Experimental Report

Proposal: **6-04-265** **Council:** 4/2010

Title: The alpha-relaxation in amorphous polymers seen by scattering methods: a synergistic NSE & XPCS approach

This proposal is a new proposal

Researh Area: Soft condensed matter

Main proposer: **LUND Reidar**

Experimental Team: COLMENERO Juan
LUND Reidar
ARBE Maria

Local Contact: FOUQUET Peter

Samples: deuterated poly(alkylene oxides): [CD2-CD((CD2)m-CD3)-O-]n, m=1,3,5

Instrument	Req. Days	All. Days	From	To
IN11	11	7	15/11/2012	22/11/2012

Abstract:

In this work, we aim to directly follow the dynamics of the a-relaxation in polymers in an unprecedented time/temperature range by using neutron spin-echo spectroscopy (NSE) at ILL in synergy with x-ray photon correlation spectroscopy, XPCS available at ESRF. While both techniques nowadays are able to measure the dynamic density correlation functions around the inter-chain structure factor peak located at relatively high scattering vectors (approx 0.5-1Å-1), they have an interesting complimentary dynamic window. Fast times in the picosecond (ps) – nanosecond (ns) range will be covered by NSE, and XPCS can cover times from milliseconds (ms)- hours. Hence, by combining the two complimentary techniques, we will be able to directly follow the generic structural al-relaxation towards the freezing at the glass transition (Tg) – a task so far not accomplished with scattering techniques. We believe that sufficient signal-to-noise ratios can be obtained by choosing deuterated as well as halogenated polymers that exhibit structure factor peaks at rather low Q and strong coherent scattering cross sections for both x-rays and neutrons. Combination with dielectric spectroscopy and computer

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Unfortunately the XPCS approach was not successful due to severe polystyrene sample degradation (radiation damage). Being this an experiment focused on the synergetic combination of XPCS and NSE instruments, it was not meaningful to invest the NSE beamtime on this sample. For this reason, we asked the SCO office to change the nature of the samples to investigate.

The experiment was focused on the study of the α-relaxation monitoring the decay of the dynamic structure factor in a series of poly(alkylene oxides) (PAOs). In previous diffraction experiments combined with molecular dynamics simulations on PAOs [1], we had proved the nanosegregation of main chains and side groups in these polymers by identifying the origin of the correlations giving rise to the first peak (Q_I) and second peak (Q_{II}) of the static structure factor (see Figs. 1 and 2). Thus, as predicted by coarse-grained simulations [2], the nanosegregation scenario found in other comb-like polymers also applies for highly flexible main-chain systems. The question to be addressed here was whether the dynamics of the α-process associated to the relaxation of the side group subsystem (Q_{II}) in these systems also shows the anomalous properties exhibited by other comb-like polymers like poly(n alkyl methacrylates) (PnMAs) [3,4], or such peculiar features are just a consequence of the dynamic asymmetry between backbone and side-group atoms present in those polymers. In the case of PAOs, the very flexible poly(ethylene oxide)-like main chain is expected to display a high mobility, like the alkyl side groups and thus the dynamic asymmetry is very weak.

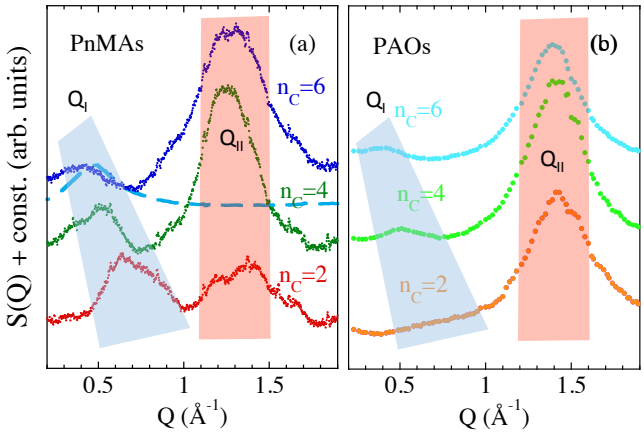

Fig. 1: Structure factor measured on deuterated PnMAs (a) and PAOs (b). The dashed line in (a) corresponds to the partial structure factor of a sample with deuterated main chain and protonated side group (n_c=6). The shadowed areas mark the regions of peaks I and II.

