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| ESRF | **Experiment title:**<br>Confinement effects in one-dimensional polymer arrays | **Experiment number**:<br>SC2938 |
| **Beamline**:<br>ID13 | **Date of experiment**:<br>from: 20/07/2011 to: 22/07/2011 | **Date of report**:<br>09/08/2012 |
| **Shifts:**<br>6 | **Local contact(s)**: Michael REYNOLDS | *Received at ESRF:* |


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## Report:

Wetting of porous anodic aluminium oxide (AAO) templates has been used for the preparation of 1D poly(vinylidene fluoride) (PVDF) nanostructures. This technique is based on the fact that polymer melts and solutions tend to wet the walls of nanoporous templates avidly if the walls exhibit high surface energy [1]. Scanning μ-XRD with 1 μm beam diameter was performed along the cross section of the sample (Figure 1), from the residual PVDF film (bulk) to the nanorod array. The synchrotron beam was carefully aligned perpendicular to the nanorod axis and the 2D-diffraction patterns were recorded in transmission geometry. Analysis of the 2D-patterns has allowed us to investigate the spatial evolution of degree of crystallinity, crystal orientation and what is even more interesting the solid-solid phase transition from the α non polar crystal form (bulk) to the γ polar ferroelectric form (nanorod array) [2].

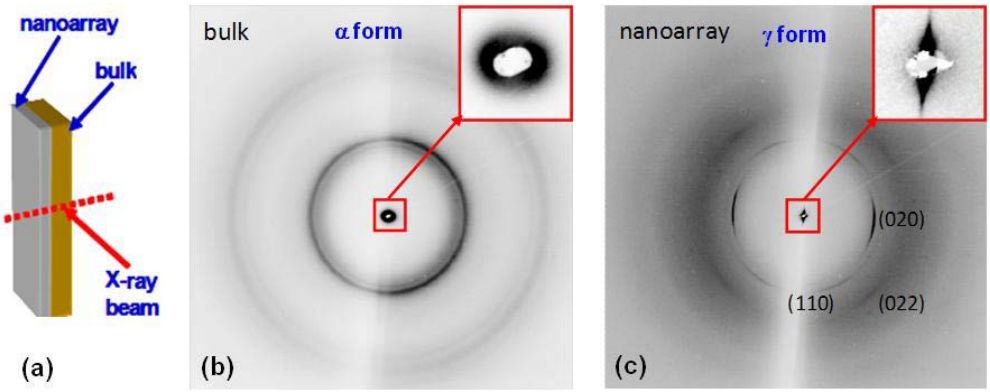


**Figure 1.** (a) Schematic view of the scanning μ-XRD geometry. (b) Diffraction pattern of the residual PVDF film. (c) Diffraction pattern of the nanorod array.

In conclusion, the work already published on these results [2] shows that solution template wetting is a versatile method to produce arrays of isolated ferroelectric γ-type nanorods connected by a paraelectric α-structure supporting film. The AAO walls template polymer crystallization orienting the lamellar crystals flat-on growing along the nanorrods long axis. The method is based upon a phase transition induced by the confinement of PVDF into nanoporous and by its interaction with the walls of the AAO membrane. The advantage of this method using porous anodic aluminum oxide as a template is the high versatility of the method.

Based on the previous experience, we extended our research to poly(vinylidene-co-trifluoroethylene) (PVDF-TrFE) random copolymer nanoarrays. Scanning the sample with 1 μm diameter X-ray beam, from the residual polymer film (bulk) to the nanorod array, we have investigated the effects of confinement on crystal phase transition, degree of crystallinity and crystal orientation with the aim of optimizing the ferroelectric properties of polymer nanostructures for their application in organic electronics [3]. In this case the polymer nanoarrays were prepared by melt and solution wetting.

Figure 2(a) shows the diffraction pattern of the residual P(VDF-TrFE) 50/50 film prepared by melt wetting and Figure 2(b) that of P(VDF-TrFE) 50/50 prepared by solution wetting. The small angle X-ray scattering (SAXS) region of the patterns has been enlarged and presented with the figure as insets. Similar diffraction patterns are obtained for other P(VDF-TrFE) compositions (i.e. 70/30 and 80/20) suggesting that the main structural features depend more on the processing method (i.e. melt or solution) than on the copolymer composition.

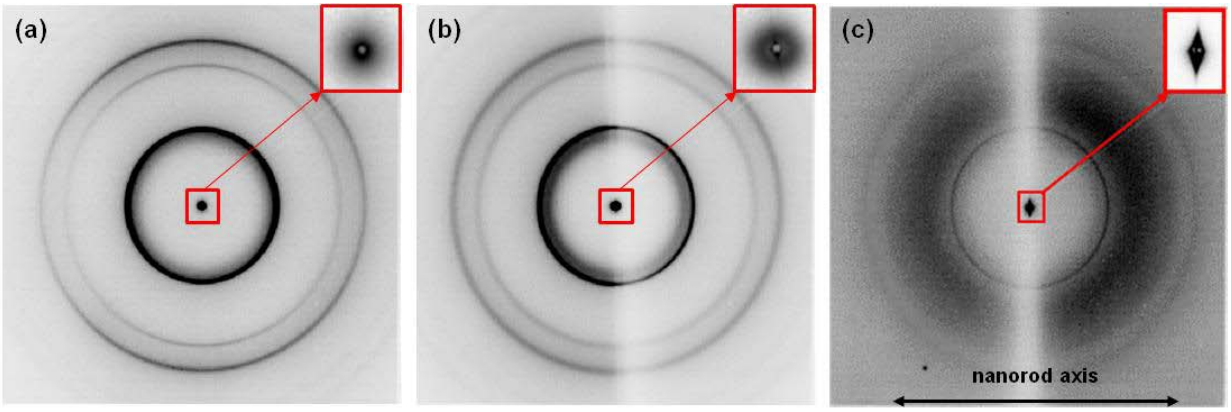


**Figure 2.** (a) Diffraction pattern of the residual P(VDF-TrFE) 50/50 film prepared by melt wetting. (b) Diffraction pattern of the residual P(VDF-TrFE) 50/50 prepared by solution wetting. (c) Diffraction pattern of the nanorod array.

