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A Critical Temperature-Pressure Window for Attaining a Giant Piezoelectric Voltage Coefficient in Poly(vinylidene fluoride)

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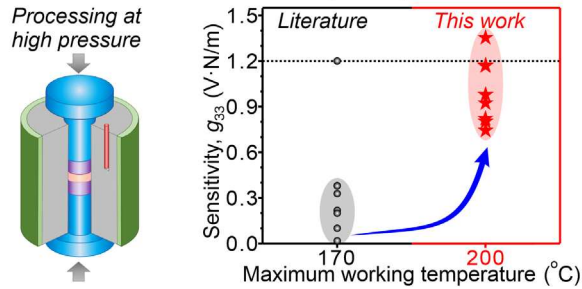
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High pressure.

For Table of Contents use only

New Record PVDF Piezoelectric Response
based on extended-chain polar crystal forms



Abstract: Polymeric piezoelectric sensors are increasingly important in the context of advancing artificial intelligence and soft robotics. It is known that electric response to mechanical stress of poly(vinylidene fluoride) (PVDF) increases with increasing fraction of non-centrosymmetric (or “polar”) β and γ crystal forms ($X_{\beta+\gamma}$), as well as with increasing fraction of extended-chain crystals (F_{ECC}). Here we describe a temperature-pressure (T - P) window for achieving both high $X_{\beta+\gamma}$ and high F_{ECC} , through intervention of the high-pressure hexagonal mesophase. Importantly, we show that high $X_{\beta+\gamma}$ and F_{ECC} can be achieved under considerably milder conditions, hundred °C and hundred MPa below the equilibrium T - P range of the mesophase. By rapidly pressure-quenching the melt significantly below the triple-point temperature, direct melt-crystallization is bypassed and the system enters a heavily superpressed and supercooled metastable range of the mesophase. This enables the lamellae of the mesophase to grow and thicken, subsequently transforming to largely extended-chain β and γ forms. Thus a T - P processing window opens up, leading to a marked increase in piezoelectric response. This way we achieved a record PVDF piezoelectric voltage constant g_{33} of $1.35 \text{ V} \cdot \text{m} \cdot \text{N}^{-1}$. Moreover, the chain extension involved also raises the melting point of the polymer by $\sim 30^\circ\text{C}$, making the sensors usable at higher temperatures. This study offers guidance

for the development of high-sensitivity PVDF-based piezoelectric sensors for applications across a broad temperature range.

1. Introduction

The ability of piezoelectric materials to convert mechanical energy into electrical and vice versa has a wide range of applications in the fields of actuators, sensors, medical monitoring, and energy harvesting. Each application requires different piezoelectric properties.^{1,2,3} For sensors a large piezoelectric voltage constant g (the ratio of electric field produced to the mechanical stress applied) is critical to their performance and represents a key figure of merit for evaluating their sensitivity. Though the conventional piezoelectric ceramics, such as BaTiO₃, PbTiO₃, and Pb(Zr, Ti)O₃, often have large piezoelectric coefficient (d) and high dielectric constant (ϵ), their piezoelectric voltage constant, $g = d/\epsilon$ is relatively limited. The important g constant of piezoelectric ceramics g_{33} (the force is impressed on the same surface from which the charge is collected) is usually in the range from 0.02 to 0.12 V·m·N⁻¹.^{4,5,6} In contrast, poly(vinylidene fluoride) (PVDF) has larger g_{33} (~0.29 V·m·N⁻¹),^{7,8,9} making it a desirable sensor material. Since the discovery of piezoelectricity in mechanically stretched PVDF in 1969,¹⁰ PVDF-based polymers have become increasingly important for their applications in portable, miniaturized and wearable electroactive devices due to their high flexibility, easy fabrication into complicated shapes and mechanical robustness.^{11,12,13}

PVDF can crystallize in five different crystal forms, α , β , γ , δ , and ϵ . α and ϵ forms are centrosymmetric, whereas β , γ , and δ are non-centrosymmetric or

1 “polar”, hence are ferroelectric, thermoelectric and piezoelectric.^{7,11,14,15} It is
2 well accepted that piezoelectric performance can be improved by maximizing
3 the polar form fraction. Although β form is the thermodynamically stable phase,
4 PVDF commonly crystallizes in α form as it is kinetically favored.¹⁶ An increased
5 fraction of polar forms β and γ has been achieved in the past by adding
6 fillers,^{17,18} by chemical modification,^{19,20} mechanical stretching,^{21,22,23}
7 electrospinning,^{24,25} crystallization or annealing under pressure^{26,27,28} and by
8 other methods.^{29,30,31,32,33}

9 When it comes to applications at high temperature, here PVDF is severely
10 limited by its relatively low melting point (160-170 °C). Crystallization of PVDF
11 under high pressure can induce the more thermally stable extended-chain
12 crystals (ECC),^{26,27,34} which is a promising way to produce high-temperature
13 PVDF sensors. Most past studies of PVDF crystallization under pressure have
14 focused on achieving β -form ECC through the hexagonal columnar liquid crystal
15 phase above the triple point ($T = 300$ °C, $P = 320$ MPa = 3.2 kbar).^{26,34,35} The
16 combination of high pressure and temperature imposes stringent requirements
17 on processing equipment for mechanical endurance and to prevent melt
18 leakage, thereby largely restricting its practical application.^{36,37,38} The previous
19 study has reported that a mixture of α -, β -, and γ -ECCs can be obtained by
20 cooling PVDF from the melt at 210 °C under pressure of 200 MPa or higher.²⁷
21 To explain their observation, the authors suggested that a metastable hexagonal
22 phase exists at relatively low temperatures when PVDF is cooled from melt
23 under high pressure.²⁷ However, it is not clear if such treatment actually results
24 in a high value of g_{33} . Also, it is not known if the conditions applied in the above
25 study are optimal for achieving the desired PVDF structure and piezoelectric

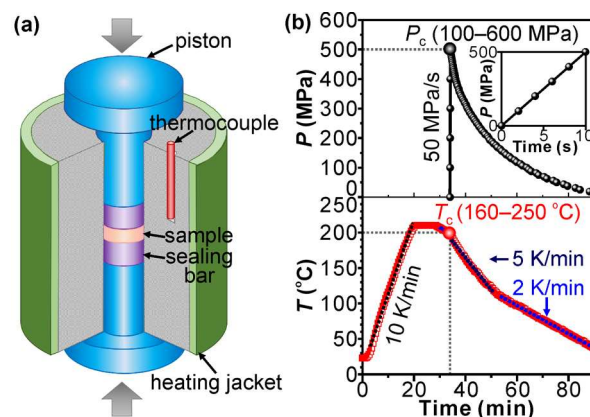
performance. The growth competition between crystal polymorphs and between ECC and FCC remains poorly understood, and even less is documented on the critical T - P range for the formation of PVDF that consists of largely polar crystal forms and, at the same time, has its chains largely extended, referred to here as “polar ECC”.

