# Poly(vinylidene fluoride) Phase Structure and Identification

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Poly(vinylidene fluoride) (PVDF) is one of the most interesting semicrystalline polymers and is often used in sensors, actuators, energy harvesters, etc., because of its high biocompatibility, film-forming ability, low cost, excellent chemical stability, and good electroactive characteristics, including piezo-, pyro-, and ferro-electric properties.

poly(vinylidene fluoride) wearable sensor nanogenerator energy harvester

## 1. Introduction

The development and utilization of renewable, sustainable, and environmentally friendly energy sources are essential to mitigate the continuously rising global energy demand, shortage of fossil fuels, and environmental pollution caused by non-renewable sources [1][2][3]. To this end, various energy harvesting, storage, and recycling technologies based on external sources (e.g., solar power, thermal energy, and chemical energy) have been developed. Among them, mechanical energy sources are readily available in nature and daily human activities, such as human movement with fingers, hands, arms, legs, etc., speaking, respiration, airflow, vibrations, frictional forces, water precipitation, and hydraulics (waves in nature, blood flow inside organisms, etc.) [4][5][6][7]. Over recent years, self-powered wearable sensors and human energy harvesters based on nanogenerators (NGs) have attracted considerable attention, including piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs). These wearable sensors can be used to detect, monitor, and record real-time information on the human physiological status.

Poly(vinylidene fluoride) (PVDF) is one of the most interesting semicrystalline polymers and is often used in sensors, actuators, energy harvesters, etc., because of its high biocompatibility, film-forming ability, low cost, excellent chemical stability, and good electroactive characteristics, including piezo-, pyro-, and ferro-electric properties [8][9][10][11]. Notably, PVDF-based NGs can effectively harvest energy from organic systems and human activities, such as body motion and even breathing [12][13][14][15]. In addition, the excellent biocompatibility of PVDF-based polymers makes them desirable for application in flexible membranes, energy sensors, energy-harvesting electronic skins (e-skins), and even implantable devices and artificial prosthetics [16]. However, they still have some drawbacks, such as low ionic conductivity, low crystallinity, and shortage of reactive groups [17]. The low crystallinity especially can limit their piezoelectric properties, charge mobility, and dielectric constant.

Moreover, two copolymers of PVDF are popular candidates for self-powered electronics and energy harvesting. The first one, poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), is promising due to its thermodynamic stability and high crystallinity. TrFE has a more rigid and ordered structure compared to the vinylidene fluoride (VDF) monomer in PVDF. This structural difference promotes the formation of crystalline regions within the copolymer, where it allows for efficient alignment of polymer chains, resulting in enhanced charge generation in response to mechanical stress or strain. However, the high cost, poor thermal stability, limited stacking integrity, chemical reactivity, and poor ferroelectric dipole density of P(VDF-TrFE) restrict its large-scale device fabrication. Although the copolymerization units of TrFE can improve the crystallinity of PVDF, their crystal defects often cause current leakage paths [18][19]. Compared with P(VDF-TrFE), PVDF homopolymers exhibit a higher dipole density and thermal stability. The other PVDF copolymer, poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)), has a relatively higher piezoelectric sensitivity and electrostrictive strain [20][21][22][23]. Furthermore, the piezoelectric coefficient of P(VDF-HFP) (13.5 with 5% HFP) is much higher than those of PVDF (≈12.9) and P(VDF-TrFE) (≈10.4) copolymers [24]. Furthermore, the P(VDF-HFP) copolymer has a unique piezoelectric response, which makes it more suitable for fabricating self-powered wearable, stretchable electronic devices, compared with the other polymers. The PVDF- and PVDF-HFP-based materials exhibit immense potential as electrolytes in solid-state lithium-ion batteries, owing to their large dielectric constant, chemical stability, and high mechanical strength [25][26].