At first sight, the wide angle X-ray scattering (WAXS) signal from the residual P(VDF-TrFE) 50/50 film prepared by melt wetting appears to suggest a slightly oriented crystalline pattern compared to that of the same material prepared by solution wetting. The information obtained from the small angle X-ray scattering (SAXS) is complementary to WAXS due to the difference in length scales being probed. It is worth noting that for both samples the SAXS signals are isotropic but while for the sample prepared by solution wetting (Figure 2(b)) the SAXS signal consists of a well resolved ring, corresponding to a long period of 15 nm related to the nanostructure of semicrystalline polymers. For the sample prepared by melt wetting (Figure 2(a)) the SAXS intensity is concentrated around the beam stop corresponding to higher correlation lengths related to a larger polymer long period.

Further analysis of the WAXS patterns reveals, however, that the differences between patterns (a) and (b) in Figure 2 are not only due to orientation effects, but also due to a crystal phase transformation. Azimuthally integrating the WAXS region of patterns 2(a) and 2(b) and those corresponding to P(VDF-TrFE) copolymers with different compositions, the corresponding 1-D intensity profiles were obtained and are presented in Figure 3. Bragg reflections have been indexed according to the ferroelectric (FE) orthorhombic with pseudo-hexagonal nature and the paraelectric (PE) hexagonal crystalline forms respectively [4]. Figure

3(a) shows 1-D intensity profiles from samples of P(VDF-TrFE) 50/50 and 70/30 prepared from the melt, a pure ferroelectric phase is observed for both copolymers. However, samples of P(VDF-TrFE) 50/50 and 80/20 prepared from solution present 1-D intensity profiles with mixed ferroelectric and paraelectric phases as it is seen in figure 3(b).

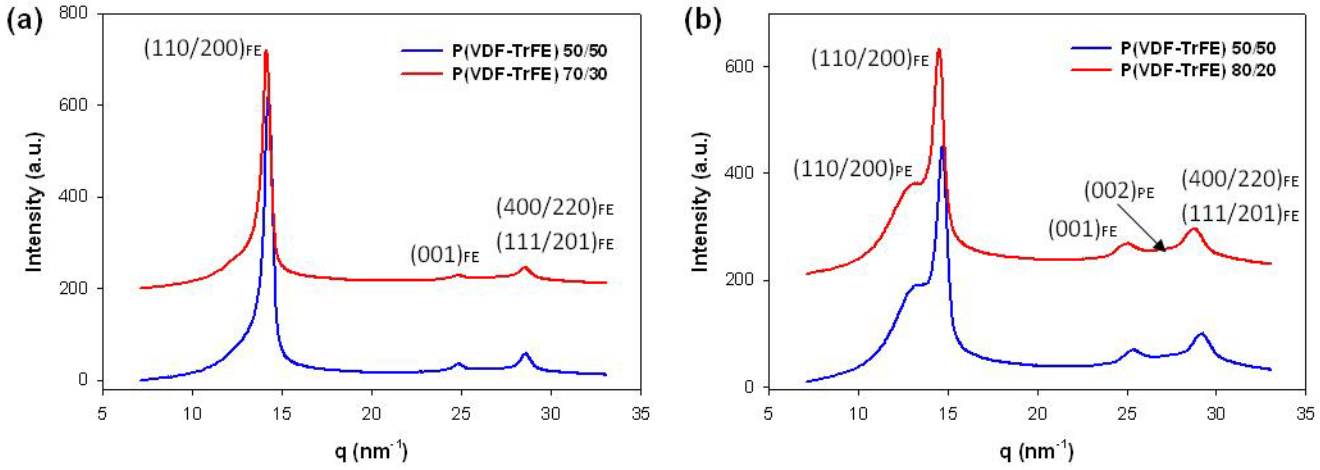


**Figure 3.** (a) 1-D intensity profiles from samples of P(VDF-TrFE) 50/50 and 70/30 prepared from the melt. (b) 1-D intensity profiles from samples of P(VDF-TrFE) 50/50 and 80/30 prepared from solution wetting.

It is worth noting that while the residual polymer films (Figure 2) show different diffraction patterns related to the ferroelectric phase or to a mixture of ferroelectric and paraelectric crystalline forms for the samples prepared from the melt or from solution respectively, for all the copolymers infiltrated within the AAO membranes either by melt wetting or by solution wetting the polymer nanoarrays (Figure 2c) present an almost isotropic WAXS pattern characteristic of the pure ferroelectric phase and the SAXS intensity (inset) concentrated on the meridian that corresponds to correlation lengths related to the pores of the AAO membrane, but no signal of the polymer long period is evidenced.

From diffraction patterns collected between the residual polymer film and the nanorod array for the different samples, the effects of confinement on crystal phase transition and the degree of crystallinity have been spatially investigated and a work on this topic is under preparation for publication.

## References


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