Crystallization kinetics in hydrogen bonded pseudo-blockcopolymers measured by *in-situ* SAXS

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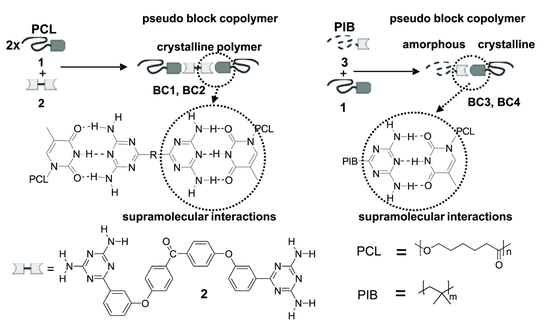
Introduction:

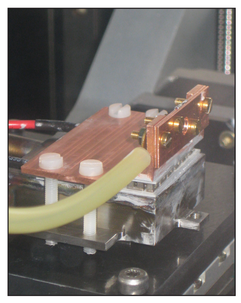
In this work the kinetics of structure formation of novel polymeric samples has been investigated via *in-situ* Small Angle X-ray Scattering (SAXS). The samples consist of PCL (poly(ε-caprolactone)) and PIB (poly(isobutylene)) blocks, which are weakly connected by hydrogen – bonds. These hydrogen-bonds appear between the thymine and 2,6-diaminotriazine groups which are linked to the individual blocks and lead to a so called supramolecular interaction between them.

To describe the isothermal crystallization of PCL, the kinetic theory of Avrami was applied. Herefrom one gets the growth rate constant k, the crytallization halftime $t_{1/2}$ and with an additional Arrhenius plot the activation energy E_a of the crystallization process. All measurements were carried out in a laboratory X-ray device (NanoStar, Bruker AXS) equipped with a rotating copper anode (wavelength 0.1542 nm) and a 2D gas detector with microgap technology (Vantec 2000).

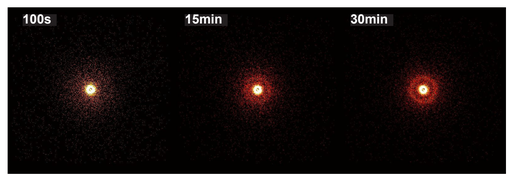
Samples, Experimental Setup and Data Collection:



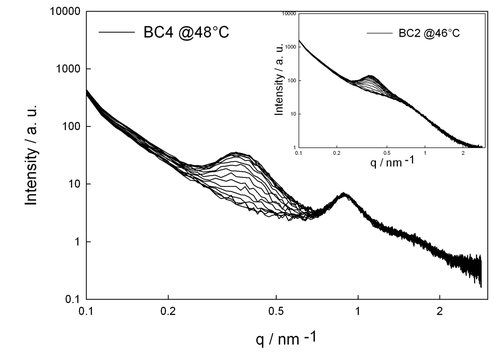
Structure of the supramolecular pseudo blockcopolymeres [1]. The results are restricted to BC2 and BC4.



Sample holder and Peltier-cooling device. Samples are placed between aluminium foils.



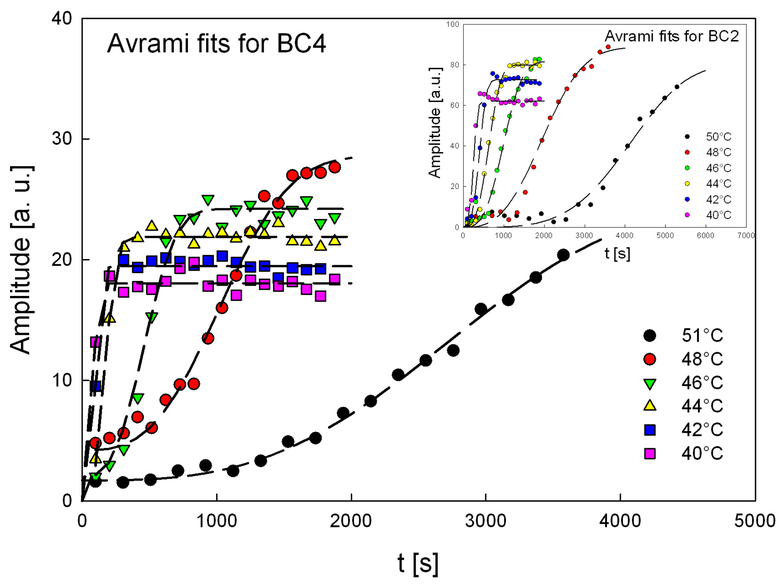
Time dependent evolution of a diffraction ring in the scattering pattern of sample B2, crystallization at 46°C.



Scattering curves of the isothermal crystallization for both samples: BC4 (large graph) and BC2 (small graph).

Results:

The intensities obtained from the SAXS pattern allow the application of the Avrami theory. Measurements at differerent temperatures enable the determination of the activation energy of the crystallization process.



