Experimental report

11/03/2021

Proposal:	**9-11-1948**	**Council:**	10/2019
Title:	CONFINING PVDF IN DYNAMICALLY ASYMMETRIC BLENDS AND ALL-POLYMER NANOCOMPOSITES		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples:	deuterated poly(methyl methacrylate) protonated poly(vinylidene fluoride)

Instrument	Requested days	Allocated days	From	To
D7	2	2	25/09/2020	27/09/2020
IN16B Si 111 BATS	6	0		

Abstract:

PVDF in its beta-phase is a ferroelectric polymer with interest for data storage. Neat PVDF films generally crystallize in the non-ferroelectric alpha-phase. Blending with PMMA, the beta-phase can be produced. However, almost nothing is known about: (i) the dynamics of PDVF in the blends with different compositions; (ii) how this dynamics can affect the formation of the different crystalline phases; and (iii) whether the confinement and heterogeneous effects reported for PEO in PEO/PMMA and in PEO/PMMA-based-SCNPs can also be observed for PVDF in PVDF/PMMA and in PVDF/PMMA-based-SCNPs ('universality').

Here, we want to characterize the self-atomic motions of amorphous PVDF in blends with linear PMMA and nano-composites with PMMA-based SCNPs. For high PMMA contents we want to explore the analogies with PEO/PMMA systems, to confirm the universality of the phenomenology found attributed to (i) confinement by a surrounding amorphous rigid matrix, and (ii) trapping of segments by internal loops of the SCNPs. For low PMMA concentrations --the phase of interest for applications-- the effects of additional confinement by the own crystalline fraction shall be characterized.

CONFINING PVDF IN DYNAMICALLY ASYMMETRIC BLENDS AND ALL POLYMER NANOCOMPOSITES

The mixtures (‘all-polymer nano-composites’) prepared in this work contained protonated linear poly(vinylidene fluoride) (hPVDF) chains and deuterated Single Chain Nanoparticles (SCNPs). These SCNPs were obtained from deuterated linear copolymer precursors (dPrec) of P(MMA-*co*-AEMA) via Michael addition reaction mechanism following a procedure reported in ref [1]. As reference, we also investigated the blends consisting of linear hPVDF and the dPrec linear chains.

We investigated the homopolymers (hPVDF and both, the dPrec and dSCNPs) as reference samples, and the following four different compositions for the mixtures: 25hPVDF/75dPrec, 25hPVDF/75dSCNPs, 75hPVDF/25dPrec and 75hPVDF/25hSCNPs. Molecular weights M_w were 180 kDa for hPVDF and around 100 kDa for dPrec and dSCNPs. The glass-transition temperatures T_g measured by DSC were 340 K (dPrec) and 369 K (dSCNPs), while hPVDF sample presents a crystallization peak at 408 K and a melting peak at 440 K. Samples were filling flat aluminum sample holders, and the thicknesses were calculated to yield a transmission of 90%.

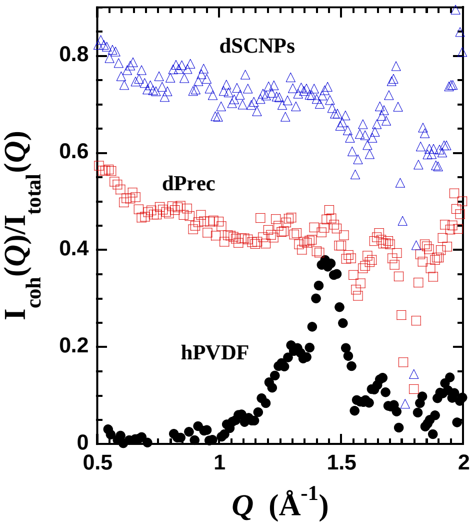

Figure 1. Ratio between coherent and total differential cross sections obtained by D7 at 300 K for reference samples: hPVDF, dPrec and dSCNPs. dPrec and dSCNPs samples were multiplied by a factor 1.4 and 2.1 respectively, for comparison reasons.

D7 experiments were carried out where the incident neutron wavelength was set to 4.8768 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 homopolymers were studied at 300 K as reference. The results are plotted in Figure 1. PVDF homopolymer shows a clear crystalline peak centered at 1.43 Å^{-1}, while dPrec and dSCNPs samples present smooth patterns characteristic for their amorphous character.

Additionally, all mixtures were studied at three different temperatures, at 300, 395 and 450 K. The obtained results are plotted in Figure 2.

