Experimental report

14/02/2020

Proposal: **9-11-1901** **Council:** 10/2018

Title: COMPONENT DYNAMICS IN AN ALL-POLYMER NANO-COMPOSITE BASED ON SINGLE-CHAIN NANO-PARTICLES

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
d / h polytetrahydrofurane
Blends of Poly(vinylidene fluoride) $C_2H_2F_2$ and Poly(methyl methacrylate) $C_5H_8O_2$
Blends of Poly(styrene-butadiene) (SBR) (C_8H_8-C_4H_6) and low molecular resins (C_nH_m)

Instrument	Requested days	Allocated days	From	To
IN5	3	3	01/10/2019	04/10/2019
IN16B	6	5	27/09/2019	02/10/2019
D7	2	2	25/09/2019	27/09/2019

Abstract:

The (few) investigations carried out until now suggest that the addition of single-chain nano-particles (SCNPs) to long linear polymer chains induces their disentanglement. Surprisingly, in an all-polymer nano-composite where the linear chains in the matrix are precursors of the SCNPs (and therefore their segmental dynamics are identical) we observe, together with tube dilation, an acceleration of the initial decay of the dynamic structure factor of the chains. With these experiments we want to selectively investigate the component dynamics in this all-polymer nano-composite at segmental level, trying to shed light on this unexpected result.

COMPONENT DYNAMICS IN AN ALL-POLYMER NANO-COMPOSITE BASED ON SINGLE-CHAIN NANO-PARTICLES

The mixtures contained protonated or deuterated Single-Chain Nano-Particles (SCNPs) based on tetrahydrofuran (THF). These SCNPs were obtained from protonated or completely deuterated linear copolymer precursors (hPrec and dPrec) respectively, via copper click chemistry mechanism. Nano-composites consisting of mixtures of linear precursors and SCNPs were prepared.

To separately follow the two components, samples where the SCNPs are deuterated and the precursor (the matrix) is protonated and samples where the SCNPs are protonated and the matrix is deuterated were prepared. Two different compositions were studied (75% and 50% in Prec): 75hPrec/25dSCNPs, 75dPrec/25hSCNPs, 50hPrec/50dSCNPs and 50dPrec/50hSCNPs. Molecular weights M_w were 21 kg/mol for hPrec and 36 kg/mol for dPrec as reference samples. The glass-transition temperatures T_g measured by DSC were 202 K (hPrec) and 210 K (hSCNPs), while their deuterated counterparts exhibit ±2 K of difference in the temperature. Samples were filling flat aluminum sampleholders, and the thicknesses were calculated to yield a transmission of 90%.

All samples were studied at 300 K by D7 instrument. On IN16B and IN5, at 285, 320 and 360 K experiments were carried out in order to determine the T-dependence of the segmental relaxation in both nanocomposite components. For comparison reasons, same experiments were done in the bulk linear precursor and SCNPs as reference samples.

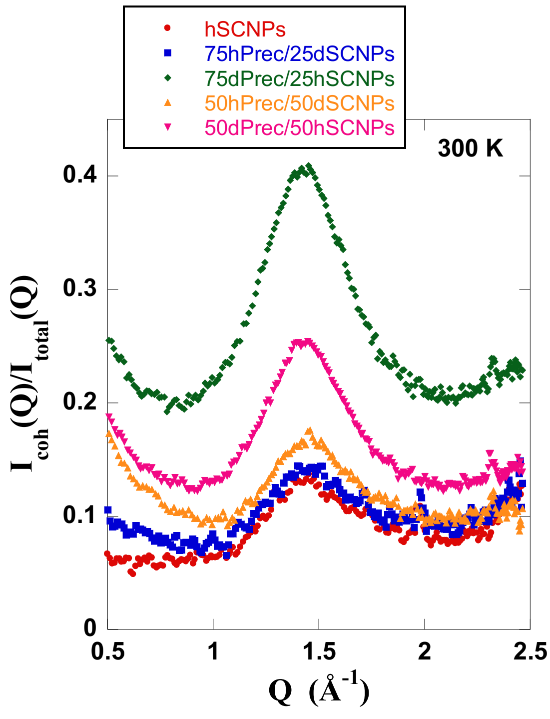

Figure 1. Ratio between coherent and total differential cross sections obtained by D7 at 300 K on samples with protonated and deuterated precursor and SCNPs mixtures.

