Polymers under Multiple Constraints

# Polymer- & Soft-Matter-Seminar

**Tuesday, 29th November 2016**

at: **5.15pm**

VDP4 1.27, Von-Danckelmann-Platz 4, 06120 Halle


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### "The influence of chain topology on the crystallization of polycaprolactones (PCLs): cyclic versus linear chains"


Narrow polydispersity cyclic PCL samples (C-PCLs) were prepared by means of controlled click chemistry techniques in the group of Scott Garyson at Tulane University (USA). Linear PCL counterparts (L-PCLs) of almost identical molecular weights were also obtained in a Mn range spanning 2 to 22 kg/mol. The samples were studied by Differential Scanning Calorimetry (DSC), Transmission Electron Microscopy (TEM) and Polarized Light Optical Microscopy (PLOM). The morphology, nucleation and overall crystallization kinetics were studied, as well as their self-nucleation behavior and SSA (Successive Self-nucleation and Annealing) thermal fractionation. Cyclic PCLs were found to nucleate and crystallize faster than linear PCLs. Two reasons are responsible for this peculiar behavior: (a) faster diffusion of C-PCL chains as compared to linear chains and (b) larger supercoolings of C-PCLs at any given crystallization temperature, as compared to L-PCLs, since a larger value of the equilibrium melting temperature was determined for C-PCLs as compared to L-PCLs.

When small quantities of L-PCL are added to C-PCL a decrease in overall isothermal crystallization kinetics much stronger than predicted on the basis of a linear mixing law is observed. The results are explained by realizing that new topological effects are created upon mixing L-PCL chains with C-PCL molecules. When these linear chains come into contact with cyclic PCL chains a threading effect is produced that dramatically affects chain dynamics by forming a transient entanglement network. As a consequence cyclic molecules relax and diffuse much more slowly than anticipated decreasing both nucleation and growth kinetics. The results have important implications for cyclic samples "contamination" with linear chains.