

Research Article

Fabrication and Raman Analysis of Aligned Electrospun PVDF Nanofibers

Akira Ueda^{1*}, Omar Ali¹, Andrey Zavalin¹, Sergey Avanesyan¹, Warren E. Collins¹, Richard Mu², S. Keith Hargrove²

¹Center for Physics and Chemistry of Materials, Fisk University, USA

²TIGER Institute, Tennessee State University, USA

***Corresponding authors:** Akira Ueda, Research Assistant Professor in Physics, Center for Physics and Chemistry of Materials, Fisk University, Nashville TN 37208, USA. Tel: +16153298684; Email: akiraueda2014@gmail.com; aueda@fisk.edu Richard Mu, TIGER Institute, Tennessee State University, USA. Email: rmu@tnstate.edu

Citation: Ueda A, Ali O, Zavalin A, Avanesyan S, Collins WE, et al. (2018) Fabrication and Raman Analysis of Aligned Electrospun PVDF Nanofibers. Biosens Bioelectron Open Acc: BBOA-111. DOI: 10.29011/BBOA-111.100011

Received Date: 26 December, 2017; **Accepted Date:** 06 January, 2018; **Published Date:** 12 January, 2018

Abstract

We have fabricated uniaxially aligned Polyvinylidene Fluoride (PVDF) nanofibers by electrospinning technique in order to investigate the molecular configuration by using Raman spectroscopy. PVDF is a piezoelectric and pyroelectric material in the β -phase molecular configuration, and it is recently found the way to align nanofibers by using a set of grounded electrodes during electrospinning. We have developed a mathematical formalism of analysis for Raman spectroscopy for (1) the signal-to-noise ratio and (2) the degree of β -phase in the phase mixture of PVDF nanofibers. We observed many sharp peaks in the Raman spectra from a single PVDF nanofiber, which were not able to see in bulk materials. In order to see the accurate vibration modes, in general, the Raman spectroscopy on nanofiber may contribute to the detail analysis of polymers.

Abstract

We have fabricated uniaxially aligned Polyvinylidene Fluoride (PVDF) nanofibers by electrospinning technique in order to investigate the molecular configuration by using Raman spectroscopy. PVDF is a piezoelectric and pyroelectric material in the β -phase molecular configuration, and it is recently found the way to align nanofibers by using a set of grounded electrodes during electrospinning. We have developed a mathematical formalism of analysis for Raman spectroscopy for (1) the signal-to-noise ratio and (2) the degree of β -phase in the phase mixture of PVDF nanofibers. We observed many sharp peaks in the Raman spectra from a single PVDF nanofiber, which were not able to see in bulk materials. In order to see the accurate vibration modes, in general, the Raman spectroscopy on nanofiber may contribute to the detail analysis of polymers.

Introduction

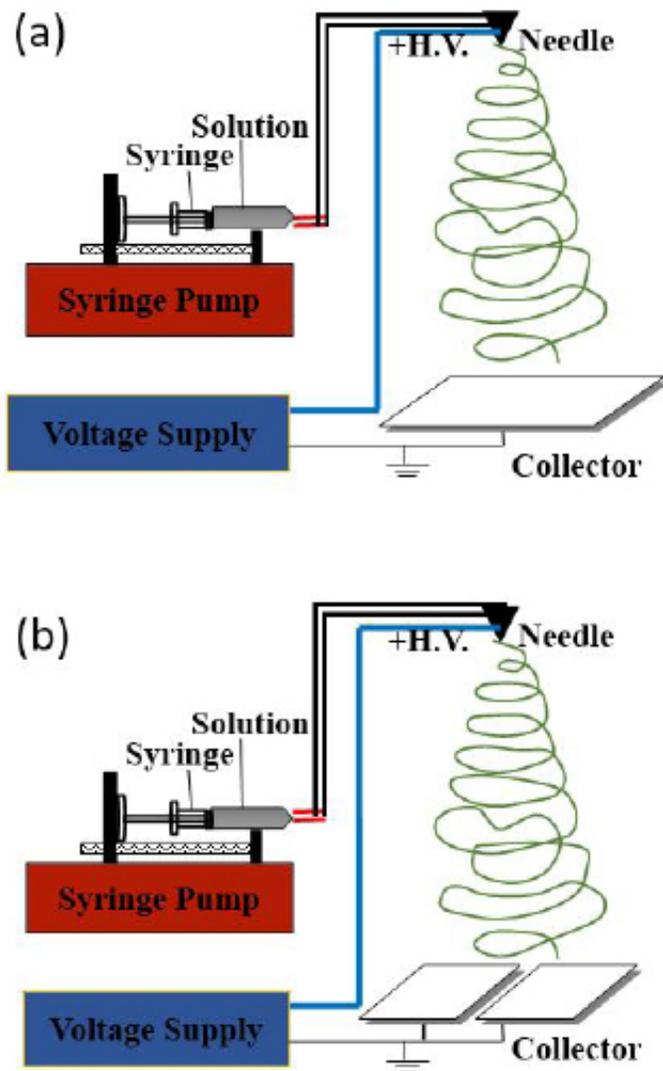
Electrospinning has been used as a simple and versatile method for drawing fibers from several kinds of polymer solutions. In a typical process, the polymeric fluid is extruded from the orifice of a needle to form a small droplet in the presence of a strong electric field. When the electric field is sufficiently strong, charges

