Experimental Report

04/11/2013

Proposal:	**9-11-1587**	**Council:**	4/2012
Title:	Amoeba-like behavior of a polymer chain confined in 2D: poly(ethyleneoxide) intercalated in graphite oxide		

This proposal is resubmission of: 9-11-1543

Researh Area: Soft condensed matter

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Samples: blends of protonated and deuterated poly(ethylene oxide) intercalated in graphite oxide
solutions of PMMA-AEMA copolymers and nanoparticles (C9.5H14O4.1) in deuterated dimethyl formamide (DCON(CD3)2)

Instrument	Req. Days	All. Days	From	To
IN15	8	8	19/11/2012	27/11/2012

Abstract:

MD-simulations on 2D polymer chains have found that highly correlated amoeba-like fluctuations of the fractal contours of the compact (sub)chains are the dominant dynamics mechanism. We want to provide experimental evidence for such an intriguing
behavior by investigating the single chain dynamic structure factor of poly(ethylene oxide) intercalated in graphite oxide layers. We have demonstrated that in this system the chains are forced to adopt a completely planar conformation with a one-monomer thickness, i.e. exactly the conditions of 2D-conformation. With SANS measurements and applying contrast variation we have already addressed the single chain form factor of the 2D-confined PEO chains thereby confirming the predictions by molecular dynamics simulations.

Amoeba-like behavior of a polymer chain confined in 2D: poly(ethyleneoxide) intercalated in graphite oxide

We performed measurements on samples consisting of mixtures of protonated (hPEO) and deuterated (dPEO) poly(ethylene oxide) (22% hPEO and 78% dPEO in weight) intercalated in graphite oxide (GO). With this concentration, the scattering of the matrix should be matched, according to the composition and estimated density of GO. Two molecular weights of PEO, 8000 and 1300 g/mol, were considered. Figure 1 shows diffraction results obtained with polarization analysis on IN15 on the 8000 g/mol sample. The increase of the data at low Qs indicates that the matrix scattering is not perfectly matched, probably due to a non-perfect filling. Nevertheless, we can see that in the Q-region 0.1-0.3Å^{-1} the signal of the sample is about one order of magnitude higher than that of the matrix, i.e., the experiments were feasible from the point of view of the scattered intensities.

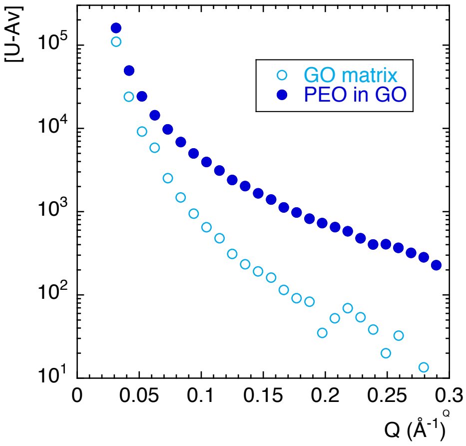

Figure 1: Difference between the 'Up' and the 'Average' signals obtained in diffraction mode by IN15 on the GO-matrix (empty circles) and the sample of PEO (8000 g/mol) intercalated in GO (filled circles).

The confined PEO dynamics was explored at three Q-values: 0.06, 0.1 and 0.2Å^{-1}. These samples suffer severe decomposition at high temperatures. Therefore, the upper temperature limit for the investigation was 400K. Unfortunately, even at such high temperature for both samples a completely elastic signal was observed for the three Q-values investigated. As an example, Figure 2 shows the results corresponding to the 8000 g/mol sample. Thus, apparently, the confined single chain dynamics of PEO is too slow to be detected in the NSE dynamic window in