In this work, we have used a commercially available PVDF and a piston-cylinder apparatus to study the interplay between different crystalline forms (α , β , γ) and morphologies (FCC, ECC) in the crystallization of PVDF over a wide temperature (160-250 °C) and pressure range (100-600 MPa, or 1-6 kbar). T - P windows for obtaining in practice both the β, γ crystal forms and ECC morphology are determined. A steady increase in g_{33} is observed with increases in both crystallinity of the polar forms ($X_{\beta+\gamma}$) and the fraction of ECC (F_{ECC}). Gratifyingly, the combination of the increases in both also raises the usable temperature range of PVDF sensors by up to 30 °C. Applying the processing conditions thus defined, we achieve a g_{33} parameter of 1.35 V·m·N⁻¹, the highest reported so far, and more than 3 times higher than the commonly reported value for PVDF.^{39,40,41,42,43,44,45,46,47,48}

2. High-Pressure Crystallization of PVDF

A piston-cylinder apparatus was used to prepare high-pressure crystallized PVDF samples. As shown in **Figure 1a**, the sample was placed between two copper sealing pellets in the cylindrical channel of the press. The pressure applied to the sample was controlled by a hydraulic jack through the piston, and measured via a digital pressure gauge with an accuracy of ± 1 MPa. The temperature of the PVDF sample was regulated by a heating jacket,

1 temperature controller and a thermocouple. The disk-shaped PVDF sample had
 2 a diameter of 20 mm and a thickness of 0.5 mm. It was first heated to 210 °C at
 3 a heating rate of ~ 10 K/min, and held isothermally for 8 min to eliminate thermal
 4 history. The sample was then heated or cooled to the crystallization temperature
 5 (T_c , 160-250 °C). Once the set temperature was reached, the pressure (P_c , 100-
 6 600 MPa) was applied. The applied pressure increased the equilibrium melting
 7 temperature (T_m^0) of PVDF, thereby increasing the undercooling ($\Delta T = T_m^0 - T_c$)
 8 without altering the crystallization temperature. The pressurization rate was ~50
 9 MPa/s (see the inset in **Figure 1b**), which leads to an increase in undercooling
 10 at a rate of ~18.5 K/s, based on pressure dependence of T_m^0 of 0.37 K/MPa for
 11 PVDF.³⁷ This amounts to what can be termed pressure quenching. Immediately
 12 after pressure reached the preset value, the sample was cooled to room
 13 temperature (**Figure 1b**). The formation of polar phases and ECC in these high-
 14 pressure crystallized samples, as well as their structure-piezoelectricity
 15 relationship, were studied using a combination of wide- and small angle X-ray
 16 scattering (WAXS/SAXS), Fourier transform infrared (IR) spectroscopy,
 17 differential scanning calorimetry (DSC), scanning electron microscopy (SEM),
 18 and piezoelectric response measurements, as detailed in **section 5**.



19
 20 **Figure 1.** (a) Schematic of the piston-cylinder apparatus, and (b) the recorded pressure

and temperature vs. time for PVDF crystallization at 500 MPa and 200 °C. Inset shows the expanded view of the pressure ramp.

3. Results and Discussion

3.1. Polymorphic PVDF Crystals Formed at 300 MPa. Polymorphic composition of PVDF after crystallization at $P_c = 300$ MPa and different temperatures T_c was studied by WAXS and IR. The results are shown in **Figure 2**. For $T_c = 160$ °C, typical α -form X-ray reflections are observed in WAXS (**Figure 2a**), which is further confirmed by the IR absorption bands at 763 cm^{-1} (CF_2 bending and skeletal bending), 795 cm^{-1} (CH_2 rocking), 974 cm^{-1} (CH_2 twisting), and 1210 cm^{-1} (CF_2 stretching and CH_2 wagging) in **Figure 2b**. These bands correspond to the TGTG' conformation of the α -form.^{49,50} By keeping P_c constant and increasing T_c (200, 220, 240, and 250 °C), the WAXS profiles show a new diffraction peak at $2\theta=20.8^\circ$ ($d = 0.43$ nm, **Figure 2a**). This can be assigned to an overlap of $(110, 200)_\beta$ and $(021)_\gamma$ reflections. This is consistent with the observed IR bands (**Figure 2b**) at 840 cm^{-1} (CH_2 rocking) and 1276 cm^{-1} (CH_2 rocking, CF_2 antisymmetric stretching and rocking) characteristic for the all-trans (TTTT) conformation (β -form), as well as those at 832 cm^{-1} (CF_2 symmetrical stretching and C–C stretching) and 1233 cm^{-1} (CF_2 asymmetrical stretching and rocking) for the TTTGTTTG' conformation (γ -form). As the two non-centrosymmetric crystal forms, β and γ , are not easily resolved quantitatively by X-ray diffraction due to peak overlap, and as the two forms behave very similarly in the present experiments (see below), we shall hitherto refer to them collectively as the “polar forms”.

The combination of the above WAXS and IR results thus reveal a clear

temperature range for the formation of polar forms in PVDF crystallized at 300 MPa. **Figure 2c** shows the crystallinity X of the polar β - and γ -forms ($X_{\beta+\gamma}$) and the nonpolar α -form (X_α) calculated from WAXS data (columns).⁵¹ Additionally, it presents the fraction of polar forms ($F_{\beta+\gamma}$), which is estimated from both WAXS (empty squares) and IR data (filled squares). Pure α -form is observed when PVDF crystallizes at 300 MPa and 160 °C. As T_c increases, the polar forms begin to grow at 200 °C, ultimately becoming dominant at 220 °C and higher. The increase in $F_{\beta+\gamma}$ with increasing T_c is basically due to the higher melting temperature of the polar forms in comparison to that of the α -form.^{27,35,52} Consequently, only those PVDF samples crystallized at T_c can suppress the crystallization of kinetically favored α -form, which enables the formation of polar forms. Whereas for PVDF crystallized at $T_c=160$ °C, crystallization of the α -form dominates due to the increased undercooling—more on this in **section 3.5**. The highest total crystallinity develops at 220 °C. This phenomenon can be attributed to the fact that pressure quench-induced nucleation is more pronounced at lower temperatures, whereas the crystal growth occurs at an accelerated rate at higher temperatures.

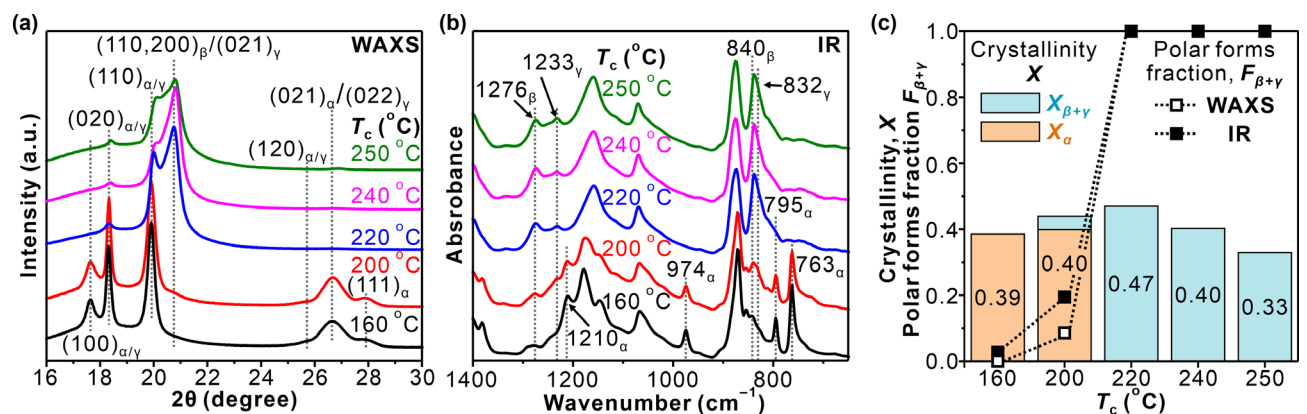


Figure 2. (a) WAXS profiles and (b) IR spectra of PVDF crystallized at 300 MPa and different temperatures (160 °C, 200 °C, 220 °C, 240 °C and 250 °C), (c) crystallinity

(bar chart) of polar (β - and γ) and non-polar (α) forms, and the fraction of polar forms $((\beta+\gamma)/(\alpha+\beta+\gamma))$ (squares) as a function of T_c .