built up on the surface of the droplet will overcome the surface tension to induce the formation of a liquid jet that is subsequently accelerated toward a grounded metal plate (the collector). As the solvent is evaporating, the liquid jet is stretched to produce continuous and thin fibers of the polymer. By using a syringe pump, it is possible to continuously feed the liquid in order to obtain fibers in a relatively short time.

(Figure 1(a)) shows a typical setup of electrospinning. In this case, the electrospun fibers are often collected as randomly oriented structures in the form of nonwoven mats or membranes. Although these mats are of great interest for applications that include texturing, composite reinforcement, membrane-based separation, sensor, enzyme immobilization, and tissue engineering [1,2,3], these disordered structures may not be used for device fabrications such as microelectronics and photonics. For this reason, well-aligned and ordered structures are required [4,5,6].

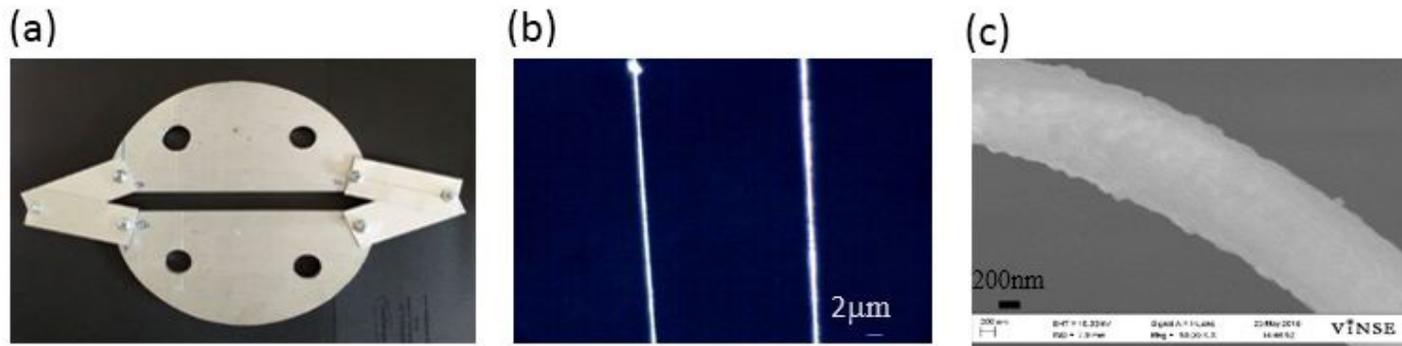
D. Li et al. initiated [7] that the control of the spatial orientation of electrospun nanofibers by using a set of separated grounded metal or semiconducting plates as the collector, as schematically shown in (Figure 1(b)). Their explanation of this effect is as follows: At the gap of two separated collecting plate edges, the electric field becomes opposite directions. Just before an electrospun

nanofiber reaches the collector, the nanofiber is pulled toward both edges of the metal plates, the forces are in the direction perpendicular to the edges. Therefore, as the result, landed fiber aligned perpendicular to the edges, and it turns out that those fibers orient parallel each other in certain degree.



Figures 1(a-b): Experimental setup for electrospinning. (a) Typical electrospinning setup with solid collecting conducting plate grounded. (b) The collector consists of two conducting plates grounded separately with some gap.

(Figure 2(a)) shows the gap adjustable collector plate made of aluminum with a gap size of 10 mm. (Figure 2(b)) is an optical micrograph that shows an example of the collected nanofibers in the gap of collector and the directions of fibers are nearly perpendicular to the gap edges. (Figure 2(c)) is an SEM micrograph of a single fiber fabricated under the similar conditions to the one in (Figure 2(b)). The average diameter of these fibers is approximately 1 μm , and we better call the fibers “Microfibers” in this case. However, in this paper we call them “Nanofibers” since we also fabricate submicron-size fibers under similar conditions.