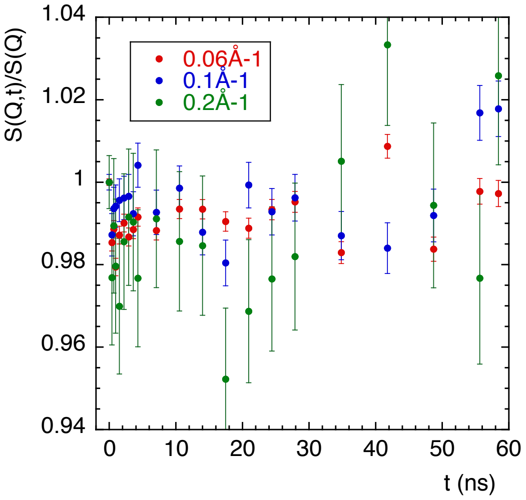

Figure 2: Dynamic structure factor measured at the three Q-values indicated for PEO (8000g/mol) intercalated in GO.

the temperature range where the degradation effects are still assumable. We tried to get some results increasing further the temperature, but the signal was still elastic, within the uncertainties, and we found clear signatures of decomposition.

In view of the impossibility of measuring any dynamics on these samples, we decided to invest the rest of the beam time on test experiments on soft nanoparticles in solution.

The soft nanoparticles (NPs) investigated were obtained from the copolymer P(MMA-co-AEMA) with M_w=58000 g/mol and 35% AEMA. The NPs were synthesized through Michael addition-mediated multidirectional self-assembly of appropriate individual polymeric chains at room temperature in tetrahydrofuran, by following a procedure recently reported in Ref. [1]. Ehylene glycol diacrylate (EGDA) was used as intrachain cross-linking agent. We considered solutions in deuterated DMF with ϕ=0.05 polymer volume fraction –well below the overlap volume fraction– and two temperatures, -10 and 70ºC. At the highest temperature, we also investigated the equivalent solution of the precursor (linear copolymer prior to crosslinking). Figure 3 shows a Kratky plot comparing the form factors of the NPs and the precursor. While the latter shows a close to Debye-like behavior characteristic for a random coil, the peak displayed by the data corresponding to the NPs reveals a compact structure, confirming the globule-like form induced by internal crosslinking.

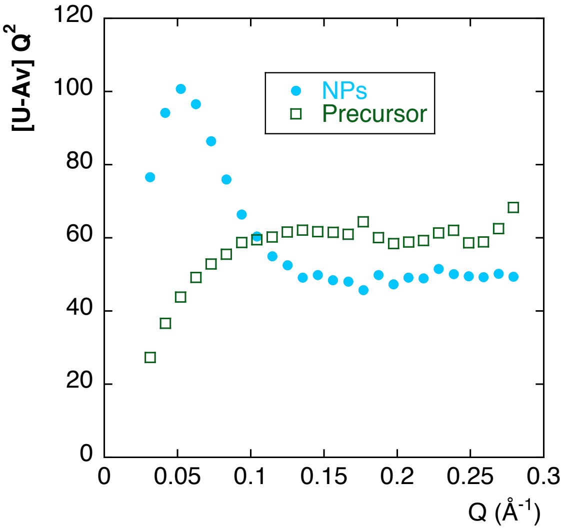

Figure 3: Kratky plot for the NPs and the precursors in solution. The data have been obtained from the difference between the 'Up' and the 'Average' signals obtained in diffraction mode by IN15.

Using λ=16, 10.5 and 8Å we investigated the dynamics in the Q-region between 0.02 and 0.3Å^{-1}. For three selected Q-values, Figure 4 shows the dynamic structure factor measured for both samples at 70ºC. Data are corrected for background scattering from the deuterated solvent. In a first approach, these functions can be well described by KWW functions $\exp[-(t/\tau)^{\beta}]$. The values obtained for the β-exponent are represented in Fig. 5(a). They differ from 1 (corresponding to purely diffusive dynamics), indicating the contribution of internal degrees of freedom in the explored Q- and time window. Accordingly, the characteristic times do not follow a Q^{-2}-law but steeper dependences are observed (see Fig. 5(b)). The results suggest a smaller diffusion coefficient [determined by the inverse of the constant asymptotic $Q \rightarrow 0$ value of the magnitude represented in Fig. 5(b)] for the NPs than for the linear precursors. This would be in contradiction with an effectively smaller size of the NPs according to their globule-like form factor. We suspect this finding to be due to a possible aggregation of the NPs. The interpretation of these results requires further analyses and complementary measurements.

