

A short review on working with β - and γ - phases of electroactive polymer PVDF and their perks

Udit Singh Pathania^a, Sumit Bhardwaj^b

Department of Physics, University Institute of Sciences, Chandigarh University, Mohali, Punjab-140413

Abstract

In this review paper, we will talk about the electroactive phases of Poly (vinylidene fluoride), PVDF, their identification, processing, and applications. We will find and tabulate the problems that occur in the identification of different phases of PVDF. PVDF exists in five phases α , β , γ , δ , and ϵ -phases. These electroactive properties have applications in energy generation and storage, biomedical applications, smart scaffolds, sensors and actuators, nanofilms, filters, and spin-valve devices. We will also discuss the different processing methods of β - and γ - phases. PVDF and its copolymers have significantly large applications. Also, we will discuss the conclusions of different techniques to identify; quantitatively and qualitatively the different polymorphs of the PVDF. There are different methods of processing these polymorphs, phase transition method can be used to get one polymorph from another. And an insight into the development and utilization of polymorphs of PVDF.

Keywords: piezoelectric effect; PVDF; electroactive; β -phase.

1. Introduction

PVDF shows electroactive responses including piezoelectric, pyroelectric, and ferroelectric effects. PVDF shows the highest dielectric constant among other semicrystalline polymers, β -phase has the highest electric dipole moment $\approx 8 \times 10^{-30} \text{Cm}$, and the piezoelectric effect is greater than γ -phase. The dipole moment ranges from 5 to $8 \times 10^{-30} \text{Cm}$ [1]. This electric dipole moment is due to the fluorine's high electronegativity and every chain has the dipole moment perpendicular to the polymer chain. The α and ϵ -phases are non-polar due to the antiparallel packaging of dipoles while others are polar. PVDF has applications in separation membrane and filtration membrane. The structures α , β , and γ -phases have been studied extensively.

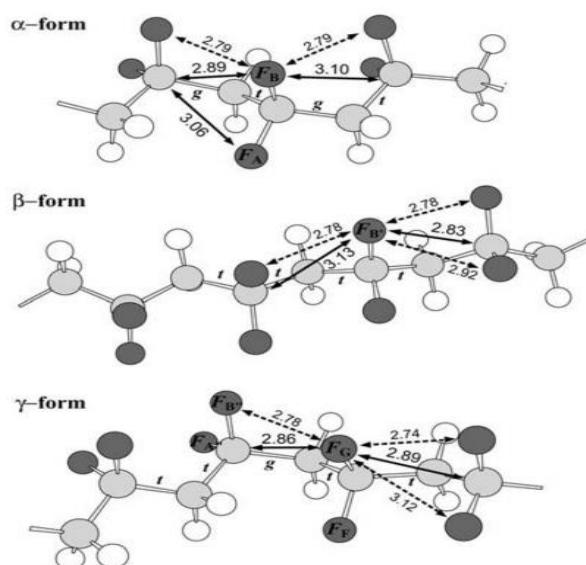


Fig. 1. α -phase has TG TG' confirmation, β -phase has TTT conformation and γ -phase has TTTGTTG' conformation[2].

The α and δ -phase have the same conformation, γ and ϵ -phases have T₃GT₃G¹ conformation, but only the β -phase has the TTT conformation[3]. Due to trans (TTT) conformation β -phase has better electroactive responses than other polymorphs. The α -phase is most common as it can be directly obtained from the melt but β and γ -phases can both be processed from the α -phase and melts. With different processing methods, the yield is different, quantitatively and qualitatively. This provides us with the required usability of the material.

2. Results

2.1. Difficulties in the characterization of PVDF

Many different techniques are used to distinguish between these polymorphs, but no one technique can independently differentiate between these polymorphs. The methods used are Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, and differential scanning calorimetry (DSC).