Figures 2(a-c): The collector and collected fibers. (a) The gap adjustable collector plate made of aluminum with a gap size of 10 mm. (b) The collected nanofibers in the gap of collector. (c) The SEM image of a single fiber that was fabricated under the similar condition.

Our current interest is the uniaxially aligned nanofibers of PVDF. PVDF has been extensively investigated due to its mechanical, ferroelectric, and electrical properties, such as piezoelectric as well as pyroelectric characters, which makes it suitable for applications in electro-optics and electro-mechanical devices [8,9]. However, there are four molecular phases of PVDF (α -, β -, γ -, and δ -phases). Most stable α -phase is the nonpolar, which does not have piezoelectric property and can be obtained directly from the melt. This phase is formed by $(CH_2-CF_2)_n$ chains in a TG+TG-conformation and monoclinic crystallographic form. In the polar β -phase, PVDF chains adopt a zig-zag planar conformation, which leads to an orthorhombic cell, which has high value of electric polarization [10]. The phase transition from the non-polar α -phase to the polar β -phase of PVDF was investigated using micro-Raman spectroscopy [11]. They started from α -phase PVDF film sheets and observed the phase transition to β -phase by stretching the films. Although their study was interesting, the peak assignments and resolution are our concerning.

In our electrospinning, PVDF solution becomes fibers by stretching with electric field while the solvent is evaporating. From the uniaxially aligned nanofibers, we may detect the degree of β -phase in PVDF fibers. We measured the Raman signals by rotating the incident excitation laser polarization respect to the fiber axis.

Since polymers have large molecular, the degree of freedom for vibration modes should be large. The assignments of bands or peaks in the literature are possibly indistinct. Many sharp peaks are overlapped and form broad bands. Raman spectroscopy on a

single nanofiber could be useful to distinguish these sharp peaks rather than signals from bulk materials because the signals from bulk materials may average out to become blurred. Using our analysis formalism, we may have a detailed understanding of Raman individual peaks for the phase changes of polymers.

Mathematical Background for Analysis

In order to analyze data, we introduce two mathematical concepts below. One is the degree of random noise level compared with real signals. Another is the component analysis of β -phase of PVDF distinguished from α -phase spectra.

Signal to Noise Ratio

Suppose that we take two Raman spectra of PVDF which may not be the same due to random noise:

$$\psi_1(\omega) = \psi_0(\omega) + \varepsilon_1(\omega) \quad (1a)$$

$$\psi_2(\omega) = \psi_0(\omega) + \varepsilon_2(\omega) \quad (1b)$$

where $\psi_0(\omega)$ is the ideal spectrum of a specific PVDF sample, which is practically unknown because of the additional random noise spectra $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. However, since the spectra are averaged over several scans, the noise spectrum portion can be reduced down to a certain level. On the other hand, since we take spectra from a single PVDF nanofiber, the ideal spectrum $\psi_0(\omega)$ can be weak. Therefore, we have the following two cases:

$$(A) |\psi_0(\omega)| \gg |\varepsilon_1(\omega; t)|, |\varepsilon_2(\omega; t)| \quad \text{for Low noise level case}$$

$$(B) |\psi_0(\omega)| \ll |\varepsilon_1(\omega; t)|, |\varepsilon_2(\omega; t)| \quad \text{for High noise level case}$$

In order to distinguish the noise level, we introduce the following correlation coefficient R:

$$R_{12} \equiv \frac{\int_{\omega_1}^{\omega_2} \psi_1(\omega) \psi_2(\omega) d\omega}{\sqrt{\int_{\omega_1}^{\omega_2} [\psi_1(\omega)]^2 d\omega} \sqrt{\int_{\omega_1}^{\omega_2} [\psi_2(\omega)]^2 d\omega}} \quad (2)$$

For the extremely low noise level case (1): $\frac{|\varepsilon_i(\omega)|}{|\psi_0(\omega)|} \rightarrow 0$ ($i = 1, 2$), $\frac{|\varepsilon_i(\omega)|}{|\psi_0(\omega)|} \rightarrow 0$ ($i = 1, 2$), $\psi_1(\omega) \rightarrow \psi_0(\omega)$ and $\psi_2(\omega) \rightarrow \psi_0(\omega)$

In this case, the correlation coefficient of this extreme case becomes

$$R_{12} = \frac{\int_{\omega_1}^{\omega_2} \psi_0(\omega) \psi_0(\omega) d\omega}{\sqrt{\int_{\omega_1}^{\omega_2} [\psi_0(\omega)]^2 d\omega} \sqrt{\int_{\omega_1}^{\omega_2} [\psi_0(\omega)]^2 d\omega}} \rightarrow 1 \quad (3)$$

