

Experimental report

26/04/2022

Proposal: 9-11-2046

Council: 4/2021

Title: CONFINING PVDF IN DYNAMICALLY ASYMMETRIC BLENDS AND ALL-POLYMER NANOCOMPOSITES

Research area: Soft condensed matter

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Samples: protonated poly(vinylidene fluoride)
deuterated poly(methyl methacrylate) and (2-acetoacetoxy)ethyl methacrylate

Instrument	Requested days	Allocated days	From	To
IN16B Si 111 BATS	3	3	17/05/2021	20/05/2021

Abstract:

Poly(vinylidene fluoride) (PVDF) and its copolymers are highly appreciated polymers due to their excellent data storage properties. PVDF can crystallize in 4 different phases, unfortunately, neat PVDF films cannot be used for above mentioned applications because they generally crystallize in the non-ferroelectric alpha-phase. Depending always on concentrations and conditions used, PVDF when blended with the miscible poly(methyl methacrylate) (PMMA), may crystallize dominantly in the ferroelectric beta-phase. The modulation of crystallinity and polymorphism of these mixtures is well studied and explained in the literature, however, almost nothing is known about: (i) the structural and dynamic properties of the amorphous regions of this type of nanocomposites, (ii) the relation between the dynamics and the formation of different polymorphic phases and, (iii) the confinement effects observed and reported before for analogous PEO/PMMA-based-SCNPs systems.

We propose here to characterize the self-atomic motions of confined amorphous PVDF in nanocomposites with PMMA-based SCNPs and their precursors as reference.

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Mixtures of poly(methyl methacrylate) (PMMA)-based Single Chain Nanoparticles (SCNPs) and poly(vinylidene fluoride) (PVDF) are prepared in this investigation to form so-called “all-polymer nanocomposites”. These samples are compared with the corresponding reference blends where PVDF is mixed with the linear precursor chains of the SCNPs (random copolymers of deuterated MMA and 2-aminoethylmethacrylamide hydrochloride (AEMA)). The SCNPs were synthesized via Michael addition reaction mechanism following a procedure reported in ref [1]. The aim of this study was to determine the effect of the presence of the PMMA-like component on the hydrogen dynamics of PVDF, and in particular the impact of the internal cross-links within the slow chains on the PVDF local dynamics.

We investigated the following four different compositions for the mixtures: PVDF/Prec and PVDF/SCNPs (75/25 wt%), and PVDF/Prec and PVDF/SCNPs (25/75 wt%) samples, and the PVDF homopolymer as reference. Molecular weights M_w were 180 kDa for PVDF and around 100 kDa for Prec and SCNPs samples. The glass-transition temperatures T_g measured by Differential Scanning Calorimetry (DSC) were 329 K (Prec) and 353 K (SCNPs), while PVDF sample presents a crystallization peak (T_c) at 411 K and a melting peak (T_m) at 440 K. Samples were filling flat aluminum sample holders, and the thicknesses were calculated to yield a transmission of 90%.

Quasielastic Neutron Scattering (QENS) experiments using the IN16B spectrometer in the BATS mode were carried out. For these experiments, an incident wavelength of 6.28 Å was used covering a Q-range between 0.19 and 1.9 Å⁻¹. Three different temperatures were studied. First, at 425 K above the T_g and T_c values of different components. Then, at 455 K above T_m (value in the molten state) and finally again at 425 K, above the T_c value (in the supercooled liquid regime), to study the differences before and after melting processes in all the samples. Figure 1 shows some representative examples for the measured dynamic structure, normalized to its value at $\hbar\omega = 0$.