Apart from PVDF co-polymers (e.g., P(VDF-TrFE) and P(VDF-HFP)), other polymers such as polypropylene (PP), Nylon11, polylactic acid (PLLA), and poly (lactic-co-glycolic acid) (PLGA) also exhibit piezoelectric properties [27]. Moreover, their soft property is suitable for wearable electronics. Although several traditional ceramic materials such as lead zirconate titanate (PZT) can efficiently convert mechanical energy into electrical energy, they are rigid and difficult to manipulate and machine. On the other hand, owing to its flexibility, PVDF shows excellent long-term stability and does not depolarize when exposed to extremely strong alternating electric fields. Consequently, PVDF-based flexible films have gained immense popularity in recent years.

# 2. PVDF Phase Structure and Identification

## 2.1. PVDF Phase Structure

It has been widely established that the semicrystalline PVDF polymer shows five distinct crystalline phases: the α-, β-, γ-, δ-, and ε-phases [28][29][30][31][32][33][34][35][36][37], which have different stereochemical macromolecular conformations. Firstly, the α-phase, the most thermodynamically stable polymorph, is a non-electroactive, nonpolar, and paraelectric phase with no piezoelectricity, and has a centrosymmetric ($P2_1/c$) monoclinic unit cell with alternating trans and gauge linkage (TGTG’) conformation [38][39]. On the other hand, the β-phase, the most electroactive phase with excellent piezoelectricity, has an orthorhombic crystal structure with all trans (TTT) planar zigzag conformation [40]. In PVDF, the electroactive β-phase is the most preferred, due to its superior piezo-, pyro-, and ferro-electric performance [41]. Usually, it is important to transform the α-phase into β- phase, because the α-phase is the major component of PVDF films [42]. High isothermal crystallization temperatures often result in the formation of the γ-phase, which also possesses an orthorhombic crystal structure with a $T_3GT_3G'$ conformation [33][34][35]. The δ- and ε-phases are the polar and antipolar analogues of the α- and γ-phases, respectively [31][32][36][43].

Compared with the α-phase, the δ-phase has a non-centrosymmetric ($P2_1cn$) unit cell, rendering it piezoelectric, pyroelectric, and ferroelectric [44]. Similar to the β-phase, the δ-phase has superior memory functionality [45][46]. Therefore, the δ-phase is a promising alternative to the β-phase in PENGs. Among the five phases, the α-, β,- and γ-phases are the most widely investigated.

Furthermore, the electromechanical coupling factor, *k*, is one of the dominate parameters for the preparation and application of PVDF-based materials. It presents the efficiency in the mechanical to electrical transformation. High crystallinity and preferred orientation in PVDF crystallites can lead to high remnant polarization, which increases the electromechanical coupling factor. PVDF with different phases have distinct electromechanical coupling factors, and they are also influenced by temperature, poling condition, etc. [47]. Another significant parameter, $d_{33}$, is used to represent the piezoelectric constant in PVDF-based materials, which often has a negative sign conversion resulting from the crystal structure and molecular alignment. It signifies that the resulting electric field is in the opposite direction to the applied stress or strain.

## 2.2. PVDF Phase Identification

Although the β- and γ-phase have a similar conformation, the piezoelectric effect of the β-phase is stronger than that of the γ-phase. Therefore, effective strategies for obtaining the electroactive phase of PVDF have garnered considerable research attention, and the identification of the α-, β-, and γ-phases is a crucial step in realizing this goal. Among the identification approaches, Fourier-transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) are considered to be the most reliable ones. Usually, both these techniques are simultaneously used to better discern the β- and γ-phases.

It has been reported that the α-, β-, γ-, and δ-phases have distinct characteristic bands in the FTIR spectrum (**Table 1**). The intensity of these bands indicates the orientation of the $CF_2$ dipole moment. For example, the broad spectral band at 840 $cm^{-1}$ results from the overlap of the β- and γ-phases, so other identification approaches must be applied to discriminate between the two phases.