On the other hand, the *High noise level case*: $\frac{|\psi_0(\omega)|}{|\varepsilon_i(\omega)|} \rightarrow 0$ ($i = 1, 2$), $\psi_1(\omega) \rightarrow \varepsilon_1(\omega)$ and $\psi_2(\omega) \rightarrow \varepsilon_2(\omega)$

In this case, the correlation coefficient becomes

$$R_{12} = \frac{\int_{\omega_1}^{\omega_2} \varepsilon_1(\omega) \varepsilon_2(\omega) d\omega}{\sqrt{\int_{\omega_1}^{\omega_2} [\varepsilon_1(\omega)]^2 d\omega} \sqrt{\int_{\omega_1}^{\omega_2} [\varepsilon_2(\omega)]^2 d\omega}} \rightarrow 0 \quad (4)$$

The Degree of β -Phase in a Mixture

Suppose that there are PVDF nanofibers of purely α -phase and β -phase, and their spectra are given by, respectively: $\phi_\alpha(\omega)$ and $\phi_\beta(\omega)$

These spectral functions are not orthogonal, in general:

$$G_{ij} \equiv \int_{\omega_1}^{\omega_2} \phi_i(\omega) \phi_j(\omega) d\omega \neq 0 \quad (5)$$

The spectral function for the mixture of purely α -phase $\phi_\alpha(\omega)$ and β -phase $\phi_\beta(\omega)$ is given by

$$\psi(\omega) \equiv C_\alpha \phi_\alpha(\omega) + C_\beta \phi_\beta(\omega) \quad (6)$$

where the coefficients C_α and C_β are the quantities that express the contributions of α -phase and β -phase in the mixture, respectively.

They can be obtained in the following method: Multiplying both sides by $\phi_i(\omega)$ and integrating over the specified region, we have

$$\int_{\omega_1}^{\omega_2} \phi_i(\omega) \psi(\omega) d\omega = C_\alpha \int_{\omega_1}^{\omega_2} \phi_i(\omega) \phi_\alpha(\omega) d\omega + C_\beta \int_{\omega_1}^{\omega_2} \phi_i(\omega) \phi_\beta(\omega) d\omega, (i = \alpha, \beta)$$

These are a set of simultaneous equations for C_α and C_β :

$$S_i = C_\alpha G_{i\alpha} + C_\beta G_{i\beta}, (i = \alpha, \beta) \quad (7)$$

where S_i is given by

$$S_i \equiv \int_{\omega_1}^{\omega_2} \phi_i(\omega) \psi(\omega) d\omega_\alpha \quad (8)$$

In the 2-D matrix form, Eq. (7) becomes

$$\begin{bmatrix} G_{\alpha\alpha} & G_{\alpha\beta} \\ G_{\beta\alpha} & G_{\beta\beta} \end{bmatrix} \begin{bmatrix} C_\alpha \\ C_\beta \end{bmatrix} = \begin{bmatrix} S_\alpha \\ S_\beta \end{bmatrix} \quad (9)$$

Therefore, using the inverse of G-matrix, C_α and C_β can be obtained by

$$\begin{bmatrix} C_\alpha \\ C_\beta \end{bmatrix} = \begin{bmatrix} G_{\alpha\alpha} & G_{\alpha\beta} \\ G_{\beta\alpha} & G_{\beta\beta} \end{bmatrix}^{-1} \begin{bmatrix} S_\alpha \\ S_\beta \end{bmatrix} \quad (10)$$

Here, as well known, the inverse of G-matrix is given by

$$\begin{bmatrix} G_{\alpha\alpha} & G_{\alpha\beta} \\ G_{\beta\alpha} & G_{\beta\beta} \end{bmatrix}^{-1} = \frac{1}{\det G} \begin{bmatrix} G_{\beta\beta} & -G_{\beta\alpha} \\ -G_{\alpha\beta} & G_{\alpha\alpha} \end{bmatrix}, \quad (11)$$

Experimental

Sample preparation and measurement of Raman spectra are briefly described below.

Sample preparation

PVDF powder (MW: ~534,000) was purchased from Aldrich Chemistry, N-N-Dimethylformamide (DMF) and Acetone were purchased from Fisher Scientific. PVDF nanofibers are produced

by the electrospinning method, as previously mentioned in the introduction section. PVDF solution was prepared as follows: First, we made a solvent mixture of DMF and acetone with a volume ratio of (DMF): (acetone) = 60%: 40%. PVDF powder was resolved in the solvent mixture with a concentration of 12 wt.% of PVDF and was thoroughly mixed with a magnet stirrer at 45°C for 12 hours.