Two different series of samples can be distinguished in these measured blends. First, those samples where the rich component is deuterated P(MMA-*co*-AEMA) (Figure 2a and 2b), and, second, those samples rich on protonated PVDF fraction (Figure 2c and 2d). At 450 K, where all the samples are in molten state, one main peak is observed in the Q-range between 0.5 and 2.0 Å^{-1} centered around 1.2 Å^{-1} for all the samples studied here. The correlations giving rise to this peak, thus, do not seem to be appreciably modified by the composition.

At temperatures lower than the melting point, Figure 2c and 2d show clear PVDF crystalline peaks around Q ~ 1.2-1.9 Å^{-1}. In these cases, the PVDF content is around 75 wt%; the peaks thus are clear in both cases when PVDF is mixed both, with the linear

Prec and the SCNPs. On the other hand, in Figure 2a these crystalline peaks are also observed at temperatures lower than the melting point when the PVDF is blended with the linear Prec. This means that these samples are able to crystallize even with c_{PVDF}<0.5. This has never been reported in PVDF-based mixtures. When PVDF is mixed with the SCNPs (Figure 2b), this behavior seems also to be present, though much less pronounced.

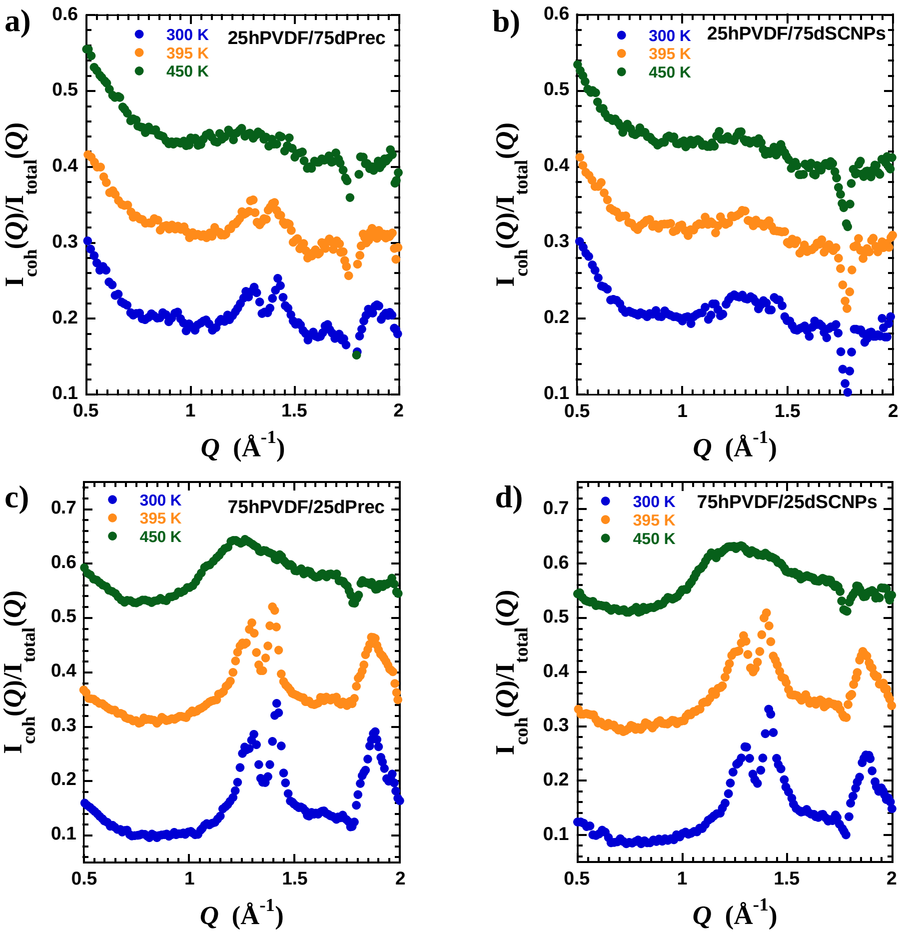

Figure 2. Ratio between coherent and total differential cross sections obtained by D7 at three different temperatures: 300 K (blue filled circles), 395 K (orange filled circles) and 450 K (green filled circles) for (a) 25hPVDF/75dPrec sample, (b) 25hPVDF/75dSCNPs sample, (c) 75hPVDF/25dPrec sample and (d) 75hPVDF/25dSCNPs sample.

In addition to this important insight into the structure of the mixtures, these results are very important also to determine the *Q*-ranges where the coherent scattering contribution is more or less pronounced, in order to properly analyze and interpret our future QENS results on these samples.

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.