Microstructure and thermal properties of modified polyethylene

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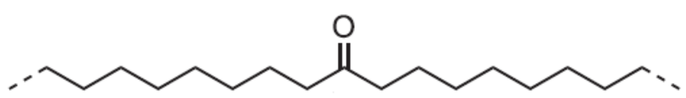
Questions

- How do the samples behave during heating and cooling?
- Are melting and crystallization temp. comparable to HDPE?
- What are the structural properties of the samples in relation to the crystalline and amorphous layer thickness?

Samples

- important property of the modified polyethylene samples: Degradability

	HDPE Total	PE Keto 1,6	PE Keto 1,0	PE Keto 0,6
M_n	27,7x10³ g/mol	160x10³ g/mol	130x10³ g/mol	220x10³ g/mol
CO Content	-	1,6 mol%	1,0 mol%	0,6 mol%



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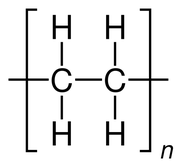
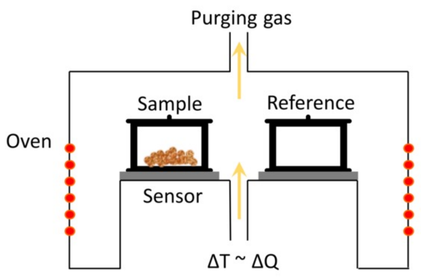


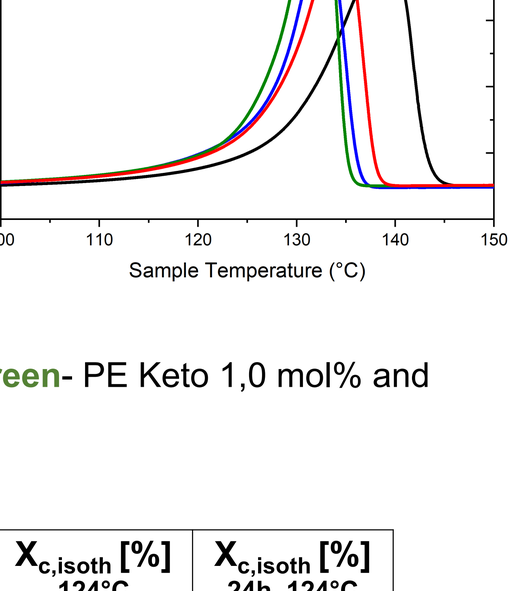
Differential scanning calorimetry (DSC)

- Measurement of (specific) heat capacity

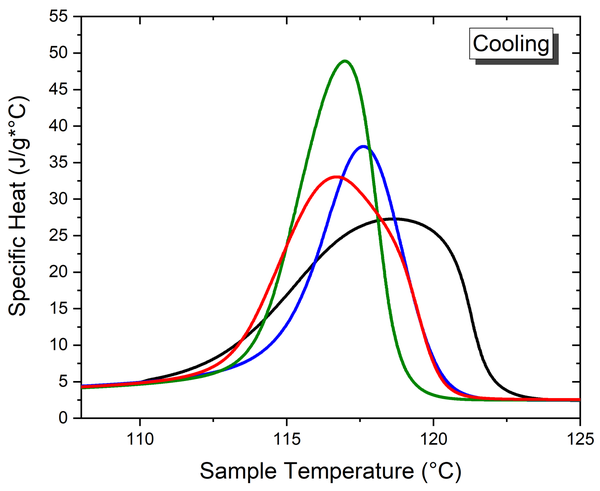
$$c_p = \frac{\text{Heat flow}}{\text{Heating rate} * m} \quad [\text{J/(g*°C)}]$$