2.1.1. FTIR

The absorption FTIR band identifies clearly the α -phase as shown in the table.1, but the shouldered peak in the absorption band in the γ -phase is close to that of the β -phase, therefore, it is difficult to distinguish between the γ and β -phase. The absorption band of β -phase at 510 cm⁻¹ and γ -phase at 512 cm⁻¹ are very close and the 840 cm⁻¹ and 1279 cm⁻¹ absorption bands are in both[4]. So, only the α -phase is accurately identified by FTIR absorption at 489, 795, and 976cm⁻¹ peaks[5]. FTIR is also used in the quantification of the polymorphs of PVDF. To calculate the relative percentage of β and γ content from a PVDF sample of α , the β -phase content[6], F(β) is given by

$$F(\beta) = \frac{A_{\beta}}{(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}} \dots\dots\dots(a)$$

Where A _{α} and A _{β} are the absorbances at comparable wave numbers and K _{α} and K _{β} are the absorption coefficients at the respective wave numbers.

Similarly, as in equation (a), the γ -phase content, F(γ) will be given by

$$F(\gamma) = \frac{A_{\gamma}}{(K_{\gamma}/K_{\alpha})A_{\alpha} + A_{\gamma}}$$

But the quantification of γ -PVDF is again difficult because of the shouldered absorption peak shown by it at 840cm⁻¹.

Table 1. An absorption bands characteristics of polymorphs of PVDF[4], [5], [7].

α -PVDF	β -PVDF	γ -PVDF
408cm ⁻¹	510cm ⁻¹	512cm⁻¹
532cm ⁻¹	840cm ⁻¹	776cm ⁻¹
614cm ⁻¹	1279cm ⁻¹	812cm ⁻¹
766cm ⁻¹		833cm ⁻¹
795cm ⁻¹		840cm⁻¹
		1234cm ⁻¹

So, α -phase identification is easy but more work needs to be done to differentiate between β and γ -phase.

2.1.2. XRD

By studying the diffractogram of the different phases of PVDF with the help of the wide-angle X-ray diffraction technique. We can identify the diffracted peaks only exclusive to a certain phase. As this works on Bragg's law,

$$2d \sin\theta = n\lambda \dots\dots\dots (b)$$

Where n is the order of reflection, d is the crystal plane spacing, θ is the angle between lattice plane and incident light. The α has a characteristic peak at $2\theta = 17.66$ and β has a characteristic diffraction peak at $2\theta = 20.26$, but γ -phase diffraction peaks $2\theta = 18.50$ and $2\theta = 20.04$ relative to the diffraction planes (020) and (110) close to that of α - phase $2\theta = 18.30$ and $2\theta = 19.90$ relative to the diffraction planes (020) and (110), making it difficult to differentiate between them[4]. The β -phase is clearly identified.

2.1.3. DSC

Differential Scanning Calorimetry (DSC), gives us insight into the thermogram of the PVDF phases. This method cannot differentiate between the α and β -PVDF as they have the same endothermic peaks. According to Gregorio – Cestarini and Prest – Luca the endothermic peak of the α -phase is at 167°C and 172°C respectively[6]. γ -phase is clearly identified as having different melting peaks than the α and β - phase but the peak depends upon how the γ -phase is obtained, if it is obtained from melts then the temperature is 179°C – 180°C, and if from the interphase transformation of α to γ then the temperature is 189°C – 190°C, 8°C and 18°C higher than α -PVDF (figure 4). So, we see the melting peaks in DSC morphology and the crystalline phase characteristics. Hence, this method is complementary to X-ray diffraction and FTIR. The conclusion from these techniques is that no one can differentiate between all three polymorphs but by application of all three we can deduce correctly the phase of a given sample.

Table 2. Distinguish and undistinguished phases of PVDF by techniques.

