Experimental report

14/02/2020

Proposal:	**9-11-1894**	**Council:**	10/2018

Title: CHAIN CONFORMATION AND DYNAMICS INAN INTERNALLY CROSS-LINKED POLYMERMELT: DISAPPEARENCE OF ENTANGLEMENTS

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Arantxa (Maria Aranzazu) ARBE**

Experimental team:
Timo BRAENDEL
Paula MALO DE MOLINA

Local contacts:
Ingo HOFFMANN
Lionel PORCAR
Peter FALUS

Samples: d / h polytetrahydrofurane

Instrument	Requested days	Allocated days	From	To
D22	1	1	10/09/2019	11/09/2019
IN15	7	5	11/09/2019	16/09/2019

Abstract:

Recent experiments on Single-Chain-Nano-Particles in bulk reveal that the structural relaxation is hardly sensitive to internal cross-links, while macroscopic rheology shows a spectacular disentanglement with respect to the linear chains' melt counterpart. A new emerging relaxation process at intermediate length scales --also detectable by dielectric spectroscopy-- seems to be the mechanism controlling the viscous flow in the SCNPs. We want to search for the microscopic signatures of such a process in the single chain dynamic structure factor, and provide experimental evidence for the internal loops structure predicted by MD-simulations through SANS.

Chain conformation and dynamics in an internally cross-linked polymer melt: disappearence of entanglements

Proposal 9-11-1894. Experimental report

Single-Chain Nano-Particles (SCNPs) are nano-objects obtained by intra molecular cross-linking of individual macromolecular chains (‘precursors’). Recent experiments had shown that melts of SCNPs exhibit a markedly different rheological behavior compared to their linear counterparts with the same molecular weight. The aim of this experiment was to search for the microscopic signatures of such an effect in the single chain dynamic structure factor. For this purpose we investigated the single chain static (SANS) and dynamic (NSE) structure factor of SCNPs in bulk compared to its linear precursor. The SCNPs were synthesized based on a poly(THF-co-glycidyl azide) precursor that is internally cross-linked via click reaction with propargyl ether as a linker. In order to enhance the contrast, both in the case of precursor and SCNPS, we used 10% of hydrogenated polymer in the rest deuterated. The hydrogenated precursor had a molecular weight of $M_w = 31.0$ kDa (PDI=1.18) and the deuterated had $M_w = 36.0$ kDa (PDI=1.19).
SANS experiments on the instrument D22 were carried out at room temperature (295K). We used a neutron wavelength λ=6 Å and 2 different configurations of sample-to-detector / collimation distances (2 m/2.8 m and 17.6 m/17.6 m) to cover a Q interval from 0.003 to 0.45 Å^{-1}. The linear precursor exhibits the typical scattering for a polymer chain. Preliminary fits with a generalized chain form factor suggest that the chain has an R_G=6.2 nm and a Flory parameter of $\nu = 0.51$. However, the SCNP curve shows a more complex scattering pattern including a peak around 0.07 Å^{-1}. We suspect that this might be due to the presence of impurities from the synthesis procedure. We plan to confirm this in future experiments.

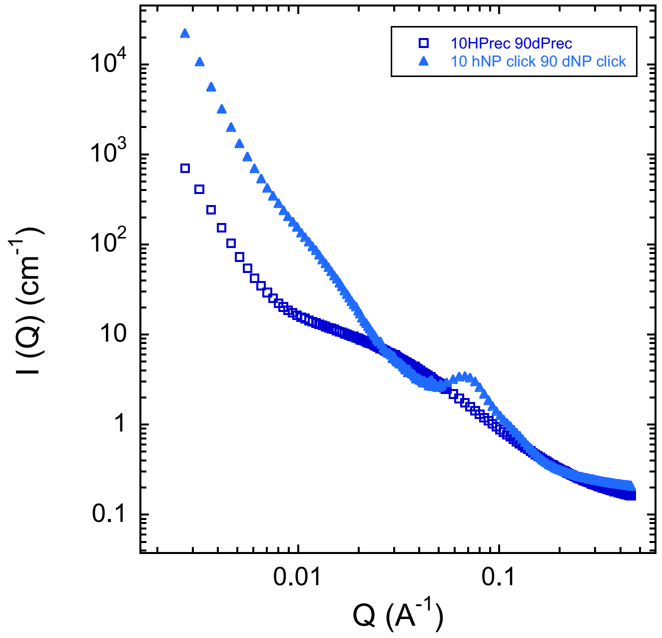

Figure 1. Small angle neutron scattering curves of 10% hydrogenated linear precursor in deuterated precursor (squares) and 10% hydrogenated SCNPs in deuterated SCNPs (triangles).

For the IN15 neutron spin echo experiments we used the same blend of protonated and deuterated chains of precursor and SCNP, respectively. In these kinds of samples the coherent scattering coming from the contrast between the protonated chains and the deuterated matrix reveals the single chain dynamic structure factor $S(Q,t)/S(Q,0)$. By means of IN15, with λ = 13.5 Å and three scattering angles we could gain access to Q values of 0.05, 0.09, and 0.13 $Å^{-1}$ and reaching up to 480 ns. The samples were measured in a flat niobium holder with 2 mm thickness and the temperature of the experiment was 382 K. Figure 2 shows that the curves of the SCNPs are very similar to those of the precursor, suggesting that the dynamic differences that lead to the different rheological behavior are out of the NSE experimental window. Further detailed analysis and comparison with the macroscopic measurements will help elucidate the underlying mechanisms in the SCNP dynamics compared to its linear precursor.

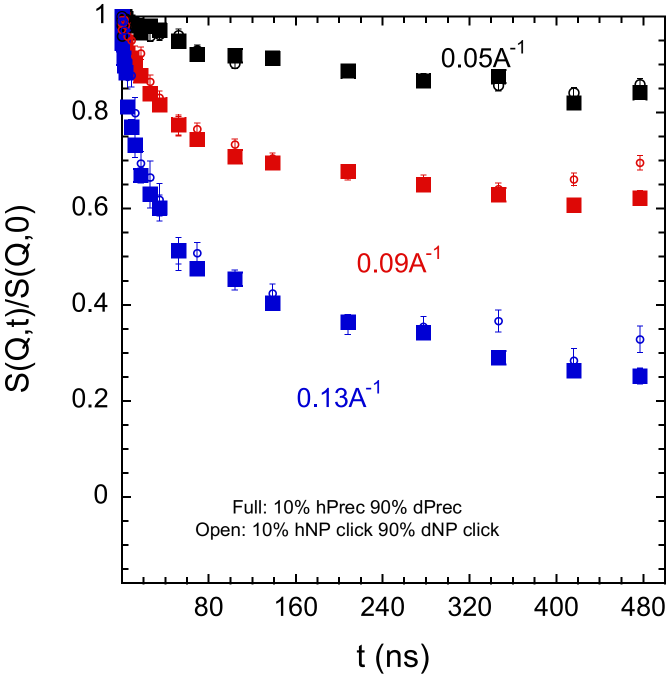

Figure 2. Intermediate scattering function obtained by neutron spin echo of 10% hydrogenated linear precursor in deuterated precursor (full squares) and 10% hydrogenated SCNPs in deuterated SCNPs (open circles) at the indicated Q values.

In addition, we performed test measurements on SCNP and linear chains in deuterated DMF solutions at room temperature.