Just before electrospinning, the PVDF solution was mixed again with a magnet stirrer at 45°C for 1 hour. The outlet of PVDF solution was an 18-gauge stainless steel needle with a high voltage of 14.5 kV controlled with a high voltage power supply (ES100P-5W, Gamma High Voltage Research). The solution pumping speed was 4.5 ml/h controlled with a syringe pump (NE-300, New Era Pump System, Inc.). The fiber collector was made of two aluminum plates and they were separately grounded to a common ground. The separation gap between two aluminum plates was 10 mm. The distance between the needle tip and the collector was 17 cm.

Raman Spectroscopy

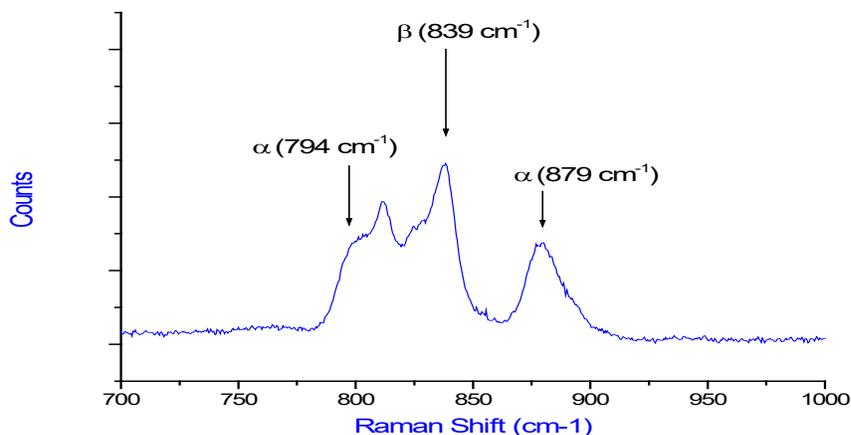
The Raman spectra were taken with a micro-Raman spectroscope (Lab RAM HR, Jobin Yvon Technology/Horiba Scientific) with 532 nm laser beam from a diode laser (Ventus, Laser Quantum) in the range of 700-1000 cm⁻¹. The x100 objective lens was used with a power of 38 mW. Exposed time was 2 secs and 100 repetitions were set for the accumulation of averaging. The polarization plane was adjusted by rotating the relative angle of a half-wave plate to the laser polarization.

Results and Discussion

Signal-to-Noise Ratio

Raman spectra were taken from (A) a PVDF sample made by drying PVDF solution droplet and (B) a single PVDF nanofiber by the aligned electrospinning method (Figure 3).

(A) Dried PVDF Solution Droplet



(B) Aligned PVDF Electrospun Nanofiber

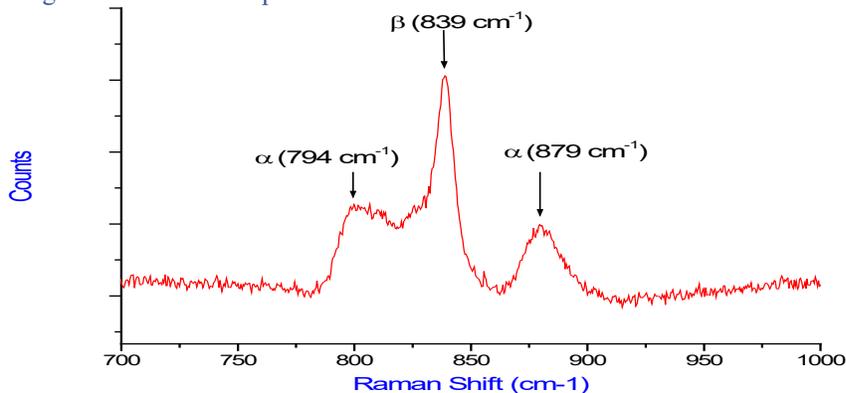


Figure 3: Raman spectra from (A) a sample of dried PVDF solution and (B) a single PVDF nanofiber by the aligned electrospinning method in the range between 700 cm^{-1} and 1000 cm^{-1} . Assignments of peaks are given according to Ref. 11.

The spectrum (A) is supposed to show α -phase because the sample was made without any stress. However, the peak at 839 cm^{-1} is one of strong peaks in this spectral region. The bands for β -phase at 794 cm^{-1} and 879 cm^{-1} are pronounced, but the band at 794 cm^{-1} is only at the shoulder of broad band. The spectrum (B) shows a relatively strong sharp peak at 839 cm^{-1} , which is for β -phase. The reason why the β -phase pronounced is the sample was made by the electrospinning. These assignments especially for β -phase at 839 cm^{-1} is in question for spectrum (A).