Technique	Distinguishable	Indistinguishable
FTIR	α	β, γ
XRD	β	α, γ
DSC	γ	α, β

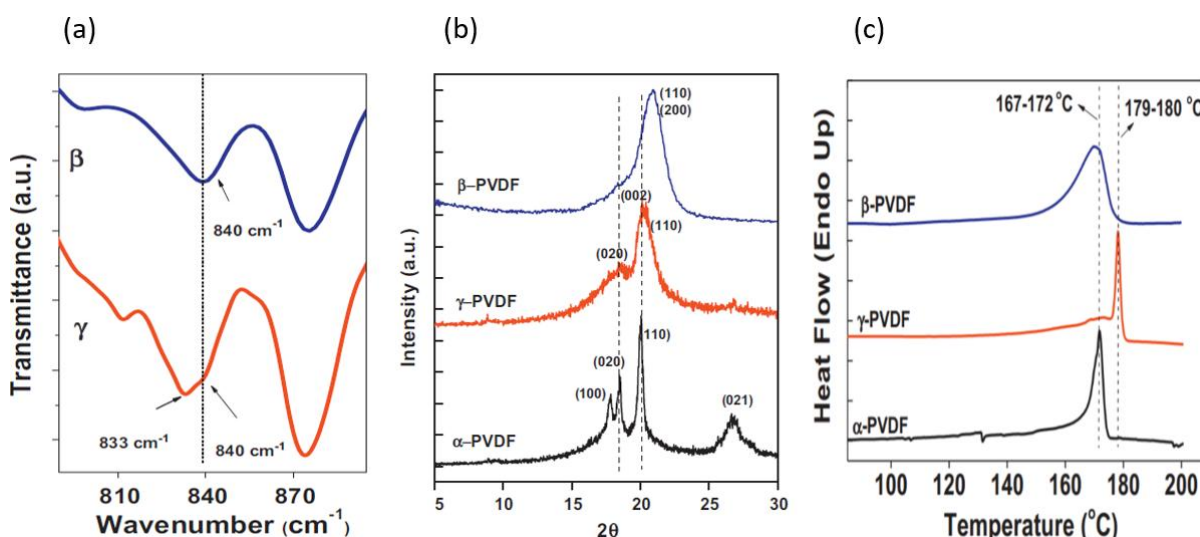


Fig. 2. (a) FTIR resemblance pattern of β and γ -phases (b) XRD identification diffraction pattern of α , β and γ -phases (c) DSC signature of three PVDF phases.[8], [9]

2.2. Processing methods of β and γ -phases

There are many different processes to produce β and γ -PVDF but the most common is the form α - phase, from melts and from different fillers. Let us compare the results of these methods:

2.2.1. From melts

The pressure quenching of α -phase at high pressure and temperature can yield the pure β -phase formation with higher MP than α - phase about 27°C higher, making its MP at 185°C. High pressure was applied to the α - conformation PVDF to obtain the β -phase such as 4000 kg/cm², so, increasing the quenching pressure from 200 to 800 MPa will result in the increase in the β -phase content, at quenching pressure around 800MPa we will get the pure β -phase. Some of the process's conditions are tabulated below:

Table 3. β -phase from the melts

Preparation	Observation
The temperature of at least 280°C pressure quenching 500 MPa or more	Pure β -phase
Pressure quenching initial 100 MPa to 700 MPa	Pure β -phase
Non- isothermal crystallization at ultra-high cooling rates of 150 K/s	Partial β -phase

In the case of the γ -phase, melt crystallization at a high temperature of about 170°C we can only obtain 34.8% γ -phase content from the melts. So, other methods are needed to get a higher content γ -phase.