**Table 1.** Characteristic FTIR absorption bands of α-, β-, γ-, and δ-phase PVDF.

| Phase | Band Position ($cm^{-1}$) | References |
|---|---|---|
| α | 530 | [48][49] |
| | 615 | [48][49][50] |
| | 763–765 | [48][49][50][51][52][53] |
| | 795–797 | [48][49][50][53] |
| | 976 | [49][51][53] |
| | 1218 | [54] |

| Phase | Band Position ($cm^{-1}$) | References |
|---|---|---|
| β | 510 | [48][49][55] |
| | 836 | [50] |
| | 840 | [47][48][51][55] |
| | 845 | [49] |
| | 1210 | [47][54] |
| | 1274–1279 (shoulder) | [54][56] |
| | 1383 | [54][56] |
| | 1423 | [54] |
| | 1431 | [54] |
| γ | 812 | [47] |
| | 833 (sharp) | [57] |
| | 838 (broad) | [58][59] |
| | 1233–1234 (shoulder) | [54][59] |
| δ | 1182 | [60] |
| | 1209 | [60] |

The relative proportion of electroactive phases ($F_{EA}$) can be utilized to distinguish some phases. For example, taking the band at 840 $cm^{-1}$ as an example, S. Maji et al. [61] deconvoluted the FTIR spectrum (900–750 $cm^{-1}$ bands) and quantified the relative fraction of electroactive phases ($F_{EA}$), including both β- and γ-phases, using the following equation:

$$F_{EA} = \frac{I_{EA}}{\left(\frac{K_{840}}{K_{763}}\right) I_{763} + I_{EA}} \times 100 \qquad (1)$$

where $F_{EA}$ represents the proportion of the electroactive phase; $I_{763}$ and $I_{EA}$ are the absorption intensities at 763 and 840 $cm^{-1}$, respectively; and $K_{763}$ and $K_{840}$ are the absorption coefficients at the respective wavenumbers [62]. The individual β- and γ-phases of PVDF films can also be defined by curve deconvolution of the band at 840 $cm^{-1}$. The ratio of the electroactive β- and γ-phases can be obtained as follows [63]:

$$F(\beta) = F_{EA} \times \left(\frac{A_\beta}{A_\beta + A_\gamma}\right) \times 100\% \qquad (2)$$

and

$$F(\gamma) = F_{EA} \times \left(\frac{A_\gamma}{A_\beta + A_\gamma}\right) \times 100\% \quad (3)$$

where $A_\beta$ and $A_\gamma$ are the total regions under the deconvoluted curves of the β and γ-phases centered at the 840 cm$^{-1}$ band.

It has been widely accepted that the absorption band at 840 cm$^{-1}$ is common to both β and γ-phases, but it exists as a strong band only for the β-phase, while it appears as a shoulder of the 833 cm$^{-1}$ band for the γ-phase.

It can be seen in **Table 1** that some peaks of the α-, β- and γ-phases overlap with each other, so it is difficult to distinguish them just by FTIR spectroscopy. XRD characterization is another auxiliary approach to discriminate the structures. The representative crystal diffraction planes and diffraction angles of the various phases of PVDF are listed in **Table 2**. The peak at 20.6° is attributed to the (110) and (200) crystal planes of the β-phase, while the peaks at 18.5°, 19.2°, and 20.4° correspond to the (020), (002), and (110) crystal planes of the γ-phase. Although both the α- and δ-phases have similar chain conformations, the intensities of peaks at 2θ = 17.6° and 25.6° corresponding to (100) and (120) planes are different for the two phases. After heat treatment at 170 °C, the lattice shape and size as well as the symmetry of the unit cell lattice are changed [64]. However, some peaks cannot be easily distinguished. For example, the characteristic peak of the α-phase at 18.3° (020) is often overlapped with that of the γ-phase at 18.5° (020); the broad peak at 20.5° often results from the overlap of the β-phase signal at 20.6° and the γ-phase signal at 20.4°. Sometimes a broad double peak appears around 20.4°, indicating the coexistence of β- and γ-phases [37].