3.2. Formation of Polar ECC at 300 MPa.

Having established the temperature range of polar forms crystallization at 300 MPa, we now turn to the formation of ECC and its relationship with crystal form. SAXS profiles of PVDF crystallized at 300 MPa at different temperatures are presented in **Figure 3a**. Crystallization at 160 and 200 °C results in a broad SAXS peak centered at $q = 0.54 \text{ nm}^{-1}$. This indicates the formation of folded-chain crystals (FCC) with a long period L of 11.6 nm, if the simple Bragg equation is used. DSC of these samples shows an endotherm at *ca.* 170 °C (**Figure 3b**), attributable to melting of FCC crystals of α -form, as corroborated by the WAXS and IR results presented in **Figure 2**. When T_c is increased to 220 °C or higher, the SAXS peak associated with folded-chain crystals persists. However, based on WAXS and IR results, these are now identified as polar forms FCC. Furthermore, their DSC melting peaks are now shifted to *ca.* 178 °C, slightly higher than the melting point of α -form FCC (α -FCC). In addition to the FCC scattering peak, a new SAXS shoulder is observed near the beamstop ($q \approx 0.15 \text{ nm}^{-1}$). Its presence suggests the formation of crystals with extended chain, or at least chains with substantially extended fold length, as the associated L can be estimated to exceed 40 nm. In the following we refer to the morphology of such highly extended fold length as ECC. The formation of ECC is further substantiated by the appearance of a distinct and pronounced new DSC melting peak at 198 °C. Confirmatory *in-situ* WAXS/SAXS experiments will be described in the following section. Consequently, we can already state that predominantly polar ECC

crystals are produced when PVDF is crystallized at 300 MPa and at around 220 °C. However, as T_c is increased further, a decrease in intensity of the low- q SAXS shoulder is observed (**Figure 3a**). In concord, the DSC melting peak around 198 °C diminishes, indicating a reduction in ECC fraction. **Figure 3c** plots the T_c -dependence of FCC and ECC melting enthalpies (ΔH_{FCC} and ΔH_{ECC} , vertical bars), along with the ECC fraction, $F_{ECC} = \Delta H_{ECC}/(\Delta H_{ECC} + \Delta H_{FCC})$ (square symbols). Like the formation of polar forms, formation of ECC starts at elevated temperatures (> 200 °C) and increases further at higher T_c .

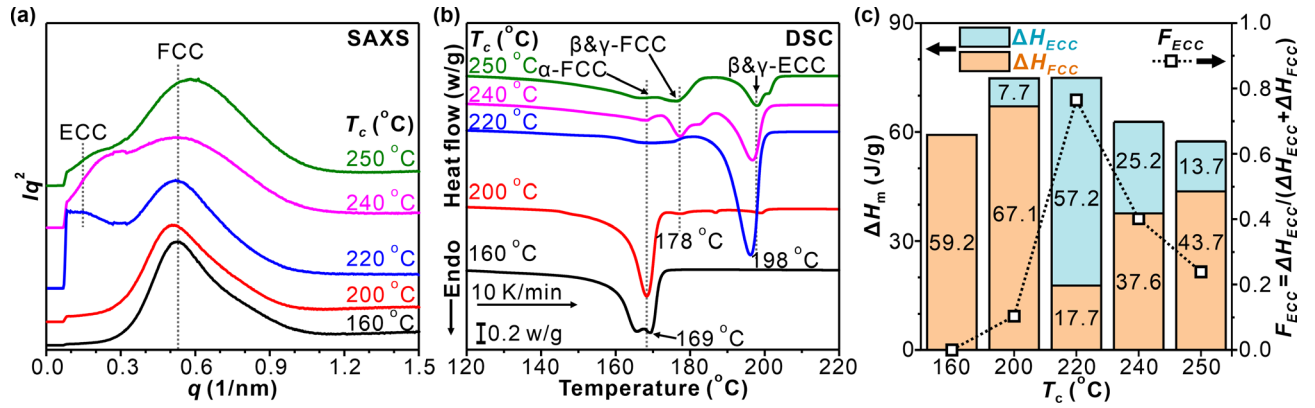


Figure 3. (a) Lorentz-corrected SAXS profiles and (b) DSC curves of PVDF crystallized under 300 MPa at different temperatures: 160 °C, 200 °C, 220 °C, 240 °C and 250 °C. (c) Melting enthalpies (vertical bars) of ECC and FCC, and the fraction of ECC (square symbols) as a function of crystallization temperature T_c .

3.3. Crystalline Morphology of FCC and Polar ECC. Crystalline morphology of the α -form FCC and polar ECC was studied using SEM. Two PVDF samples were selected for this study: one was crystallized at a pressure of 300 MPa and a temperature of 220 °C (**Figures 4a and 4b**), and the other under the same pressure at 160 °C (**Figures 4c and 4d**). The former sample

was composed predominantly of polar forms, with ~80% as ECC, while the latter consisted entirely of α -form FCC, as was shown above by ex-situ WAXS, SAXS, IR, and DSC. Unlike the typical spherulitic morphology associated with the α -form of PVDF crystallized at 300 MPa and 160 °C (**Figures 4c** and **4d**), the cigar-shaped morphology was observed for PVDF crystallized at 300 MPa and 220 °C (**Figures 4a** and **4b**). The thickness of the cigar-shaped morphology is approximately 50 nm, which is significantly larger than that of the α -spherulites (~10 nm), consistent with the SAXS and DSC results (**Figures 3a** and **3b**). Although the thickness of the cigar-shaped morphology is smaller than the average chain length of ~ 500 nm in the all-trans conformation which is possibly due to the head-to-head and tail-to-tail defects, this cigar-shaped morphology closely resembles the ECC of polyethylene,⁵³ which will be discussed further in **section 3.6**.