2.2.2. By α -phase transition

When stress is applied to the α -phase PVDF film, we can obtain the β -phase by this stretching mechanism but there is some percentage of α -phase still present in the film. The temperature is changed from 80°C to 140°C and R, the stretch ratio from 1 to 5. At temperature 80°C and a stretch ratio(R) of 5 had given maximum β -phase with 20% of the α still present. The transformation to β -phase depends upon the R than the temperature. The ferroelectric behavior and the piezoelectric responses are highest in this case. The piezoelectric coefficient is given by

$$d_{33}^T = \left(\frac{\partial S_3}{\partial E_3} \right)_T \dots\dots\dots (c)$$

Where d_{33}^T is the piezoelectric coefficient at the S, strain due to the external electric field E, and at T.

d_{33} value is found to be equal to 34pCN⁻¹, with increasing temperature at R =5 the piezoelectric effect will decrease as the β - phase content decreases. β - phase with the stretch ratio between 3 to 5 can be obtained from α - phase transformation under temperatures below 100°C[10],[11]. But β - phase formed by low-temperature transformation does not have a piezoelectric effect due to the random crystal orientation. So, to obtain a sufficient piezoelectric effect high electric field is applied 100 – 400mV/m which causes the β - crystal to align with a better piezoelectric effect[12]. This process of varying the electric field is called poling and also by poling of δ - phase.

In the case of the γ -phase as we have seen in the DSC the change can be induced in the α -phase to transform into the γ -phase thermally. The α -phase crystals are annealed near the melting point of PVDF to obtain the γ -phase but the content is very small in samples crystallized below 155°C and even at higher temperatures does not have significant change[13].

2.2.3. Solvent casting

Solvent casting involves electrospinning, spin-coating, and Langmuir- Blodgett processes. Electrospinning DMF solution in a dissolved PVDF solution forms the β - PVDF nanofibers which have many applications in biomedical, cell phones, sensors, batteries, etc. Langmuir- Blodgett technique is used to form nanoscale films forming ferroelectric β - PVDF which is formed directly. A pure β - phase can be prepared with 2nm monolayer thickness and a piezoelectric coefficient of - 49.4pm/V[14]. The spin-coating process can be used to obtain thin uniform polymer film by spinning a planer substrate in the solution of dilute PVDF. The thickness and the roughness of the layer will be dependent on the spinning speed and the humidity respectively. By taking acetone and DMF as solvents with single-crystal Si wafer 2 μ m PVDF film can be made by Benz et al[15].

2.2.4. Fillers

More focused studies on forming β - phase by doping of filler material have been made and it has been found that the β - phase piezoelectric content was increased to about $\sim 90\%$ by incorporation of the BaTiO_3 ceramic, ferrite nanoparticles, and organometallic modified clays. It was observed that the piezoelectric was increased (33 pC/N) until $\sim 90\%$ when the filler was ferrite nanomaterial, and $\sim 80\%$ when BaTiO_3 ceramic filler was incorporated into the chain [16], [17]. The change in the electroactive β - phase is dependent on the filler size not on the content of the filler. Melt mixing process of clay with PVDF forms electroactive PVDF clay nanocomposite. There are many more fillers that can be used to tweak the electroactive the β - phases such as palladium nanoparticles, carbon nanotubes, hydrated salt added to the polymeric solution, and nano TiO_2 . In the case of γ - phase KBr powder, zeolite, clay, organ-modified silicon copolymer L-20 melting at different temperatures, and crystallization of γ - phase has increased the electric conductivity of the PVDF sample.

3. Applications

3.1. Magnetolectric materials and electrolytes

Practical application of ME material is a challenging field having very large applications such as memories for data storage, switching, sensors, actuators, spin-wave generation, and diodes polarisation filters. This can be done by the application of an electric field we can vary the induced magnetization of the material which can vary electric polarization. Hence, serving as the bridge between both magnetic and electric properties. Metglas/PVDF ME laminates sensors for detection of weak ac and dc magnetic fields are being used to have a strong coupling effect at room temperature. It is difficult to use single-phase ME materials because they have weak ME coupling and require low temperatures. PZT (lead zirconate titanate), BaTiO_3 (barium titanate), and Terfenol-D are the most used as ME composites as they have a high piezoelectric effect three times the single-phase ME composites but they are still limited by their cost, brittleness, fragility [18]–[21].

