Structural Evolution of PVDF under Heat and Pressure: Crystallinity and Phase Composition via FTIR and XRD Analysis

By

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Abstract

This study investigates the synergistic effects of temperature (30–210°C) and pressure (10,000 lbs) on the crystalline phase evolution of poly(vinylidene fluoride) (PVDF), focusing on enhancing its electroactive β-phase content. Triplicate PVDF samples were processed under controlled thermal and pressure conditions, followed by structural characterization via X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Non-pressurized samples exhibited dominant α-phase crystallization (2–3% β-phase) below 150°C, with a minor β-phase increase (3–4%) near melting temperatures. In contrast, pressurized samples demonstrated accelerated β-phase nucleation, achieving 6–7% β-phase at 70–130°C and a peak of 9.6% at 170°C, near the α-phase melting point. This marked increase highlights pressure's role in reducing energy barriers for all-trans chain alignment, stabilizing the polar β-phase. However, post-melting treatments (190–210°C) under pressure reverted β-phase content to baseline levels (1–2%), emphasizing that phase transitions are contingent on maintaining sub-melt conditions. Statistical reproducibility across triplicates confirmed robust trends. These findings underscore the potential of pressure-assisted thermal processing to tailor PVDF's polymorphic behavior, offering a solvent-free pathway to enhance piezoelectric performance for applications in sensors and energy harvesting. The study bridges processing parameters with functional outcomes, providing actionable insights for optimizing PVDF's electromechanical properties.

Chapter 1: Introduction

Property of PVDF

Poly(vinylidene fluoride), or PVDF, is a remarkable polymer that bridges the gap between everyday plastics and high-performance functional materials. At first glance, it might seem like just another flexible, lightweight plastic, but what sets PVDF apart is its hidden talent: it can generate electricity when squeezed or bent. This unique property, known as piezoelectricity, arises from its molecular structure, where alternating $–CH_2–$ and $–CF_2–$ groups create strong dipole moments. When mechanically stressed, these dipoles align, producing a measurable voltage—a phenomenon that has made PVDF a star player in cutting-edge technologies like wearable sensors, medical devices, and energy-harvesting textiles.[1]

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer that exhibits both a glass transition temperature and a melting point. The glass transition temperature of PVDF typically ranges is -40°C, marking the transition of its amorphous regions from a rigid, glassy state to a flexible, rubbery phase. This transition is influenced by PVDF's molecular structure, particularly the balance between chain flexibility and dipole-dipole interactions , as well as its molecular weight and tacticity. The melting point of PVDF lies between 171 to 180°C, reflecting the melting of its crystalline domains, which are predominantly composed of the α-phase under standard processing conditions.[2] Higher crystallinity correlates with improved thermal stability and mechanical strength due to the ordered packing of polymer chains in crystalline regions.

So, how does PVDF pull this off? The secret lies in its molecular structure. Imagine a chain of carbon atoms where every other carbon is bonded to two fluorine atoms ($–CF_2–$) and two hydrogen atoms ($–CH_2–$). This alternating pattern creates tiny electric dipoles along the polymer

chain. When these dipoles align in a specific direction—like soldiers standing in formation—the material becomes polar, enabling it to convert mechanical stress into electrical signals.

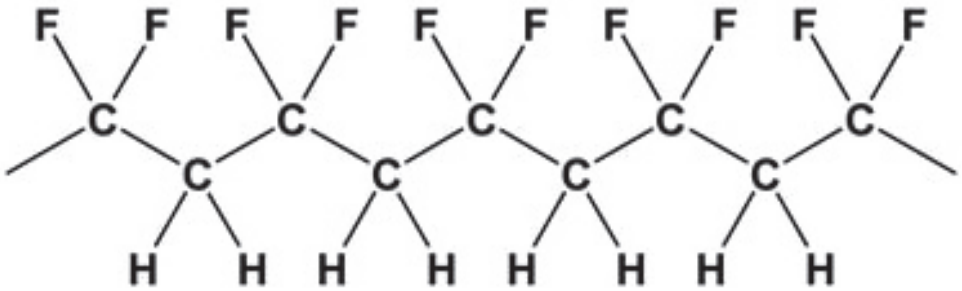

Figure 1: Molecular structure of PVDF[3]

Amorphous and Crystalline Phase

In materials science, the crystalline phase refers to a highly ordered arrangement of atoms, ions, or molecules in a repeating three-dimensional lattice structure. This long-range order results in distinct properties such as sharp melting points, anisotropy (direction-dependent behavior), and well-defined diffraction patterns in techniques like X-ray diffraction (XRD). Examples include metals, salts, and the α- or β-phase regions in semicrystalline polymers like poly(vinylidene fluoride) (PVDF). In contrast, the amorphous phase lacks long-range order, with molecules arranged in a random, disordered configuration. Amorphous materials, such as glass, rubber, or the non-crystalline regions in polymers, exhibit isotropic behavior (uniform properties in all directions), gradual softening upon heating (glass transition), and broad, diffuse XRD patterns. Semicrystalline polymers like PVDF contain both phases: crystalline domains provide mechanical strength and thermal stability, while amorphous regions contribute to flexibility and impact resistance. The balance between these phases governs material performance, with processing conditions (e.g., cooling rate, pressure) critically influencing their relative proportions.

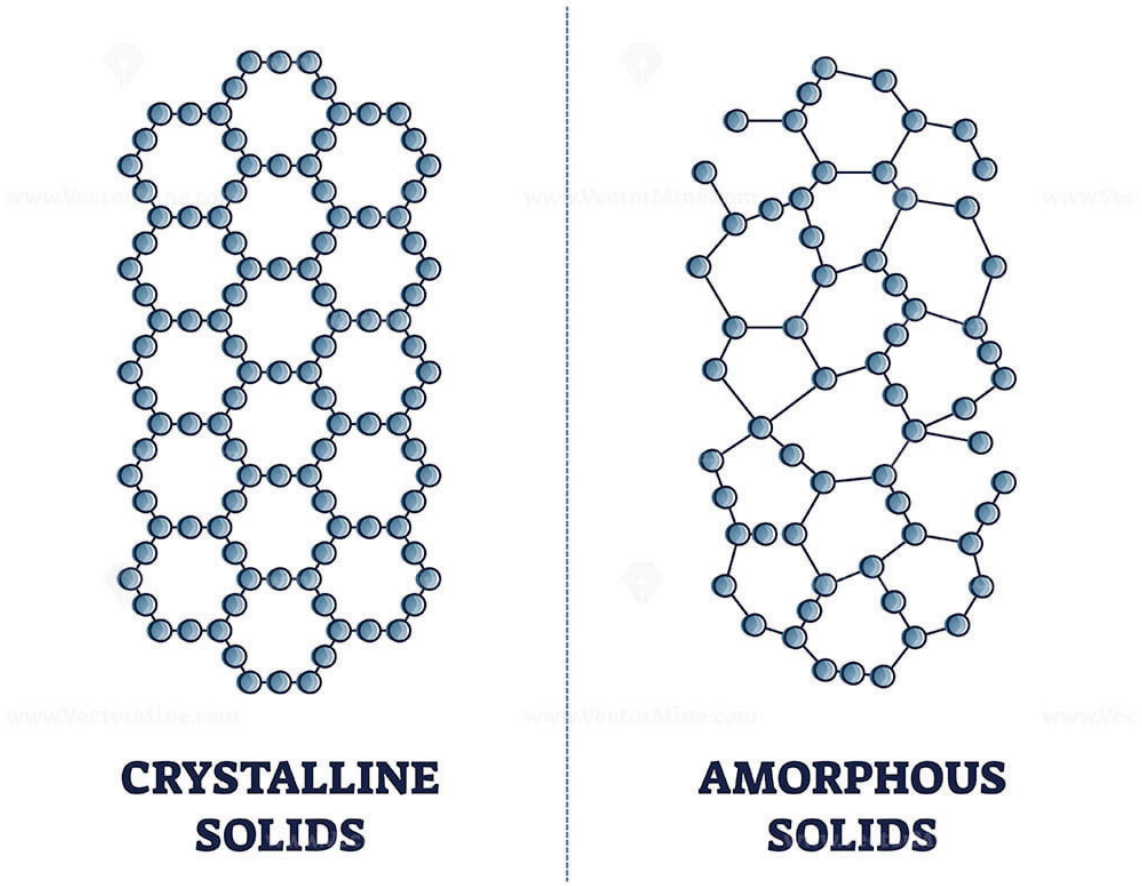

Figure 2: Amorphous and Crystalline Phase Structure[2]

Alpha and Beta Phase of PVDF

Not all PVDF is created equal. The way it's processed determines which of its "personalities" dominates. For instance:

- The α-phase of poly(vinylidene fluoride) (PVDF) represents its thermodynamically stable but functionally modest state. In this phase, PVDF molecules adopt a trans-gauche (TGTG') conformational arrangement, where alternating segments of the polymer chain twist into relaxed, low-energy configurations. This disordered structure results in a nonpolar crystalline symmetry, rendering the α-phase largely inert for piezoelectric

applications. Typically formed under conventional processing methods such as melt-casting or slow cooling from solution, the α-phase dominates in the absence of external stimuli like mechanical stretching or electric poling. While its stability and ease of formation make it industrially convenient, the α-phase exhibits minimal piezoelectric activity (d_{33} < 5 pC/N), limiting its utility in advanced technologies [4].

- In stark contrast, the β-phase embodies PVDF's high-performance potential. When subjected to mechanical stretching, high-pressure annealing, or electric field poling, PVDF chains undergo a dramatic conformational shift into an all-trans (TTTT) arrangement. This alignment locks the strong dipoles of $–CF_2$ and $–CH_2$ groups into a parallel orientation, creating a polar crystalline structure with spontaneous polarization. The β-phase boasts exceptional piezoelectric coefficients (d_{33} ≈ 20–30 pC/N), but with superior flexibility and biocompatibility [4]. Recent studies highlight its pivotal role in self-powered wearable sensors, where β-phase PVDF films convert subtle biomechanical motions (e.g., finger bending or pulse waves) into measurable electrical signals.

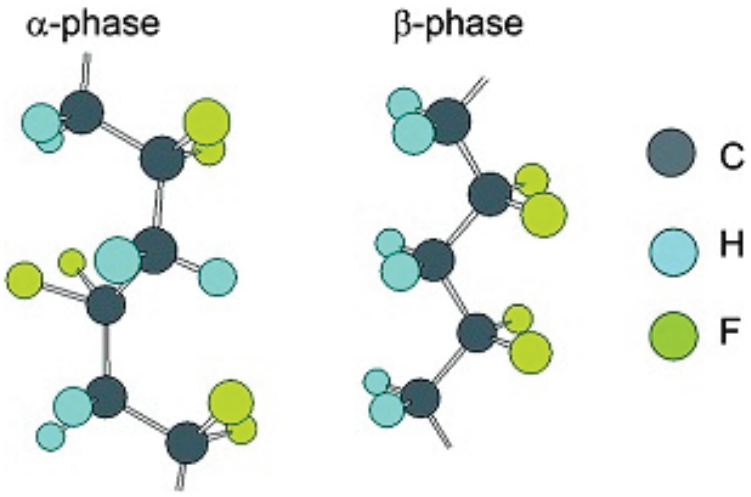

Figure 3: Alpha- and Beta-phase Structure of PVDF[3]

The polymer's performance hinges on its crystalline phases. While the non-polar α-phase dominates under standard processing conditions, the polar β-phase—responsible for its strongest piezoelectric response—requires strategic engineering through methods like high-pressure annealing or electrospinning. Research demonstrates that optimizing processing parameters (e.g., temperature gradients, mechanical stretching) can enhance β-phase content. However, challenges remain in scaling these methods cost-effectively. Getting PVDF to embrace its β-phase isn't straightforward. While heat can nudge its molecules into motion, and pressure can force them into order, the relationship between these factors is delicate. Too little pressure, and the dipoles remain disorganized; too much heat, and the material might lose its structural integrity. This balancing act is why researchers are digging into how temperature and pressure work together to shape PVDF's behavior.

