Experimental report

16/12/2016

Proposal: 6-04-275 **Council:** 4/2016

Title: Impact of Nano-Structuration on the alpha-Relaxation: Collective and Self-Motions of Melt Systems Composed by Single-Chain Nano-Particles

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: protonated single chain nano-particles based on THF
protonated linear copolymer based on THF
deuterated single chain nano-particles based on THF-d8
deuterated linear copolymer based on THF

Instrument	Requested days	Allocated days	From	To
IN16B	6	0		
IN11	9	5	10/11/2016	15/11/2016

Abstract:

We want to characterize the dynamic structure factor (collective motions) and the incoherent scattering function of hydrogens in bulk samples composed of single-chain nano-particles (SCNPs) in comparison to melts of the precursor (linear polymers) counterparts. In this way, we will determine the possible impact of internal cross-link on the microscopic motions involved in the dynamics of the structural relaxation. We are now in the position to face this problem thanks the availability of fully deuterated SCNPs based on THF, which in addition do not crystallise and display a very low glass-transition temperature.

Impact of Nano-Structuration on the α-Relaxation: Collective and Self-Motions of Melt Systems Composed by Single-Chain Nano-Particles

We investigated by IN11C (λ=5.5Å) the dynamic structure factor of melts of fully deuterated precursor macromolecules (dPrec) and melts of single-chain nano-particles obtained from them by internal cross-link (dNP). With three multidetector positions (20º, 50º and 80º for the scattering angle in the middle of the detector) we covered Q-values in the range $0.15 \leq Q \leq 1.7 Å^{-1}$. The molecular weight of the precursors was Mw=36820g/mol with PDI=1.23, and the radius of gyration (determined in good solvent conditions) was of about 7.5nm. The temperatures investigated were 280K, 300K (only in the dNPs), 320K and 360K. In addition, we studied a melt of protonated precursor molecules (hPrec, Mw=33220g/mol, PDI=1.55) at 320K. In this case, the intermediate incoherent scattering function of the hydrogens was the dominant component in the NSE signal.

The resolution function was determined from the scattering of the samples at low temperature. This was realized at 2K for the hPrec sample. However, during the measurements of the dNP sample at such low temperature an unexpected progressive depolarization of the signal was observed that prevented using such measurements as resolution function. We tried to repeat these 2K measurements on the dNP sample but the same result was obtained. We could not identify the origin of this phenomenon (apparently, no magnetic fields were applied in neighbouring instruments during such measurements). We thus finally determined the resolution from the scattering al 220K (close to the glass-transition temperature), which we checked to be elastic by comparison with TiZi results. We also used measurements at 220K for deconvoluting the spectra of the dPrec sample.

With circles, Figure 1 shows the results from the deuterated samples at $1.27 Å^{-1}$ (i.e., about the structure factor maximum Qmax) at the intermediate temperature investigated. The decay of the intermolecular correlations there monitored –due to the α-relaxation—takes place in an almost indistinguishable way for both kinds of melts, independently of the presence of internal cross-links. This is a non-trivial result, which is in agreement with the finding of nearly identical values of the glass transition temperatures in both systems. The similarity of the dynamical features for both materials is observed for the three temperatures investigated in the Q-range around the main structure factor peak Qmax, as can be appreciated in Fig. 2. There, the characteristic times have been represented as function of Q for the three common temperatures studied. However, a striking result is found for Q-values below $0.6 Å^{-1}$, when the intermediate length scales region is entered: the decay of the dynamic structure factor becomes much more stretched and takes place at much longer times for the dNP-bulk than for the linear chains system. This is well illustrated in Fig. 1, where we have also plotted the results corresponding to the lowest Q accessed in the experiments ($0.15 Å^{-1}$) with squares. While for the precursor the characteristic time at this Q-value is clearly faster than at Qmax, for the dNPs system the relaxation time is not resolvable by IN11C. Also, these results seem to follow an extremely stretched functional form. This feature has prevented the determination of the characteristic time in the low-Q range of the dNPs system in a first analysis. A detailed evaluation of the data in this regime will be performed in the future.