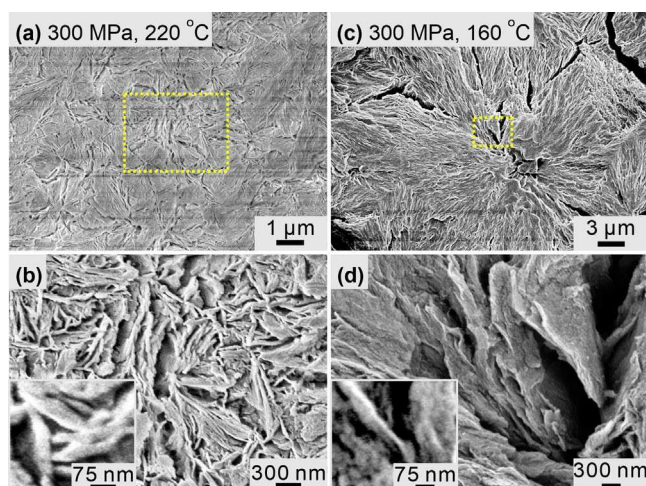


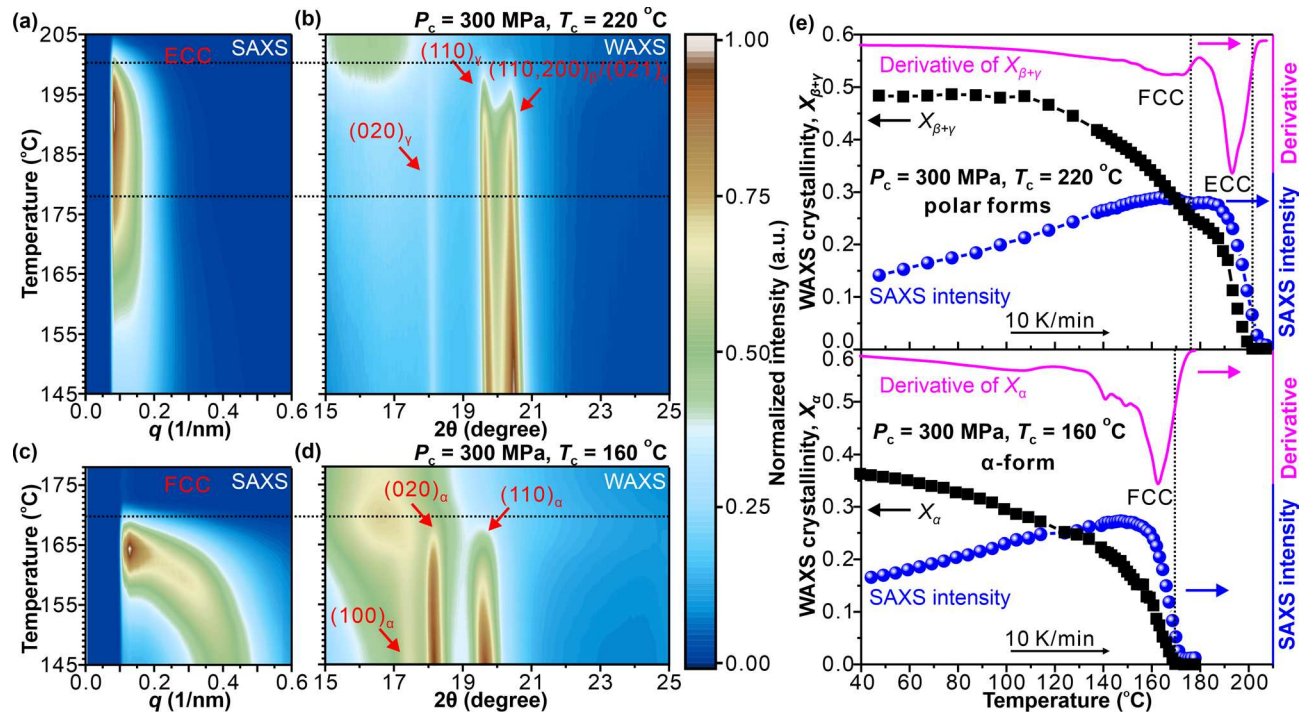
Figure 4. SEM observations of PVDF crystallized at 300 MPa and 220 °C (**a**, **b**) and at 300 MPa and 160 °C (**c**, **d**). (**b**) and (**d**) are enlarged views, indicated by yellow dashed boxes of (**a**) and (**c**), respectively. The insets in (**b**) and (**d**) illustrate the morphologies of ECC and FCC, respectively.

1 **3.4. Melting Behavior of FCC and Polar ECC.** Melting process of the α -form
2 FCC and polar ECC was further studied by time-resolved simultaneous SAXS
3 and WAXS. **Figures 5a** and **5b** show, respectively, SAXS and WAXS 2D $I(q, T)$
4 plots of intensity (false color) vs. q and temperature recorded on heating for
5 samples crystallized at 300 MPa and 220 °C. The precise position of the SAXS
6 peak could not be determined as instrumental low- q resolution limit is reached.
7 However, it can be said that the long period, if there is a period, exceeds 60 nm
8 and that there is no indication of its increasing significantly during the heating
9 run. At the same time, WAXS shows the presence of exclusively polar forms,
10 with their diffraction intensity diminishing with increasing temperature.

11 **Figures 5c** and **5d** show the T -dependent SAXS and WAXS intensity profiles
12 of the sample crystallized also at 300 MPa but at a lower T_c of 160 °C. This
13 sample has a substantially smaller long period which, however, increases quite
14 steeply above 145 °C, with the SAXS peak shifting drastically to low q and
15 disappearing at melting point that is >30 K below that of the ECC. The multifold
16 increase in L of the FCC during the relatively fast (10 K/min) heating is a
17 testament to the high longitudinal mobility of PVDF chains even in the ordered
18 3D crystalline forms.^{54, 55} However, even though L apparently reaches or
19 exceeds 60 nm at or near the melting point, we do not consider them in the
20 same category as ECC, since their melting point is still ca. 30 K below that of
21 the pressure-crystallized ECC. The WAXS in **Figure 5d** shows that the T_c =
22 160 °C sample contains pure α -form.

23 **Figure 5e** displays the T -dependence of WAXS crystallinity (black squares)
24 and SAXS intensity integrated (blue spheres) during the described heating runs
25 for samples pressure-crystallized at (top) 220°C and (bottom) 160°C. The

1 diagrams also include the derivative of the crystallinity (purple line). The initial
2 increase in SAXS intensity observed in both PVDF samples is normally
3 attributed to increasing density difference between crystalline and amorphous
4 layers which results from the difference in their thermal expansivities. A
5 contribution also comes from partial melting of individual, usually thinner,
6 lamellae within the stacks.⁵⁶ The crystallinity of the 220 °C sample exhibits a
7 two-stage reduction, concluding at ca. 178 °C and 200 °C, respectively. The
8 corresponding derivative reveals two peaks that are consistent with those in the
9 DSC (**Figure 3b**); they correspond to melting, respectively, of polar FCC and
10 polar ECC. In contrast, the 160 °C sample shows a gradual reduction in
11 crystallinity and finally melts completely at ~169 °C.



12 **Figure 5.** SAXS (a, c) and WAXS (b, d) recorded simultaneously during heating of
13 PVDF crystallized under a pressure of 300 MPa and at temperatures of 220 °C (a, b)
14 and 160 °C (c, d). Heating rate was 10 K/min. SAXS/WAXS profiles were recorded at
15 2K intervals, and are shown in false color representing normalized intensity. (e)

Crystallinity (black squares), its derivative (purple line), and SAXS intensity integrated in the range up to $q=1.5 \text{ nm}^{-1}$ (blue spheres) plotted against temperature.