How can we reliably coax PVDF into its high-performing β-phase using nothing but heat and pressure—no solvents, no complex additives? By mapping how these two variables dance together, we aim to unlock simpler, greener ways to engineer PVDF for real-world applications. Whether it's improving the sensitivity of a medical sensor or making energy-harvesting fabrics more efficient, the answers could ripple far beyond the lab bench.

Processing Techniques for Phase Control

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer whose functional properties, particularly its piezoelectric and ferroelectric performance, are intrinsically linked to its crystalline phase composition. Among its polymorphs, the polar β-phase is highly desirable for applications requiring strong electromechanical coupling, such as sensors, energy harvesters, and flexible electronics. However, achieving high β-phase content in PVDF demands precise control

over processing conditions. Two techniques—mechanical stretching and high-pressure annealing—have emerged as critical strategies for phase engineering in PVDF, enabling tailored crystallinity and enhanced performance.

Mechanical stretching is a widely adopted method to induce β-phase formation in PVDF by forcibly aligning polymer chains into a conformation favorable for dipole orientation. When PVDF films or fibers are subjected to uniaxial or biaxial stretching at elevated temperatures, the applied stress overcomes the energy barrier required for molecular rearrangement. During this process, the polymer chains transition from the relaxed trans-gauche (TGTG') conformation of the α-phase to the extended all-trans (TTTT) arrangement characteristic of the β-phase. However, mechanical stretching is not without limitations. Excessive strain rates or uneven stretching can introduce microstructural defects, such as voids or cracks, which compromise mechanical integrity and dielectric strength. Additionally, the β-phase formed through stretching may revert to the α-phase under prolonged thermal exposure, necessitating post-stretching stabilization methods like annealing.[5]

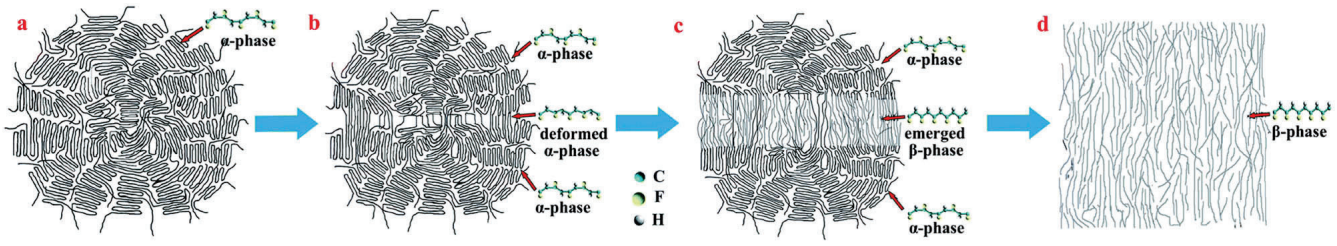

Figure 4: Schematic drawing of the transformation process from α-crystal to β-crystal of PVDF by mechanical stretching[6]

High-pressure annealing combines thermal treatment with externally applied pressure to manipulate PVDF's phase behavior. Unlike conventional annealing, which relies solely on

temperature to promote crystallization, this method applies pressures ranging from 10,000 to 20,000 psi at temperatures near or above the polymer's melting point. The simultaneous application of heat and pressure suppresses molecular relaxation, forcing chains into ordered configurations. Under high pressure, the free volume between polymer chains is reduced, effectively lowering the energy barrier for dipole alignment. This promotes the nucleation and growth of β-phase crystallites, even at temperatures where α-phase formation would otherwise dominate. The pressurized environment also enhances crystallite orientation, as evidenced by sharp XRD peaks and reduced full-width-at-half-maximum (FWHM) values, indicating larger and more ordered crystalline domains. A key advantage of high-pressure annealing is its ability to stabilize metastable phases. Unlike mechanically stretched PVDF, which may suffer phase reversion under thermal cycling, pressure-treated samples retain β-phase content even after repeated heating and cooling. This stability is attributed to the "locked-in" dipole alignment achieved under high stress, which resists conformational changes. Furthermore, the technique improves mechanical properties such as tensile strength and thermal stability, making it suitable for high-temperature applications.[7]

Chapter 2: Methods

Melt Casting

The fabrication of PVDF samples involved a meticulously controlled melting cast procedure, with 21 independent casts prepared to ensure statistical reliability and reproducibility. The process commenced by preheating a thermal plate to 275°C, a temperature selected to achieve complete polymer melting while minimizing thermal degradation. To prevent adhesion and ensure easy demolding, a custom mold was constructed using a double-layered aluminum foil base, leveraging aluminum's high thermal conductivity and non-reactive surface properties. Prior to melting, PVDF pellets (1.0 g ± 0.05 g per sample) were meticulously weighed, fragmented into smaller pieces to enhance melting uniformity, and subjected to two sequential ethanol washes. This purification step aimed to eliminate surface contaminants and residual additives that could interfere with crystallization kinetics. The cleaned PVDF was then evenly distributed within the mold cavity to minimize thickness variations. The mold assembly was positioned on the preheated thermal plate, and a glass enclosure was placed over the setup to stabilize the thermal environment and mitigate convective heat loss. The polymer was maintained at 275°C for 1 hour to ensure thorough homogenization and erase prior thermal history—a critical step for achieving consistent crystallographic outcomes. Following the melting phase, the mold was rapidly quenched in an ice bath to induce rapid solidification. This quenching step suppressed spontaneous α-phase crystallization by restricting molecular reorganization, thereby preserving metastable phases that are pivotal for enhancing piezoelectric functionality. The combination of precise temperature control, impurity removal, and rapid thermal quenching ensured uniform sample morphology and repeatable phase characteristics across all 21 casts.

Hydraulic Press

The crystalline phase behavior of poly(vinylidene fluoride) (PVDF) was investigated using a Carver Auto Series Hydraulic Press equipped with temperature-controlled stainless steel plates. Cylindrical PVDF tablets were initially pre-formed using melting casts, and samples designated for heat-pressure treatment were positioned between the hydraulic press's dual plates. The press system allowed simultaneous application of heat and compressive force, with temperatures set to a gradient spanning 30°C to 210°C to probe PVDF's phase transitions across its melting regions. A constant pressure of 10,000 lbs was applied for 15 minutes based on prior studies demonstrating its efficacy in inducing chain alignment and β-phase nucleation in semicrystalline polymers.

The procedure commenced by preheating the bottom plate to the target temperature. Once the sample contacted both plates, a 10-minute equilibration period ensured uniform heating. Pressure was then applied while maintaining thermal conditions, facilitating molecular reorganization under combined stress. After processing, samples were cooled to room temperature under sustained pressure to stabilize the crystalline structure. This approach aimed to mimic industrial-scale polymer processing while enabling precise control over phase morphology. The selected temperature range allowed observation of PVDF's α-phase dominance at lower temperatures and β phase formation at elevated temperatures. The high pressure reduced energy barriers for dipole alignment, promoting polar phase nucleation.

Set 1	Set 2
PVDF 30°C	PVDF 30°C with 10,000lbs
PVDF 50°C	PVDF 50°C with 10,000lbs

PVDF 70°C	PVDF 70°C with 10,000lbs
PVDF 90°C	PVDF 90°C with 10,000lbs
PVDF 110°C	PVDF 110°C with 10,000lbs
PVDF 130°C	PVDF 130°C with 10,000lbs
PVDF 150°C	PVDF 150°C with 10,000lbs
PVDF 170°C	PVDF 170°C with 10,000lbs
PVDF 190°C	PVDF 190°C with 10,000lbs
PVDF 210°C	PVDF 210°C with 10,000lbs

Table 1: Thermal Treatment Conditions for PVDF Samples With and Without Applied Pressure

2-D X-Ray Diffraction

The crystalline phase behavior of poly(vinylidene fluoride) (PVDF) was characterized using a Bruker D8 Discover 2D X-ray Diffractometer (XRD), a non-destructive analytical technique critical for probing polymer crystallinity and polymorphic transitions. PVDF samples were analyzed to evaluate the influence of processing conditions on phase composition. The system employed a copper (Cu) X-ray tube operating at 40 kV and 40 mA, coupled with a Vantec-500 Xe-CO2 gas-filled detector positioned 20 cm from the goniometer center.

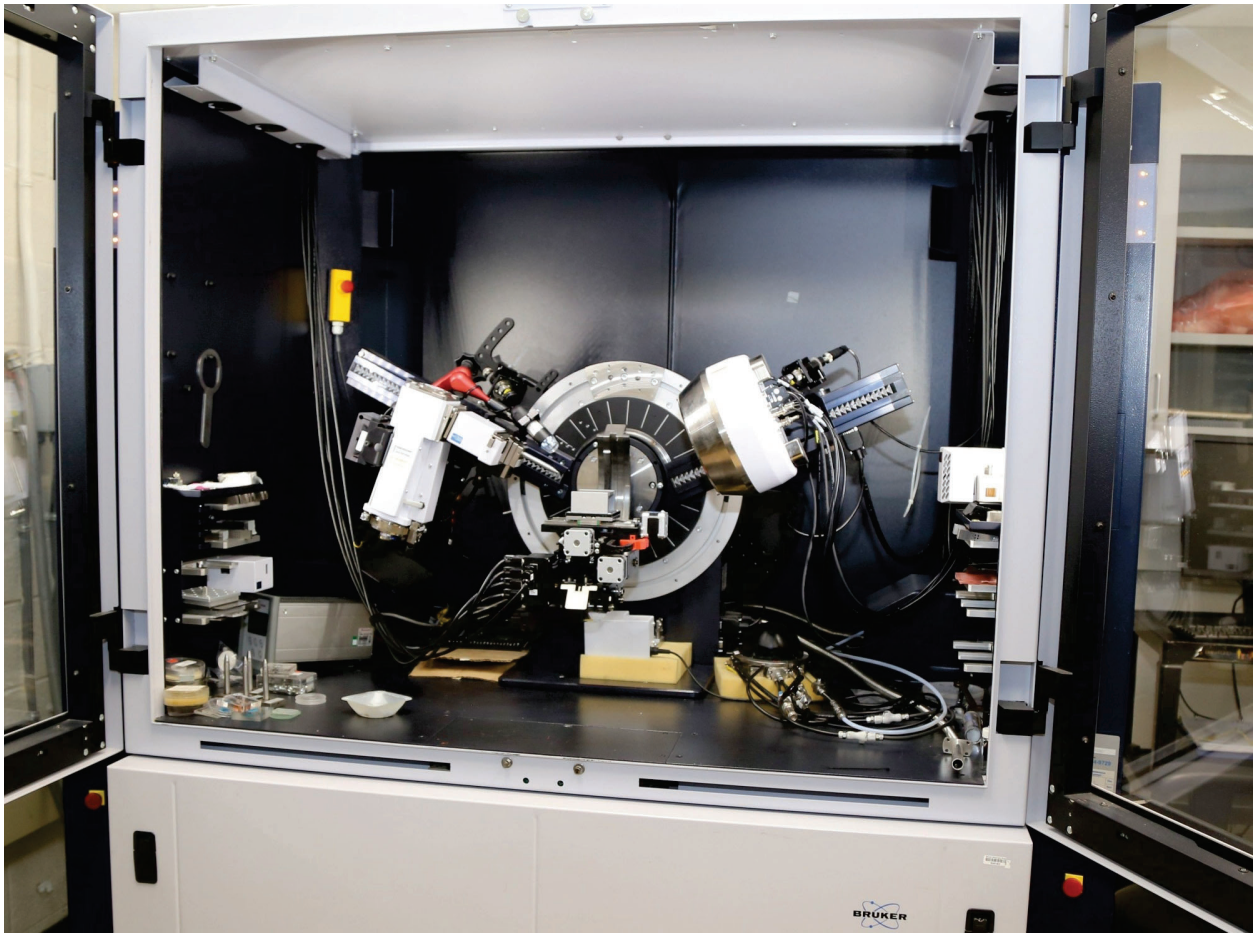

Figure 5: X-Ray Diffractometer Used for PVDF Crystalline Phase Analysis

Samples were mounted on glass slides to minimize background interference. Three distinct regions were scanned. Diffraction patterns were acquired across a 2θ range of 20° to 80° with a step size of 25° and an exposure time of 60 seconds per step. Prior to scanning, the X-ray beam alignment was calibrated by adjusting the z-plane until the dual laser beams converged into a singular focal point on the sample surface.