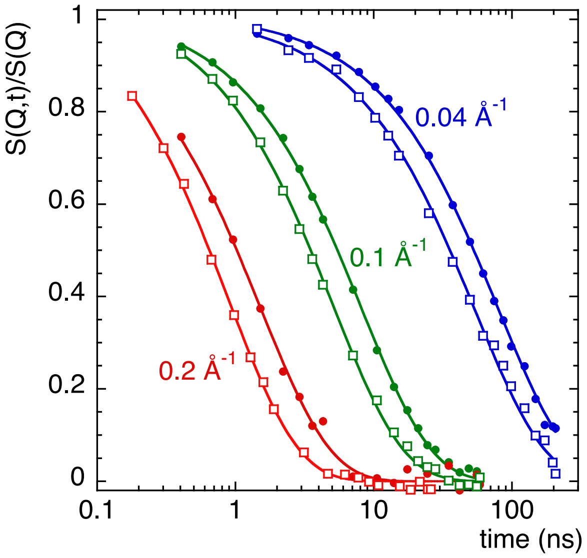

Figure 4: Dynamic structure factor measured on the NPs solution (filled circles) and on the precursors solution (empty squares) at Q=0.04Å^{-1} (blue), 0.1Å^{-1} (green) and 0.2Å^{-1} (red). Lines are fits with KWW functions.

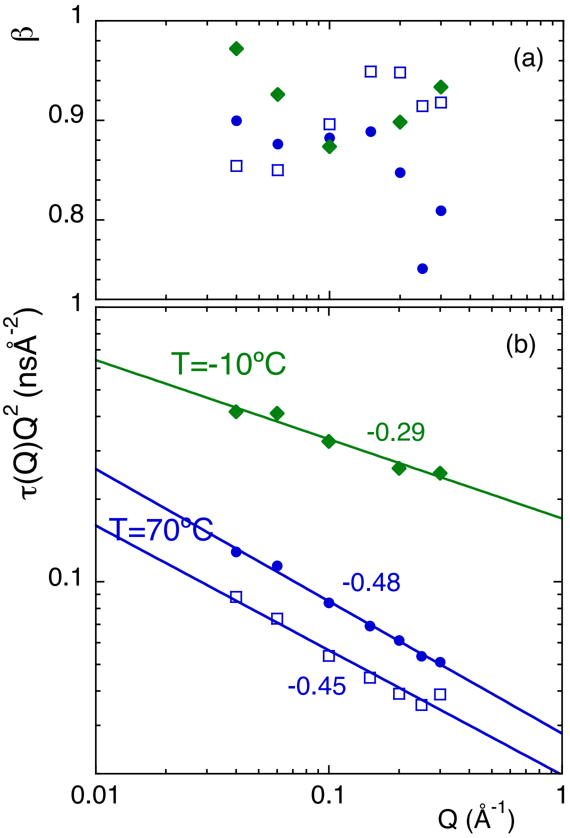

Figure 5: Q-dependence of beta (a) and the product $\tau(Q)Q^2$ (b) for the NPs (filled symbols, diamonds at T=-10ºC and circles at 70ºC) and the precursors (empty squares, T=70ºC). The solid lines are fits to power laws with the given exponents.

References

[1] Sanchez-Sanchez, A.; Akbari, S.; Etxeberria, A.; Arbe, A.; Gasser, U.; Moreno, A. J.; Colmenero, J.; Pomposo, J. A. *ACS Macro Letters* 2013, *2*, 491–495.