**Table 2.** Diffraction angles and crystal planes of α-, β-, γ-, and δ-phase PVDF.

| Phase | 2θ (°) | Crystal Plane | References |
|---|---|---|---|
| α | 17.6–17.7 | (100) | [33][48][55][58][65] |
| | 17.9 | (110) | [66] |
| | 18.68, 18.3–18.5, | (020) | [33][48][55][58][65][66] |
| | 19.9 | (021) | [65] |
| | 19.9, 20.38 | (110) | [33][48][55][58] |
| | 20.2 | (021) | [66] |
| | 20.8 | (011) | [33] |
| | 26.5 | (021) | [48][55][58] |

| Phase | 2θ (°) | Crystal Plane | References |
|---|---|---|---|
| | 27.6, 25.6 | (120) | [33][39] |
| | 27.8,27.9 | (111) | [65][66] |
| | 35.7, 36.1 | (200) | [65][66] |
| | 39.0 | (002) | [65][66] |
| | 57.4 | (022) | [65] |
| β | 20.6–20.8 | (110)/(200) | [33][48][55][65][66] |
| | 36.3 | (200) | [48] |
| | 36.6 | (020, 101) | [65][66] |
| | 56.1, 56.9 | (221) | [65][66] |
| γ | 18.5 | (020) | [55][65][66][67] |
| | 19.2 | (002) | [55] |
| | 20.1–20.4 | (110) | [55][65][66][67] |
| | 26.8 | (022) | [65][66] |
| | 36.2 | (200) | [58] |
| | 38.7 | (211) | [65][66] |
| δ | 18.3 | (020) | [39][68] |
| | 17.6 | (100) | [64] |
| | 19.9 | (110) | [39][68] |
| | 25.6 | (120) | [64] |
| | 26.7 | (021) | [39][68] |
| | 28.1 | (111) | [39][68] |

The overall crystallinity ($X_c$) is calculated according to the crystalline and amorphous regions isolated from the XRD patterns by the Gaussian function, as follows:

$$X_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100\% \tag{4}$$

where $\sum A_{cr}$ and $\sum A_{amr}$ are the sums of integrated areas from crystal diffraction peaks and the amorphous halo. The crystallite size can be determined using the Debye–Scherrer formula, as follows:

$$\mathrm{t} = \frac{\lambda}{B\cos\theta} \tag{5}$$

where t is the crystallite size, *B* is the FWHM of the diffraction peak in radians, and λ is the X-ray wavelength.

Other auxiliary approaches can be implemented, based on the physical properties of PVDF. For example, the melting temperature of the α-phase is lower than that of the polar β- and γ-phases in PVDF, so differential scanning calorimetry (DSC) is suitable for identifying the α-phase in relation to the β- and γ-phases [69][70].

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## References

1. Kumar, C.N. Energy collection via Piezoelectricity. J. Phys. Conf. Ser. 2015, 662, 012031.
2. Sinha, S.; Chakraborty, S.; Goswami, S. Ecological footprint: An indicator of environmental sustainability of a surface coal mine. Environ. Dev. Sustain. 2017, 19, 807–824.
3. Harris, P.; Litak, G.; Bowen, C.R.; Arafa, M. Arafa, M. A composite beam with dual bistability for enhanced vibration energy harvesting. In Energy Harvesting & Storage: Materials, Devices, & Applications VII; SPIE: Bellingham, WA, USA, 2016; p. 98650K.
4. Mao, Y.; Geng, D.; Liang, E.; Wang, X. Single-electrode triboelectric nanogenerator for scavenging friction energy from rolling tires. Nano Energy 2015, 15, 227–234.
5. Fan, X.; Chen, J.; Yang, J.; Bai, P.; Li, Z.; Wang, Z.L. Ultrathin, Rollable, Paper-Based Triboelectric Nanogenerator for Acoustic Energy Harvesting and Self-Powered Sound Recording. ACS Nano 2015, 9, 4236–4243.
6. Zhang, G.Y.; Cheng, T.; Zheng, M.H.; Yi, C.G.; Pan, H.; Li, Z.J.; Chen, X.L.; Yu, Q.; Jiang, L.F.; Zhou, F.Y. Peroxisome proliferator-activated receptor-γ (PPAR-γ) agonist inhibits transforming growth factor-beta1 and matrix production in human dermal fibroblasts. J. Plast. Reconstr. Aesthetic Surg. 2010, 63, 1209–1216.
7. Zhao, Z.; Pu, X.; Du, C.; Li, L.; Jiang, C.; Hu, W.; Wang, Z.L. Freestanding Flag-Type Triboelectric Nanogenerator for Harvesting High-Altitude Wind Energy from Arbitrary Directions. ACS Nano 2016, 10, 1780–1787.
8. Vinogradov, A.; Holloway, F. Electro-mechanical properties of the piezoelectric polymer PVDF. Ferroelectrics 1999, 226, 169–181.
9. Gomes, J.; Nunes, J.S.; Sencadas, V.; Lanceros-Méndez, S. Influence of the β-phase content and degree of crystallinity on the piezo-and ferroelectric properties of poly(vinylidene fluoride). Smart

Mater. Struct. 2010, 19, 065010.