3.5. Formation of Polar ECC under Different Pressures. Equipped with knowledge of polar ECC in PVDF crystallized at 300 MPa, we proceed to examine the formation of that state under different pressures. **Figure 6** shows the WAXS (**Figures 6a, 6d**), IR (**Figures 6b, 6e**) and DSC (**Figures 6c, 6f**) results of PVDF crystallized at 200 MPa (**Figures 6a-6c**) and 400 MPa (**Figures 6d-6f**). Analogous results for PVDF crystallized at additional pressures of 100, 500, and 600 MPa are reported in **Figure S1**. For PVDF crystallized at 100 MPa, only a small fraction of the polar forms can be formed at a high T_c of 240 °C (see **Figure S1a, S1b**). Polar forms are present entirely as FCC according to the DSC heating curves (**Figure S1c**). When the pressure is increased to 200 MPa, the temperature range of polar form expands. A predominance of polar forms can be achieved when $T_c \geq 200 \text{ °C}$, as confirmed by WAXS and IR (**Figures 6a, 6b**). Meanwhile, high temperature melting peaks are observed by DSC (**Figure 6c**), indicating the formation of ECC. However, when compared to PVDF crystallized at 300 MPa, the ECC melting peaks are still relatively small. On the other hand the application of a higher pressure of 400 MPa produces exclusively polar forms at $T_c \geq 200 \text{ °C}$ (**Figures 6d, 6e**), although a significant polar ECC melting peak is seen only at $T_c = 220 \text{ °C}$ (**Figure 6f**).

These results demonstrate that elevated temperature and pressure conditions favor the formation of polar forms in PVDF. Specifically, at a pressure of 200 MPa or greater, a predominance of polar forms can be obtained over a broad temperature range. In contrast, the formation of ECC necessitates a more

stringent temperature-pressure (T - P) window. Thus, to successfully produce polar ECC, it is necessary to establish the T - P window that ensures the formation of both the polar forms and ECC.

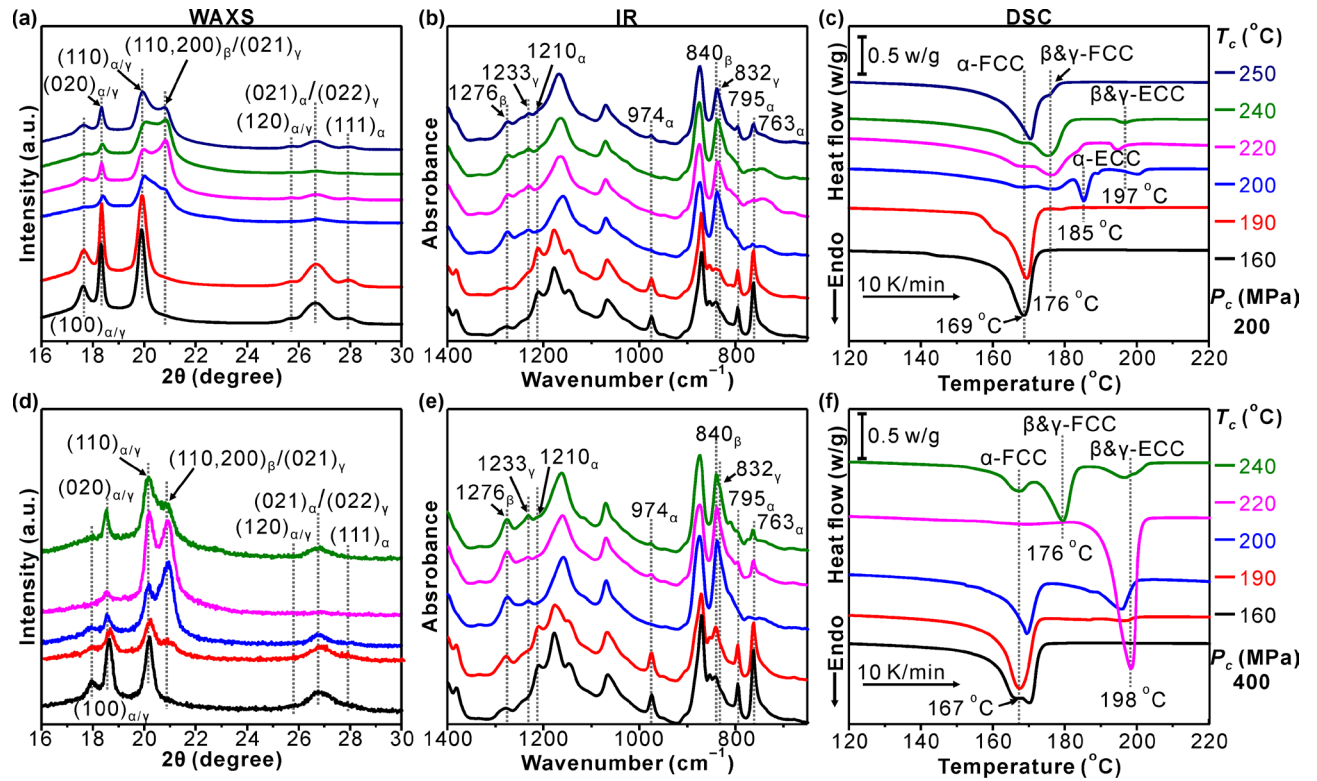


Figure 6. (a), (d) WAXS profiles, (b), (e) IR spectra and (c), (f) DSC curves of PVDF crystallized at two pressures; top row (a-c) 200 MPa and bottom row (d-f) 400 MPa. The curves are color-coded according to T_c as defined on the right.

3.6. T - P windows for growing polar forms and ECC. The results presented above allow for the estimation of crystallinity of the polar forms ($X_{\beta+y}$) as well as the fraction of ECC (F_{ECC}) in the crystallized material. Contour maps giving F_{ECC} and $X_{\beta+y}$ as a function of T_c and P_c are presented in **Figures 7a** and **7b**. Interestingly, although the formation of ECC requires higher temperatures and pressures in comparison to the formation of polar forms, both F_{ECC} and $X_{\beta+y}$ exhibit a similar dependence on temperature and pressure, both with a

1 maximum around 300-400 MPa and 220-230 °C, for the particular crystallization
2 protocol applied.

3 Added to **Figure 7a** is the equilibrium *T-P* phase diagram of PVDF.^{26,27, 35,37}
4 This diagram is shown with black dashed lines. It delineates the phase
5 boundaries between melt, the hexagonal mesophase and the crystal. Being an
6 equilibrium diagram, it strictly applies only to ECC morphology. Typically for
7 columnar mesophases in main-chain polymers,⁵⁷ the *T*-range of the hexagonal
8 mesophase is seen to broaden with increasing pressure.^{58 , 59} In
9 thermodynamic terms this means that

$$\frac{S_{hex} - S_{cr}}{S_{melt} - S_{cr}} > \frac{V_{hex} - V_{cr}}{V_{melt} - V_{cr}}$$

11 Here *S* and *V* denote entropy and volume of the hexagonal, crystal and melt
12 phases per monomer unit. In other words the above inequality means that the
13 mesophase is closer to melt in entropy than in volume, or that it is a “high-
14 entropy low-volume” phase, as in the high-pressure hexagonal phase in
15 polyethylene.⁵⁸ This is in contrast to the plastic crystal, the so-called “rotator”
16 phase in *n*-alkanes, where the above inequality is reversed.⁵⁹ Compared to the
17 crystal, the high *S_{hex}* in PVDF comes from a combination of increased volume
18 and comparatively high number of conformational defects in the mesophase,
19 schematically depicted in **Figure 8**. Both factors contribute to high chain mobility
20 which allows relatively rapid chain extension in the mesophase. It also enables
21 the achievement of the energetically favored *all-trans* and *TTTGTTTG'*
22 conformations that characterize the polar crystal forms β and γ.

