

¹H-NMR Investigation of Chain Ordering Effects in Polymer Crystallization

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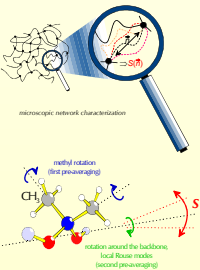
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Introduction

In our own DSC measurements and in literature [1] chemically and physically crosslinked samples (networks and entanglements) of PDMS (poly (dimethylsiloxane)) displayed an enhanced tendency to crystallize. This is an atypical behavior concerning the geometric constraints (entanglements, netpoints and loops) of these systems, which have to accumulate in the amorphous phase, and the viscosity dependence of the crystal growth-rate in classical models of crystallization theory [2]. The motivation of this project was to approve and quantify these results by means of NMR.

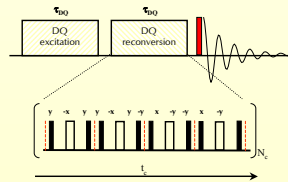
¹H Double-Quantum NMR and Chain Order



Multiple-quantum NMR can be used to measure the residual dipolar coupling between protons of the methyl groups in PDMS [3]. Couplings are extracted from normalized double-quantum build up curves.

Residual couplings are a measure of the dynamic order parameter S describing the time-averaged stability of the local backbone orientation as constrained by crosslinks and topological restrictions (entanglements).

Hindrances & Constraints

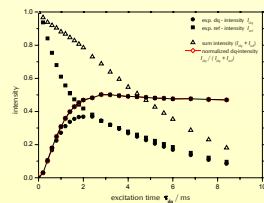


Static multi-quantum experiments [4] with variable excitation / reconversion time $\tau_{DQ} = N_c \cdot \tau_c$

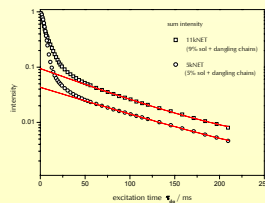
Investigated PDMS Samples

- (a) Linear, $M_n = 5717$ g/mol, $P = 2.55$ [5kLIN]
- (b) Network made of (a), sol = 5% [5kNET]
- (c) Linear, $M_n = 11573$ g/mol, $P = 2.55$ [11kLIN]
- (d) Network made of (c), sol=10% [11kNET]
- (e) Linear PDMS, $M_n = 102000$ g/mol [102kLIN]

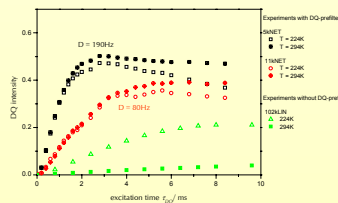
5kNET – Example of Build Up Analysis



Sum Intensity → Sol Fraction



Build Up Curves – Temperature Dependence

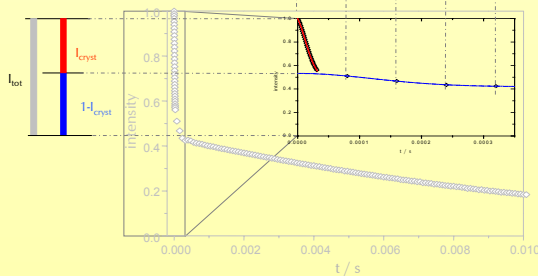
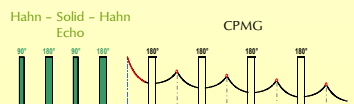


No Measurable Chain Order for 5kLIN and 11kLIN

Principles of Crystallization Kinetics Experiments

Analysis of the relaxation function [5].

- fast initial decay from crystalline parts
- slow decay from amorphous parts.



Degree of Crystallinity

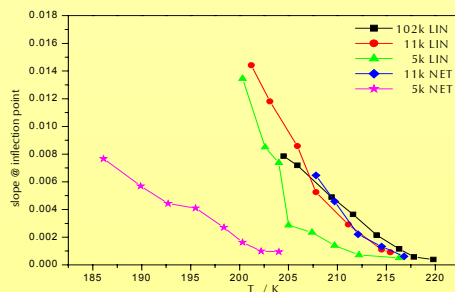
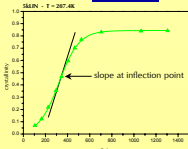
$$\phi_c = \frac{I_{cryst}}{I_{tot}} = 1 - \frac{(1 - I_{cryst})}{I_{tot}}$$

Isothermal Crystallization

Samples were cooled from a temperature above the equilibrium melting point T_f^0 to the desired crystallization temperature T_c . The degree of crystallinity was determined at different crystallization times θ . The slope of the crystallization isotherm at the inflection point has been taken as a measure for the crystallization rate.

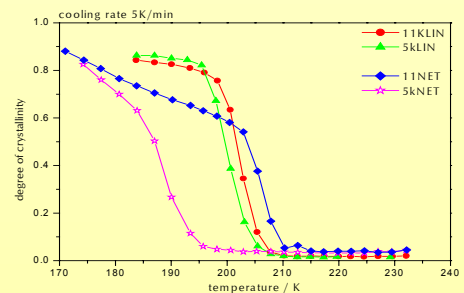
Isothermal Crystallization Rates

Example of a Crystallization Isotherm



Non - Isothermal Crystallization

The degree of crystallinity was measured after certain crystallization times θ respectively at different temperatures, with cooling rates equivalent to the DSC measurements.



Summary and Outlook

- ➔ Isothermal and non-isothermal NMR kinetic experiments do not display the behavior found in DSC measurements
- Exclude magnetic field dependence of NMR results
- Exclude disturbing effects present in DSC measurements
- Investigate chain ordering effect on a series of defined mixtures of linear low MW and high MW ($>M_c$) PDMS

References

- [1] T. Dollase, H. W. Spiess, M. Gottlieb, R. Yerushalmi-Rozen, *Europhys. Lett.* **60** (3), 390-396 (2002)
- [2] J.D. Hoffman, G.T. Davis, J.I. Lauritzen, in *Treatise on Solid State Chemistry*, Vol. 3 (Plenum Press, 1976), p. 497
- [3] K. Saalwächter, *Chem. Phys. Lett.* **362**, 331-350 (2002)
- [4] J. Baum, T. Pines, *J. Am. Chem. Soc.* **108**, 7447-7454 (1986)
- [5] R. H. Ebengou, J. P. Cohen-Addad, *polymer* **35**, 2962-2969 (1994)