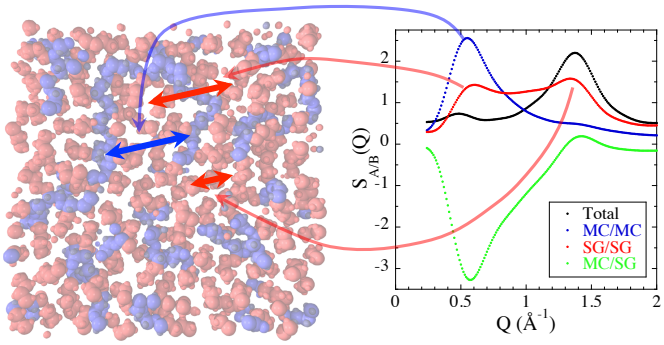

Fig. 2: Snapshot of the simulated cell of PAO with n_c = 4 [1] showing the nanosegregated structure. Red color corresponds to SG atoms and blue color to MC atoms. On the right, decomposition of the structure factor in MC, SG and cross-correlations.

With the available beamtime we followed the decay of the dynamic structure factor of PAOs with two different side-group lengths namely 4 and 6 carbon atoms –PHO and POO respectively–, at the two characteristic wavevectors Q_I and Q_{II} and at different temperatures. The wavelength used was 5.5Å and the samples were fully deuterated.

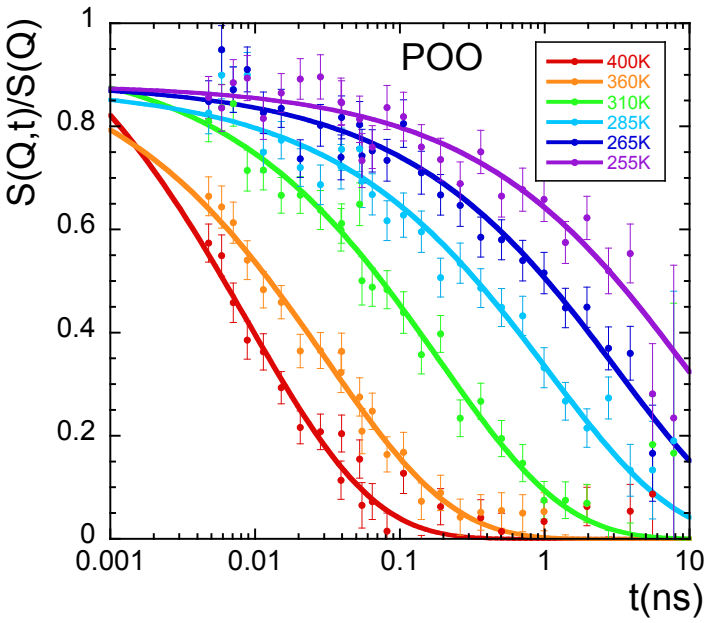

Fig. 3: Dynamic structure factor measured on POO at the temperatures indicated and Q_{II}=1.35Å^{-1}. Lines are KWW fits with β fixed to 0.5.

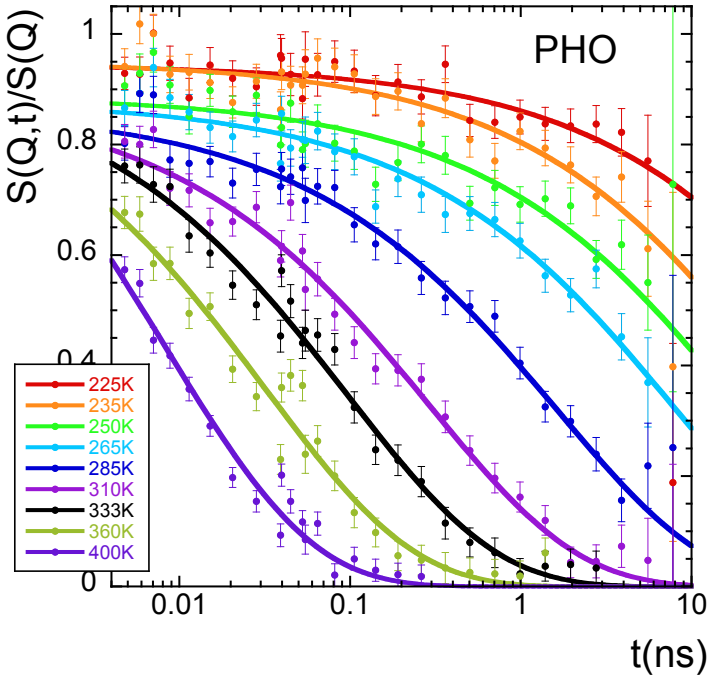

Fig. 4: Dynamic structure factor measured on PHO at the temperatures indicated and Q_{II}=1.35Å^{-1}. Lines are KWW fits with β fixed to 0.5.

