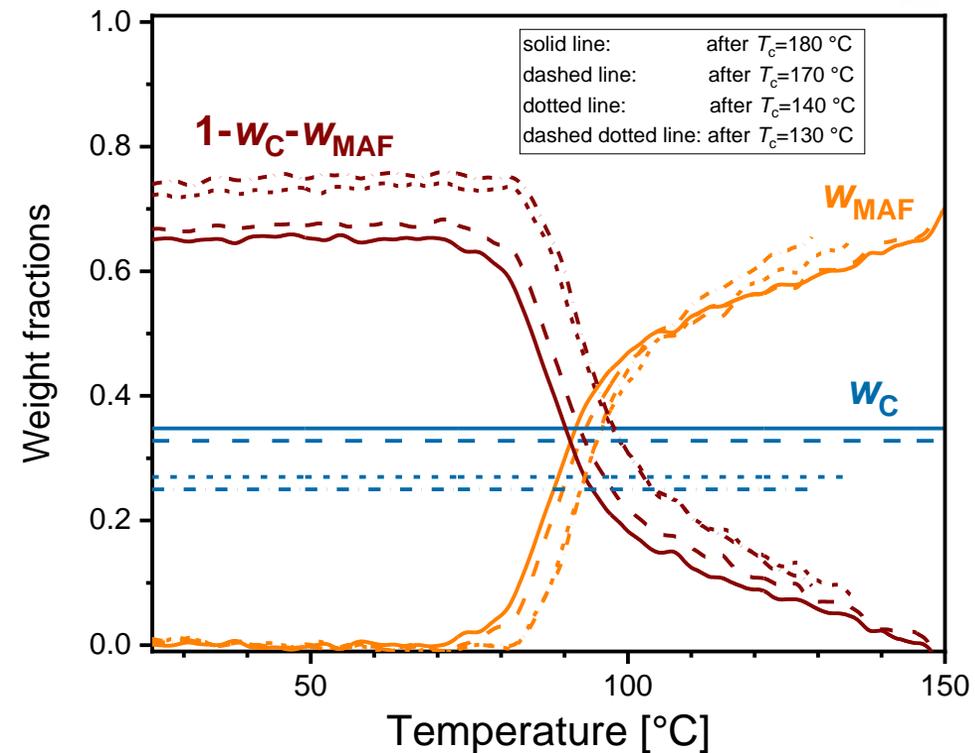
G. Stoclet, G. Gobius du Sart, B. Yeniad, S. de Vos, J.M. Lefebvre, *Polymer* 2015, 72, 165–176

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## PEF: temperature dependence of the RAF



With increasing temperature, RAF decreases from the value at  $T_g$  to zero at approximately **150 °C**



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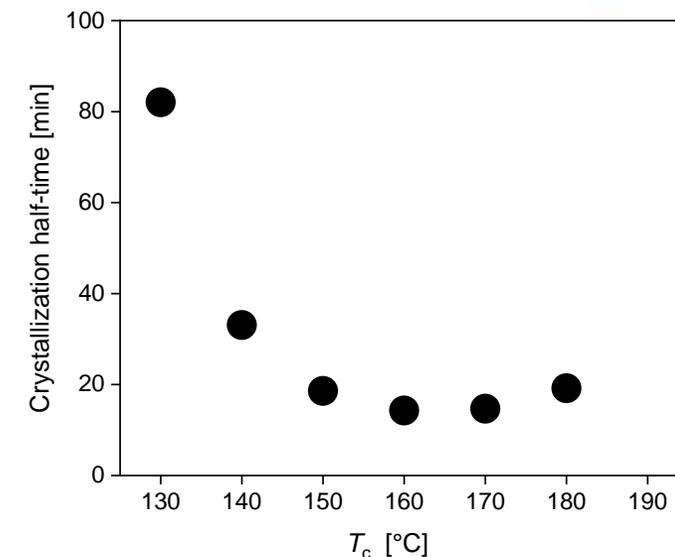


Correlation between this temperature limit and the crystallization rate

The minimum of the PEF crystallization half-time is located  
at temperatures slightly above **150 °C**

The more ordered  $\alpha$ -crystals grow only at temperatures higher than **150 °C**

**PEF**: complete mobilization of the amorphous segments occurs around **150 °C**  
total absence of constraints on the amorphous segments mobility



DENSITY

$$\rho_{MAF} = 1.370 \pm 0.003 \text{ g/cm}^3$$

$$\rho_{RAF,\alpha'} = 1.3 \pm 0.2 \text{ g/cm}^3$$

$$\rho_{RAF,\alpha} = 1.2 \pm 0.2 \text{ g/cm}^3$$

The RAF density is lower than the MAF density

Thank you  
for your kind attention