

## Tuning physical properties of polymers by nanoconfinement

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### Abstract

Arrays of polymer nanostructures exhibit an interesting behavior that makes them promising candidates for use in photonics, electronics, mechanical, and sensor devices [1-3]. High aspect ratio (length/diameter) one-dimensional (1D) nanostructures are also appropriate for studying size-dependent processes with length scales comparable to the nanostructures' size.

Material properties strongly depend upon molecular order and orientation. Crystallization is one of the simplest molecular-scale self-organization processes capable to control spatially the ordering of molecules and hence to tune the properties of partially crystalline polymer nanostructures, as they will largely depend upon the properties of their crystalline domains. Recent studies of polymer crystallization in restricted geometries shed some light on the possibility of controlling crystallization at the nanoscale. Some of the methods used allow well-defined nanostructures to be generated, such as via nanoimprint lithography (NIL) [2], and template wetting [1, 3].

Wetting of porous anodic aluminum oxide (AAO) templates has been used in this work for the preparation of 1D polymer nanostructures. This technique is based on the fact that both polymer melts and solutions tend to wet the walls of nanoporous templates avidly if the walls exhibit a high surface energy [4] (see Figure 1).

This contribution will cover recent research on these phenomena, demonstrating the use of wetting nanoporous alumina (AAO) template with polymer solution to produce arrays of poly(vinylidene fluoride) (PVDF) ferroelectric  $\gamma$ -type nanorods supported onto a nonpolar  $\alpha$ -structure film (Figure 2). The method is based upon a crystal phase transition due to PVDF confinement within alumina nanoporous [5]. Based on the previous experience, we extended our research to poly(vinylidene-co-trifluoroethylene) (PVDF-TrFE) random copolymer nanoarrays. X-ray microdiffraction using synchrotron radiation has been performed at ID13 beamline (European Synchrotron Radiation Facility). Scanning the sample with 1  $\mu\text{m}$  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 [6].

### Acknowledgements

The authors thank the financial support from the MICINN (grant MAT2011-23455).

### References

- [1] C. R. Martin, *Science*, **266** (1994) 1961.
- [2] Z. Hu, M. Tian, B. Nysten, A.M. Jonas, *Nat. Mater.*, **8** (2009) 62.
- [3] M. Steinhart, R.B. Wehrspohn, U. Gösele, J.H. Wendorff, *Angew. Chem. Int. Ed.* **43** (2004) 1334.
- [4] M. Zhang, P. Dobriyal, J.T. Chen, T.P. Russell, J. Olmo, A. Merry, *Nano Lett.*, **6** (2006) 1075.
- [5] M.C. García-Gutiérrez, A. Linares, J.J. Hernández, D.R. Rueda, T.A. Ezquerra, P. Poza, R. Davies, *Nano Lett.*, **10** (2010) 1472.
- [6] S.J. Kang, I. Bae, Y.J. Shin, Y.J. Park, J. Huh, S-M. Park, H-C. Kim, C. Park, *Nano Lett.*, **11** (2011) 138.

## Figures

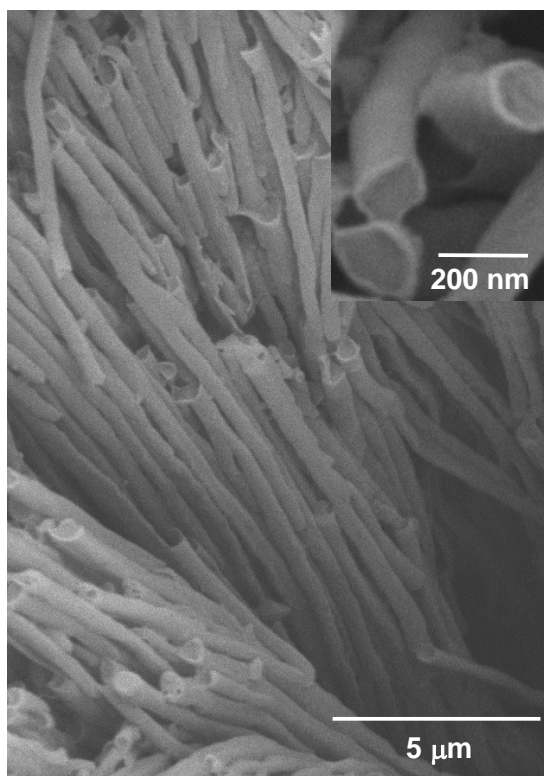


FIGURE 1. SEM image of PVDF nanostructures prepared by solution template wetting. Side view and top view (inset) showing the nanorod morphology when the alumina template has been removed.

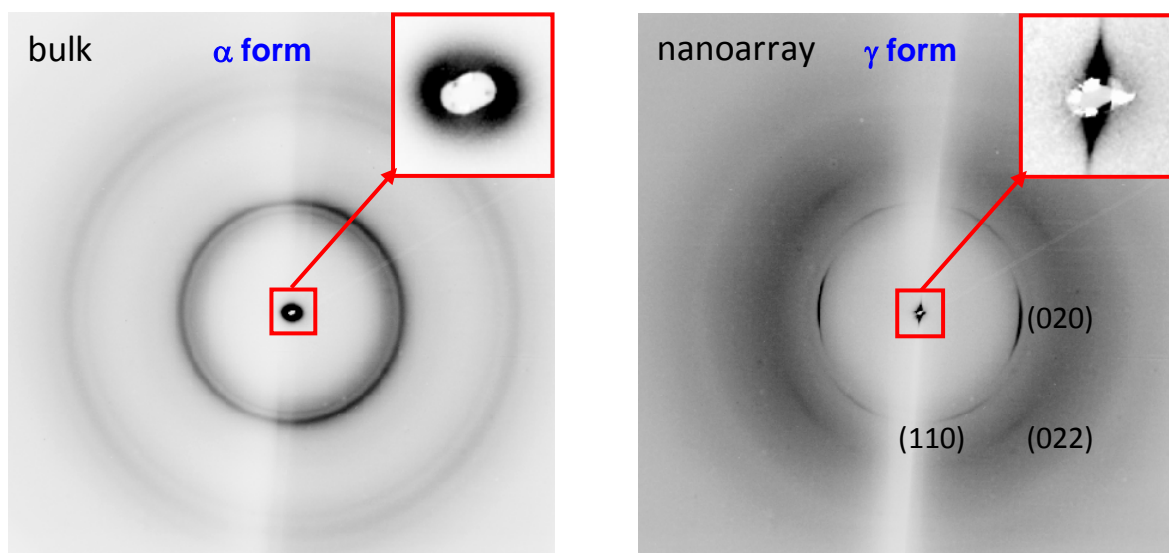


FIGURE 2. Two-dimensional X-ray diffraction patterns recorded in transmission geometry. (left) Diffraction pattern of the residual PVDF film and (right) diffraction pattern of PVDF nanorods inside porous alumina. The SAXS region of the patterns has been enlarged and presented as insets.