10. Gallantree, H. Review of transducer applications of polyvinylidene fluoride. IEE Proc. I-Solid-State Electron Devices 1983, 130, 219–224.
11. Costa, C.; Lanceros-Mendez, S. Recent advances on battery separators based on poly(vinylidene fluoride) and its copolymers for lithium ion battery applications. Curr. Opin. Electrochem. 2021, 29, 100752.
12. Hansen, B.J.; Liu, Y.; Yang, R.; Wang, Z.L. Hybrid nanogenerator for concurrently harvesting biomechanical and biochemical energy. ACS Nano 2010, 4, 3647–3652.
13. Sun, C.; Shi, J.; Bayerl, D.J.; Wang, X. PVDF microbelts for harvesting energy from respiration. Energy Environ. Sci. 2011, 4, 4508–4512.
14. Wang, F.; Tanaka, M.; Chonan, S. Development of a PVDF piezopolymer sensor for unconstrained in-sleep cardiorespiratory monitoring. J. Intell. Mater. Syst. Struct. 2003, 14, 185–190.
15. Lee, S.; Bordatchev, E.V.; Zeman, M.J. Femtosecond laser micromachining of polyvinylidene fluoride (PVDF) based piezo films. J. Micromech. Microeng. 2008, 18, 045011.
16. Chen, X.; Han, X.; Shen, Q.D. PVDF-based ferroelectric polymers in modern flexible electronics. Adv. Electron. Mater. 2017, 3, 1600460.
17. Wu, Y.; Li, Y.; Wang, Y.; Liu, Q.; Chen, Q.; Chen, M. Advances and prospects of PVDF based polymer electrolytes. J. Energy Chem. 2021, 64, 62–84.
18. Zhu, H.; Yamamoto, S.; Matsui, J.; Miyashita, T.; Mitsuishi, M. Ferroelectricity of poly(vinylidene fluoride) homopolymer Langmuir–Blodgett nanofilms. J. Mater. Chem. C 2014, 2, 6727–6731.
19. Fujisaki, S.; Ishiwara, H.; Fujisaki, Y. Low-voltage operation of ferroelectric poly(vinylidene fluoride-trifluoroethylene) copolymer capacitors and metal-ferroelectric-insulator-semiconductor diodes. Appl. Phys. Lett. 2007, 90, 162902.
20. Künstler, W.; Wegener, M.; Seiß, M.; Gerhard-Multhaupt, R. Preparation and assessment of piezo-and pyroelectric poly(vinylidene fluoride-hexafluoropropylene) copolymer films. Appl. Phys. A Mater. 2001, 73, 641–645.
21. He, X.; Yao, K.; Gan, B.K. Phase transition and properties of a ferroelectric poly(vinylidene fluoride-hexafluoropropylene) copolymer. J. Appl. Phys. 2005, 97, 084101.
22. Huan, Y.; Liu, Y.; Yang, Y.; Wu, Y. Influence of extrusion, stretching and poling on the structural and piezoelectric properties of poly(vinylidene fluoride-hexafluoropropylene) copolymer films. J. Appl. Polym. Sci. 2007, 104, 858–862.