Post-acquisition, the 2D diffraction images and spectra were processed using DIFFRAC.SUITE.EVA software. Background scattering from the glass substrate was systematically subtracted, and data were exported as .xy files for quantitative analysis. Distinct

diffraction peaks corresponding to PVDF's α-phase (e.g., 17.95°, 18.6°, 20.0°,26.8°), β-phase (20.8°), were identified, enabling precise phase fraction calculations. This approach provided critical insights into how thermal and mechanical processing altered chain conformation and crystallite orientation, essential for optimizing PVDF's electromechanical performance in applications such as energy storage and flexible electronics.

Fourier-Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique used to identify and characterize materials by measuring their absorption of infrared light. Unlike traditional infrared spectroscopy, FTIR employs an interferometer, typically a Michelson setup, which splits light into two beams that reflect off moving and fixed mirrors, creating an interferogram through path differences. This interferogram, capturing all frequencies simultaneously, is converted into a readable spectrum via a Fourier Transform algorithm, enhancing speed and accuracy. Key advantages include rapid data acquisition (multiplex advantage), high sensitivity, superior resolution, and improved signal-to-noise ratios. FTIR is versatile, analyzing solids, liquids, and gases with minimal sample preparation, often non-destructively.

Fourier-transform infrared spectroscopy (FTIR) was employed to characterize the crystalline phase composition of PVDF samples. Each sample underwent three consecutive scans. Distinct absorption bands at 763 cm^{-1} (α-phase, corresponding to CF_2 bending and CH_2 rocking modes) and 840 cm^{-1} (β-phase, attributed to CF_2 stretching and all-trans chain conformation) were monitored to quantify phase fractions.

The β-phase content (fβ) was calculated using the empirical relationship:

$$f_\beta = \frac{I_\beta}{1.26 \times I_\alpha + I_\beta}$$

Figure 6: Equation Used to Calculate the β-Phase Fraction in PVDF

where Iα and Iβ represent the integrated intensities of the α- and β-phase peaks, respectively. The coefficient 1.26 accounts for differences in absorption coefficients between the two phases, as established in prior literature. Peak integration was performed using Spectragryph software. To ensure statistical reproducibility, triplicate scans were conducted for each sample, and the resulting fβ values were averaged. Standard deviations were calculated to assess measurement consistency, confirming that intra-sample variability remained below 5%.[8]

Deconvolution on Fityk

Deconvolution is a critical method for quantifying and interpreting the X-ray diffraction spectra of polyvinylidene fluoride (PVDF), a semi-crystalline polymer with distinct crystalline phases (e.g., α, β, γ) that influence its piezoelectric, ferroelectric, and mechanical properties. This technique involves mathematically separating overlapping peaks in the XRD spectrum into individual Gaussian or Lorentzian components, allowing precise identification of the crystalline phases and calculation of their relative proportions. For PVDF, deconvolution is particularly essential due to the coexistence of multiple polymorphs, which often produce overlapping diffraction peaks. In this study, XRD data for PVDF samples were acquired using a diffractometer and exported from DIFFRACT.SUITE.EVA as .xy files for compatibility with the

open-source Fityk software. Manual analysis was performed to fit the experimental spectra with a series of peaks, each representing a distinct crystalline domain. Baseline correction and peak position constraints (based on literature values for PVDF phases) were applied to optimize the fit quality.

Chapter 3: Results

This chapter presents the experimental findings on the phase transitions of PVDF as a function of temperature (30–210 °C) and applied pressure (0 vs. 10,000 lbs). The results are organized into two main sections: X-ray diffraction (XRD) analysis and Fourier-transform infrared spectroscopy (FTIR) analysis. In each section, the evolution of PVDF's crystalline structure—particularly the growth or decline of the electroactive β-phase—is examined for both non-pressurized and pressurized samples. All data points represent the average of triplicate samples (Tri A, B, C) with error trends noted where relevant, ensuring the statistical reliability of observed trends. Key findings include the influence of pressure on overall crystallinity, the temperature-dependent emergence of β-phase crystallites, and the synergistic effect of combined high pressure and high temperature on stabilizing the β-phase. The integrated interpretation of XRD patterns and FTIR spectra is provided to give a comprehensive understanding of PVDF's structural evolution under the tested conditions.

XRD Data and Deconvolution

The X-ray diffraction results reveal how the crystalline structure of PVDF evolves with thermal treatment from 30 °C up to 210 °C, both for samples crystallized under ambient (non-pressurized) conditions and for those crystallized under an applied pressure. For each sample, the total crystalline content was calculated by the crystalline area divided by the crystalline area added to the amorphous area. (The sample notation "PVDF XX NoP" refers to a PVDF sample treated at XX °C with No Pressure, whereas "PVDF XX P" refers to a sample treated at XX °C under Pressure.) Below, we discuss the XRD-derived crystallinity and β-phase content at each treatment temperature, highlighting trends with increasing temperature and the effects of pressure on the phase composition.

Low-Temperature Regime (30 °C and 50 °C)

30 °C (Baseline): At room temperature (30 °C), the non-pressurized PVDF sample (PVDF 30 NoP) exhibits a semicrystalline structure with approximately 38.7% crystalline content (and correspondingly ~61.3% amorphous content). This indicates a moderate degree of crystallinity for the as-prepared PVDF at ambient conditions. Notably, only a very small portion of this crystalline phase is the polar β polymorph – in PVDF 30 NoP the β-phase accounts for roughly 2.7% of the material. The dominant crystalline phase is therefore the non-polar α-phase (the thermodynamically stable form of PVDF at ambient conditions), with the β-phase present as a minor component.

When PVDF is processed under pressure at 30 °C (PVDF 30 P), the overall crystallinity is slightly lower (~36.6% crystalline), indicating that the applied pressure at room temperature marginally reduces the degree of crystallization (and thus increases the amorphous fraction to ~63.4%). Despite the slight drop in total crystallinity, the β-phase content is a bit higher in the pressurized sample: PVDF 30 P contains about 3.2% β-phase. In other words, applying pressure during crystallization at 30 °C has a subtle influence that favors β-phase formation to a small extent (increasing its fraction from ~2.7% to ~3.2%), even as it slightly suppresses overall crystallinity. This suggests that pressure can influence chain packing at the molecular level, promoting the all-trans conformation characteristic of the β-phase in a small subset of crystallites. Nevertheless, at 30 °C the β-phase remains a very minor fraction in both cases, and the PVDF microstructure is largely amorphous with α-phase crystals comprising the bulk of the crystalline portion.

30°C NoP	30°C P

Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
38.7	61.3	2.7	36.6	63.4	3.2

Table 2: Phase Composition of PVDF at 30 °C With and Without Applied Pressure (10,000 lbs)

50 °C: Mild heating to 50 °C during processing leads to a slight increase in crystallinity for both non-pressurized and pressurized samples. The non-pressurized sample PVDF 50 NoP shows about 40.6% crystalline content, up from 38.7% at 30 °C. This indicates that even a modest thermal treatment can enhance crystallization, likely by providing the polymer chains enough mobility to arrange into crystalline domains more readily. The amorphous content correspondingly drops to ~59.4% at 50 °C (NoP). The β-phase fraction in PVDF 50 NoP remains very low (~3.0%), essentially unchanged within experimental error from the 2.7% at 30 °C. This means that although total crystallinity increased slightly from 30 °C to 50 °C without pressure, the fraction of those crystals that adopt the β-phase did not significantly rise – the new crystalline content formed at 50 °C is still predominantly α-phase. Such behavior is consistent with PVDF's natural tendency to crystallize into the α-form under quiescent conditions, especially at relatively low temperatures where the kinetics favor the more stable phase.

Under pressure at 50 °C, a somewhat different outcome is observed. The PVDF 50 P sample has a crystalline content of ~40.3%, essentially on par with the no-pressure sample at 50 °C (the slight difference is within a fraction of a percent). Thus, by 50 °C the applied pressure no longer significantly suppresses overall crystallinity – both samples crystallize to a similar degree (~40% crystalline) at this temperature. However, the β-phase percentage in PVDF 50 P is about 4.0%, which is modestly higher than the ~3.0% in the no-pressure case. This persistent enhancement of β-phase formation under pressure (now a difference of roughly 1 percentage point in β-phase

content compared to the NoP sample) suggests that even at mild annealing temperatures, an applied pressure biases the polymorphic outcome slightly toward the β-phase. In absolute terms the effect at 50 °C is still small – the pressurized sample is ~96% α-phase vs. 97% in the non-pressurized sample – but it establishes a trend that will become more pronounced at higher temperatures. In summary, by 50 °C both samples have gained crystallinity relative to room temperature, and pressure-treated PVDF shows a comparable crystallinity with a subtly higher portion of β-phase than its ambient-pressure counterpart.

50°C NoP			50°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
40.6	59.4	3.0	40.3	59.7	4.0

Table 3: Phase Composition of PVDF at 50 °C With and Without Applied Pressure (10,000 lbs)

Moderate Temperatures (70 °C and 90 °C)

70 °C: Further increasing the processing temperature to 70 °C continues to raise the crystallinity of PVDF in the non-pressurized condition. PVDF 70 NoP is about 41.6% crystalline, a slight uptick from ~40.6% at 50 °C. This trend of gradually increasing crystalline fraction with annealing temperature (for NoP samples) reflects the enhanced mobility of polymer chains at higher temperature, allowing more perfect or additional crystals to form. However, an interesting feature at 70 °C is observed in the β-phase content for the no-pressure sample: PVDF 70 NoP contains only ~2.6% β-phase, slightly lower than the ~3.0% measured at 50 °C. In fact, 70 °C represents a local minimum in β-phase fraction for the non-pressurized series (down from 3.0% at 50 °C to 2.6% at 70 °C). This suggests that at 70 °C under ambient pressure, the conditions particularly favor the α-phase crystallization to the near exclusion of β-phase. It is possible that 70 °C is within a temperature regime where the kinetics or thermodynamics of crystallization lead to predominantly α-phase formation, causing the already minor β-phase to become even less

prevalent. Essentially, as the crystalline content grows, it is almost entirely adding α-phase crystals at the expense of any β-phase ordering, resulting in the lowest observed β-phase percentage in the no-pressure samples around this temperature.

In stark contrast, the pressurized PVDF sample at 70 °C (PVDF 70 P) shows a very different behavior concerning β-phase. The overall crystallinity of PVDF 70 P is ~40.1%, which is actually slightly lower than the 41.6% of 70 NoP (indicating pressure may still mildly hinder full crystallization at this temperature). But notably, PVDF 70 P contains approximately 6.6% β-phase, a dramatic increase compared to both its no-pressure counterpart (2.6%) and to its own β-phase content at 50 °C (4.0%). This means that under pressure, raising the temperature from 50 °C to 70 °C led to a significant jump in the fraction of β-phase crystals (from 4% to 6.6%). The pressurized 70 °C sample has over twice the β-phase content of the non-pressurized 70 °C sample. Such a result indicates that pressure has a strong synergistic effect with this moderate annealing temperature to promote the formation of the polar β-phase. In practical terms, while ~60% of PVDF 70 P is still amorphous and ~33.5% is α-phase, a measurable portion (~6.6%) is β-phase – a polar phase content considerably higher than seen at lower temperatures or without pressure. This demonstrates that the combination of pressure and a 70 °C treatment drives more PVDF chains into the all-trans conformation characteristic of β-phase, even though the total crystallinity under pressure hasn't exceeded that of the no-pressure sample. It's a clear divergence in polymorphic outcome induced by pressure by the time we reach 70 °C.