(Figure 4) shows two spectra taken from the same PVDF single nanofiber sequentially at two different times (1:09 a.m. and 1:33 a.m.) on a day with a delay of about 24 minutes, since one scan of spectrum took about 20 minutes. Readers may think that the counts are low and that these spectra have a high level of noise. In order to compare the features, these spectra have been positioned with a vertical off-set.

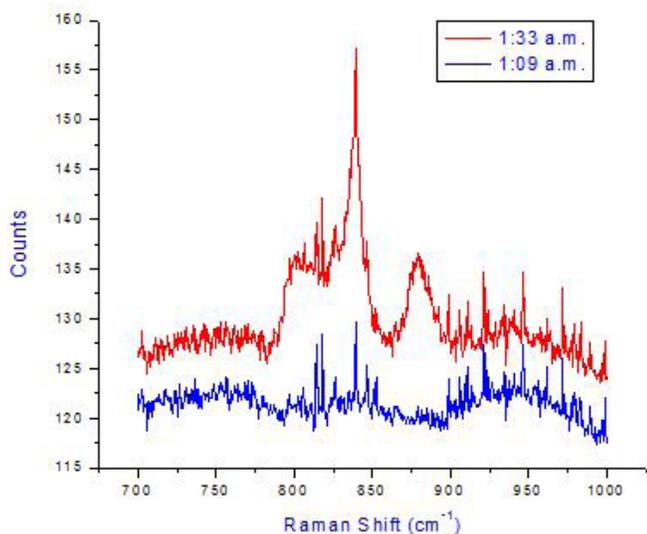


Figure 4: Two spectra taken from the same PVDF single nanofiber sequentially with a delay of about 24 minutes.

By comparing these two spectra, it is interesting that Red spectrum (top) has strong three bands and that Blue spectrum (bottom) does not have such features. However, there is a sharp peak at 839 cm⁻¹ in Blue, which corresponds to the highest peak at 839 cm⁻¹ in Red spectrum, which is for β-phase band. There are more sharp peaks in Blue spectrum, which show up in Red spectrum overlapping on the broad bands.

For the analysis, we divide these spectra into 3 regions: (I) 700-780 cm⁻¹, (II) 780-900 cm⁻¹, and (III) 900-1000 cm⁻¹. Let us investigate the regions (I) and (III) first. These two segments are replotted in (Figure 5). For the analysis from numerical data, instead we calculate the summation from its numerical data, of the integration in Eq. (2), as follows:

$$\int_{\omega_1}^{\omega_2} \psi_1(\omega) \psi_2(\omega) d\omega \rightarrow \sum_{m=0}^M \psi_1(\omega_m) \psi_2(\omega_m) \Delta\omega.$$

(M+1) is the number of data points in the integrating range

between ω_1 and ω_2 , and $\Delta\omega$ is the resolution of the measurement. The correlation coefficient is given by

$$R_{12} \rightarrow \frac{\sum_{m=0}^M \psi_1(\omega_m) \psi_2(\omega_m) \Delta\omega}{\sqrt{\sum_{m=0}^M [\psi_1(\omega_m)]^2 \Delta\omega} \sqrt{\sum_{m=0}^M [\psi_2(\omega_m)]^2 \Delta\omega}} \quad (2')$$

Dropping the common factor of $\Delta\omega$ from numerator and denominator, R_{12} was calculated as

$$R_{12} \rightarrow \frac{\sum_{m=0}^M \psi_1(\omega_m) \psi_2(\omega_m)}{\sqrt{\sum_{m=0}^M [\psi_1(\omega_m)]^2} \sqrt{\sum_{m=0}^M [\psi_2(\omega_m)]^2}} \quad (2'')$$

For (I) 700-780 cm⁻¹, the correlation coefficient becomes

$$R_{12} = 0.999974$$

For (III) 900-1000 cm⁻¹, the correlation coefficient becomes

$$R_{12} = 0.999977$$

In these regions, the noise levels are very low.

