Experimental report

21/11/2016

Proposal: 9-11-1741 **Council:** 4/2015

Title: Searching for entanglement tube dilation in all-polymer nano-composites: linear chains with stars

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: deuterated/protonated polyisoprene

Instrument	Requested days	Allocated days	From	To
D11	2	1	25/05/2016	26/05/2016
IN15	10	6	10/06/2016	16/06/2016

Abstract:

Recently, a spectacular entanglement tube dilation of linear polymer chains has been observed by NSE on a nano-composite with single-chain polymer nano-particles (SCNPs). This effect was attributed to indirect confinement effects produced by compression of the linear chains close to interfaces with the SCNPs. Such compression was corroborated by SANS measurements on the nano-composite. It was argued that the special topology of SCNPs leading to an enhanced amount of interfaces would magnify the impact of the presence of NPs on the linear chains behavior. Here we aim to check whether chain contraction and subsequent tube dilation are also present in linear chains under the presence of star polymers, which shall also provide a great amount of interfaces in the mixture.

Searching for entanglement tube dilatation in all-polymer nanocomposites: linear chains with stars

One key question in the field of polymer physics is the effect of small particles on the dynamics of linear chains in all-polymer nanocomposites. A major challenge is to distinguish between topological effects and other specific interactions between the polymer matrix and the filler particles. This limitation can be overcome by having both components with the same density, segmental mobility and monomer excluded volume. For this purpose we investigated the single chain static (SANS) and dynamic (NSE) structure factor of linear chains in a mixture with stars of the same polymer: polyisoprene (PI). The samples contained 10% labeled protonated linear chains immersed in deuterated material. The molecular weight of the linear chains (≈ 80000 g/mol) is well above the entanglement mass of PI (Me≈6000 g/mol), while the arms of the stars are just Me. In this way, we should avoid entanglements between stars and linear chains. We explored two functionalizations — 8 and 18 arms — leading to different interfacial area. The stars concentration was 23% in volume.

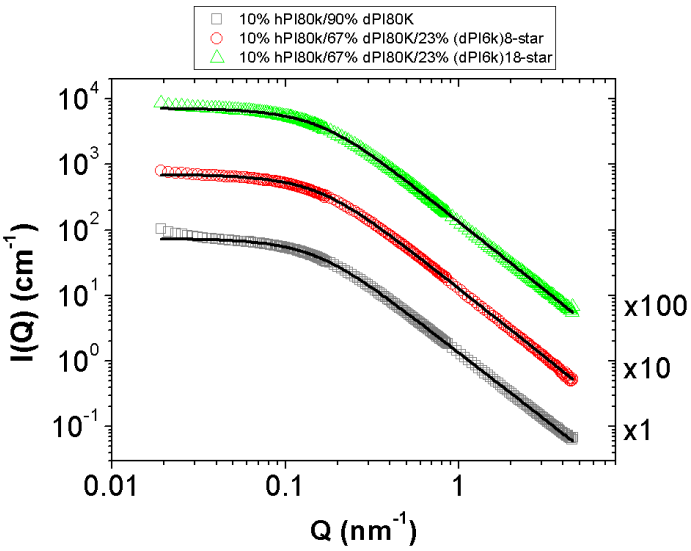

Figure 1. Small angle neutron scattering curves of 10% hydrogenated linear polyisoprene in a deuterated matrix of linear polymer (grey squares) and mixtures of linear and star polymers with 8 (red circles) and 18 arms (green triangles). Lines are fits to a generalized polymer coil model. The curves have been shifted vertically.

SANS experiments on the instrument D11 were carried out at room temperature (296 K). We used a neutron wavelength λ=6 Å and 3 different configurations of sample-to-detector / collimation distances (1.4 m/10.5 m, 8 m/8 m and 39 m/40 m) to cover a Q interval from 0.02 to 5 nm^{-1}. The scattering curves of the hydrogenated linear polymers in deuterated matrix fit well to a generalized

polymer coil polymer (Fig. 1). The chain configuration and size (Rg=10 nm) almost do not vary in the presence of 23 wt% of stars with 8 or 18 arms, compared to the linear polymer. Experiments with labeled protonated stars in deuterated material showed that the stars have a radius of gyration of 4.8 nm invariant of the star mass concentration in the nanocomposite across the concentration range probed.

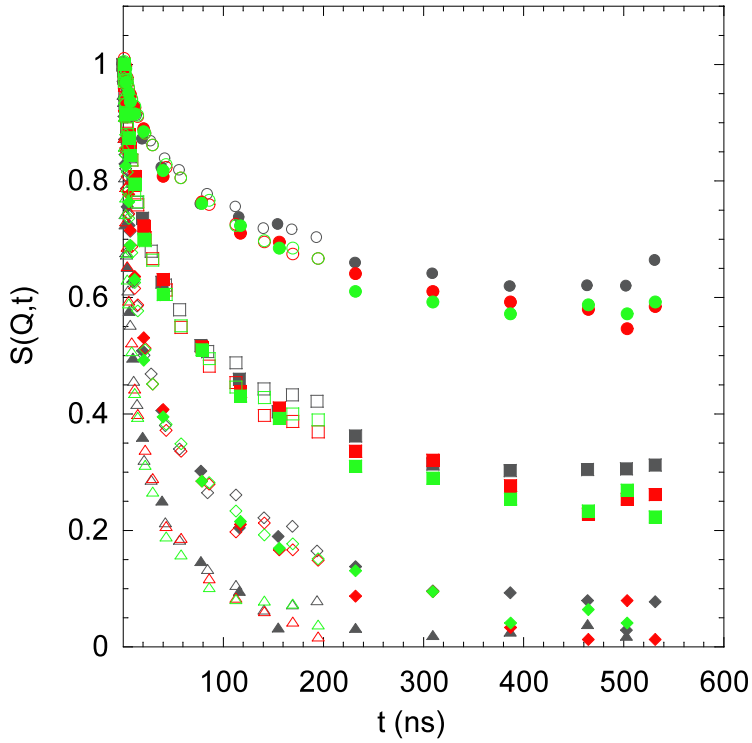

Figure 2. Intermediate scattering function obtained by neutron spin echo of hydrogenated linear polyisoprene in a deuterated matrix of linear polymer (grey) and mixtures of linear and star polymers with 8 (red) and 18 arms (green). Open symbols correspond to λ=10 Å and solid symbols to λ=14 Å for Q values 0.07 (circles), 0.1 (squares), 0.13 (diamonds) and 0.16 Å^{-1} (triangles).

For the spin echo experiments on IN15 we used two incident wavelengths λ=10 Å and 14 Å to explore the Q values 0.07, 0.1, 0.13 and 0.16 Å^{-1}, obtaining the intermediate scattering function from 0.3 to 550 ns. The dynamic measurements were performed at 423 K. The intermediate scattering functions of protonated linear chains in nanocomposites exhibit a slightly lower plateau value at long times for the linear polymer in the presence of stars, suggesting a small increase in the tube diameter corresponding to disentanglement of the linear chains (Fig. 2). These results will be compared to the tube theory for entangled polymers.

The combination of these macroscopic measurements with macroscopic dynamic measurements by dielectric spectroscopy will provide insight into the effect of small nanoparticles on the dynamics of entangled linear polymers.