70°C NoP			70°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
41.6	58.4	2.6	40.1	59.9	6.6

Table 4: Phase Composition of PVDF at 70 °C With and Without Applied Pressure (10,000 lbs)

90 °C: At 90 °C, the non-pressurized PVDF continues its trend of increasing crystallinity, though in this case the crystallinity increase from 70 °C is minimal. PVDF 90 NoP is also about 41.6% crystalline (virtually the same as at 70 °C, indicating a plateau in crystallinity around the 40–42% range for these mid-range temperatures). The lack of a large jump in crystallinity between 70 °C and 90 °C suggests that by ~70 °C the polymer might have crystallized as much as it readily can without entering a new regime of chain mobility. Regarding phases, the β-phase content in PVDF 90 NoP remains very low (~2.2%), which is consistent with the observation at 70 °C. In fact, 90 NoP still has the β-phase at only around 2.2%, about the same low level (if not slightly lower) as 70 NoP's 2.6%. This confirms that in the absence of pressure, the β-phase is highly suppressed at these intermediate temperatures – the polymer is crystallizing almost entirely into the α-phase structure at 70–90 °C. The small absolute changes (2.6% to 2.2%) are within a narrow band of low β content, so one can say broadly that no significant β-phase development occurs in no-pressure samples up to 90 °C; the β-fraction hovers around 2–3% or below, making the crystalline component overwhelmingly α-phase.

For the pressurized sample at 90 °C (PVDF 90 P), the total crystallinity is ~40.8%, which is very close to that of the no-pressure sample (41.6%). This indicates that by 90 °C, pressure is having little effect on how much of the polymer crystallizes – both samples are roughly 58–59% amorphous, 41–42% crystalline. The important difference lies again in phase composition: PVDF 90 P retains a β-phase content of about 6.6%, essentially the same high level observed at 70 P (~6.6%). In other words, the pressurized sample maintained a substantial β-phase fraction (~6–7%) at 90 °C, whereas the no-pressure sample at the same temperature had only ~2% β-phase. The fact that PVDF 90 P's β-phase percentage (6.6%) is nearly identical to PVDF 70 P's (6.6%) suggests that under pressure, the β-phase fraction might have plateaued or stabilized

in this range for the 70–90 °C window. This demonstrates that moderate temperatures (70–90 °C), when combined with applied pressure, yield a significantly higher proportion of polar β-phase in the crystalline microstructure than the same temperatures without pressure.

90°C NoP			90°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
41.6	58.4	2.2	40.8	59.2	6.6

Table 5: Phase Composition of PVDF at 90 °C With and Without Applied Pressure (10,000 lbs)

Elevated Temperatures (110 °C and 130 °C)

110 °C: By 110 °C, the PVDF samples show further changes consistent with increased chain mobility at higher annealing temperatures. The non-pressurized PVDF 110 NoP sample reaches about 42.9% crystallinity, a slight increase from ~41.6% at 90 °C. This continues the slow upward trajectory of crystallinity in the no-pressure condition. The amorphous content correspondingly falls to ~57.1%. Interestingly, the β-phase fraction in PVDF 110 NoP rises a bit to ~3.0% (from ~2.2% at 90 °C). Although 3.0% is still a very small fraction, this uptick suggests that at 110 °C (still well below the melting point of PVDF), there may be a modest increase in the tendency to form β-phase compared to the pronounced minimum seen around 70–90 °C. The β-phase content of ~3% at 110 °C is comparable to what it was at 50 °C in the no-pressure case, implying that the suppression of β-phase observed around 70–90 °C has alleviated slightly by 110 °C. One possible interpretation is that at 110 °C, the polymer chains have enough mobility to start sampling different conformations, allowing a small fraction to crystallize in the β-form again, even as α-phase remains dominant.

For the pressurized sample at 110 °C (PVDF 110 P), the crystallinity is ~43.2%, essentially the same as the no-pressure case (42.9%). This marks an interesting point: at 110 °C the application

of pressure has effectively no impact on the overall degree of crystallinity – both samples crystallize to ~43%. This parity suggests that by the time the annealing temperature is fairly high (110 °C), the kinetics of crystallization are fast and favorable enough that pressure cannot further increase or decrease the total crystallized fraction appreciably. The effect of pressure is therefore more evident in phase composition: PVDF 110 P has about 6.1% β-phase, only slightly lower than the ~6.6% at 90 P. So under pressure, the β-phase fraction remains elevated (~6% range) at 110 °C, which is roughly double the β-phase seen in the no-pressure sample at 110 °C (3.0%). In other words, even at 110 °C, pressure is managing to maintain a higher β-phase content in the crystals that form. The pressurized sample still consists mostly of α-phase crystals (since ~93.9% of the material is either α-phase crystalline or amorphous), but the minority β-phase portion is significant compared to the no-pressure scenario. The slight drop from 6.6% at 90 P to ~6.1% at 110 P might indicate a small reduction in β-phase propensity as temperature climbs further, but the value remains in the same order of magnitude. Thus, at 110 °C, pressure and no-pressure samples have converged in crystallinity but diverged in polymorph distribution, with pressure continuing to favor the β-phase about two-fold more than ambient conditions.

110°C NoP			110°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
42.9	57.1	3.0	43.2	56.8	6.1

Table 6: Phase Composition of PVDF at 110 °C With and Without Applied Pressure (10,000 lbs)

130 °C: At 130 °C, which is approaching the upper end of the typical crystallization temperature range for PVDF (but still below its melting point), the no-pressurized sample PVDF 130 NoP shows a more substantial increase in crystallinity. PVDF 130 NoP is about 45.2% crystalline, up from ~42.9% at 110 °C. This is one of the larger jumps in crystallinity observed so far in the no-pressure series, suggesting that between 110 °C and 130 °C the polymer's ability to reorder

into crystals significantly improves. Indeed, 130 °C is often near the optimal crystallization temperature for PVDF's α-phase in many cases, allowing extensive crystal growth and perfection. The amorphous fraction in 130 NoP correspondingly drops to ~54.8%. Despite this rise in total crystallinity, the β-phase content in PVDF 130 NoP decreases slightly to ~2.6% (from 3.0% at 110 °C). This reduction is subtle, but it implies that the new crystalline content gained between 110 °C and 130 °C is overwhelmingly α-phase, diluting the β-phase fraction. In fact, 2.6% is nearly as low as the minimum we saw at 70 °C for no-pressure (2.6% at 70 °C as well). The data suggest that at ~130 °C under no pressure, PVDF is crystallizing in the α-phase almost exclusively, which is consistent with the notion that 130 °C is near the peak crystallization rate for α-phase. The small β-phase fraction that is present (~2–3%) likely represents either remnants of β-phase formed at lower temperatures or a minor concurrent β-phase crystallization that never exceeds a few percent. Overall, PVDF 130 NoP is highly crystalline (~45%) but contains only about 2.6% β-phase, reaffirming that the polymer remains dominated by the non-polar α-phase under these conditions.

In the pressurized counterpart at 130 °C (PVDF 130 P), the crystallinity reaches ~43.7%, which is actually a bit lower than the no-pressure 130 °C case (45.2%). This indicates that even at 130 °C, applying pressure results in a slightly lower total crystallinity than annealing without pressure. The difference is modest (about 1.5 percentage points), but it's consistent with the earlier trend that, at most temperatures, pressure tends to either maintain or somewhat reduce the crystallinity relative to the maximum achievable at that temperature without pressure. It's possible that pressure inhibits the growth of some crystalline domains or favors smaller crystals, resulting in a marginally lower crystallinity. Importantly, however, PVDF 130 P continues to show a high β-phase fraction – about 6.8% of the sample is β-phase at 130 °C under pressure.

This is actually slightly higher than the 6.1% at 110 P, marking another local maximum in β-phase content for the pressurized series. In fact, 6.8% is the highest β-phase fraction observed so far in the pressurized samples (surpassing the ~6.6% at 70–90 °C). This suggests that at 130 °C, pressure is still strongly promoting β-phase formation, even as no-pressure conditions at the same temperature yield almost none of it. The divergence is stark: PVDF 130 P has ~6.8% β-phase while PVDF 130 NoP has ~2.6%. Thus, under pressure at 130 °C, PVDF forms roughly 2.5 times more β-phase than it does without pressure. We can infer that pressure not only biases the polymorph selection, but perhaps at 130 °C the combination of high temperature and pressure allows some additional β-phase to nucleate or persist where it otherwise would not. The data up to 130 °C demonstrate that pressure-treated PVDF consistently contains on the order of 5–7% β-phase across a broad range of sub-melting temperatures (70–130 °C), whereas non-pressurized PVDF under the same thermal history contains only ~2–3% β-phase. The total crystallinity in the pressurized samples remains slightly lower or equal to the no-pressure ones in this range, indicating that pressure's main effect is on phase composition rather than quantity of crystals (except at the very low end where it slightly reduces crystallinity).

130°C NoP			130°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
45.2	54.8	2.6	43.7	56.3	6.8

Table 7: Phase Composition of PVDF at 130 °C With and Without Applied Pressure (10,000 lbs)

Near-Melting Effects (150 °C and 170 °C)

150 °C: By 150 °C, PVDF is being annealed at a very high temperature, though still below the typical melting point (which for PVDF α-phase is around 165–170 °C). The non-pressurized PVDF 150 NoP sample reaches a crystallinity of ~46.9%, continuing the upward trend (slightly higher than 45.2% at 130 °C). This suggests that even as we approach the melting range, if the

polymer is not fully melted, it can achieve somewhat higher crystallinity. The amorphous portion is now down to ~53.1%. Interestingly, PVDF 150 NoP shows a β-phase content of ~3.4%, which is an increase compared to the 2.6% at 130 °C. In fact, 3.4% is the highest β-phase fraction observed so far in the no-pressure series (marginally exceeding the ~3.0% seen at 50 °C and 110 °C). While this is still a very small fraction, it indicates a slight uptick in β-phase at this elevated temperature. One possible explanation is that at 150 °C (just below the melt onset), a small portion of α-phase crystals might be thermally converting to β-phase, or some β-phase is able to nucleate as the mobility is extremely high but full melting is not reached. Alternatively, slight measurement variability could account for the small difference. Nonetheless, the key point is that the β-phase remains a minor component (~3%) in PVDF 150 NoP, with the vast majority of crystalline material being α-phase. The structure is highly crystalline (~47%) overall, but still predominantly non-polar in character.

The pressurized sample at 150 °C (PVDF 150 P) has a crystalline content of ~44.1%, which is a few percentage points lower than the no-pressure sample's crystallinity. Again, this continues the observation that pressure tends to yield slightly less total crystallinity at a given high temperature (44.1% vs 46.9% here). The more striking difference is in β-phase content: PVDF 150 P contains about 5.7% β-phase, down somewhat from 6.8% at 130 P but still considerably larger than the 3.4% in 150 NoP. The slight drop in β-phase fraction from 130 P to 150 P (6.8% → 5.7%) might indicate that as the temperature nears the melting point under pressure, there is a minor reduction in the stability or fraction of β-phase. It could be that some β-phase crystals start to revert to α-phase or melt away at this high temperature, causing a dip. However, 5.7% is still a significant polar phase content compared to what is seen without pressure. Thus, at 150 °C, pressure-fed PVDF retains a notable β-phase presence (~5–6%), whereas the no-pressure PVDF has only

~3%. The overall trend up to 150 °C shows that the no-pressure samples have steadily rising crystallinity and a β-phase fraction remaining very low (mostly 2–3%, slightly higher at 150 °C), whereas the pressurized samples have slightly lower crystallinity and a consistently higher β-phase fraction (peaking around 6–7% in the 70–130 °C range and slightly tapering at 150 °C). At 150 °C, both samples are on the verge of the melting transition, which sets the stage for a major structural change at 170 °C.