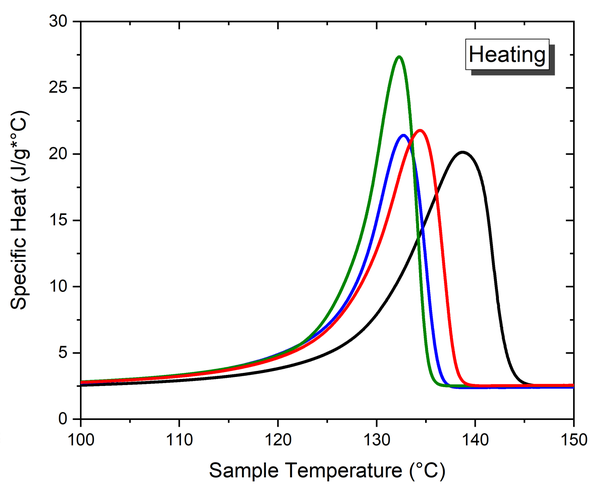
- melting enthalpy H_m indicates degree of crystallinity → area under peak





Heating and cooling scans





- second heating and cooling scan
- **black**-HDPE, **blue**-PE Keto 1,6 mol%, **green**- PE Keto 1,0 mol% and **red**-PE Keto 0,6 mol%

Isothermal measurements

	T_m [°C]	T_c [°C]	$X_{c,isoth}$ [%] 124°C	$X_{c,isoth}$ [%] 24h, 124°C
Keto 1,6	132,9	117,63	52,63	55,97
Keto 1,0	132,27	116,96	59,16	64,87
Keto 0,6	134,59	116,81	59,72	65,36
HDPE	138,71	118,65	65,98	-

Equation for degree of crystallinity:

$$X_c = \frac{H_m}{H_\infty} * 100\%$$

- for Polyethylene: H_∞= 293 J/g
- results show that the modified PE have very comparable values to HDPE

X-ray scattering

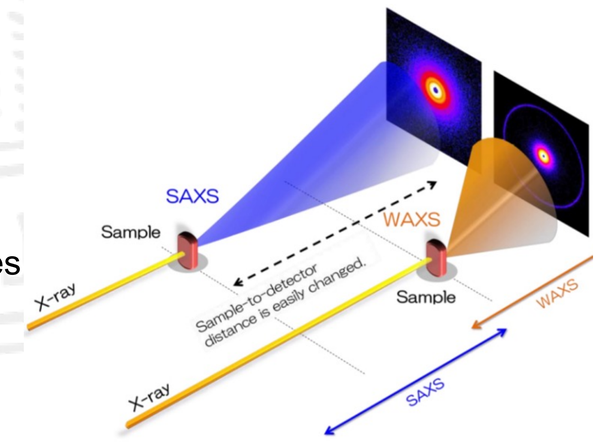
- **wide-angle scattering (WAXS):** resolves crystalline structure in order of 0.3 to 0.5 nm → order crystalline structures
- **small-angle scattering (SAXS):** Resolution from 1 to 200 nm

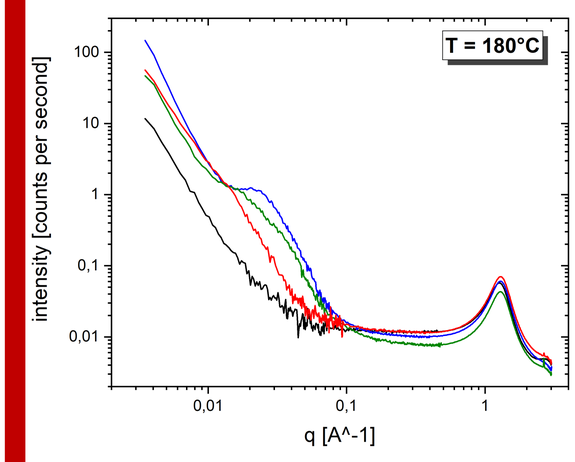
→ information about inner structure, size of semi-crystalline structures

