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GIWAXS Measurement of Ultrathin Organic Ferroelectric Polymers

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Abstract
In this study, stretched ultrathin films of polyvinylidene fluoride (PVDF) homopolymer blended with varying weight percentages of graphene oxide or GO sheets) with a thickness of 100~500 μm were fabricated using the hot-press technique. The β phase of PVDF is known to exhibit a large ferroelectric character due to the presence of long chains of C-F and C-H dipoles in its all-trans (TTTT) configuration. In this study, the polarization orientation arising from the electric dipoles of PVDF when blended with GO and hot-pressed was investigated using grazing wide-angle X-ray scattering (GIWAXS). From the GIWAXS measurement, it was found that the fabricated stretched PVDF ultrathin films exhibited the formation of ferroelectric β crystal arrangement in a random direction (200/110) direction. However, upon stretching more times, PVDF started to reveal the paraelectric α phases again with random crystal orientation. The GIWAXS measurements provide insights into the crystal arrangement of ferroelectric polymers like PVDF which will further help in improving the ferroelectric properties.

Keywords: GIWAXS, PVDF, ferroelectricity, polymer blends

Background and Objective
Ferroelectric (FE) materials are those which exhibit electrically switchable spontaneous polarization due to the existence of non-centrosymmetric inversion symmetry[1]. Ultrathin FE materials are essential for the growing need for future miniaturized devices like FE random access memory. The direction of spontaneous electric polarization (up or down) in these FE thin films can be switched by the application of an external electric field leading to the formation of two electrically bi-stable states representing binary information “0” and “1”. The switched polarization is retained even after the removal of the external electric field giving rise to nonvolatility which forms the basis of memory devices. In this context, we aim to develop high-performance polymer-based ultrathin organic FE materials as an alternative to the existing inorganic materials. Currently, organic FE materials are promising alternatives for their counterparts mainly for their flexibility, ease of fabrication, and performance. In the context of organic FE, polyvinylidene fluoride or PVDF has successfully emerged as a novel alternative FE polymer material for applications in piezoelectric energy harvesting, wearable electronics, biomedical implants, wireless sensors, etc[2] Alternative materials like PVDF can also be used for future FE memories and neuromorphic computation. FE-based memristor is one such two-terminal device technology wherein FE polarization controls the resistance of the FE device[3]. Since ferroelectricity is a directional quantity, properties such as crystallinity, crystal plane orientation, and molecular configuration become highly crucial for the overall FE properties. X-ray scattering experiments could provide information on the crystal structure and orientations.

Experimental:
The ultrathin PVDF samples were fabricated by the hot-press technique. In this method, 0.01~2 wt% of GO was blended with PVDF in dimethylformamide was dropped on the metal plate. The temperature was raised to 200 ºC and pressed with another metal plate at 30 MPa pressure for 5 mins. Subsequently, the samples were cooled naturally under pressure. The obtained films were folded and the process was repeated (for stretching multiple numbers times). The number of folding and stretching cycles also varied from 1~4 times.

Grazing incidence X-ray scattering is a technique to analyze the crystal structure of thin films mainly for organic and semiconductor materials which can reveal the crystal structure within ~10 nm from the surface distinctly. Ultrathin Organic materials and polymers have weakly scattering crystals unlike in-organic materials with high orderliness and crystallinity, hence synchrotron radiation of high brilliance and photon flux is necessary. Refractive indices of many materials have a refractive index less than one for X-rays resulting in total reflection. Grazing incidence angles produce a large beam footprint which increases the X-ray sample interaction. A simple experimental schematic of a typical Grazing incidence wide-angle scattering

(GIWAXS) is shown in Fig. 1, where X-rays are incident on the sample at the grazing angle (0.5° ~ 2°). A beam stopper was placed on the direct beam path to avoid damage to the detector. For collecting the scattered X-rays at wide angles, a 2D detector (Pilatus 300 K) was placed at 10~30 cm from the samples. Beam energies of ~12.3 keV along with a are used in the current experiment.