150°C NoP			150°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
46.9	53.1	3.4	44.1	55.9	5.7

Table 8: Phase Composition of PVDF at 150 °C With and Without Applied Pressure (10,000 lbs)

170 °C: The treatment at 170 °C represents a critical point in the thermal analysis of PVDF. This temperature is at or just above the typical melting temperature for PVDF's α-phase crystals (often reported around 167–172 °C). Therefore, exposure to 170 °C likely induces partial or full melting of the crystalline regions in the samples, especially if held for some time. The XRD results reflect a dramatic change in the material's structure at this condition, particularly for the pressurized sample. In the non-pressurized sample PVDF 170 NoP, the crystallinity has continued to increase, reaching ~48.7% crystalline. This is the highest crystallinity seen so far in the no-pressure series, consistent with the idea that annealing up to just before melting can maximize the crystalline fraction (through processes like crystal perfection, recrystallization, or growth into formerly amorphous regions). The material is now nearly half crystalline and half amorphous (51.3% amorphous). The β-phase content in PVDF 170 NoP is ~2.8%, which is slightly lower than the 3.4% at 150 °C. This slight drop might suggest that as the sample hits the melting threshold without an external pressure, there is no further increase in β-phase – in fact the fraction falls back into the ~2–3% baseline range. It's possible that any β-phase that might

have formed at 150 °C does not survive as temperature climbs to 170 °C; the structure likely reorganizes to favor α-phase or simply melts away less stable crystallites. In any case, PVDF 170 NoP remains predominantly α-phase (over 45% of the material is α-phase crystalline, given total crystallinity 48.7% and β-phase 2.8%), and the β-phase is still a negligible minority. There is no obvious anomaly in the no-pressure sample aside from achieving high crystallinity – the β-phase fraction staying low is expected since without special processing, PVDF typically crystallizes in the α form even upon cooling from near melt.

The pressurized sample at 170 °C, however, shows an anomalous and pronounced shift in phase composition. PVDF 170 P is measured to be only ~42.0% crystalline, which is significantly lower than the no-pressure sample's crystallinity at the same temperature (48.7%). In fact, the crystallinity of the pressurized sample drops compared to what it was at 150 P (44.1%), whereas the no-pressure crystallinity increased from 46.9% to 48.7%. This suggests that under pressure, heating to 170 °C caused a partial melting or dissolution of crystalline structures that was not fully recovered upon cooling – effectively, the sample lost some crystalline content. This makes sense: at 170 °C, PVDF crystals (especially α-phase crystals) would start to melt. Under pressure, the melting point can be somewhat elevated, but even so, the data imply that a considerable portion of the crystals did melt or become disordered. The amorphous content in PVDF 170 P is consequently about 58%, much higher than in 170 NoP (~51%). What's even more remarkable is that despite having less overall crystallinity, the β-phase content in PVDF 170 P skyrockets to ~9.7%. This is by far the highest β-phase fraction observed in any sample in this study – roughly one tenth of the material is β-phase in the pressurized 170 °C sample. Compared to the mere 2.8% β-phase in 170 NoP, this is a more than threefold increase in β-phase fraction due to the application of pressure at 170 °C. In fact, even in absolute terms, PVDF 170 P

has a greater absolute amount of β-phase (9.7% of the sample) than any other sample, pressurized or not.

This striking result indicates that applying pressure at a temperature right around PVDF's melting point induces a significant β-phase transformation. One possible interpretation is that under pressure, some of the PVDF that might have melted or re-crystallized underwent a phase transformation from α to β. The loss of overall crystallinity suggests many original crystals (likely α) were destabilized by the heat, but apparently the conditions favored re-nucleation or reorganization into β-phase for a portion of the polymer. Pressure often promotes close packing; in PVDF, the all-trans β-phase is a tightly packed conformation. In essence, pressure + near-melt temperature caused a polymorphic shift, sacrificing some crystalline order (hence lower total crystallinity) but greatly enriching the β-phase content of what did crystallize. This phenomenon has been noted in literature – high-pressure annealing just below the melting point can result in enhanced β-phase, whereas processing above the melt yields mostly α-phase. Our observations are consistent with such findings: the PVDF 170 P sample contains an unusually high β-phase fraction, in line with reports that pressure can facilitate β-phase formation when crystallization occurs below the melting point. Meanwhile, the corresponding no-pressure sample doesn't show this effect, highlighting that pressure is the key factor enabling the β-phase in this regime.

170°C NoP			170°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
48.7	51.3	2.8	42.0	58.0	9.6

Table 9: Phase Composition of PVDF at 170 °C With and Without Applied Pressure (10,000 lbs)

Post-Melting High Temperatures (190 °C and 210 °C)

Beyond 170 °C, PVDF samples were treated at 190 °C and 210 °C. These temperatures are well above the normal melting point of PVDF, meaning that during the treatment the polymer would be in a molten state (fully amorphous liquid) before cooling and recrystallizing. The XRD data for samples treated at these temperatures therefore reflect the crystallization behavior of PVDF upon cooling from a melt, for both non-pressurized and pressurized conditions. 190 °C: The non-pressurized sample PVDF 190 NoP, after being heated to 190 °C and cooled, shows a crystallinity of ~49.5%, which is nearly as high as the 48.7% at 170 NoP. Essentially, allowing the polymer to fully melt at 190 °C and then recrystallize (presumably upon cooling to room temperature) results in a highly crystalline solid (~50% crystalline). This level of crystallinity is consistent with or slightly higher than the maximum achieved without melting (48.7% at 170 °C), suggesting that a full melt–recrystallization did not diminish the crystalline fraction and may have even allowed slight perfection (49.5% at 190 vs 48.7% at 170). The amorphous content in 190 NoP is ~50.5%. The β-phase content in PVDF 190 NoP is measured at ~3.7%, which interestingly is a bit higher than what was observed at 170 NoP (2.8%) and is actually the highest β-fraction seen in the no-pressure series. While 3.7% is still small, its increase relative to pre-melt conditions might indicate that quenching or crystallizing from a melt at 190 °C allows a slight formation of β-phase in the otherwise α-dominated matrix. It is known that rapid crystallization or certain thermal histories can trap a small amount of β-phase even without stretching, so this ~3–4% could be a result of the specific cooling conditions or minor stress as the sample solidified. Nonetheless, the PVDF 190 NoP sample remains predominantly α-phase (~46% of the material if ~3.7% is β out of ~49.5% crystalline) with the vast majority of crystals being α. The β-phase presence, while a tad higher than at lower temps, is still marginal. There are no extraordinary anomalies in the no-pressure 190 °C case aside from it retaining high

crystallinity and a low polar phase fraction – essentially the microstructure one would expect from PVDF cooled from a typical melt.

The pressurized sample PVDF 190 P, on the other hand, exhibits distinct differences owing to the combination of high temperature and pressure during crystallization. PVDF 190 P ends up ~45.4% crystalline, which is noticeably lower than the 49.5% of 190 NoP. This follows the prior trend: when crystallizing PVDF from the melt under pressure, it appears to form slightly less total crystalline content than when crystallizing without pressure. (One reason could be that pressure might suppress the mobility upon cooling or favor fewer but larger spherulites that don't fully fill the volume, leaving somewhat higher amorphous content.) The amorphous portion in 190 P is ~54.6%. More striking is the β-phase content in PVDF 190 P: only ~1.3%. This is an extremely low β-phase fraction, even lower than what we saw in any of the lower temperature pressurized samples. In fact, at 190 °C under pressure, the β-phase that was so prominent at 170 °C has virtually disappeared – dropping from 9.7% at 170 P to just 1.3% at 190 P. Such a drastic reduction indicates that when PVDF is fully melted and then recrystallized under pressure, the resulting crystalline phase is almost exclusively the α-phase (non-polar). Essentially, the pressurized 190 °C sample behaves similarly to a typical melt-crystallized PVDF, with pressure not able to retain the high β-phase content once the polymer has been liquefied. This aligns with literature observations that if the processing (annealing) temperature far exceeds the melting point, PVDF will crystallize into the stable α-phase upon cooling even under pressure. Thus, by 190 °C we see that the effect of pressure in promoting β-phase is nullified once the polymer has been fully melted.

190°C NoP			190°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%

49.5	50.5	3.7	45.4	54.6	1.3

Table 10: Phase Composition of PVDF at 190 °C With and Without Applied Pressure (10,000 lbs)

210 °C: Finally, at the highest temperature studied, 210 °C, the behavior established at 190 °C continues. PVDF 210 NoP, after melting and recrystallizing, attains the highest crystallinity observed in the whole series: ~50.9% crystalline, with ~49.1% amorphous. This is essentially the upper limit of crystallinity under these conditions (just over 50%). The β-phase content in PVDF 210 NoP is ~3.2%, slightly lower than the 3.7% at 190 NoP but in line with the general ~3% baseline for no-pressure samples. This again underscores that cooling from a full melt without pressure yields only a minimal β-phase fraction (on the order of a few percent), and the majority of crystals are α-phase. The fact that 210 NoP has about the same β% as some of the lower temperature no-pressure samples indicates that no extraordinary β-phase generation occurs simply by going to a higher melt temperature; the outcome is controlled by PVDF's innate crystallization preference for α-phase.

For the pressurized sample at 210 °C (PVDF 210 P), the total crystallinity is ~45.9%, very similar to what was seen at 190 P (45.4%). The no-pressure sample still has a higher crystallinity (~51%), so this difference persists at 210 °C: pressure leads to a slightly lower crystalline fraction upon solidification. The β-phase content in PVDF 210 P remains extremely low at ~1.4%, essentially unchanged from the 1.3% at 190 P. This confirms that at temperatures well above the melt (210 °C in this case), the presence of pressure during crystallization does not foster any significant β-phase – the structure is overwhelmingly α-phase, just as at 190 P. The polymer under pressure at 210 °C crystallizes into its stable form and the special conditions

needed to produce β-phase (like those at 170 P) are absent because the material had been fully molten. In summary, PVDF 210 P is ~46% crystalline, ~54% amorphous, with only ~1–1.5% β-phase, which is effectively negligible. This mirrors the 190 P result and indicates reproducibility of the fact that high-pressure, high-temperature treatment yields almost no β-phase.

210°C NoP			210°C P		
Crystalline%	Amorphous%	Beta Phase%	Crystalline%	Amorphous%	Beta Phase%
50.8	49.2	3.2	45.9	54.1	1.4

Table 11 : Phase Composition of PVDF at 210 °C With and Without Applied Pressure (10,000 lbs)

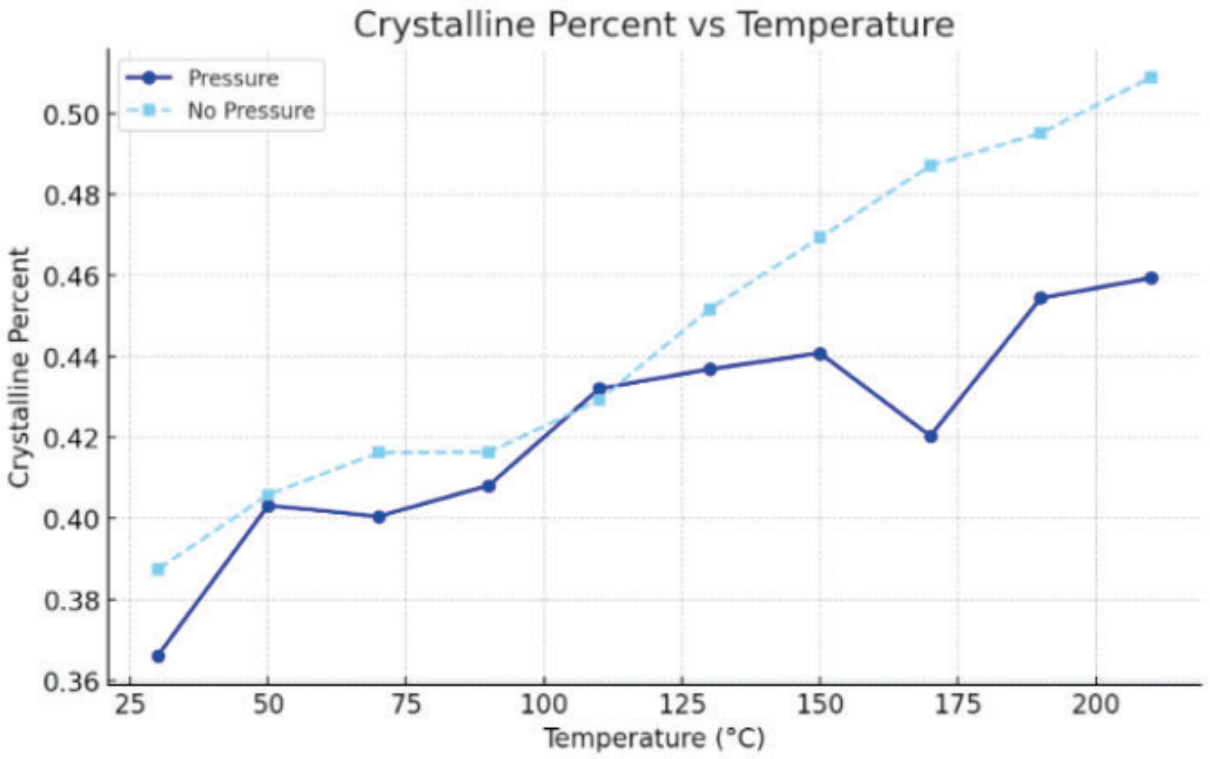

Figure 27: Temperature-Dependent Crystalline Fraction of PVDF Samples With and Without Pressure