D7 experiments were carried out where the incident neutron wavelength was set to 4.89 Å to cover a Q-range from 0.15 to 2.5 Å^{-1}. A Vanadium sheet was used to calibrate the detector efficiency. The obtained results are plotted in Fig. 1. One main peak is observed in the Q-range between 1.0 and 2.0 Å^{-1} centered around 1.4 Å^{-1} for all the samples studied here. The short-range order, thus, seems to be not modified by the composition. The value of these results is also to determine the Q-ranges where the coherent scattering contribution is more or less pronounced, in order to properly analyze and interpret the QENS results.

The QENS experiments on the protonated reference samples and on the protonated/deuterated nanocomposites were carried out on the backscattering IN16B spectrometer and the time-of-flight IN5 instrument, to cover a wide dynamic range. For the IN16B experiments an incident wavelength of 6.28 Å was used covering a Q range between 0.19 and 1.9 Å^{-1}. For the IN5 experiments two incident wavelengths were applied: 6 and 9 Å. As mentioned before, three temperatures (285, 320 and 360 K) well above T_g were studied. The analysis of the quasielastic spectra was done by Fourier transforming the data to the time domain and then deconvoluting from the instrumental resolution, to obtain the intermediate scattering function in the time domain $S\,(Q,t)$.

Figure 2 shows the IN16B and IN5 combined QENS results after this procedure. They correspond to a fix Q-value of 0.95 Å^{-1} at 285 K for the four samples studied. From the D7 experiments (Fig. 1), we know that at this Q-value the coherent contribution is minimized, and the obtained results are strongly dominated by the incoherent scattering of the protons in the corresponding sample. The QENS results can be well described above ≈ 2 ps by means of Kohlrausch-Willians-Watts (KWW) or stretched exponential function. As can be seen, at short times ($t = 10^{-12}$ to 10^{-11} s, in the IN5 window) the results observed here are quite similar for all the samples, although for the hSCNPs bulk sample the dynamics observed starts being slower than that of the linear precursor chains. This difference becomes much more evident when we move to longer times ($t = 10^{-10}$ to 10^{-9} s accessed by IN16B). There, the scattering function corresponding to the self-motions of the protons in the SCNPs samples (hSCNPs and 75dPrec/25hSCNPs) reveal a much slower underlying dynamics than those corresponding to the linear chains; on the other hand, the dynamics of the linear chains is almost undistinguishable for the hPrec based bulk sample and its nanocomposite.

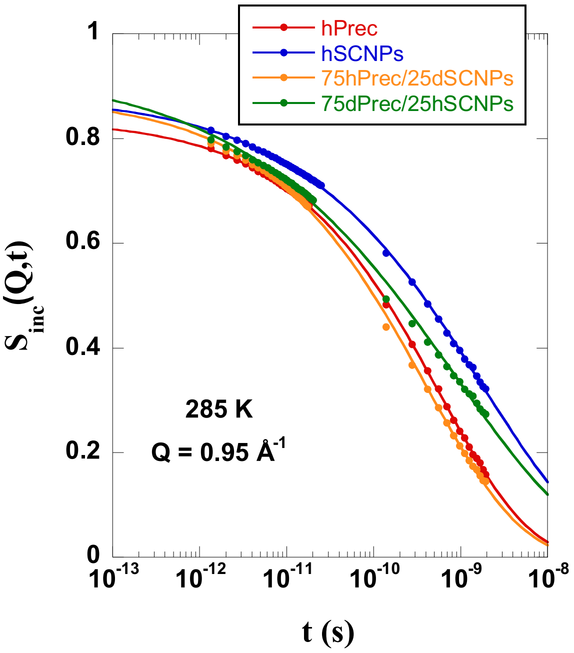

Figure 2. Fourier transformed and deconvoluted QENS spectra obtained from IN16B and IN5 instruments on the hPrec, hSCNPs and mixtures of 75hPrec/25dSCNPs and 75dPrec/25hSCNPs nanocomposites, studied at 285 K and corresponding to 0.95 Å^{-1}. Solid lines are KWW fits for each sample.