23. Wegener, M.; Künstler, W.; Richter, K.; Gerhard-Multhaupt, R. Ferroelectric polarization in stretched piezo-and pyroelectric poly(vinylidene fluoride-hexafluoropropylene) copolymer films. J. Appl. Phys. 2002, 92, 7442–7447.
24. Lu, X.; Schirokauer, A.; Scheinbeim, J. Giant electrostrictive response in poly(vinylidene fluoride-hexafluoropropylene) copolymers. IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2000, 47, 1291–1295.
25. Lun, P.; Chen, Z.; Zhang, Z.; Tan, S.; Chen, D. Enhanced ionic conductivity in halloysite nanotube-poly(vinylidene fluoride) electrolytes for solid-state lithium-ion batteries. RSC Adv. 2018, 8, 34232–34240.
26. Liang, Y.F.; Deng, S.J.; Xia, Y.; Wang, X.L.; Xia, X.H.; Wu, J.B.; Gu, C.D.; Tu, J.P. A superior composite gel polymer electrolyte of Li7La3Zr2O12-poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) for rechargeable solid-state lithium ion batteries. Mater. Res. Bull. 2018, 102, 412–417.
27. Smith, M.; Kar-Narayan, S. Piezoelectric polymers: Theory, challenges and opportunities. Int. Mater. Rev. 2022, 67, 65–88.
28. Lovinger, A.J. Annealing of poly(vinylidene fluoride) and formation of a fifth phase. Macromolecules 1982, 15, 40–44.
29. Furukawa, T. Ferroelectric properties of vinylidene fluoride copolymers. Phase Transit. Multinatl. J. 1989, 18, 143–211.
30. Mohammadi, B.; Yousefi, A.A.; Bellah, S.M. Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films. Polym. Test. 2007, 26, 42–50.
31. Levi, N.; Czerw, R.; Xing, S.; Iyer, P.; Carroll, D.L. Properties of polyvinylidene difluoride-carbon nanotube blends. Nano Lett. 2004, 4, 1267–1271.
32. Manna, S.; Batabyal, S.K.; Nandi, A.K. Preparation and characterization of silver−poly(vinylidene fluoride) nanocomposites: Formation of piezoelectric polymorph of poly(vinylidene fluoride). J. Phys.Chem. B 2006, 110, 12318–12326.
33. Dillon, D.R.; Tenneti, K.K.; Li, C.Y.; Ko, F.K.; Sics, I.; Hsiao, B.S. On the structure and morphology of polyvinylidene fluoride–nanoclay nanocomposites. Polymer 2006, 47, 1678–1688.
34. Park, J.-W.; Seo, Y.-A.; Kim, I.; Ha, C.-S.; Aimi, K.; Ando, S. Investigating the crystalline structure of poly(vinylidene fluoride)(PVDF) in PVDF/silica binary and PVDF/poly(methyl methacrylate)/silica ternary hybrid composites using FTIR and solid-state 19F MAS NMR spectroscopy. Macromolecules 2004, 37, 429–436.
35. Dang, Z.M.; Wang, H.Y.; Zhang, Y.H.; Qi, J.Q. Morphology and dielectric property of homogenous BaTiO3/PVDF nanocomposites prepared via the natural adsorption action of nanosized BaTiO3.

Macromol. Rapid Commun. 2005, 26, 1185–1189.

