Experimental Report

Proposal: **TEST-2080** **Council:** 10/2011

Title: Dynamics of Cyclic Polyethylene Glycolis in the Melt

This proposal is a new proposal

Researh Area:

Main proposer: **GOOSSEN Sebastian**

Experimental Team: GOOSSEN Sebastian
GUPTA Sudipta

Local Contact: FALUS Peter

Samples: Polyethylene glycol (C2H4O)n

Instrument	Req. Days	All. Days	From	To
IN15	6	9	27/10/2012	05/11/2012

Abstract:

Experimental report on experiment TEST-2080

The scope of this experiment was to measure the coherent intermediate structure factor by Neutron Spin Echo spectroscopy for the investigation of the dynamics of poly(ethylene glycol) (PEG) ring polymers. These are of fundamental interest due to the lack of chain ends. This experiment was a continuation of previous dynamic experiments to enhance the microscopic understanding of relaxation mechanisms in the case of entangled ring polymers and with special regard to the dynamics in blends of cyclic and linear polymers.

Experimental setup and samples
Six polymer melts were investigated at a distinct temperature of 413 K accessing the Q-range from 0.03 to 0.2 $Å^{-1}$ at six different Q-values. The samples were measured to maximum Fourier times of 600 ns.

PEG rings with a molecular weight of about 10 kg/mol were investigated in four different deuterated PEG matrices: rings with a molecular weight of 10 kg/mol, linear chains with a molecular weight of 2 kg/mol, linear chains with a molecular weight of 10 kg/mol, and linear chains with a molecular weight of 80 kg/mol.

Additionally, linear polymer chains with a molecular weight of 10 kg/mol in a matrix of deuterated linear analogues of the same molecular weight were measured as reference sample.

Furthermore, for the first time a vice versa blended sample was investigated: linear polymer chains with a molecular weight of 5kg/mol in a matrix of deuterated polymer rings of the same molecular weight.

Results and Discussion
First studies of cyclic PEG with a molecular weight of about 2 kg/mol allowed to highlight the effect of chain ends on the polymer dynamics for short polymer chains below the entanglement molecular weight M_e [1]. Cyclic polymers were found to diffuse much faster (by a factor of 1.8) than linear polymer chains and hence to exhibit dynamics faster than Rouse-like diffusion.

Investigating slightly bigger polymers with a molecular weight of about 5 kg/mol (~2.5 M_e) ring polymers were found to fulfill the Rouse model while in the linear analogues the onset of entanglements slowed down the dynamics already. [2]

Increasing the molecular weight up to 10 kg/mol (~5 M_e) in this experiment cyclic polymers finally start to deviate from Rouse-like behavior and exhibit slower dynamics. This might be the first experimental finding of topological ring-ring interactions in a polymer melt. However, compared to the linear reference sample ring polymers are still found to have much faster dynamics as shown in figure 1.

The investigation of cyclic polymers in a matrix of linear chains of varying molecular weight showed a drastic slow down of the dynamics with increasing molecular weight of the matrix. Finally, plateaus were obtained for the longest matrix of 80 kg/mol (~40 M_e).

The dynamics of linear chains in a matrix of cyclic polymers were found to be significantly faster than in a pure melt of linear chains. This is in contrast to recent simulation work that predicts the same diffusion independently of the topology of the matrix [3].

Detailed evaluation and modeling of the experimental data is still ongoing.

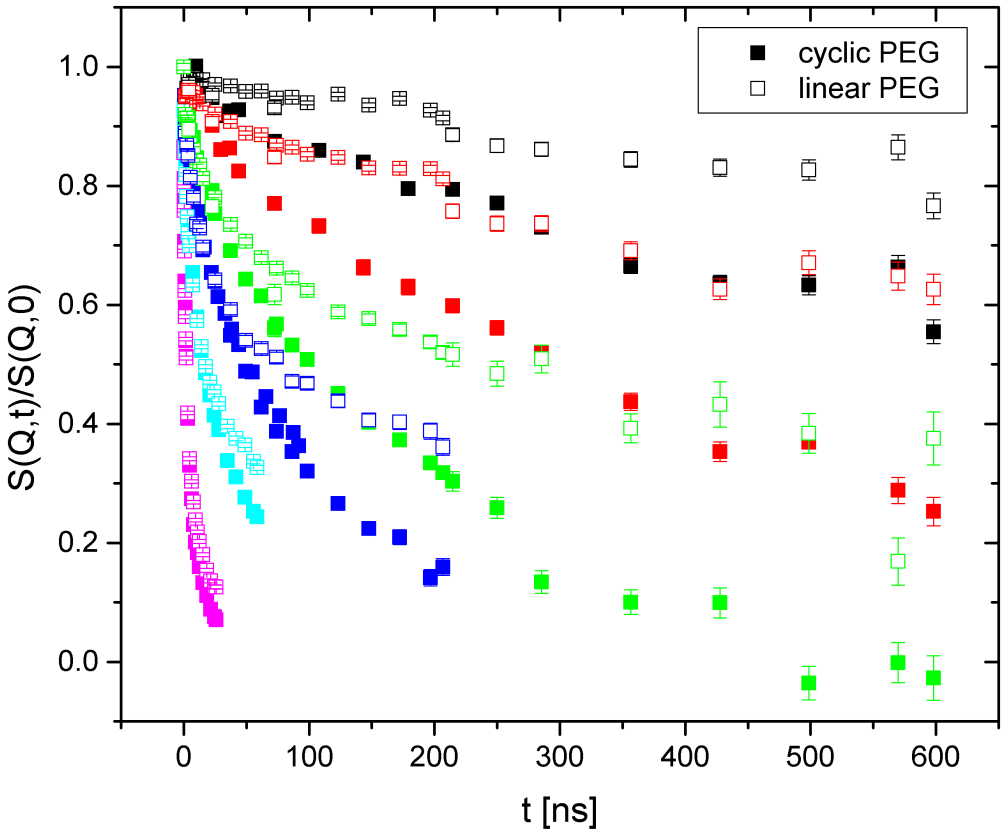

Figure 1: *Comparison of cyclic polymers in a matrix of deuterated cyclic polymers (full symbols) and linear polymer chains in a matrix of deuterated linear polymer chains (open symbols) of a molecular weight of about 10 kg/mol . Six distinct Q-values of 0.03 Å^{-1} (black), 0.05 Å^{-1} (red), 0.08 Å^{-1} (green), 0.10 Å^{-1} (blue), 0.13 Å^{-1} (cyan), and 0.20 Å^{-1} (magenta) measured at 413 K at the IN15 Neutron Spin Echo spectrometer are presented.*

References

[1] A. R. Brás, R. Pasquino, T. Koukoulas, G. Tsolou, O. Holderer, A. Radulescu, J. Allgaier, V. G. Mavrantzas, W. Pyckhout-Hintzen, A. Wischnewski, D. Vlassopoulos, D. Richter, *Soft Matter*, 7, 11169, **2011**.

[2] Experimental report on experiment 9-11-1501.

[3] J. D. Halverson, G. S. Grest, A. Y. Grosberg, K. Kremer, *Physical Review Letters*, 108, 038301, **2012.**