The updated Crystalline Percent vs Temperature chart clearly shows that PVDF's overall crystallinity rises with annealing temperature under both conditions. In the non-pressurized series (dashed light-blue line), crystallinity increases steadily from about 38% at 30 °C to roughly 51% by 210 °C. The pressurized samples (solid blue) follow the same upward trend but are consistently a few percentage points lower at each temperature. Notably, the pressurized curve shows a slight plateau around 125–150 °C and even a small dip at 175 °C, whereas the no-pressure curve climbs almost monotonically. In short, the line graph visualizes that higher temperatures drive more crystal formation in PVDF, and that applying 10,000 lbs pressure during crystallization marginally suppresses the total crystalline fraction. The figure thus reinforces the textual finding that temperature is the dominant factor for crystallization and that pressure produces only a subtle reduction in crystallinity across the range.

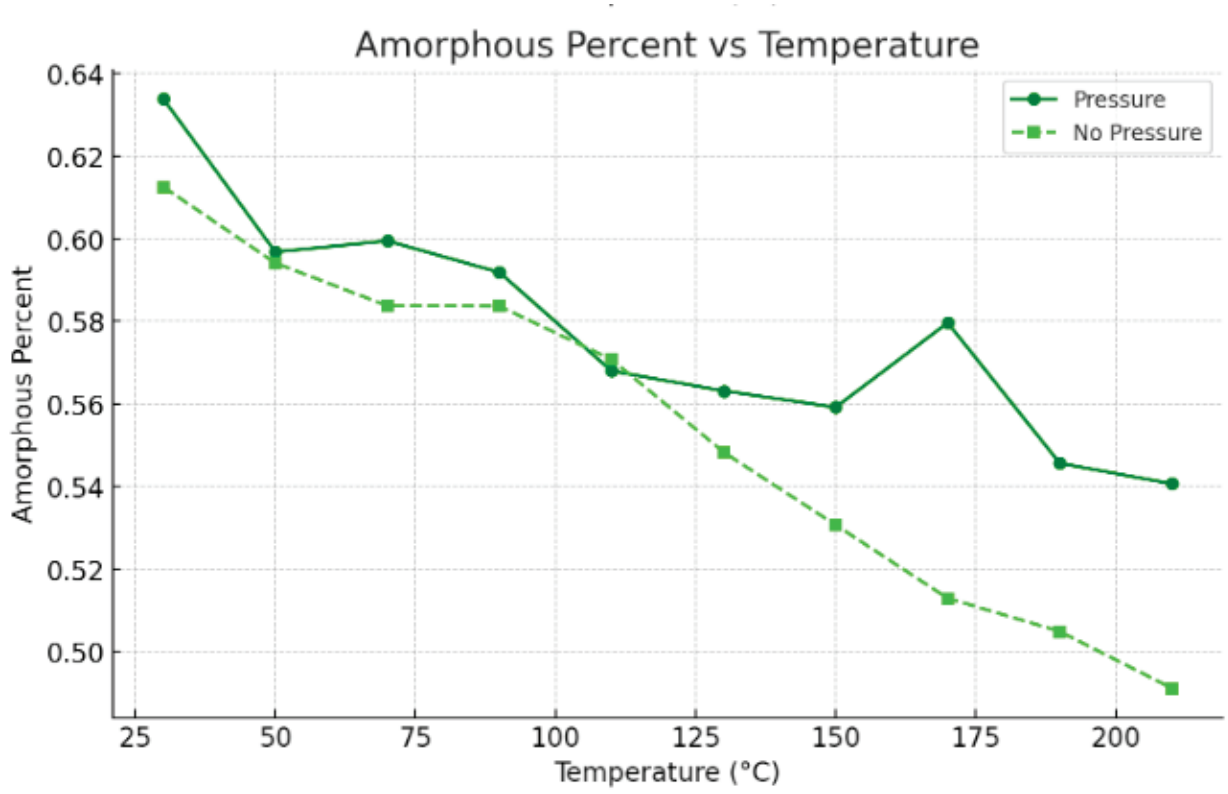

Figure 28: Amorphous Content of PVDF as a Function of Thermal Treatment Under Pressurized and Non-Pressurized Conditions

Correspondingly, the Amorphous Percent vs Temperature plot (green lines) is essentially the mirror image of crystallinity: amorphous content declines as temperature rises. In the no-pressure case (dashed green), amorphous fraction falls steadily from about 62% at 30 °C to roughly 50% at 210 °C. Under pressure (solid green), the amorphous content begins slightly higher, decreases overall to about 54% by 210 °C, but with minor fluctuations – notably a small local increase around 175 °C. These trends emphasize the complementary relationship: as crystals form at higher temperature, the amorphous proportion necessarily drops. The graph clearly quantifies this conversion. Comparing conditions, the pressurized samples retain a slightly higher amorphous fraction at each temperature, consistent with their slightly lower crystallinity. Overall, the chart supports the text's observation that temperature-driven chain mobility converts amorphous regions into crystals, and that pressure slightly delays this transformation, leaving more disorder in the pressurized samples at a given temperature.

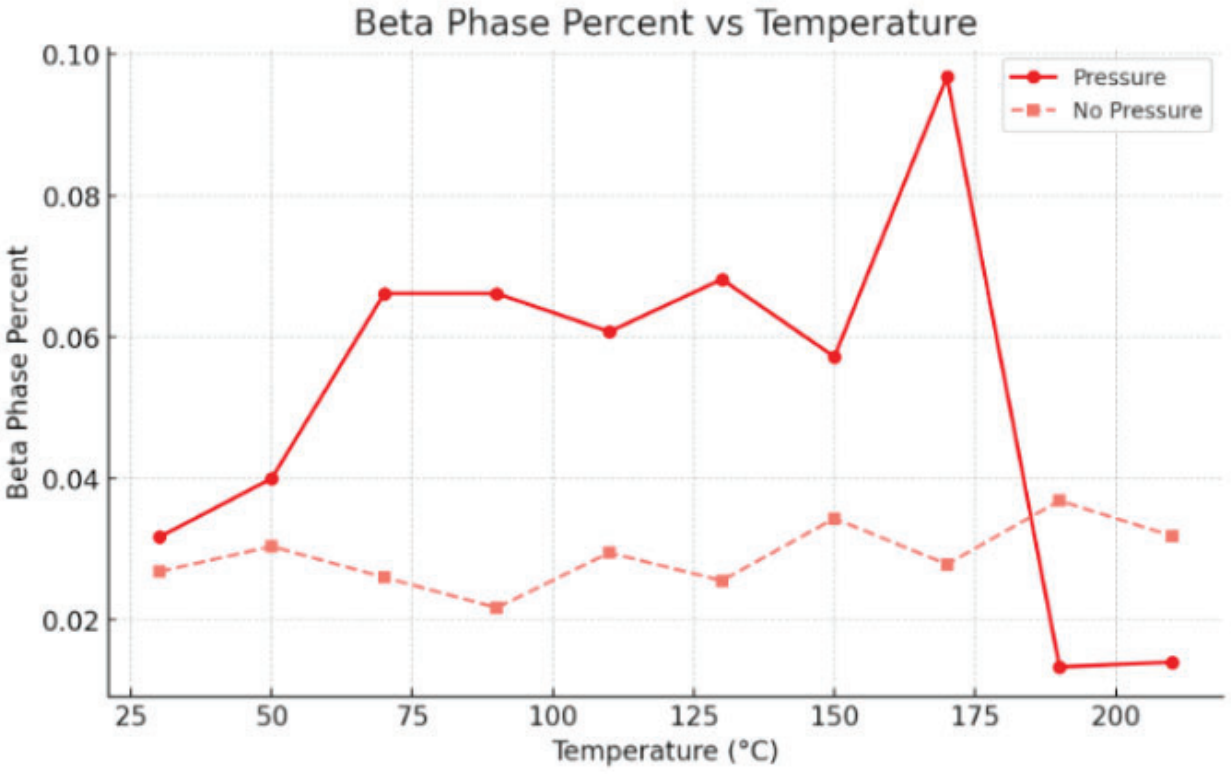

Figure 29: XRD-Derived β-Phase Content in PVDF Across Temperature Treatments With and Without Applied Pressure

The Beta-Phase Percent vs Temperature graph highlights the minor but temperature-sensitive fraction of electroactive β-crystallites. Both curves remain low across all temperatures. Under pressure (solid red), the β-phase fraction grows from ~3% at 30 °C to a local maximum near 9–10% around 170 °C, before plunging back toward ~1–2% by 210 °C. In contrast, the no-pressure samples (dashed coral line) hover roughly flat at ~2–3% β-phase at all temperatures. This visual underscores what the tabulated XRD data show: pressurization significantly enhances β-phase formation at intermediate temperatures while having little effect at the extremes. The sharp spike at 175 °C for the pressurized series reflects rapid β-crystal generation just before the melt, whereas the subsequent drop illustrates that once fully molten (above ~190 °C), the β-fraction collapses. The figure thus makes explicit that although β-phase remains a small subset of total crystallinity, its fraction is markedly higher under pressure at mid-range temperatures – qualitatively supporting the discussion that combined high pressure and near-melt conditions briefly stabilize more β-phase.

Fourier-Transform Infrared (FTIR) Data

Fourier-transform infrared (FTIR) spectroscopy was used alongside XRD to characterize the crystalline phases of PVDF and to verify the phase assignments made by XRD. FTIR is sensitive to the molecular conformation of PVDF: different crystalline phases produce distinct vibrational absorption bands. In particular, the non-polar α-phase is identified by a strong band near 763 cm^{-1}, attributed to CF_2 bending and CH_2 rocking modes in the TGTG′ chain conformation, along with auxiliary α-phase bands at ~795 cm^{-1}. The polar β-phase is most clearly indicated by an

absorption band around 840 cm^{-1}, arising from CH_2 rocking and CF_2 stretching vibrations in the all-trans (TTTT) chain conformation unique to β-PVDF. (A weaker band near 510 cm^{-1} is also exclusive to the β-phase, but this region can be obscured by other signals.) By monitoring the 763 cm^{-1} (α marker) and 840 cm^{-1} (β marker) peaks in each FTIR spectrum, we qualitatively and quantitatively assessed changes in phase content. In fact, a known semi-quantitative method to estimate the β-phase fraction, F(β), uses the absorbance intensities at these two wavelengths.