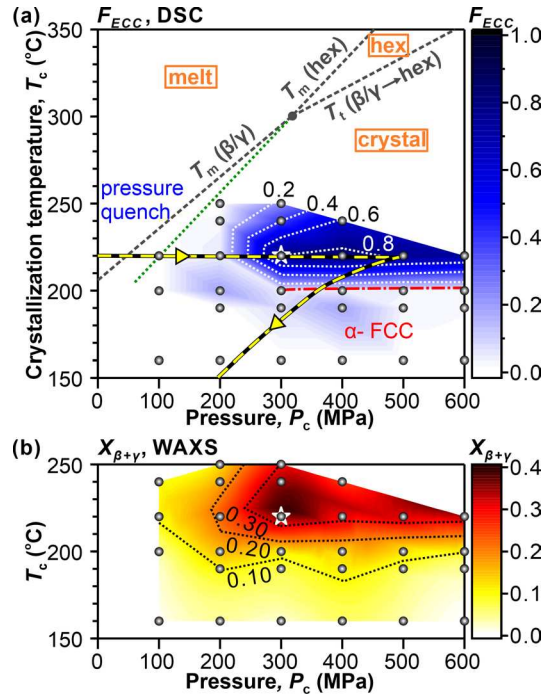


Figure 7. Contour maps of ECC fraction, F_{ECC} (a), and polar forms crystallinity, $X_{\beta+\gamma}$ (b) of PVDF crystallized at different temperatures (160 °C-250 °C) and pressures (100 MPa-600 MPa). Extended-chain fraction F_{ECC} and crystallinity of polar forms $X_{\beta+\gamma}$ are shown using color scales on the right. Additionally, F_{ECC} and $X_{\beta+\gamma}$ of the sample crystallized at $P_c = 300$ MPa, $T_c = 220$ °C for an extended period of 40 min, yielding g_{33} of $1.35 \text{ V} \cdot \text{m} \cdot \text{N}^{-1}$, is shown marked by a star. The pathway for crystallization of a specific sample, $P_c=500$ MPa, $T_c=220^\circ\text{C}$, is shown by black-yellow dashed lines.

However, just as crystallization from melt does not start at or near equilibrium melting point but at significant supercooling, so the formation of hexagonal mesophase can also occur at significant supercooling and superpressure, well below the thermodynamic triple point temperature. The horizontal black-yellow dashed line in **Figure 7a** traces the pressure quenching part of the processing cycle applied here to one sample, as an example. The arrow crosses not only the $T_m(\beta/\gamma)$ line, but also the extrapolated metastable $T_m(\text{hex})$ line (green),

1 meaning that both crystal and mesophase now have a lower free energy than
2 melt. Although at the end of the pressure ramp crystal free energy is the lowest,
3 formation of the disordered mesophase is kinetically favored, and once formed
4 it allows rapid chain extension.^{26,60} Thus fold lengths of 600 Å or more are
5 reached. This state is referred to here as “ECC”, even though the majority of
6 chains still contain one or more folds.

7 The growth and thickening of a mesophase lamella are schematically shown
8 in **Figure 8**. The appearance of the lamella is based on the cigar-shape of
9 hexagonal mesophase domains in polyethylene at high pressure and
10 temperature, observed by Hikosaka *et al.* using a polarized optical microscope
11 with a high-pressure cell.⁵³ In this study of PVDF crystallized under high
12 pressure and temperature, we assume that the mesophase morphology is
13 similar to that in polyethylene, with some support from SEM (**Figures 4a,b**).
14 Following the formation of the hexagonal phase, the mesophase→ β/γ crystal
15 transition then happens during cooling and pressure release, arresting the value
16 of F_{ECC} and $X_{\beta+\gamma}$ as at the transition. It should be mentioned that, once formed,
17 the β -form crystals do not thicken easily as the asymmetry of their all-trans
18 chains prevents the flip-flop motion that allows orthorhombic polyethylene
19 lamellae to thicken on annealing.^{61,62}

20 The horizontal red dash-dot line at 200°C in **Figure 7a** indicates the lower T -
21 limit of the formation of hexagonal mesophase using the currently applied
22 pressure and temperature protocol. At the large supercoolings below $T_c=200^\circ\text{C}$
23 the large thermodynamic stability of the crystal overrides the advantage of a low
24 barrier for mesophase formation. Thus crystal phase forms directly from melt,

1 giving FCC of the non-polar α form. Similarly, to the left of the dark colored
2 region in **Figures 7a,b**, below 200 MPa, even though the green dashed
3 metastable equilibrium $T_m(\text{hex})$ line may have been crossed during the pressure
4 quench, the driving force for mesophase formation (free energy difference
5 between melt and mesophase) was too small to compete with the much larger
6 melt $\rightarrow$ crystal free energy drop. So again at $P_c < 200$ MPa crystallization occurred
7 directly from melt.

8 The contour maps in **Figure 7** confirm and expand on the finding by Li et al.²⁷
9 that the polar forms and ECC can be obtained under considerably milder
10 pressures and temperatures than the equilibrium phase diagram would suggest;
11 in fact they can form a hundred °C and a hundred MPa below the triple point.
12 However, below 200 MPa and 190 °C the predominant structure formed is α -
13 FCC, accompanied by a small fraction of polar FCC (**Figure S2**).

14 We should mention that the high T limit of the “windows” in **Figure 7** is
15 somewhat arbitrary and is defined by the rates of cooling and pressure release
16 applied. As supercooling and superpressure get smaller, crystallization slows
17 down, and what had already crystallized may even melt again if T_m drops below
18 T_c through pressure drop that is too fast.

19 To show that $X_{\beta+\gamma}$ and F_{ECC} could be increased beyond the values achievable
20 through the T - P vs. time protocol in **Figure 1b**, a PVDF sample was allowed to
21 crystallize isothermally at 220 °C for 40 min at $P_c = 300$ MPa. The point is shown
22 as asterisk in **Figure 7a, 7b**. The values of $X_{\beta+\gamma}$ and F_{ECC} reached 0.50 and 0.92,
23 respectively (**Figure S3**), compared to 0.47 and 0.76 without isothermal
24 annealing.

One may also ask why $X_{\beta+\gamma}$ and, to some extent F_{ECC} , decrease somewhat past the maximum as P_c increases beyond 300 MPa. Again, this could be due to the superpressure and thus supercooling being too large to completely suppress direct crystallization, unmediated by the mesophase. There may be other reasons as well such as, possibly, suboptimal rate of reduction of pressure and/or temperature after pressure quench.