Figures 3 and 4 show the results obtained for the two systems at Q_{II}=1.35Å^{-1}, revealing thus the structural relaxation within the alkyl nanodomains. Within the uncertainties, these functions can be described by KWW functions $\exp[-(t/\tau)^{\beta}]$ with a fixed β-value of 0.5. This kind of description was impossible in the case of the analogous results on PnMAs, where β-values of the order of 0.2…0.3 had to be invoked. We note that $\beta \approx 0.5$ is the usually value found for the dynamic structure factor in regular glass-forming polymers. With these results we thus prove that the

behavior found in PnMAs is a consequence of confinement effects induced by the dynamic asymmetry –inexistent or very weak in PAOs.
We also investigated the dynamic structure factor at Q_I revealing the α-process at the main-chain level. Figures 5 and 6 show the results obtained. Despite the long measuring times employed –about 5h—the statistics is very poor. This is due to the extremely low intensities in this Q-region (see Fig. 1). As expected, the results would in principle be compatible with the same 'standard' KWW description, as can be seen in these figures.

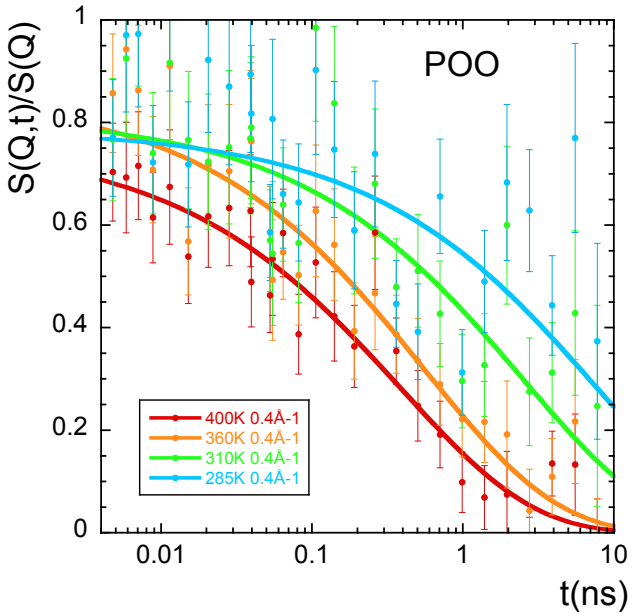

Fig. 5: Dynamic structure factor measured on POO at the temperatures indicated and Q_I=0.4Å^{-1}. Lines are KWW fits with β fixed to 0.5.

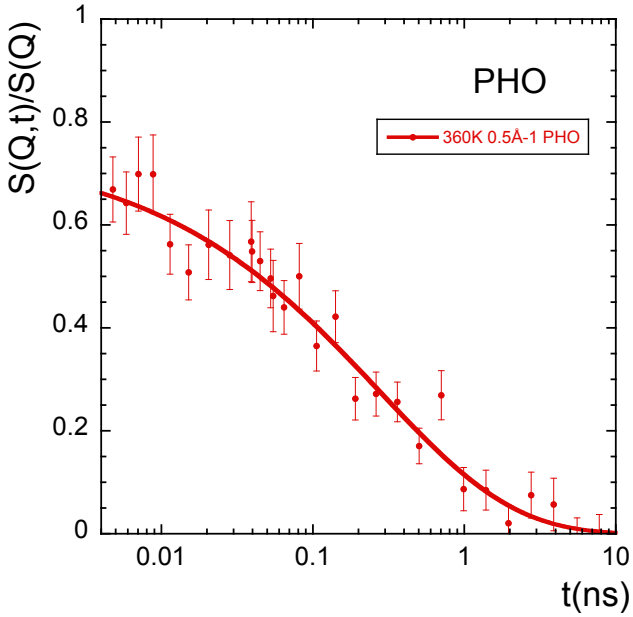

Fig. 5: Dynamic structure factor measured on PHO at the temperatures indicated and Q_I=0.45Å^{-1}. The line is a KWW fit with β fixed to 0.5.

REFERENCES

[1] C. Gerstl, M. Brodeck, G. J. Schneider, Y. Su, J. Allgaier, A. Arbe, J. Colmenero, D. Richter, Macromolecules 45 (2012) 7293.
[2] A. Moreno, A. Arbe, J. Colmenero, Macromolecules 44 (2011) 1695.
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[4] A. Arbe, A.-C. Genix, S. Arrese-Igor, J. Colmenero, D. Richter, Macromolecules 43 (2010) 3107.