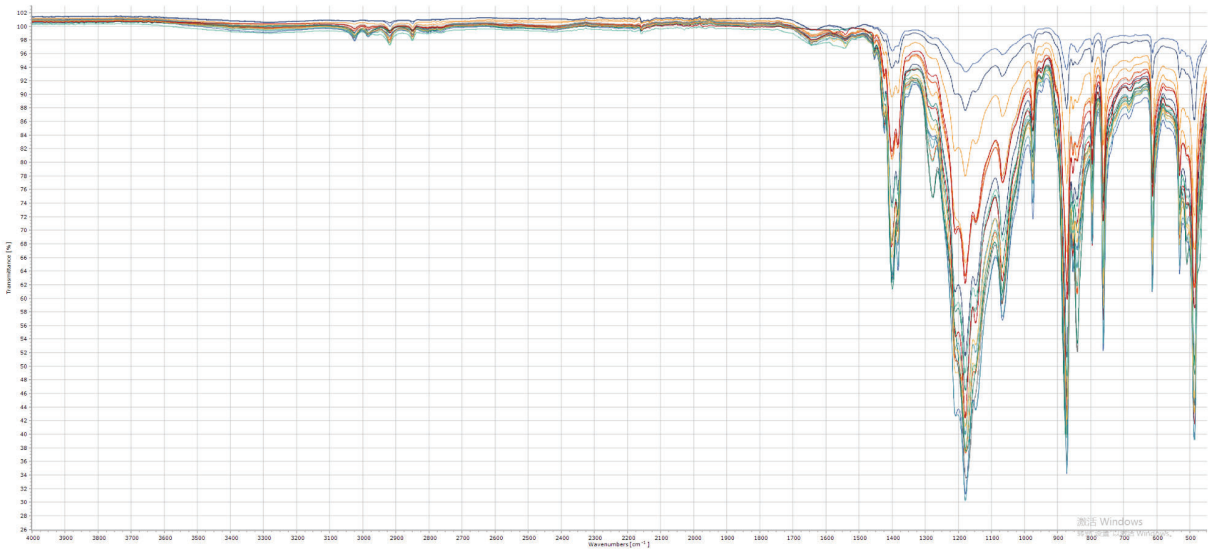

Figure 30: Overlay of FTIR Spectra for PVDF Samples Across All Thermal Conditions (30 °C to 210 °C)

Non-Pressurized Samples (NoP)

In the NoP condition, the β-phase content peaks dramatically at 30 °C (~67%), likely reflecting the quenched state where the polymer chains are rapidly frozen into a metastable, partially oriented state. This high β fraction at low temperature is not strongly supported by XRD, which measured only ~2.7% β at 30 °C NoP. The discrepancy likely arises because FTIR can detect conformational order even in small or imperfect crystalline domains, whereas XRD is sensitive only to long-range crystalline order. Thus, the elevated β signal at 30 °C may result from local

β-like chain segments that are insufficiently ordered to yield a strong β reflection in XRD but are still optically active in IR.

As temperature increases from 50 °C to 130 °C, the β-phase fraction in NoP samples declines sharply and stabilizes around 30–35%, suggesting a transition to predominantly α-phase crystallization as chain mobility improves. This trend directly matches the XRD data, which consistently showed very low β-phase content (typically 2–3%) and rising total crystallinity dominated by α-phase throughout this temperature range. The low β-phase fractions in both techniques confirm that thermal annealing without applied pressure favors α-phase formation.

Interestingly, a modest increase in FTIR β content is observed again between 150–210 °C, peaking slightly at ~35% by 210 °C. This rise loosely mirrors the XRD observation that β-phase fraction in NoP samples reaches a minor peak (~3.7% at 190 °C) following full melt-recrystallization. This may be due to rapid quenching from high temperature trapping a small amount of β-conformation. Still, both FTIR and XRD confirm that NoP samples remain largely α-phase dominated at all temperatures ≥50 °C.

Pressurized Samples (P)

In the pressurized series, FTIR shows a more stable and elevated β-phase fraction across most temperatures. After an initial dip at 50 °C (~40%), the β content increases steadily to a maximum of ~53% at 90 °C, indicating effective pressure-assisted promotion of β-phase nucleation. This coincides with the XRD data, which showed β-phase content increasing from ~4% (50 °C P) to ~6.6% (90 °C P). The discrepancy in magnitude (FTIR shows higher β%) can again be explained

by FTIR's sensitivity to local chain conformation, even in partially ordered or nanocrystalline regions.

After 90 °C, the FTIR β content gradually decreases to ~33% at 190–210 °C, following a trend consistent with the XRD β-phase drop-off observed in pressurized samples that underwent complete melting. Notably, the XRD β content peaked at 170 °C P (~9.6%), while FTIR showed a local dip at that temperature, suggesting some deviation between the techniques. One possible explanation is that the β-phase domains formed at 170 °C P are large and highly ordered, thus producing strong XRD reflections, but their overall population size is smaller—leading to a relatively reduced absorbance in FTIR.

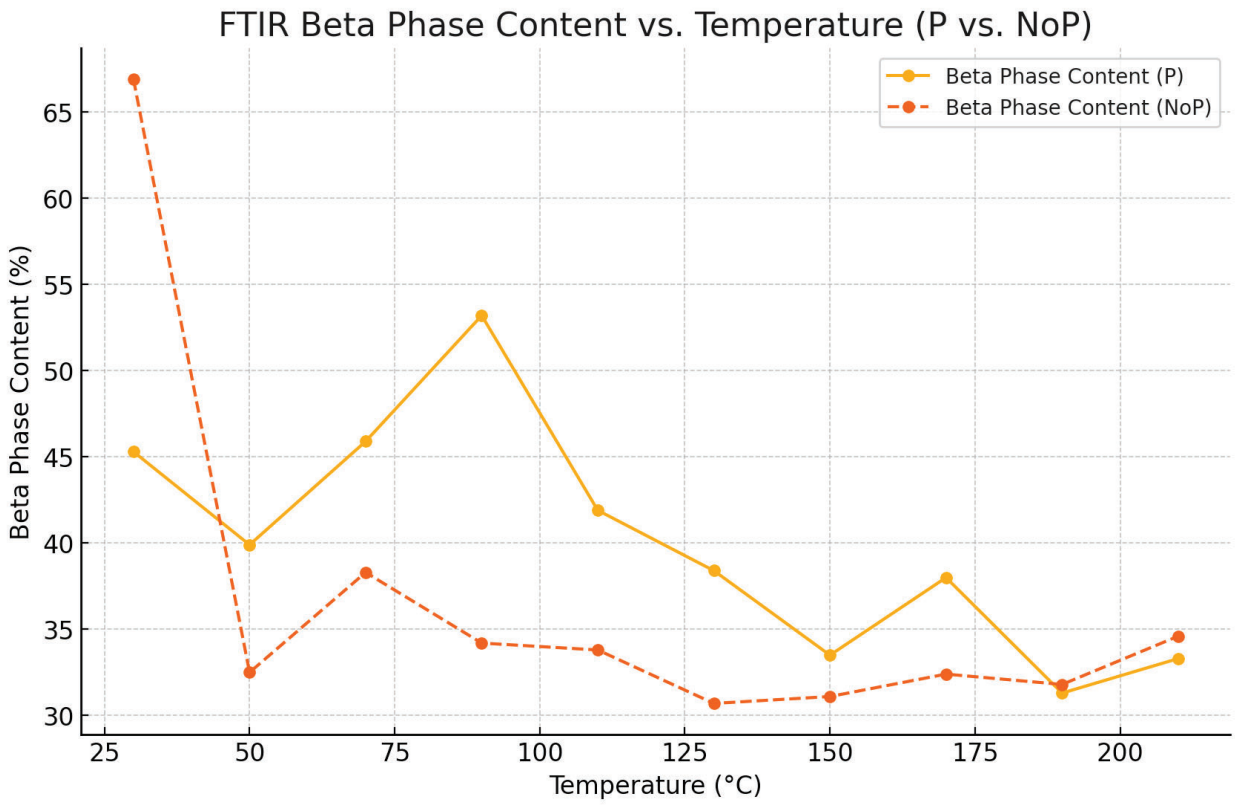

Figure 31: FTIR-Derived β-Phase Fraction of PVDF Under Thermal and Pressure Variations

Finally, the FTIR-derived β-Phase Content vs Temperature chart reveals similar trends in the two techniques, with FTIR showing much higher apparent β fractions. This visualization aligns with the XRD analysis: pressure greatly moderates the β-phase fraction and produces a pronounced peak around 90–100 °C. The chart quantifies the text's points – for example, the FTIR β-content values are plotted – and it makes clear that pressure yields a steadier, elevated β-signal across 50–150 °C. In summary, the FTIR plot corroborates that PVDF crystallized without pressure retains a large but metastable β-rich character only at the lowest temperature, whereas pressure induces a more gradual β-phase increase with temperature.

Chapter 4: Conclusions and Discussion

Discussion

The structural transitions observed in PVDF – from the α-phase to β-phase – can be understood by considering the molecular conformational changes and the thermodynamic/kinetic factors introduced by temperature and pressure. The α-phase of PVDF has a TGTG′ chain conformation (trans-gauche-trans-gauche′ sequence), which is non-polar due to cancellation of dipoles in the crystal lattice. It is the thermodynamically favored form under normal crystallization conditions because its molecular folding allows a lowest-free-energy packing at ambient pressure. The β-phase, by contrast, adopts an all-trans (TTTT) planar zigzag conformation. This arrangement maximizes the dipole alignment along the chain, making β-PVDF ferroelectric and piezoelectric. However, β-phase is typically a metastable form in PVDF; without external influences, PVDF will rarely crystallize directly into the β-phase. The challenge, then, is to overcome the energy barriers that normally favor the α-phase and instead promote the formation of β-phase domains. Our study sheds light on how thermal energy and compressive pressure together influence these energy barriers and kinetic pathways.

Role of Temperature: Temperature alone primarily affects the kinetics of PVDF's structural transitions. At higher temperatures (below the melting point), polymer chains have increased mobility and can rearrange more easily. In our no-pressure experiments, as the annealing temperature rose from 30 °C to ~110 °C, we observed an increase in overall crystallinity – this is because higher thermal energy allowed the chains to overcome kinetic hurdles to crystallization, resulting in more and larger crystalline regions (predominantly α-phase). However, temperature by itself did not significantly change the polymorph outcome: even up to 150 °C, the polymer still crystallized as mostly α-phase. There was a hint from our XRD data that at certain

intermediate temperatures (around 50–70 °C) the fraction of β-phase in no-pressure samples actually decreased slightly, creating a local minimum (~2% β at 70 °C vs ~3% at 30 °C). This suggests that at those temperatures the conditions especially favored α-phase ordering (perhaps because that temperature range allowed very efficient nucleation and growth of α crystals, leaving even less opportunity for any β ordering than either lower or slightly higher temps). In general, without pressure, raising the temperature simply helped α-phase crystallize better – it did not cause α to transform into β to any appreciable extent. Only when approaching the melting point did we see a very small uptick in β-phase in no-pressure samples (~3.4% at 150 °C, ~2.8% at 170 °C NoP, compared to ~2–3% at lower temperatures). Even these slight increases are within experimental uncertainty and may not indicate any real α→β conversion due to heat; more likely, they might result from minor kinetic effects. Overall, heat alone was insufficient to induce significant β-phase.

Role of Pressure: Applying pressure had a much more profound effect on the phase transition, affirming one of the central hypotheses of this work: that high pressure can bias the polymorphic formation towards the β-phase. There are both thermodynamic and mechanistic reasons for this. Thermodynamically, the β-phase is slightly denser than the α-phase. Under pressure, phases with lower specific volume (higher density) are favored, since the system can minimize its free energy by adopting a more compact structure. In PVDF, the all-trans conformation packs molecules more tightly, so one can intuit that pressure will stabilize the β-phase relative to the α-phase. Our results support this: even at 30 °C, a slight increase in β-phase was detected with pressure, implying that pressure lowered the free energy difference between α and β, allowing a small portion of PVDF to choose the β-phase upon crystallization. More crucial, however, is the kinetic influence of pressure. Pressure acts somewhat like an external field that constrains molecular

motion and free volume. When PVDF is crystallizing under pressure, the polymer chains are being forced closer together. This restriction in free volume likely hampers large-amplitude rotational motions about the backbone bonds that would lead to the relaxed TGTG′ conformation, and instead it "encourages" chains to crystallize in an extended conformation.