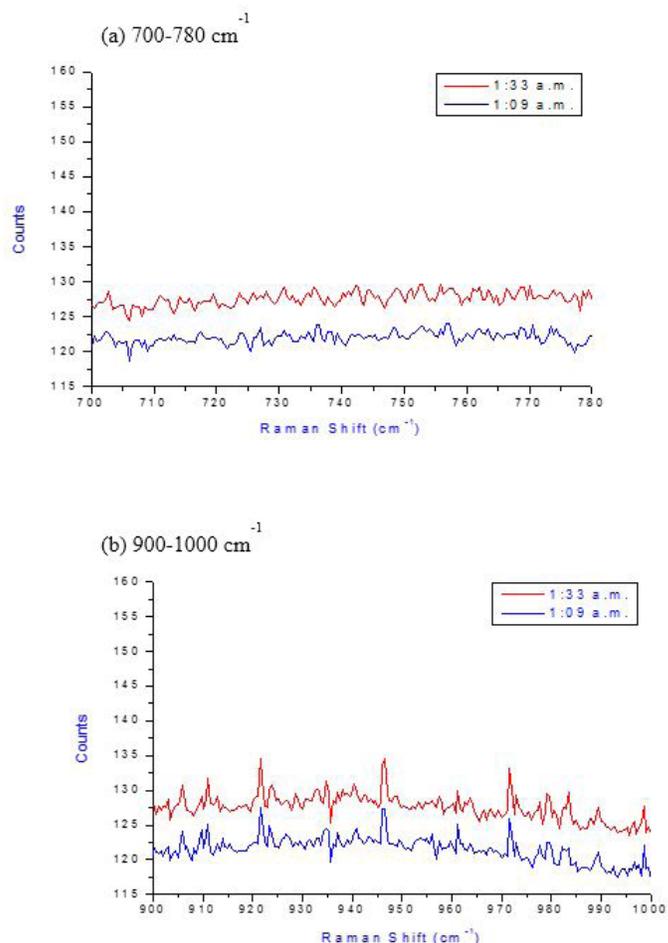


Figure 5: The two segments of spectra in (Figure 4) for the region of (a) 700-780 cm⁻¹ and (b) 900-1000 cm⁻¹. There is a vertical off-set for these two spectra.

(Figure 6) shows the same set of spectra in the region of (II) 780-900 cm⁻¹, and its correlation coefficient becomes

$$R_{12}=0.999341$$

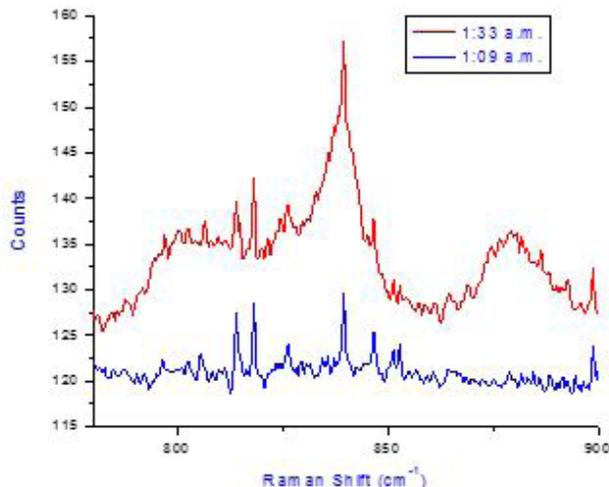


Figure 6: The two segments of spectra in (Figure 4) for the region of 780-900 cm⁻¹. There is a vertical off-set for these two spectra for comparison.

Since the correlation coefficient R_{12} is close to 1, the spectra in the region of (II) 780-900 cm⁻¹ are not noisy although the Red spectrum has three broad bands at about 794 cm⁻¹, 839 cm⁻¹, and 879 cm⁻¹. In this region (II), the correlation coefficient R_{12} is slightly worse than those for regions (I) and (III), however, R_{12} in region (II) is fairly close to 1. This means that the small sharp peaks are not noise related, but also, they are actual Raman band peaks. In order to explain more, suppose that there are N individual peaks at $\omega = \omega_p$ ($p=1,2,\dots,N$), and that one of two Raman spectra from one sample is described as

$$\psi_1(\omega) = \psi_0(\omega) + E_1(\omega) = \sum_{p=1}^N a_p \chi_p(\omega) + E_1(\omega), \quad (12)$$

Here, $\chi_p(\omega)$ is an elementary band spectrum for one mode,

whose peak is at $\omega = \omega_p$. The coefficients a_p 's are relative amplitudes of the modes. If another Raman spectrum from the same sample is described as

$$\psi_2(\omega) = k\psi_0(\omega) + E_2(\omega) = \sum_{p=1}^N k a_p \chi_p(\omega) + E_2(\omega), \quad (13)$$

