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# Morphology, polymorphism behavior and molecular orientation of electrospun poly(vinylidene fluoride) fibers

Wu Aik Yee [a], Masaya Kotaki [b,1], Ye Liu [b], Xuehong Lu [a,*]

[a] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
[b] Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

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## Abstract

The morphology, polymorphism behavior and molecular orientation of electrospun poly(vinylidene fluoride) (PVDF) fibers have been investigated. We found that electrospinning of PVDF from its *N*,*N*-dimethylformamide/acetone solutions led to the formation of β-phase. In contrast, only α- and γ-phase was detected in the spin-coated samples from the same solutions. In the aligned electrospun PVDF fibers obtained using a rotating disk collector, the β-phase crystallites had a preferred orientation along the fiber axis. The degree of orientation did not, however, vary significantly with the speed of the rotation disk collector, and the β-phase was also not significantly enhanced with the increase in the rotation speed or the decrease in the size of spinnerets. These facts indicated that the orientation was likely to be caused by Columbic force rather than the mechanical and shear forces exerted by the rotating disk collector and spinnerets. The Columbic force may induce local conformational change to straighter TTTT conformation, and hence promote the β-phase. The addition of 3 wt.% of tetrabutylammonium chloride (TBAC) into the polymer solutions effectively improved the morphology of the electrospun fibers, and led to almost pure β-phase in the fibers. With spin coating, PVDF–TBAC did not, however, show any strong β-phase diffraction peak. The synergistic β-enhancement effect of TBAC and electrospinning is possibly due to the fact that while TBAC could induce more *trans* conformers, electrospinning promotes parallel packing, and hence inter-chain registration.

*Keywords:* Poly(vinylidene fluoride) (PVDF); Electrospinning; Polymorphism

## 1. Introduction

Poly(vinylidene fluoride) (PVDF) has drawn great attention in recent years due to its attractive properties such as piezo-, pyro- and ferroelectricity, as well as flexibility, light weight and good processability. Although PVDF has a simple chemical structure, it is well established that it can exhibit five different polymorphs depending on its processing conditions. These crystal forms involve three different chain conformations, namely: (1) all-*trans* (TTTT) planar zigzag for β-phase, (2) TGTG′ for α and δ phases, and (3) $T_3GT_3G'$ for γ and ε phases [1]. When PVDF chains are packed into crystal lattices, their dipoles are either additive, which leads to a net dipole as in β, γ and δ phases, or canceled among themselves, resulting in no net dipole as in α and ε phases [1]. Among the three polar phases, the β-phase has the largest spontaneous polarization ($p$) per unit cell and thus exhibits the highest piezo-, pyro- and ferroelectric activities, which endues PVDF with great potentials for various device applications [2,3].

When PVDF is cooled from melt, it normally crystallizes in the non-polar α-phase. The polar β-phase can be obtained through various post-treatments of the melt-processed samples, such as mechanical stretching of melt-spun films/fibers in a certain temperature range [4–6] and thermal, corona or high-field room-temperature poling of the α-phase thin films [5–9]. The β-phase can also be induced directly under some special conditions, such as by melt crystallization at high pressure [10], in the process of vapor deposition of oligomeric PVDF [11,12], or by blending with carbon nanotubes [13]

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* Corresponding author. Tel.: +65 6790 4585; fax: +65 6790 9081.
*E-mail address:* asxhlu@ntu.edu.sg (X. Lu).

[1] Present address: Division of Advanced Fibro Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

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and organically modified nanoclay [14–16]. When deposited from solutions PVDF commonly crystallizes in the $\alpha$- and $\gamma$-form [17]. The $\beta$-phase has been found in solvent-cast thin films when a highly polar but toxic solvent, hexamethyl phosphoramide, was used [18], or hygroscopic/hydrated salts were added in the solutions as additives [19].

Electrospinning has been established as a simple and versatile method for drawing polymer fibers with diameters at nanometer- or submicron-scale [20–22]. The technique has been applied to fabricate PVDF nanofibers and fibrous thin films for various applications [23–26]. A previous study has shown that electrospun PVDF fibers can be semi-crystalline [26] while their polymorphic behavior has not been studied, and consequently, their electroactive properties have not been explored. This work was undertaken to investigate the crystalline phase variation in PVDF fibers electrospun under various conditions. We found that electrospinning of PVDF from its *N*,*N*-dimethylformamide/acetone solutions led to the formation of $\beta$-phase. In particular, with the addition of a small amount of tetrabutylammonium chloride (TBAC) into the PVDF solutions, the $\beta$-phase became dominant in the electrospun fibers. In contrast, for the spin-coated samples although the addition of TBAC led to a significant increase in *trans* conformers it did not promote long-range order impressively. It is believed that while TBAC induced local conformational changes electrospinning played a critical role in promoting inter-chain registration. Molecular orientation in the electrospun fibers was also examined and correlated to the polymorphism behavior of the fibers.

