Experimental report

18/09/2018

Proposal: 9-11-1833 **Council:** 4/2017

Title: Effects of star polymer functionality on the entanglement tube dilatation of the linear matrix in all-polymer nanocomposites.

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1741

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Samples: hydrogenated/deuterated polyisoprene

Instrument	Requested days	Allocated days	From	To
IN15	6	0		
D11	2	1	05/06/2018	06/06/2018

Abstract:

Our previous IN15 experiments show indications of disentanglement upon incorporation of small stars to an entangled polymer melt. Complementary dielectric spectroscopy studies in a wide concentration range reveal a strong effect of the functionalization (number of arms) of the stars on the disentanglement time of the matrix, and suggest exploring with NSE mixtures with higher star concentrations to provide robust microscopic evidence for the importance of the interface amount on the entanglement tube dilation. SANS experiments are crucial to precisely determine the form factor and thereby the chain dimensions of the macromolecules in the mixtures;an information also needed for the proper interpretation of the dielectric results.

Effects of star polymer functionality on the entanglement tube dilatation of the linear matrix in all-polymer nanocomposites.

When studying the effect of small soft particles on the dynamics of linear chains in all-polymer nanocomposites it is challenging 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 chemical composition: polyisoprene (PI). The samples contained 10% labeled protonated linear chains immersed in deuterated material. The molecular weight of the linear chains (80 kDa) is well above the entanglement mass of PI ($M_e \cong$ 6000 g/mol), while the arms of the stars are just M_e. In this way, we should avoid entanglements between stars and linear chains. We explored star polymers with 18 arms and compared them to the linear case of the same size, i.e., PI 12k. The star concentration was 50%.

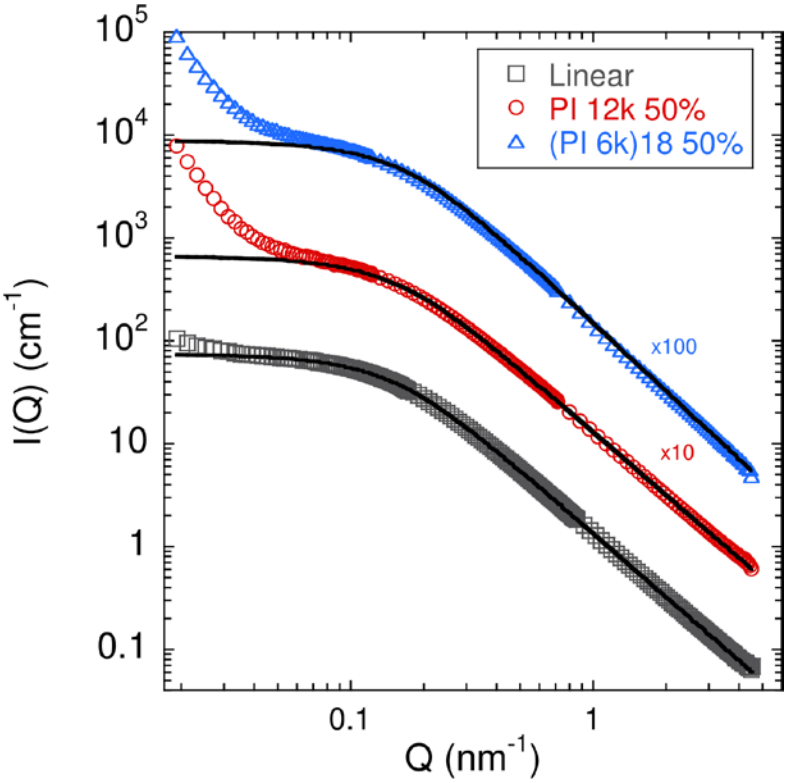

Figure 1. Small angle neutron scattering curves at 296 K of 10% hydrogenated linear polyisoprene in a deuterated matrix of linear polymer (grey squares) and mixtures of linear and 50 % linear PI 12k (red circles) and 18 arms (blue triangles). Lines are fits to a generalized polymer coil model.

SANS experiments on the instrument D11 were carried out at room temperature (296 K) and at 361 K. We used a neutron wavelength λ=6 Å and 3 different configurations of sample-to-detector / collimation distances (1.4 m/2.5 m, 8 m/8 m and 39 m/40.5 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 (see representative examples in Figure 1).

The chain conformation and size (R_g=9.98 nm) almost do not vary in the presence of 50 wt% of stars with 18 arms (R_g=9.7 nm) and short linear polymer (R_g=9.3 nm). Experiments with labeled protonated stars in deuterated linear matrix showed that the stars have a radius of gyration of 5.6 nm independent of the star mass concentration in the nanocomposite across the concentration range probed.

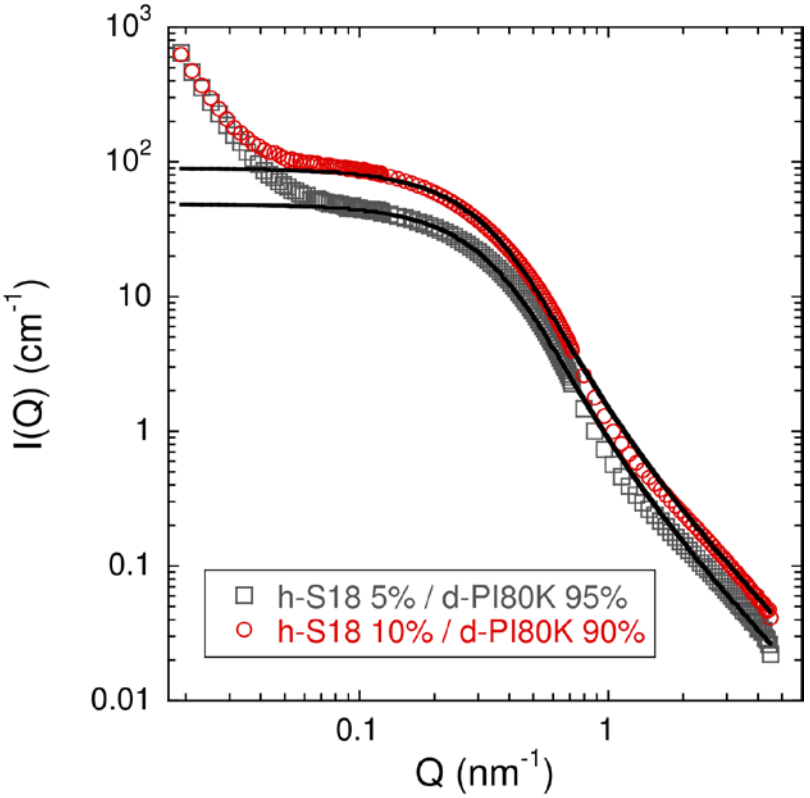

Figure 2. SANS curves at 296 K of 5% (hPI6k)8-star in deuterated linear matrix and 10% (hPI6k)18-star in deuterated linear matrix. Lines are fits to a star polymer model.

Finally, our experiments showed that the size of the linear polymer in the blends with stars and short linear chains slightly decreases with temperature with a value of $\partial \ln < {R_g}^2 > / \partial T$ of $-0.8 \cdot 10^{-3}$ K^{-1} in both cases. However, the 18-arm star polymers don´t significantly change in size at higher temperatures. We note that the temperature dependence of the polymer size is relevant for the interpretation of the dynamic data of neutron spin echo performed at high temperature and our dielectric spectroscopy results that were performed at a wide range of temperatures.