

Experimental report

06/09/2023

Proposal: 9-11-2080

Council: 10/2022

Title: Cooperativity of monomer motion within the tube confinement of highly entangled melts.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: (C₂D₆OSi)_n
(C₂H₆OSi)_n+(C₂D₆OSi)_n
(C₂H₆OSi)_m+(C₂D₆OSi)_m

Instrument	Requested days	Allocated days	From	To
IN15	5	5	18/05/2023	23/05/2023

Abstract:

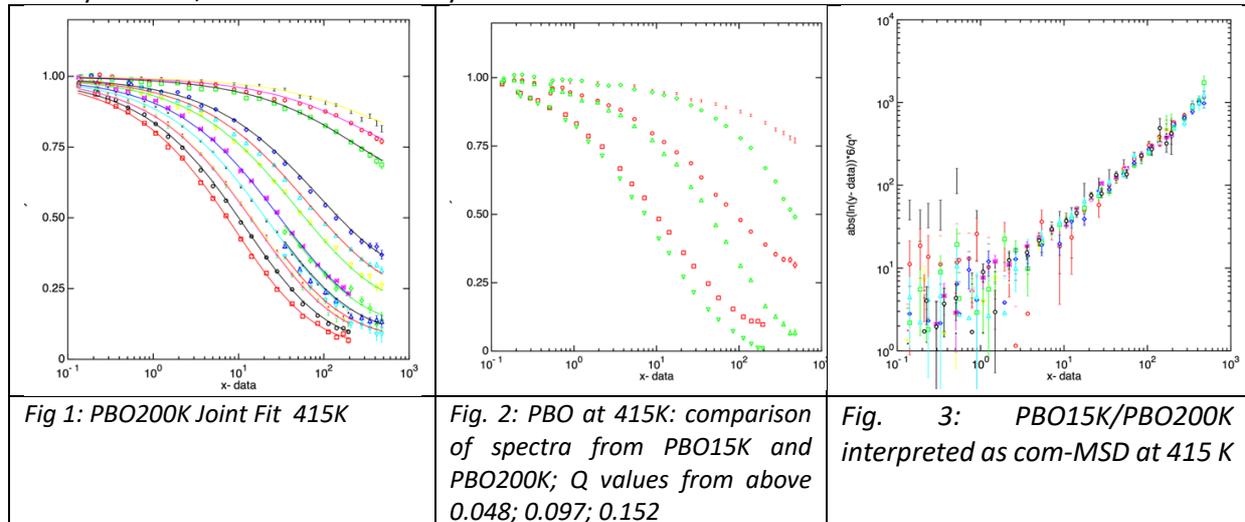
Scrutinizing the usually ignored short time regime of presently available NSE data from reptating polymers that were collected during the last 3 decades reveals that at short times and distances the dynamics significantly deviates from an expected Rouse dynamics on the entanglement blob level. The presently known experiments focused on long time plateaus and only contain limited data of limited accuracy and sampling density in this regime. In this proposal the best suitable available polymer (PDMS) is chosen to explore the dynamics details in this regime to understand the dynamic peculiarities of reptating polymers that occur at displacements around the tube dimension. 5 days of IN15 beamtime is requested.

Experimental report on Exp. 9-11-2080

Recently we have studied the dynamics of short chain tracers in long strongly entangled matrices both for PE as well as for PEO (M. Zamponi et al. Phys. Rev. Lett. 126, 187801 (2021); M. Kruteva et al. Macromolecules 54, 11384 – 11391 (2021)). Both experiments showed that independent of the tracer molecular weight cooperative motion of the tracers with the host takes place and is limited by the entanglement distance or tube diameter of the host.

With this in mind we performed an experiment on poly(butylene-oxide) (PBO) melts using a weakly entangled short chain (below $Z=2$; $M_w=12000$) in one case and a strongly entangled melt ($M_w=200000$) in the other case with the aim to scrutinize the short time Rouse regime within an entangled melt and to search for signatures of cooperativity in the long chain system. The idea was to investigate a short chain melt that should be characterized by Rouse dynamics and a highly entangled melt, where based on the tracer experiments we expected cooperative motion, which would be different to that in the short melt. We took PBO, because it has a large tube diameter (about $d = 70 \text{ \AA}$ for PBO), is rather flexible and should display a pronounced Rouse regime in the by NSE accessible dynamic structure factor. We studied both melts at two temperatures (415K and 450K) by NSE in a time window up to about 500 ns.

Let us first have a look on the 200K material. It was evaluated in terms of our new dynamic structure factor that includes Rouse behavior at short times, local reptation at longer times and allows for Non-Gaussian dynamics (M. Monkenbusch et al., J. Chem. Phys. 159, 034902 (2023)). A very good joint fit of the spectra from both temperatures was obtained. Fig 1 displays the fitting result for 415K. As may be seen, the fit describes very well the data.



In a next step we compared the spectra from the PBO15K and PBO200K samples. Fig. 2 displays NSE spectra taken from the PBO15K and the PBO200K samples at 415K. While at short times in the initial Rouse regime both sets of spectra well agree, at longer times the PBO15K spectra decay significantly faster – they are not subject of entanglement constraints and express significant contributions from translational diffusion. The **amazing observation** was that the ratio of the respective spectra from the two melts resembled a single exponential with a relaxation time following a Q^{-2} behavior suggesting that the ratio of the spectra reflects simple translational center of mass (com) Fickian diffusion of the shorter chains. Fig 3 presents these ratios in terms of a center of mass displacement $\langle r_{com}^2(t) \rangle = -\frac{6}{Q^2} \ln[(S(Q, t)_{PBO15K} / S(Q, t)_{PBO200K})]$. As may be seen, all data originating from the Q - range $0.041 \leq Q \leq 0.163 \text{ \AA}^{-1}$ collapse on a master curve relating to $\langle r_{com}^2(t) \rangle = 2.52 * t = 6 * D_R t = Wl4/3R_e^2 [\text{\AA}^2]$. A similar observation also holds for the 450K data. As it turns out the thus determined

center of mass diffusion coefficients are exactly described by the plain Rouse rate Wl^4 obtained from a fit of the PBO200K sample.

As demonstrated in a recent paper, in the cross over region from nonentangled to entangled the dynamic structure factor can be well analyzed by a Rouse mode analysis, which affects the amplitudes of the Rouse modes (Aakash Sharma et al., ACS Macro Letters 11, 1343 – 1348 (2022)). In this spirit in the fits of PB=15K the first Rouse mode amplitude was affected. Fitting the PBO15K data in addition to Fickian diffusion a strong sub-diffusive component was found. The observations well related to findings by Zamponi et al. (Journal of Physical Chemistry B **112**, 16220-16229 (2008)) on short chain polyethylene (PE) melts, which could be quantitatively interpreted by CDGLE that involved cooperative motion of in the order of 10 polymers in the melt.

But there remain mysteries apparent in the comparison of the PBO spectra! We reiterate that aside of translational center of mass Fickian diffusion the spectral shape from both samples agree quantitatively. Thus, the same cooperative motion that gives rise to sub-diffusivity in the unentangled short chain melt must also take place within the tube constraints of the long chain material. There it appears in the cross over regime to local reptation. Nevertheless, as for the short chains, where it is assumed that the early time sub-diffusive part is related to an inter-chain potential that couples the com-motion of several chains, a very similar phenomenon appears to take for the chain dynamics within the tube confinement. Also there interchain interaction between the entanglement strands gives rise to cooperative motion with the same signature in $S(q, t)$ as for the short chains. To pin down the physics behind this observation will be goal for future experiments.