Then, the correlation coefficient R_{12} becomes For the low noise

level case (1): $\frac{|E_i(\omega)|}{|\psi_0(\omega)|} \rightarrow 0$ ($i = 1, 2$), for the simplicity,

$$\psi_1(\omega) \rightarrow \psi_0(\omega) \text{ and } \psi_2(\omega) \rightarrow k\psi_0(\omega)$$

In this case, the correlation coefficient of this extreme case becomes

$$R_{12} = \frac{\int_{\omega_1}^{\omega_2} \psi_0(\omega) k\psi_0(\omega) d\omega}{\sqrt{\int_{\omega_1}^{\omega_2} [\psi_0(\omega)]^2 d\omega} \sqrt{\int_{\omega_1}^{\omega_2} [k\psi_0(\omega)]^2 d\omega}} \rightarrow 1, \quad (14)$$

which means that if two detected spectra from the same sample have the proportional spectra each other with low noise level, then we have a good correlation coefficient R_{12} close to 1. From this point of view, the broad bands are made up from many sharp peaks, and the signals from a single nanofiber can be resolved relatively easier than the signal from bulky samples. For the bulky samples such as thick film, the additional interactions among polymer molecules are expected, and the sharp features may be blurred.

The Degree of β -Phase in a Mixture

Since we could not have pure α - and β -phases, at this point we could not analyze the degree of β -phase in the mixture phases of fibers. There should have the way to analyze, and the investigation is ongoing.

Conclusions

We have fabricated uniaxially aligned PVDF nanofibers to investigate molecular configuration in the nanofibers. We developed a mathematical formalism of analysis for the signal-to-noise ratio and the degree of β -phase in the phase mixture of PVDF nanofibers. Although, at this point, we could not investigate the degree of β -phase in the mixture of nanofibers, there should be the way to find it with our formalism. In order to see the accurate vibration mode, the Raman spectroscopy on nanofibers may contribute to the detail analysis of polymers. Since polymers are large molecules, there are many vibrational modes due to the high degree of freedom. In the literature, the assignments of bands or peaks are possibly indistinct. In Raman spectra of single nanofiber, many sharp peaks are found overlapped each other and form broad bands. Raman spectroscopy on a single nanofiber could be useful to distinguish these sharp peaks rather than signals from bulk like films.

Acknowledgement

We acknowledge for the supporting grants listed below:

ARO: W911NF-15-1-0441 and W911NF-13-1-0153;

NSF: CMMI-1462329;

NEEC: N00174-16-C-008 and MSRDC CA W911SR-14-2-0001-0004.

References

1. Pawlowski KJ, Belvin HL, Raney DL (2003) Electrospinning of a micro-air vehicle wing skin. *Polymer* 44: 1309-1314.
2. Gibson P, Gibson SH, Rivin D (2001) Transport properties of porous membranes based on electrspun nanofiber. *Colloid Surf A* 187-188: 469-481.
3. Wang Y, Yan D (2003) Properties of poly (vinyl alcohol)/montmorillonite nanocomposite fiber. *Polym Prepr* 3: 213.
4. Kovtyukhova NI, Mallouk TE (2002) Nanowires as building blocks for self assembling logic and memory circuits. *Eur J Chem* 8: 4354-4363.
5. Favier F, Walter EC, Zach MP, Benter T, Penner RM (2001) Hydrogen sensors and switches from electrodeposited palladium mesowire arrays. *Science* 293: 2227-2231.
6. Kim F, Kwan S, Akana, J, Yang P (2001) Langmuir-Blodgett nanorod assembly. *J Am Chem Soc* 123: 4360-4361.
7. Li D, Wang Y, Xia Y (2003) Electrospinning of Polymeric and Ceramic Nanofibers as Uniaxially Aligned Arrays. *Nano Letter* 3: 1167-1171.
8. Yin S, Zhang QM, Chung KW, Yang R, Cheng ZY, et al. (2000) Investigation of the Electro-optic Properties of Electron-irradiated P(VDF-TrFE) Copolymer. *Opt Eng* 39: 670.
9. Vinogradov A, Holloway F (1999) Electro-mechanical properties of the piezoelectric polymer PVDF. *Ferroelectrics* 226: 169-181.
10. Kepler RG (1985) Ferroelectric, pyroelectric, and Piezoelectric Properties of Poly (vinylidene Fluoride). In: Nalwa HS. *Ferroelectric Polymers*. Marcel Dekker, Inc., USA. Pg No:183.
11. Constantino CJL, Job AE., Simoes RD, Giacometti JA, Zucolotto V, et al. (2005) Phase transition in poly (vinylidene fluoride) investigated with micro-Raman spectroscopy. *Appl Spectroscopy* 59: 275-279.