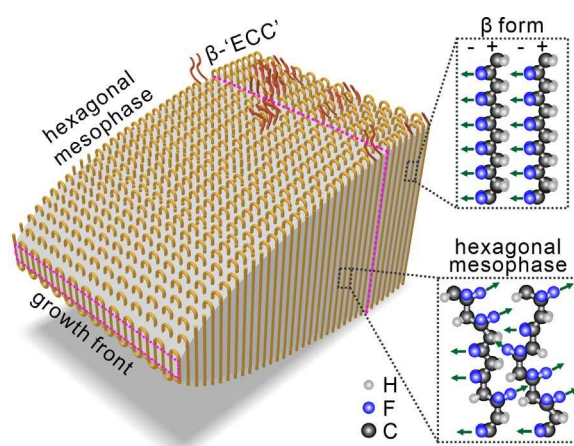


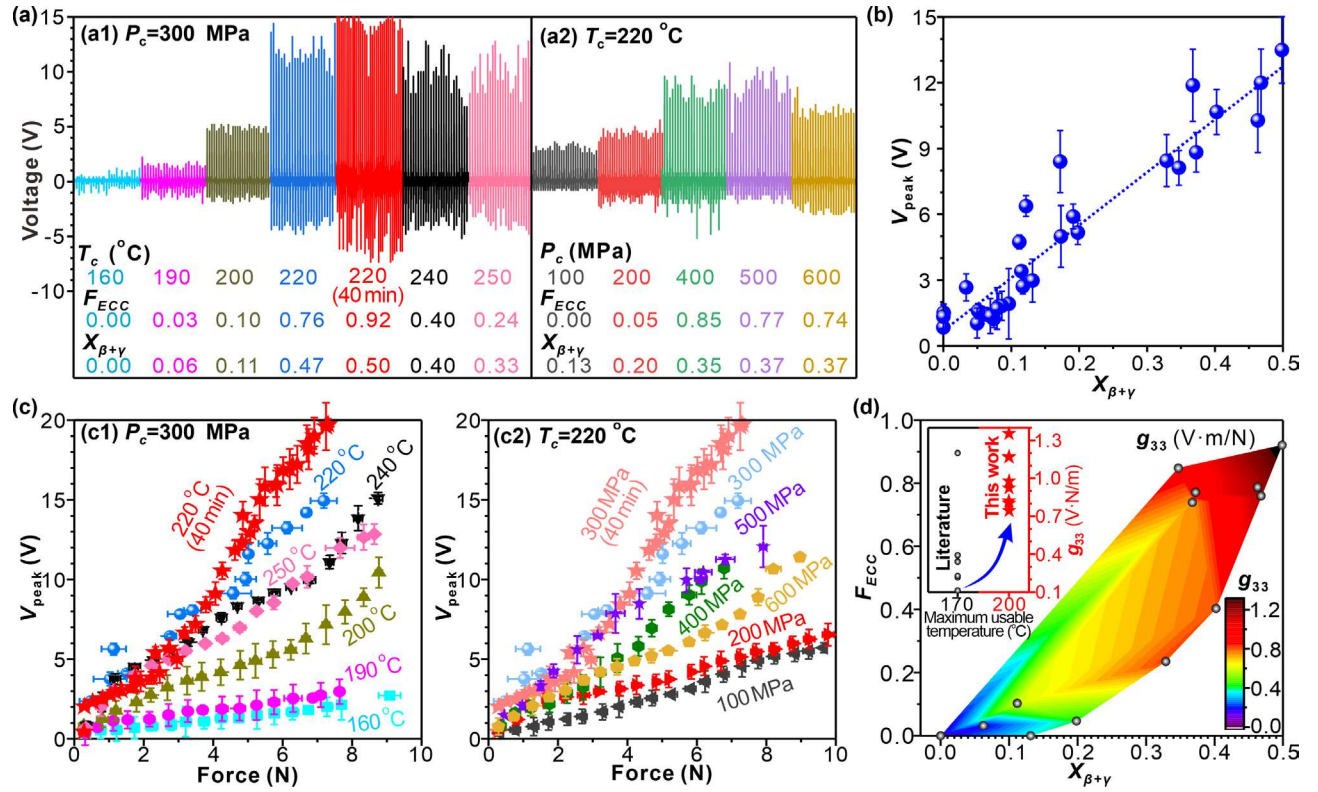
Figure 8. Schematic diagram shows the crystallization of β -form ECC through the hexagonal mesophase in PVDF. The chain conformations of hexagonal mesophase and β -form are compared.

3.7. Effect of Structure on Piezoelectric Performance. Based on the T - P windows of the polar forms and ECC, PVDF films with different values of $X_{\beta+\gamma}$ and F_{ECC} were prepared. Pressure sensors were fabricated by encapsulating the PVDF films between copper foil electrodes, the sandwich then placed between polyimide substrates, as depicted in **Figure S4**. Piezoelectric performance of the sensors was tested by measuring open-circuit voltage in response to varying applied force. **Figure 9a1** shows the voltage output of sensors containing PVDF crystallized at $P_c = 300$ MPa at different T_c . **Figure**

1 **9a2** shows the same for samples crystallized at $T_c = 220$ °C and different P_c . At
2 $P_c = 300$ MPa, an increase in T_c results in a substantial rise in output voltage,
3 achieving the highest voltage value of approximately 12 V for samples
4 crystallized at 220 °C. Even more impressive value of 14 V is obtained with
5 samples isothermally crystallized at 220 °C. For PVDF crystallized at $T_c =$
6 220 °C, the output voltage increases with increasing P_c . The trends in
7 piezoelectric response with respect to T_c and P_c are generally consistent with
8 the trend in $X_{\beta+\gamma}$, as seen in **Figure 7**. As shown in **Figure 9b**, V_{peak} of PVDF
9 sensors scales roughly linearly with crystallinity of the polar forms, as shown by
10 the dashed line. This confirms that crystallinity of the polar forms is the primary
11 factor influencing piezoelectric performance. However, it should be
12 acknowledged that certain data points deviate from the linear relationship,
13 suggesting the existence of additional influencing factors.

14 **Figure 9c** shows the relationship between V_{peak} and applied force. The data
15 show a linear increase in V_{peak} with applied stress the application of larger force
16 for all the PVDF samples (**Figures 9c1** and **9c2**), affirming their suitability for
17 pressure sensing applications. To assess the performance of these PVDF
18 sensors, the piezoelectric voltage constant (g_{33}) was derived from the slope of
19 V_{peak} vs applied force.^{7,40,41} Furthermore, the g_{33} has been plotted as a function
20 of $X_{\beta+\gamma}$, as well as another important crystalline structural feature, F_{ECC} (**Figure**
21 **9d**). We show that g_{33} increases with an increase in $X_{\beta+\gamma}$, as well as with the
22 increase in F_{ECC} . The maximum g_{33} of $1.35 \text{ V} \cdot \text{m} \cdot \text{N}^{-1}$ is attained with $X_{\beta+\gamma} = 0.50$
23 and $F_{ECC} = 0.92$. This value is the highest g_{33} reported in the literature so far,
24 and is more than three times greater than the commercially available PVDF films
25 that are produced through stretching and electrical poling.⁴⁴ The inset figure in

1 **Figure 9d** compares the value of g_{33} obtained in this work with those reported
2 in the literature.^{33,39,40,41,42,43,44,45,46,47,48} The highest g_{33} and increased maximum
3 working temperature are achieved through high-pressure high-temperature
4 processing. Furthermore, the piezoelectric sensitivity of these high pressure
5 crystallized PVDF sensors remains nearly constant, exhibiting no significant
6 degradation after 1500 measured cycles (**Figure S5**).



