Experimental report

16/09/2019

Proposal: 9-11-1861 **Council:** 4/2018

Title: Association dynamics of supramolecular star polymers

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C2H4O/C2D4O

Instrument	Requested days	Allocated days	From	To
IN11	10	12	23/07/2019	04/08/2019
IN15 Standard	5	4	31/07/2019	04/08/2019

Abstract:

The scope of this proposal is the coherent intermediate structure factor as measured by Neutron Spin Echo spectroscopy to investigate for the first time the association dynamics of supramolecular poly(ethylene oxide) (PEO) stars in the melt of covalent short PEO linear chains. The proposed investigation is a new dynamic experiment to enhance the microscopic understanding of the self-association mechanism in a symmetric 3-arm star, consisting of PEO, using directed and DNA-inspired heterocomplementary thymine (Thy) and diaminotriazine (Dat) as the supramolecular functional group. Here, the NSE dynamic structure factor and its correlation to the chain architecture and transient associated state is an indispensable prerequisite to unravel the microscopic properties of the self-assembly dynamics, and in particular the effective hydrogen bonding (H-bonding) lifetime.

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The main aim of this proposal is to extract the single chain dynamic structure factor of supramolecular PEG stars that contains the influence of the H-bonding on the overall dynamics, as well as on the mode contributions and bonding and debonding mechanisms related to transient network dynamics. Directed heterocomplementary hydrogen-bonding end-groups, thymine (THY) (one of the nucleobase in DNA) and diaminotriazine (DAT) as well as the self- complementary hydrogen-bonded 2-ureido-4[1H]- pyrimidinone (UPY) motif are used as the hydrogen-bonding functional groups [1,2,3].
This investigation is not only important from a fundamental point of view, but also for the industrialized polymers since they exhibit a large variety of architectures, involving e.g. branched and crosslinked structures and star-type polymers can be considered as the simplest prototype materials for branched systems [4,5].
Nine different samples have been measured – supramolecular hydrogenated (H) 4-arm star PEG immersed in own deuterated (D) covalent short linear PEG chains in the melt at different concentrations – at three temperatures (333K, 373K and 413K) accessing the Q-range 0.05 Å-1 and 0.2 $Å^{-1}$ at five different Q values. The samples were measured to maximum Fourier times of 300 ns.

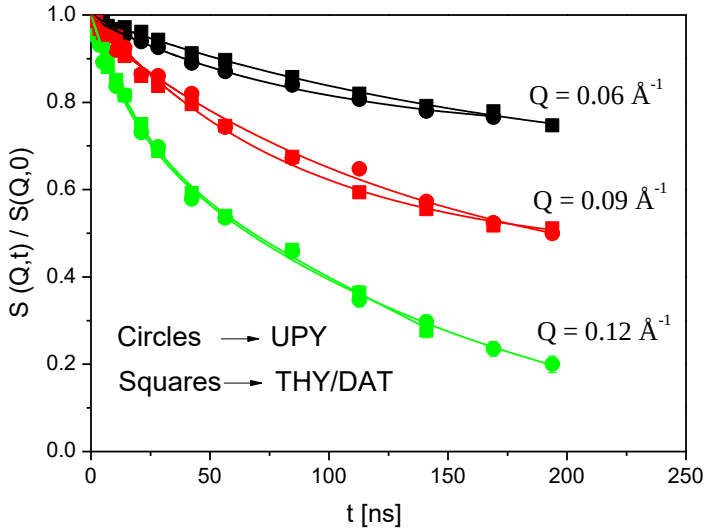

Figure 1- Dynamic structure factor vs Fourier times for 4-arm star PEG functionalized with Thy/DAT (1/1) and UPY immersed in own covalent short linear PEG chains in the melt at 20% wt% concentration at T=60ºC.

Figure 1 shows a simple qualitative comparison of the dynamic structure factor in function of Fourier times for the diluted supramolecular PEG stars. Eventhough the homocomplementary association strength of the UPY groups are 10^5 higher than THY/DAT (1:1) heterocomplementary association strength, when dissolved in own covalent short linear PEG chains, the dynamics seems very similar.
Additional quantitative analysis is ongoing for further evaluation of the results.
However the structural parameters as an essential input for the understanding of the dynamics are still missing and a continuation proposal has been submitted in ILL.

References

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