## 2. Experimental

### 2.1. Materials

PVDF powders (Solef 11008) was used as received. *N*,*N*-Dimethylformamide (DMF), acetone and acetic acid were supplied by Aldrich, and TBAC by Fluka.

### 2.2. Electrospinning

DMF/acetone mixtures were prepared at DMF/acetone weight ratio of 60/40, 70/30 and 80/20, respectively. PVDF was dissolved in the solvent mixtures at PVDF concentration, namely polymer/solvent weight ratio, of 15 and 20 wt.%, respectively. The PVDF solutions were then placed in a plastic syringe fitted with a needle of tip-diameter of 200, 30 and 1 μm, respectively. PVDF fibers were electrospun at 15 or 21 kV with a high-voltage power supply. A syringe pump was used to feed the polymer solution into the needle tip, and the feed rate of the syringe pump was fixed at 0.25 ml/h. A grounded aluminum foil was located at a fixed distance of 15 cm from the needle tip to collect the fibers. The fibers were randomly deposited on the collector plate forming a fibrous thin film (random mat). In parallel to the above, 3 wt.% of acetic acid and TBAC (the mass of the additive/the mass of solvents) were added into the 20 wt.% PVDF polymer solution (DMF/acetone = 60/40), respectively, and the solutions were electrospun at 21 kV using the 27G needle (tip-diameter = 200 μm). The 20 wt.% PVDF polymer solutions, with and without TBAC, were also electrospun at 15 kV using the setup shown in Ref. [24]. The fibers were collected using the setup shown in Ref. [27] at the rotating disk speed of 600, 1000, 1500 and 2000 rpm, respectively, with the fibers aligning in the rotation direction. All electrospun fibers were dried *in vacuo* at room temperature overnight prior to characterization.

### 2.3. Spin-coating

The 20 wt.% PVDF solutions in 60/40 DMF/acetone mixture, with and without 3 wt.% TBAC, were spin-coated at 2000 rpm using a Cost Effective Equipment (CEE) Model 100 spin-coater. The thin films obtained were dried *in vacuo* at room temperature overnight prior to characterization.

### 2.4. Scanning electron microscopy (SEM)

The morphology of the electrospun fibers was examined using *a JEOL 5600* SEM. A thin layer of gold was sputtered on the sample surface before the examination.

### 2.5. Wide angle X-ray diffraction (WAXD)

WAXD patterns were recorded with a Bruker GADDS X-ray diffractometer equipped with a two-dimensional (2D) area detector using Cu K$\alpha$ radiation. The random mats were rolled to make tubes of ~1 mm diameter for the X-ray measurement while the aligned samples were measured directly without rolling, as shown in Fig. 1. For all samples, 2D diffraction patterns were collected in the $2\theta$ range of 15°–50°, and integrated to obtain azimuthal average intensity against $2\theta$ plots using GADDS software package. To examine crystal orientation, the same software was used to obtain the radial average intensity of equatorial reflections versus azimuthal angle ($\chi$) plots.

### 2.6. Differential scanning calorimetry (DSC)

The DSC curves of the materials were measured using a TA Instruments Modulated DSC 2920. The sample was heated at 20 °C/min from 25 to 200 °C. All experiments were performed under a nitrogen purge.

### 2.7. Attenuated Fourier transform infrared spectroscopy (AT-FTIR)

FTIR spectra were collected using a Perkin Elmer FTIR System Spectrum GX equipped with a Golden Gate Single

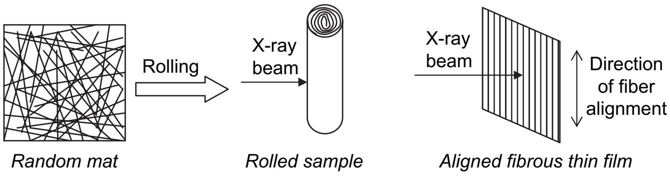

Fig. 1. A schematic of the geometries of the WAXD experiments.