36. Nam, Y.W.; Kim, W.N.; Cho, Y.H.; Chae, D.W.; Kim, G.H.; Hong, S.P.; Hwang, S.S.; Hong, S.M. Morphology and Physical Properties of Binary Blend Based on PVDF and Multi-Walled Carbon Nanotube. Macromol. Symp. 2007, 249, 478–484.
37. Yang, D.; Xu, H.; Wu, Y.; Wang, J.; Xu, Z.; Shi, W. Effect of hydroxylated multiwall carbon nanotubes on dielectric property of poly(vinylidene fluoride)/poly(methyl methacrylate)/hydroxylated multiwall carbon nanotubes blend. J. Polym. Res. 2013, 20, 236.
38. Disnan, D.; Hafner, J.; Benaglia, S.; Teuschel, M.; Schneider, M.; Garcia, R.; Schmid, U. Nanostructural and piezoelectric characterization of electro-formed δ-phase poly (vinylidene fluoride) thin films. Mater. Res. Lett. 2023, 11, 296–303.
39. Gupta, V.; Babu, A.; Ghosh, S.K.; Mallick, Z.; Mishra, H.K.; Saini, D.; Mandal, D. Revisiting δ-PVDF based piezoelectric nanogenerator for self-powered pressure mapping sensor. Appl. Phys. Lett. 2021, 119, 252902.
40. Wu, L.; Hu, N.; Yao, J.; Liu, Y.; Ning, H.; Liu, X.; Yuan, W.; Fu, S. Improvement of the piezoelectricity of PVDF-TrFE by carbon black. Mater. Res. Express 2018, 6, 025509.
41. Alam, M.M.; Sultana, A.; Sarkar, D.; Mandal, D. Electroactive β-crystalline phase inclusion and photoluminescence response of a heat-controlled spin-coated PVDF/TiO2 free-standing nanocomposite film for a nanogenerator and an active nanosensor. Nanotechnology 2017, 28, 365401.
42. Ko, E.J.; Lee, E.J.; Choi, M.H.; Sung, T.H.; Moon, D.K. PVDF based flexible piezoelectric nanogenerators using conjugated polymer: PCBM blend systems. Sens. Actuators A Phys. 2017, 259, 112–120.
43. Wang, J.; Li, H.; Liu, J.; Duan, Y.; Jiang, S.; Yan, S. On the α → β transition of carbon-coated highly oriented PVDF ultrathin film induced by melt recrystallization. J. Am. Chem. Soc. 2003, 125, 1496–1497.
44. Bachmann, M.; Gordon, W.L.; Weinhold, S.; Lando, J.B. The crystal structure of phase iv of poly(vinylidene fluoride). Ferroelectrics 1980, 51, 5095–5099.
45. Li, M.; Wondergem, H.J.; Spijkman, M.-J.; Asadi, K.; Katsouras, I.; Blom, P.W.M.; de Leeuw, D.M. Revisiting the δ-phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films. Nat. Mater. 2013, 12, 433–438.
46. Zhao, D.; Katsouras, I.; Asadi, K.; Groen, W.A.; Blom, P.W.M.; Leeuw, D.M.D. Retention of intermediate polarization states in ferroelectric materials enabling memories for multi-bit data storage. Appl. Phys. Lett. 2016, 108, 232907.

47. Martins, P.; Lopes, A.; Lanceros-Mendez, S. Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications. Prog. Polym. Sci. 2014, 39, 683–706.
48. Salimi, A.; Yousefi, A. Analysis method: FTIR studies of β-phase crystal formation in stretched PVDF films. Polym. Test. 2003, 22, 699–704.
49. Lu, F.; Hsu, S. Spectroscopic study of the electric field induced microstructural changes in poly(vinylidene fluoride). Polymer 1984, 25, 1247–1252.
50. Yuan, D.; Li, Z.; Thitsartarn, W.; Fan, X.; Sun, J.; Li, H.; He, C. β phase PVDF-hfp induced by mesoporous SiO2 nanorods: Synthesis and formation mechanism. J. Mater. Chem. C 2015, 3, 3708–3713.
51. Kim, G.H.; Hong, S.M.; Seo, Y. Piezoelectric properties of poly(vinylidene fluoride) and carbon nanotube blends: β-phase development. Phys. Chem. Chem. Phys. 2009, 11, 10506–10512.
52. Bormashenko, Y.; Pogreb, R.; Stanevsky, O.; Bormashenko, E. Vibrational spectrum of PVDF and its interpretation. Polym. Test. 2004, 23, 791–796.
53. Sharma, M.; Madras, G.; Bose, S. Process induced electroactive β-polymorph in PVDF: Effect on dielectric and ferroelectric properties. Phys. Chem. Chem. Phys. 2014, 16, 14792–14799.
54. Ramasundaram, S.; Yoon, S.; Kim, K.J.; Lee, J.S.; Park, C. Crystalline structure and ferroelectric response of poly(vinylidene fluoride)/organically modified silicate thin films prepared by heat controlled spin coating. Macromol. Chem. Phys. 2009, 210, 951–960.
55. Adhikary, P.; Garain, S.; Mandal, D. The co-operative performance of a hydrated salt assisted sponge like P (VDF-HFP) piezoelectric generator: An effective piezoelectric based energy harvester. Phys. Chem. Chem. Phys. 2015, 17, 7275–7281.
56. Kanik, M.; Aktas, O.; Sen, H.S.; Durgun, E.; Bayindir, M. Spontaneous High Piezoelectricity in Poly(vinylidene fluoride) Nanoribbons Produced by Iterative Thermal Size Reduction Technique. ACS Nano 2014, 8, 9311–9323.
57. Tamang, A.; Ghosh, S.K.; Garain, S.; Alam, M.; Haeberle, J.; Henkel, K.; Schmeisser, D.; Mandal, D. DNA-Assisted β-phase Nucleation and Alignment of Molecular Dipoles in PVDF Film: A Realization of Self-Poled Bioinspired Flexible Polymer Nanogenerator for Portable Electronic Devices. ACS Appl. Mater. Interfaces 2015, 7, 16143–16147.
58. Karan, S.K.; Mandal, D.; Khatua, B.B. Self-powered flexible Fe-doped RGO/PVDF nanocomposite: An excellent material for a piezoelectric energy harvester. Nanoscale 2015, 7, 10655–10666.
59. Lopes, A.C.; Martins, P.; Lanceros-Mendez, S. Aluminosilicate and aluminosilicate based polymer composites: Present status, applications and future trends. Prog. Surf. Sci. 2014, 89, 239–277.

