P(VDF-TrFE) NANOFIBERS: STRUCTURE OF THE FERROELECTRIC AND PARAELECTRIC PHASES THROUGH IR AND RAMAN SPECTROSCOPIES

Alessia Arrigoni, Luigi Brambilla, Chiara Bertarelli, Gianluca Serra, Matteo Tommasini and Chiara Castiglioni.

a Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

b Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

* Corresponding author: chiara.castiglioni@polimi.it

SUPPLEMENTARY INFORMATION

Figure SI1: SEM micrographs showing morphology of P(VDF-TrFE) randomly aligned nanofibers.

Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2020
Figure SI2: Diameters distribution obtained from SEM micrograph of randomly oriented nanofibers, 100 diameter measurements have been taken for the statistical analysis.

Figure SI3: SEM micrographs showing morphology of P(VDF-TrFE) macroscopically aligned nanofibers.
Figure SI4: Diameters distribution obtained from SEM micrograph of macroscopically aligned nanofibers, 100 diameter measurements have been taken for the statistical analysis.

Figure SI5: DSC thermogram of P(VDF-TrFE) nanofiber mat. A rate of 10°C/min has been set.
Table SI1. Observed Full-width-at-Half-maximum for the main Infrared bands of a P(VDF-TrFE) (80/20) film.

| Peak    | 1402 cm\(^{-1}\) | 1289 cm\(^{-1}\) | 1183 cm\(^{-1}\) | 1076 cm\(^{-1}\) | 883 cm\(^{-1}\) | 845 cm\(^{-1}\) |
|---------|------------------|------------------|------------------|------------------|----------------|----------------|
| **FWHM**| 23 cm\(^{-1}\)  | 41 cm\(^{-1}\)  | 74 cm\(^{-1}\) (pre annealing) | 58 cm\(^{-1}\) (post annealing) | 38 cm\(^{-1}\) | 20 cm\(^{-1}\) | 25 cm\(^{-1}\) |

Figure SI6: Molecular models of 10VDF and 9VDF-TrFE.

Figure SI7: (a) Experimental IR spectrum of the "ideal β phase" in P(VDF-TrFE) films obtained by subtraction (orange line). (b), (c) Simulated (DFT, B3LYP 6-31G**) IR spectra of 10VDF (blue line) and
9VDF-TrFE (green line). Bands labelled with * correspond to extra-features observed for P(VDF-TrFE) and not present in the IR spectrum of PVDF. The doublet labelled with a circle in the simulated spectrum is a marker or the TrFE unit (it corresponds to normal modes localized on the TrFE group) and allows the assignment of the experimental band at 1124 cm$^{-1}$ to TrFE "chemical defects".

Figure SI8: (a), (b) Experimental Raman spectra of a PVDF sample with a relatively high amount of $\beta$ phase (light blue line) and P(VDF-TrFE) powder (light green line). (c), (d) Simulated (DFT, B3LYP 6-31G**) Raman spectra of 10VDF (blue line) and 9VDF-TrFE (green line). Experimental features possibly ascribed to TrFE units are labelled with *. They can be put in correspondence with the two bands of the simulated spectrum at 1342-1367 cm$^{-1}$ (labelled with a circle) and 455 cm$^{-1}$, corresponding to normal modes localized on the TrFE group.
Figure SI9. Sketch of the vibrational eigenvectors (from DFT B3LYP 6-31G** calculations) corresponding to vibrational modes localized on the TrFE unit. Wavenumbers correspond to computed values, after scaling.

Table SI2. Calculated IR intensities and Raman activities corresponding to vibrational modes localized on the TrFE unit. Red and blue characters highlight the main predicted marker bands, which can be recognized in the IR and in the Raman spectrum, respectively.

| wavenumbers [cm\(^{-1}\)] | wavenumbers (scaled) [cm\(^{-1}\)] | IR intensity [km/mol] | Raman activity [Å\(^4\)/amu] |
|-----------------------------|----------------------------------|----------------------|-----------------------------|
| 465                         | 455                              | 4.24                 | 1.11                        |
| 1127                        | 1102                             | 37.67                | 0.61                        |
| 1140                        | 1115                             | 44.12                | 0.76                        |
| 1372                        | 1342                             | 8.77                 | 9.17                        |
| 1398                        | 1367                             | 6.48                 | 0.22                        |
SI – Discussion

Infrared spectrum of fibres mat: intensity behaviour of $B_1$ bands and molecular orientation. Detailed discussion based on symmetry considerations.

Based on evidence from polarized IR spectra of macroscopically oriented fibres, we know that the orientation of the axis of the trans-planar chains is mostly parallel to the fibre axis. Thus, for the fibres mat, the dipole derivative vector (parallel to the chain axis $x$ – see sketch 1) lies in the plane of the substrate, which is orthogonal to the propagation direction of the IR beam. For the dipole derivatives associated to $A_1$ and $B_2$ phonons the situation is different, and they are respectively parallel to the $z$ and $y$ directions of the molecular reference system (sketch SI1). Contrary to the chain axis ($x$), the $z$ and $y$ directions of the local molecular frame show random orientation with respect to the propagation direction of the IR beam. This is due to the cylindrical symmetry of fibres. Therefore, the dipole derivatives vectors associated to $A_1$ and $B_2$ phonons exhibit an average non-vanishing dipole component along the propagation direction of the IR beam. For all such reasons, the scalar product of the dipole derivatives with the radiation electric field vector averages in a different way for $B_1$ and $A_1$ (or $B_2$) transitions, and the resulting absorption intensity for $B_1$ bands doubles with respect to the isotropic case (e.g. film).\textsuperscript{79} Observation iv in Section 3.5, can be rationalized in the same way, provided that the corresponding vibrational transition has a dipole derivative mainly directed along the polymer chain (e.g., it belongs to $B_1$ species).

Sketch SI1. Structure of the trans-planar structure of a PVDF chain belonging to the $\beta$ crystalline phase. The Cartesian reference system adopted is indicated.