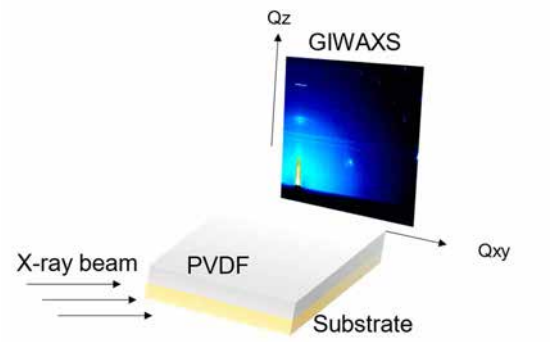

Fig. 1: Schematics of the GIWAXS experiment where an X-ray beam grazes the substrate. The scattered X-rays are collected on a 2D detector placed behind the sample.

Results and discussion:

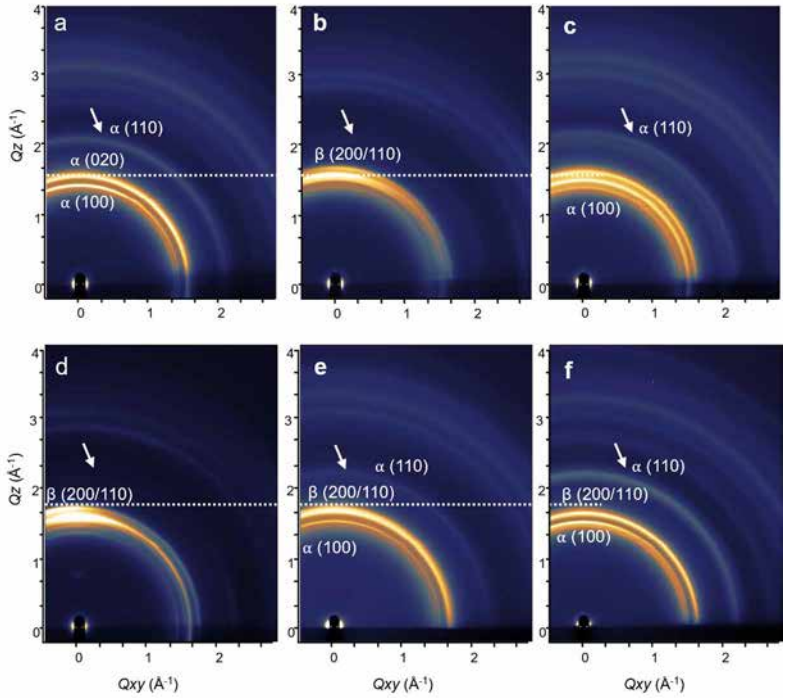

Fig. 2: GIWAXS pattern of ultrathin (a, b, c) pristine PVDF and (d, e, f) PVDF blended with GO placed on Si substrates under various stretching conditions. The white arrow in the figures indicates the α (110). The white dotted line is drawn on all figures to distinguish the slight shift of the diffraction maxima for the α and the β phases.

Figure 2(a, b, c) shows the GIWAXS pattern of 100~500 ultrathin pristine PVDF (with no GO blending, no stretch, 1 stretch, and 4 stretches are shown) placed on Si substrates while measurements. The GIWAXS pattern confirms the presence of α (110, 100, 020) in PVDF with no stretching (Fig. 2a) or hot-pressing. The white arrow in the figures indicates the α (110). The white dotted line is drawn on all figures to distinguish the slight shift of the diffraction maxima for the α and the β phases. This confirmed that PVDF didn't possess any FE property. When the same films were subjected to hot-press during which the samples were stretched, the samples with one stretch (Fig. 2b) revealed the crystallization of the FE β (110/200) phase with random orientation. However, the samples with 4 times stretching Fig. 2c) revealed a mixture of β and α phases. This result is contradicting our hypothesis where we predicted the enhancement of FE properties induced by temperature and pressure. The GIWAXS patterns for the case when the samples were blended with GO nanosheets are shown in Figure 2(d, e, f). In this case, the blended samples with no stretch (Fig. 2d) showed

crystallization of the FE β phase. The intensity of the peak at the meridian is highest indicating a slight epitaxial orientation of the 200/110 plane in the no-stretch samples. However when the samples were stretched once and four times, the α phase started to emerge as indicated by the white arrow contradicting our hypothesis.

The current measurements show that the arrangement of PVDF molecules depends on the stretching conditions which will be investigated subsequently.

References:

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