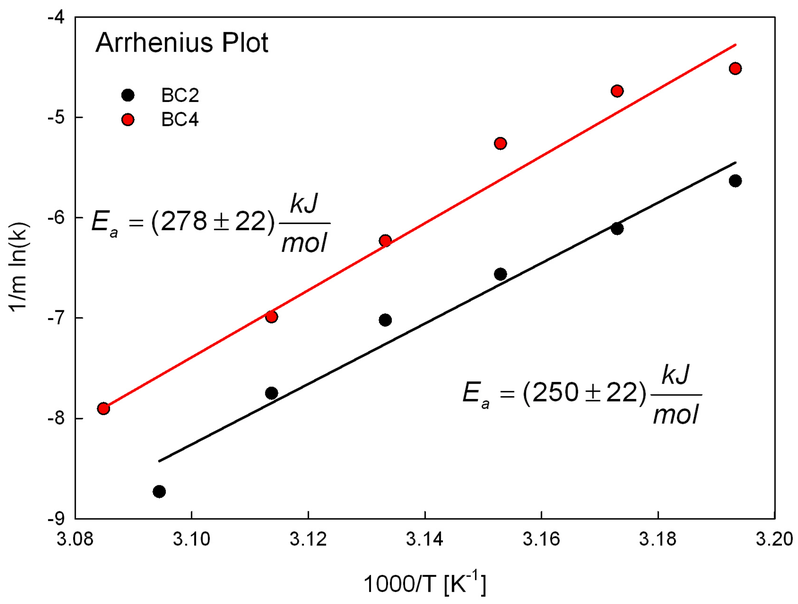
Avrami Fits at different temperatures for the BC4 sample (large graph) and the BC2 sample (small graph).

Avrami equation: $X(t) = 1 - e^{-(kt)^m}$

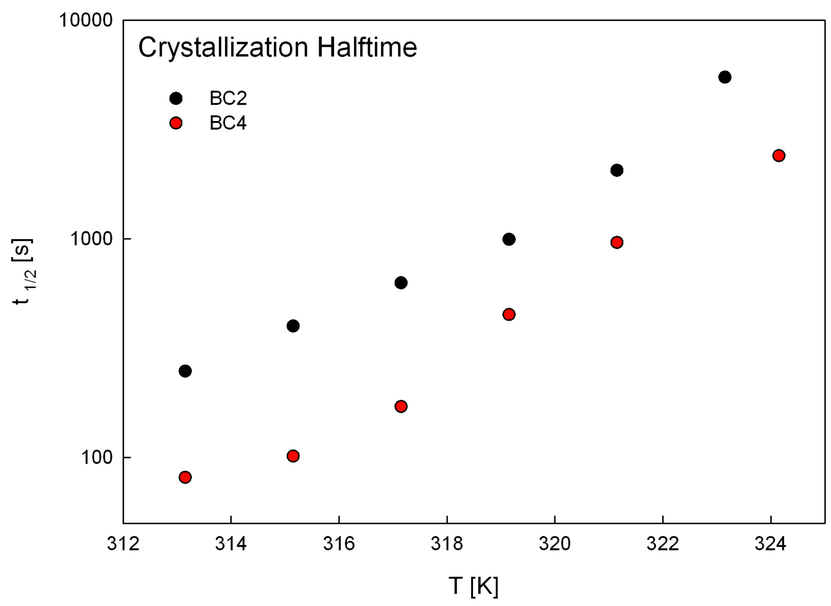
$X(t)$ ... Relative Crystallinity
k ... Growth rate constant
m ... Avrami exponent (m = 1, 2, 3 or 4)

$$k^{1/m} = k_0 \cdot e^{-E_a/RT}$$

$$t_{1/2} = \left(\frac{\ln(2)}{k}\right)^{1/m}$$



Arrhenius plots and the resulting activation energies E_a for the crystallization process.



Crystallization halftimes for different temperatures calculated from the growth rate constant k.

Conclusion:

- The crystallization kinetics of pseudo block-copolymers has been investigated via *in-situ* Small Angle X-Ray Scattering (SAXS).
- This crystallization process can be described by the kinetic theory of Avrami [2]. From this theory the growth rate constant k has been obtained.
- The value of the Avrami exponent m depends on the nucleation mechanism and growth dimension [3]. In our case m was close to 3, which suggests heterogenous nucleation.
- Using an Arrhenius plot, we were able to determine the activation energy E_a of the crystallization process.
- Further, the crystallization halftime $t_{1/2}$ has been calculated, which gives additional information on the kinetics and temperature dependence of the crystallization process.[3,4].

Literature:

[1] Ostas, E; Schröter, K.; Beiner, M; Yan, T.; Thurn-Albrecht, T., Binder, W.H. J. Polym.Sci 2011, accepted.
[2] Weinberger M., Peterlik H. et al.; Chemistry and Materials Science, Silcon, Vol. 1, Nr. 1, 2009, 19-28
[3] Jianglei Q., Shiqi Z., Zhiting L.; Journal of Applied Polymer Science, Vol. 110, Issue 5, 2008, 2615-2622
[4] Kuo-Yu C., Jen-Feng K., Journal of Applied Polymer Science; Vol. 111, Issue 1, 2009, 371-379

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