PVDF having a high dielectric constant in the β - phase of 8.4 and the strong electron-withdrawing capacity of the functional group gives it larger anodic stability due to which there is higher ionization of the lithium salt which can be used to obtain high functional polymer electrolyte by incorporating in the polymer matrix. LiCF_3SO_3 , LiBF_4 , and LiClO_4 have been used these have higher conductivity ranging from 10^{-7} to 10^{-4} S/cm at 0°C [22]–[24]

3.2. Biomedical application

PVDF is being used as the biomaterials in smart prostheses, sensors, and smart scaffolds. Tissue engineering has generated an interest in the biomedical field. By mobilizing L-lysine on PVDF membrane this can be used in tissue repair, there can be three different ways, but firstly the cell is harvested from the patient. The scaffold can directly be planted in the affected region or it can be cultured with the cells of the region where to be implanted with appropriate signals. This can also be implemented in the case of bone regeneration [25]. The sensors measure the heart rate [26]. Positively charged β - phase PVDF has osteoblast adhesion and growth is higher by of order 500 cells/ mm^2 , hence, it has a higher culture ratio for tissue regeneration.

3.3. Sensors and actuators

Due to piezoelectric and pyroelectric effects, PVDF is used in actuators and sensors, which is able to change mechanical variables into measurable electric quantities. PVDF/ Graphene, SGO/ PVDF bilayer has fast response time than pure PVDF actuator and responds to heat, moisture, and light [19], [20]. Quartz crystals are microbalance to detect vapors of the DMMP (dimethyl methyl phosphonate)

vapor when modified by PVDF[27]. ZnO₃ nanoneedle with PVDF hybrid film is used to sense the heart rate and other vital information[28]. The addition of the nanofillers to increase the piezoelectric responses of the sensors and actuators is used. A nanocomposite in presence of BaTiO₃ nucleates the electroactive β - phase up to 80%. This cause the piezoelectric effect to increase in the material which can also be tuned to the desired applications/response[29]. PZT with carbon nanotube is incorporated into the PVDF matrix increasing the dielectric constant and also transforming the α - phase to β - the phase. These are used in miniature devices such as ink jet printers.

3.4. Energy harvesting and Shape memory polymer

The mechanical vibrations and thermal fluctuations are converted into the electric energy by piezoelectric and pyroelectric effects respectively. By using the ultrasonication probe process flexible nanogenerators were fabricated with BaTiO_(1-x)Zr_xO₃ which are used in devices such as nanoscale materials, NG (nanogenerators), and other devices[30].

Using a direct laser writing technique crystal phase anisotropy can be programmed into the PVDF film where the anisotropic distribution of the α and β - phases is produced. This shape change is due to the different absorption abilities of α and β - phases for acetone. SM (shape memory) properties are seen in carbon nitride polymer film which can be folded into many shapes[31]–[33].

Conclusion

The electroactive phases of the PVDF find many applications as magnetoelectric composites, electrolytes in batteries, sensors, and actuators for sensing mechanical signals to converting them to electric signals and robotics, prosthetic arms, shape memory polymers (SMP), biomedical, tissue regeneration/ engineering, and some energy harvesting applications as NG (nanogenerators) and many more. From the 1969 work of Heiji Kawai on piezoelectricity of Poly(vinylidene Fluoride) many advancements in PVDF have been made but we require a more precise way to differentiate between this α , β , γ - phases of PVDF as no single experimental technique is able to differentiate between these electroactive PVDF phases. The filler incorporation increases the piezoelectric effect and also β - phase content but the fragility, and brittleness of the composite so formed it challenging to make these materials work. Cost-effectiveness is also something to keep in mind. Also need to understand and study the morphology of different crystal structures. PVDF and its composites have more electroactive response in magnitude than any other polymer.

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