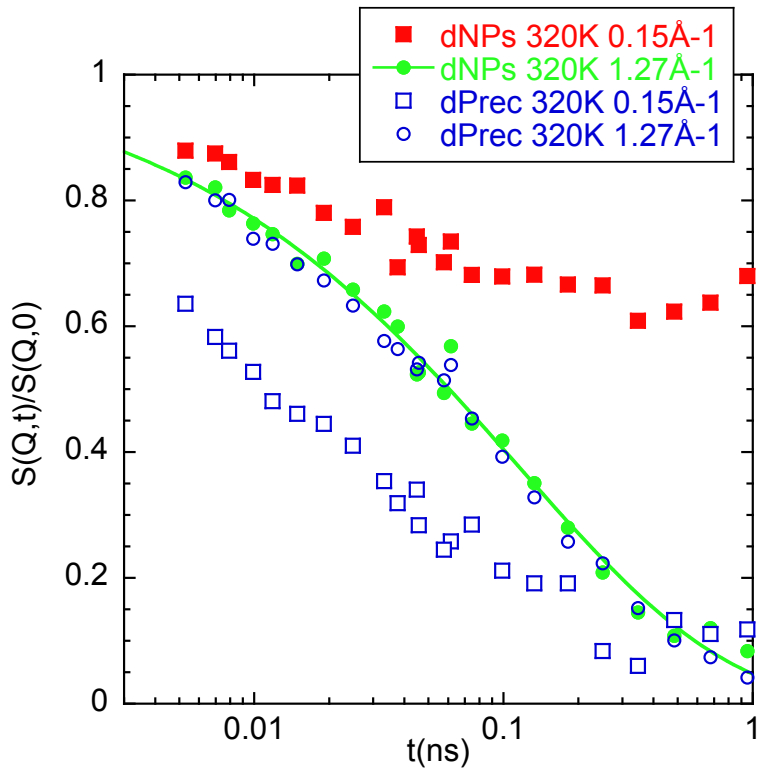

Figure 1: Dynamic structure factor measured at 320K on the melt of deuterated precursor chains (empty symbols) and on the melt of deuterated nano-particles (filled symbols) at Qmax=1.27Å^{-1} (circles) and the lowest Q accessible (squares). Solid line is a description of the dNPs data at Qmax by means of a stretched exponential with β=0.52 (value in the 'standard' range).

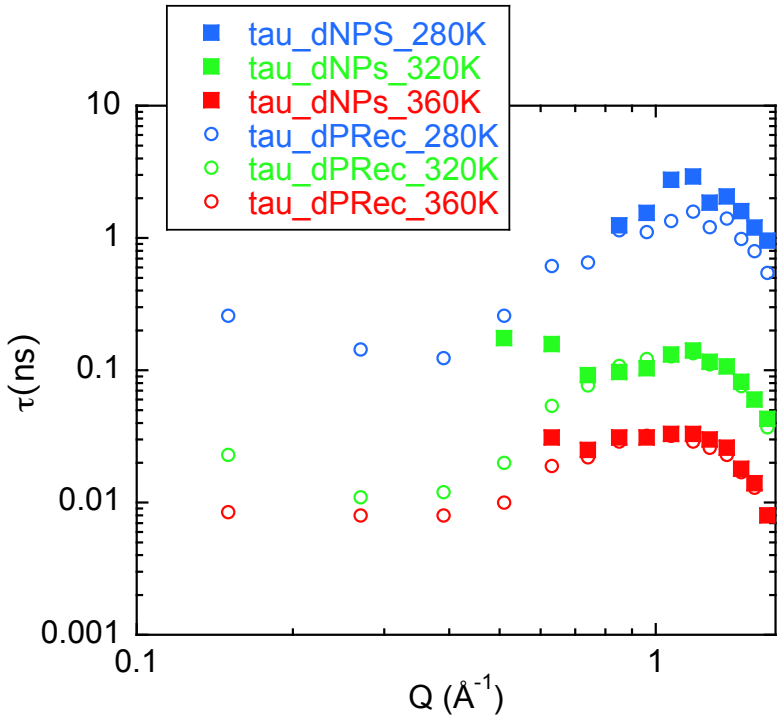

Figure 2: Characteristic times obtained from fits of stretched exponential functions to the dynamic structure factor results of the dPrec (empty symbols) and the dNP (filled symbols) samples at the three temperatures investigated. The β-values obtained followed a clear modulation with the structure factor.