60. Tashiro, K.; Yamamoto, H.; Kummara, S.; Takahama, T.; Aoyama, K.; Sekiguchi, H.; Iwamoto, H. High-Electric-Field-Induced Hierarchical Structure Change of Poly(vinylidene fluoride) as Studied by the Simultaneous Time-Resolved WAXD/SAXS/FTIR Measurements and Computer Simulations. Macromolecules 2021, 54, 2334–2352.
61. Maji, S.; Sarkar, P.K.; Aggarwal, L.; Ghosh, S.K.; Mandal, D.; Sheet, G.; Acharya, S. Self-oriented β-crystalline phase in the polyvinylidene fluoride ferroelectric and piezo-sensitive ultrathin Langmuir–Schaefer film. Phys. Chem. Chem. Phys. 2015, 17, 8159–8165.
62. Gregorio, R., Jr.; Cestari, M. Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride). J. Polym. Sci. Part B Polym. Phys. 1994, 32, 859–870.
63. Ghosh, S.K.; Alam, M.M.; Mandal, D. The in situ formation of platinum nanoparticles and their catalytic role in electroactive phase formation in poly(vinylidene fluoride): A simple preparation of multifunctional poly(vinylidene fluoride) films doped with platinum nanoparticles. RSC Adv. 2014, 4, 41886–41894.
64. Naegele, D.; Yoon, D.Y.; Broadhurst, M.G. Formation of a New Crystal Form (αp) of Poly(vinylidene fluoride) under Electric Field. Macromolecules 1978, 11, 1297–1298.
65. Esterly, D.M.; Love, B.J. Phase transformation to β-poly(vinylidene fluoride) by milling. J. Polym. Sci. Part B Polym. Phys. 2004, 42, 91–97.
66. Li, W.; Meng, Q.; Zheng, Y.; Zhang, Z.; Xia, W.; Xu, Z. Electric energy storage properties of poly(vinylidene fluoride). Appl. Phys. Lett. 2010, 96, 192905.
67. Lee, M.K.; Lee, J. A nano-frost array technique to prepare nanoporous PVDF membranes. Nanoscale 2014, 6, 8642–8648.
68. Cai, X.; Lei, T.; Sun, D.; Lin, L. A critical analysis of the α, β and γ phases in poly(vinylidene fluoride) using FTIR. RSC adv. 2017, 7, 15382–15389.
69. Damjanovic, D.; Newnham, R. Electrostrictive and piezoelectric materials for actuator applications. J. Intell. Mater. Syst. Struct. 1992, 3, 190–208.
70. Lee, J.G.; Kim, S.H. Structure development of PVDF/PMMA/TiO2 composite film with casting conditions. Macromol. Res. 2011, 19, 72–78.

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