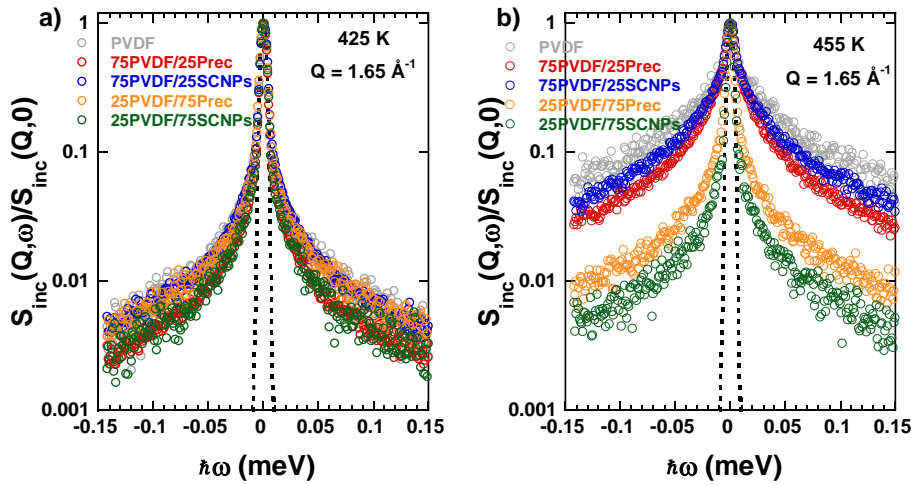


Figure 1. Normalized IN16B spectra obtained at $Q = 1.65 \text{ \AA}^{-1}$ for PVDF homopolymer and different mixtures at a) $T = 425 \text{ K}$ (before melting) and b) $T = 455 \text{ K}$. The dotted line shows the instrumental resolution function.

The chosen Q-value is 1.65 \AA^{-1} . From D7 experiments performed before (doi:10.5291/ILL-DATA.9-11-1948), 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. Results at temperatures of 425 K (before melting) and 455 K are shown in Figure 1a and 1b, respectively. A clear broadening with respect to the resolution function can be observed for all samples at both temperatures. At these temperatures, it can be observed that the spectrum corresponding to the 25PVDF/75SCNPs sample is narrower, pointing to a slower dynamics at the explored length scale.

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 $S(Q,t)$. The curves corresponding to the same representative examples as in Figure 1 are shown in Figure 2.

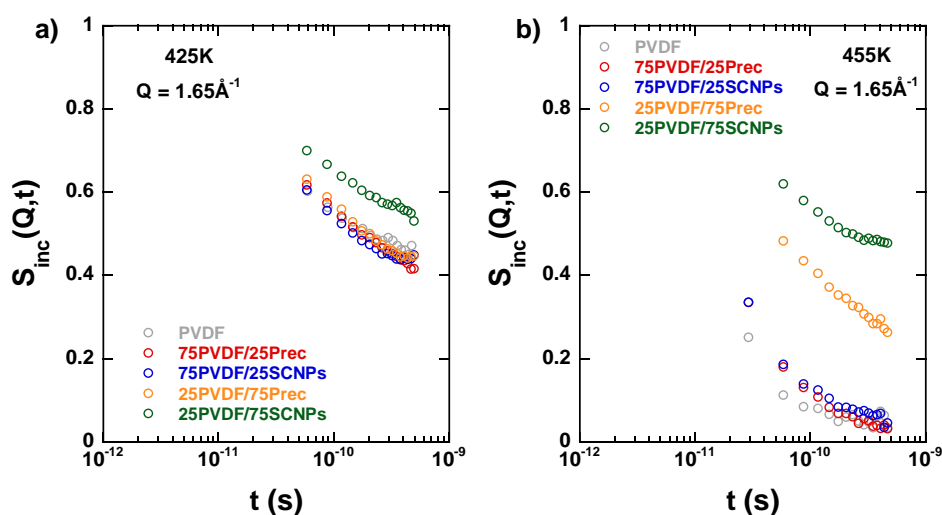


Figure 2. Fourier-transformed and deconvoluted IN16B spectra at $Q = 1.65 \text{ \AA}^{-1}$ value for PVDF homopolymer and different mixtures at a) $T = 425 \text{ K}$ (before melting) and b) $T = 455 \text{ K}$.

At 455K, the neat PVDF displays a faster dynamics compared to the rest blended samples, indicating an impact of mixing on its dynamics. The sample blended with SCNPs (25/75 wt%) shows the slowest dynamics compared to all other samples. The quantitative analysis of these results is in progress.

References

- [1] Sanchez-Sanchez, A.; Akbari, S.; Etxeberria, A.; Arbe, A.; Gasser, U.; Moreno, A. J.; Colmenero, J.; Pomposo, J. A. *ACS Macro. Lett.* **2013**, 2, 491-495.