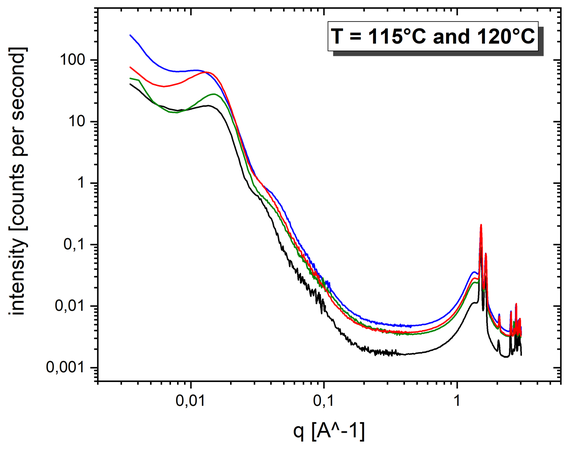
Fundamental mathematical relationship (Bragg's law):

$$n\lambda = 2d \sin\theta$$

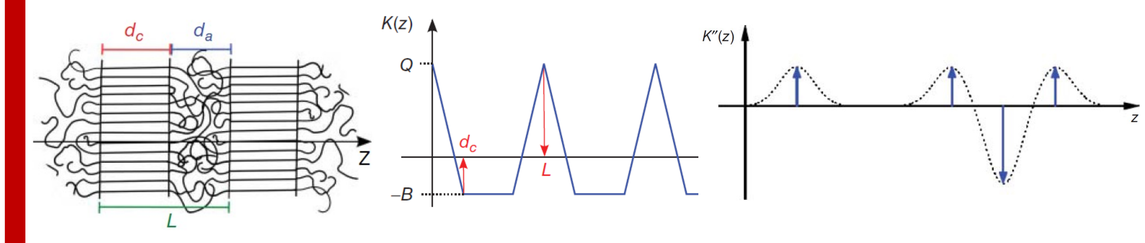
- d - distance between grid planes
- CuKα Radiation: λ=0,154 nm





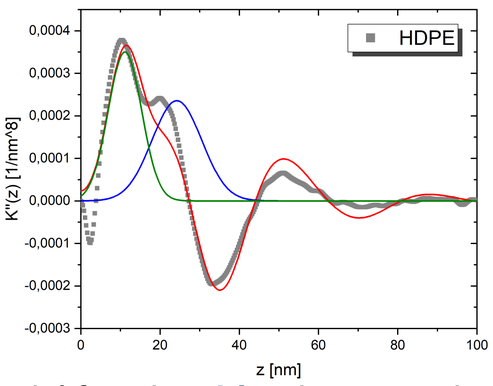


- left-180°C and right-120°C and 115°C for PE Keto samples
- **black**-HDPE, **blue**-PE Keto 1,6 mol%, **green**-PE Keto 1,0 mol% and **red**-PE Keto 0,6 mol%
- PE consist out of a lamellar structure with thickness d_c and amorphous regions with thickness d_a → long period $L = d_a + d_c$



$$K''(z) = 16\pi^3 \int_0^\infty [\lim_{s\to\infty} I(s)s^4 - s^4 I(s)] \cos(i2\pi sz)\, ds$$

	$X_{c,isoth}$ [%] 115°C	$X_{c,isoth}$ [%] 24h, 115°C
Keto 1,6	52,7	-
Keto 1,0	56,85	-
Keto 0,6	60,1	64,87
HDPE	68,54	-



- interface distribution function → **red**-model function, **blue**-h_c, **green**-h_a

$$X_c = \frac{d_a}{d_c + d_a} * 100\%$$

Conclusion

- T_M and T_C are comparable to Polyethylene
- crystal structure from HDPE and PE Keto is very similar
- d_c is smaller compared to Polyethylene
- d_a is higher compared to Polyethylene
- Properties are comparable to PE → potential alternative in view of the environmental crisis

[1] Maximilian Baur u. a. „Polyethylene materials with in-chain ketones from nonalternating catalytic copolymerization“. *Science* 374.6567 (2021), S. 604–607.

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