7 **Figure 9.** Piezoelectric performance of high-pressure crystallized PVDF. (a) Output
8 voltages of PVDF under a mechanical load of 5.1 ± 0.2 N with a frequency of 4.5 ± 0.4
9 Hz; PVDF crystallized at (a1) $P_c = 300$ MPa and different T_c , (a2) $T_c = 220$ °C and
10 different P_c . (b) Peak voltage vs. $X_{\beta+\gamma}$. (c) Peak voltage vs. applied force. PVDF was
11 crystallized at (c1) $P_c = 300$ MPa and different T_c , (c2) $T_c = 220$ °C and different P_c . (d)
12 Direct piezoelectric stress coefficient, g_{33} , as a function of $X_{\beta+\gamma}$ and F_{ECC} . g_{33} was
13 determined from the slope of plots in (c). The inset in (d) compares the values of g_{33}
14 obtained in this work with those reported in literature.^{33,39,40,41,42,43,44,45,46,47,48}

4. Conclusions

In summary, this work confirms that it is the synergy between the polar forms and ECC morphology that provides high sensitivity and service temperature of PVDF piezoelectric sensors. We show that polar ECC can form within a critical window of temperatures and pressures that are considerably lower than the equilibrium T - P range of stability of the key facilitator, the hexagonal mesophase. The formation of polar ECC thus not only yields the highest piezoelectric voltage constant reported so far ($g_{33} = 1.35 \text{ V} \cdot \text{m} \cdot \text{N}^{-1}$), but also extends the usable temperature range of the sensor. More experiments will be needed to establish if even higher piezoelectric response could be reached by the high-pressure crystallization method.

5. Experimental Section

5.1. Materials. PVDF pellets with a weight-average molecular weight (M_w) of 183 KDa and a polydispersity of 2.52 were purchased from Shanghai 3F New Materials Co., Ltd. The melting temperature was 169 °C (**Figure S6**).

5.2. Characterization. The fraction of polar forms β and γ , $F_{\beta+\gamma}$, of PVDF was determined using a Thermo Scientific Nicolet iZ10 Fourier transform infrared (FTIR) spectrometer in the attenuated total reflectance (ATR) mode. All the spectra were recorded over a wavelength range of 400-4000 cm^{-1} by averaging 32 interferograms with a resolution of 2 cm^{-1} . $F_{\beta+\gamma}$ was calculated by^{23,49}

$$F_{\beta+\gamma} = \frac{I_{840,832}}{I_{840,832} + 1.26I_{763}} \times 100\% \quad (1)$$

1 where $I_{840,832}$ and I_{763} represent the absorbances at 840/832 cm^{-1} for β - and
2 γ -forms and 763 cm^{-1} for α -form, respectively.

3 Melting behavior of PVDF was studied by a TA Instruments DSC250
4 differential scanning calorimeter in nitrogen atmosphere. All the samples (~ 5
5 mg) were heated from 30 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$. The melting peaks of FCC
6 and ECC could be clearly separated. The fractions of ECC and FCC are then
7 calculated by

$$8 \quad F_{ECC} = \frac{\Delta H_{ECC}}{\Delta H_{ECC} + \Delta H_{FCC}} \quad (2)$$

$$9 \quad F_{FCC} = \frac{\Delta H_{FCC}}{\Delta H_{ECC} + \Delta H_{FCC}} \quad (3)$$

10 where ΔH_{FCC} and ΔH_{ECC} are the melting enthalpies of FCC and ECC,
11 respectively.

12 The crystalline morphology of PVDF samples was studied using a ZEISS
13 Sigma 300 SEM. The PVDF samples were first treated with the specific etching
14 reagent⁶³ to remove the amorphous component. Then, the etched surface of
15 PVDF samples was sputter-coated with nano-gold particles and observed by
16 SEM at an operating voltage of 3 kV.

17 Simultaneous WAXS/SAXS measurements were performed at beamline
18 16B1 of the Shanghai Synchrotron Radiation Facility. The X-ray wavelength was
19 0.154 nm. 2D WAXS and SAXS patterns were collected with Pilatus 900K and
20 2M detectors, respectively. The sample-to-detector distances for WAXS and
21 SAXS were 409.5 mm and 2328.0 mm. The melting behavior of PVDF samples
22 crystallized at 300 MPa and at two different temperatures (160 $^{\circ}\text{C}$ and 220 $^{\circ}\text{C}$)
23 was also studied by in-situ WAXS/SAXS measurements using a Linkam

1 THMS600 hot stage. The samples were heated from 40 °C to 210 °C at 10 K/min.
 2 crystallinity (X_c) was estimated from the WAXS using curve deconvolution,

$$3 \quad X_c = \frac{\sum A_c}{\sum A_c + A_a} \quad (4)$$

4 where $\sum A_c$ is the sum of areas of all crystalline peaks and A_a the area of the
 5 amorphous halo. Due to peak overlaps, separate crystallinities of β - and γ -forms
 6 were not determined. (111) α , the diffraction peak characteristic of α -form, was
 7 used to separate X_α from $X_{\beta+\gamma}$. Crystallinities of the non-polar and polar forms
 8 were determined as

$$9 \quad X_\alpha = \frac{A_{(110)\alpha}/K_{(110)\alpha}}{\sum A_c + A_a} \quad (5)$$

$$10 \quad X_{\beta+\gamma} = X_c - X_\alpha \quad (6)$$

11 where coefficient $K_{(110)\alpha}$ is the ratio of (111) α reflection intensity ($A_{(110)\alpha}$) to the
 12 total intensity of all crystalline peaks ($\sum A_c$).

13 The long period of lamellar stacks was estimated from the SAXS scattering
 14 peak as $L=2\pi/q^*$, where q^* is the position of the SAXS peak in the Lorentz-
 15 corrected plot.

16 The piezoelectric response of PVDF was measured based on the direct
 17 piezoelectric effect. An oscilloscope probe (MDO34, Tektronix) equipped with a
 18 250 MHz, 10x passive voltage probe was used to monitor the output voltage (V).
 19 The force (F) applied to the PVDF sensor was recorded using a digital force
 20 gauge. The piezoelectric voltage constant g_{33} was obtained from the V - F plots
 21 according to^{8,40,41}

$$22 \quad V = \frac{g_{33}Fd}{s} \quad (7)$$

1 where d and S are the thickness and area of the sample.

2

3 **Supporting Information**

4 Additional WAXS, IR and DSC traces of PVDF crystallized under different
5 pressures; Temperature and pressure window of α form; Crystalline form and
6 melting temperature of isothermally crystallized PVDF; Schematic diagram of
7 the PVDF sensor; Stability test of PVDF sensor; Molecular weight and melting
8 temperature of as-purchased PVDF pellets.

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17 **Notes**

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