In summary, the integrated picture of the structural transitions is as follows: Under ambient conditions, PVDF crystallization yields α-phase crystals by default. When we introduce elevated temperature, we accelerate crystallization but do not change the phase – α-phase simply forms more readily. When we introduce high pressure, we alter the free energy landscape to favor a denser packing and restrict molecular rotations, thereby stabilizing the β-phase conformation to a greater extent. Pressure alone at lower temperatures can nucleate a small amount of β-phase; pressure combined with higher temperature substantially increases that amount. There appears to be an optimal window (around the onset of melting) where the combination of pressure and thermal energy allows partial transformation of existing structures and maximizes β-phase yield. Beyond that, a full melt resets the system, and the advantage of pressure is lost unless coupled with special processing. The α→β transition in PVDF is therefore not a sharp phase transition under these conditions, but rather a gradual, partial reorientation of the crystallizing polymer that can be tuned by processing parameters. Both FTIR and XRD evidence support this mechanism: FTIR showed the gradual emergence of the β conformation, and XRD quantified its extent, as pressure and temperature were varied.

Conclusion

This research has demonstrated that by tailoring processing conditions – specifically, by applying compressive pressure during thermal treatment – it is possible to influence the polymorphic

outcome of PVDF crystallization and induce a discernible amount of the electroactive β-phase that is otherwise nearly absent under standard conditions. Although the β-phase fraction achieved (up to ~10%) under our experimental pressure-temperature window is relatively limited, it decisively proves that pressure can drive PVDF's structure toward the all-trans conformation. The combination of XRD and FTIR provided a coherent verification of this phenomenon, with each method reinforcing the conclusions of the other. We conclude that the α-phase to β-phase transition in PVDF can be promoted by high pressure through a mechanism of enhanced dipole alignment and altered nucleation kinetics, even without any stretching or external electric field. However, we also conclude that moderate pressures yield only moderate increases – achieving predominantly β-phase PVDF likely requires either much higher pressures or additional processing steps (e.g. mechanical deformation or specialized thermal cycling).

Future Directions and Applications

Enhancing β-Phase Content: A clear next step is to explore methods to push the β-phase content higher than what was achieved here. Our results show the trend, but not the limit – with ~70–100 MPa we got ~10% β-phase. Future experiments could employ higher pressures or more sophisticated pressure protocols. For instance, using hydraulic presses or multi-axial compression systems capable of hundreds of MPa might dramatically increase the β-phase yield. There is of course an engineering challenge in applying such high pressures uniformly, but even if not practical for bulk manufacturing, it would be valuable scientifically to map out the β-phase fraction as a function of pressure to see if it follows a predictable trend or saturates. Implementing a cyclic thermal-pressure treatment (for example, multiple cycles of heating to near-melt under pressure, then quenching) might yield higher β-phase than a single-cycle

process. This could bridge the gap toward achieving tens of percent of β-phase or more, which would have a more significant impact on piezoelectric properties.

Applications in Sensing and Energy Harvesting: The ultimate motivation behind enhancing PVDF's β-phase content is to improve its piezoelectric and ferroelectric properties for applications. With even a modest increase in β-phase, one should see an increase in the material's polarization when poled and an increase in piezoelectric strain constants. Our pressure-conditioned PVDF samples, especially the one with ~10% β at 170 P, could be tested as an energy-harvesting element (for instance, as a film in a bending cantilever that converts mechanical vibrations to electrical signals). We anticipate a measurable boost in output compared to a purely α-phase film. For sensors (force sensors, accelerometers, etc.), having some built-in β-phase means the sensor will be active to some degree without extensive poling treatments, potentially simplifying device fabrication. Moreover, the combination of moderate β-phase and a still substantial α-phase could result in a material that has a balance of properties – the α-phase provides mechanical strength and stability, while the β-phase provides electroactivity. Some devices might benefit from this balance; for example, a flexible piezoelectric wearable might trade off absolute piezoelectric sensitivity for better mechanical robustness by not being 100% β-phase (which can be more brittle).

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Appendix

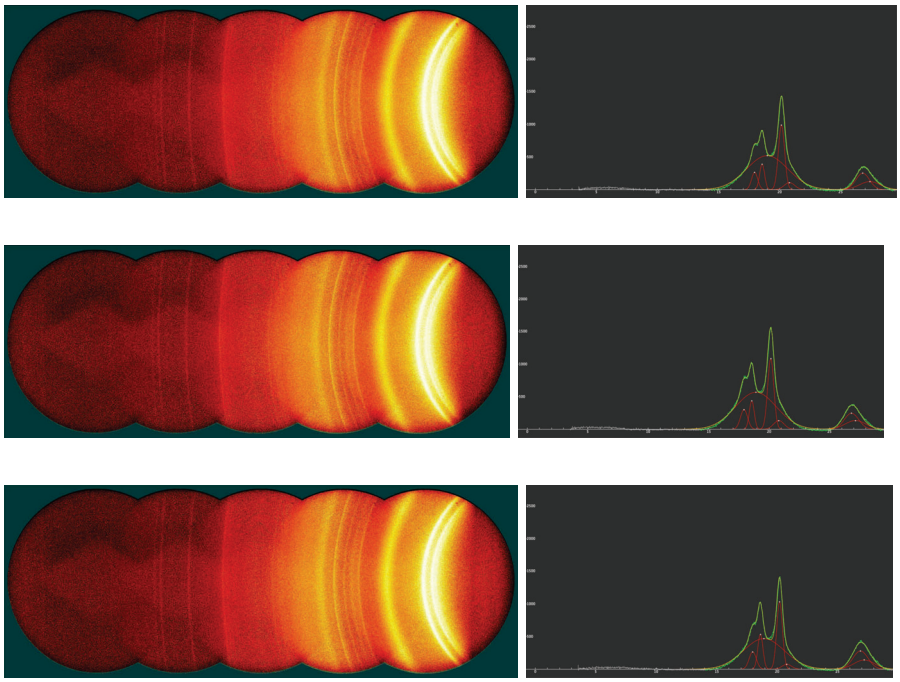


Figure 7:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 30 degrees without Pressure

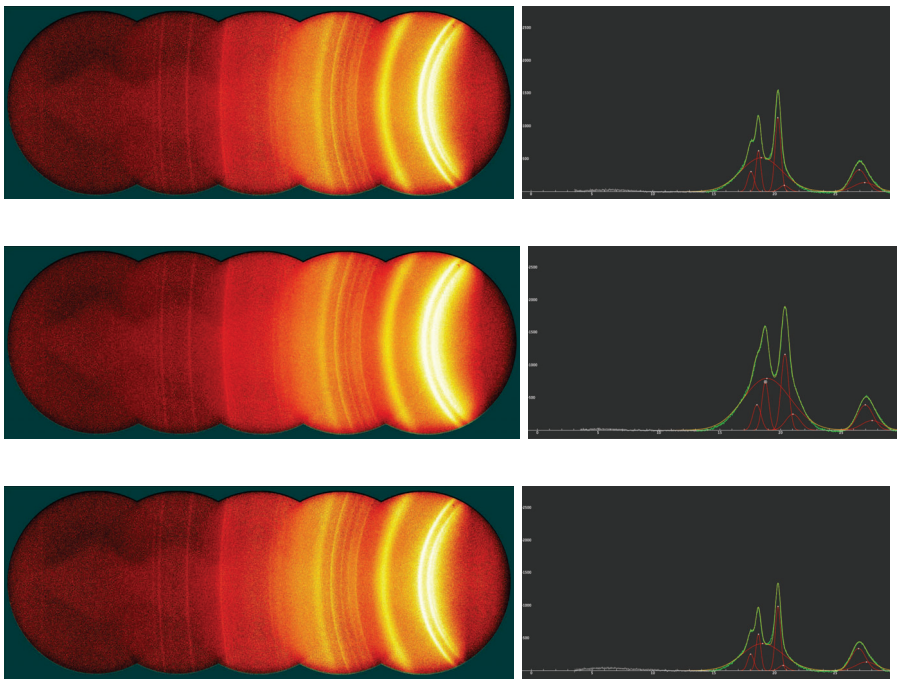


Figure 8:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 50 degrees without Pressure

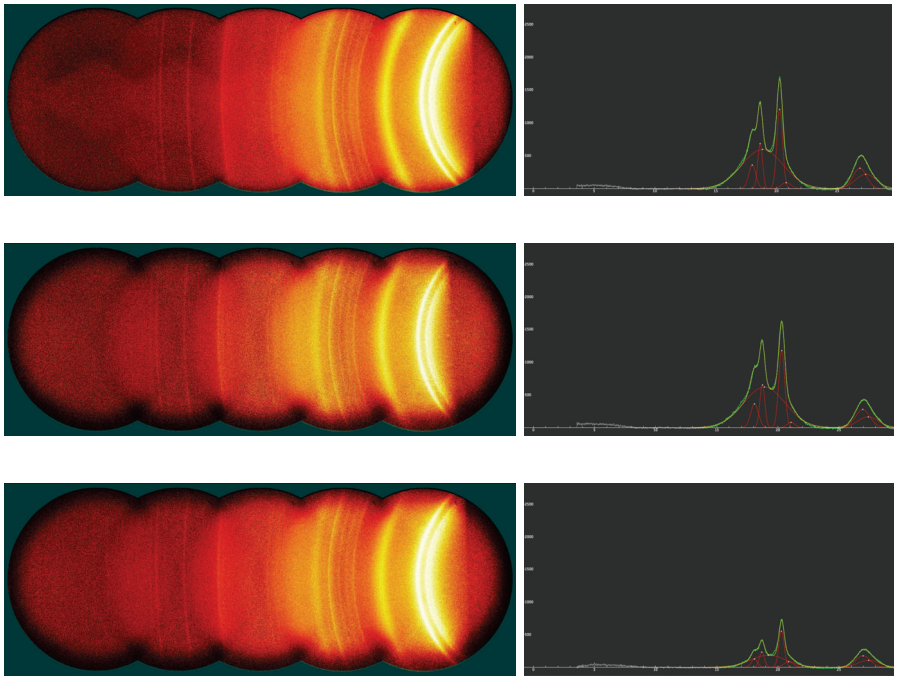


Figure 9:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 70 degrees without Pressure

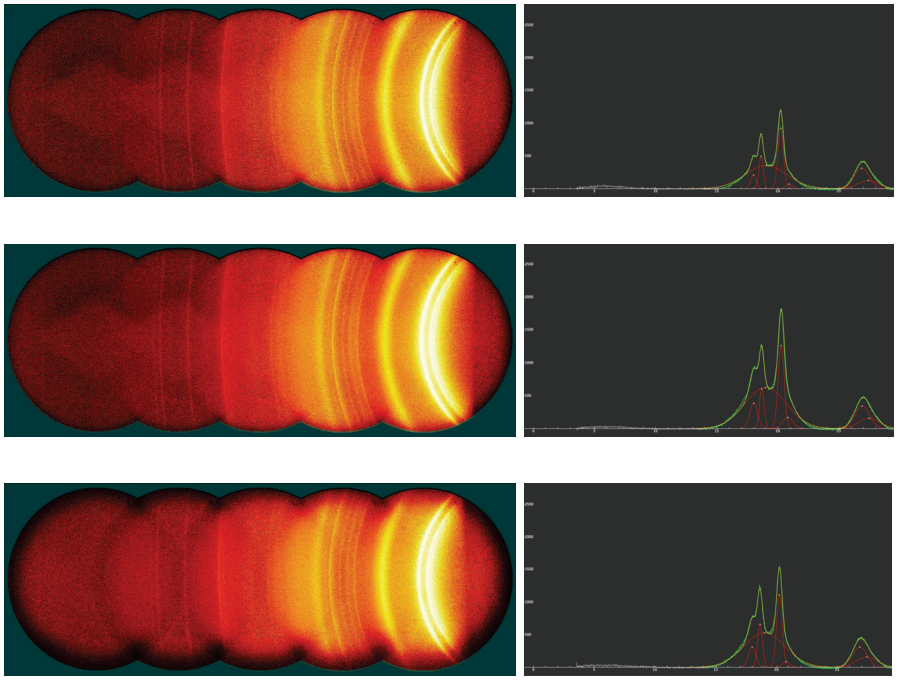


Figure 10:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 90 degrees without Pressure

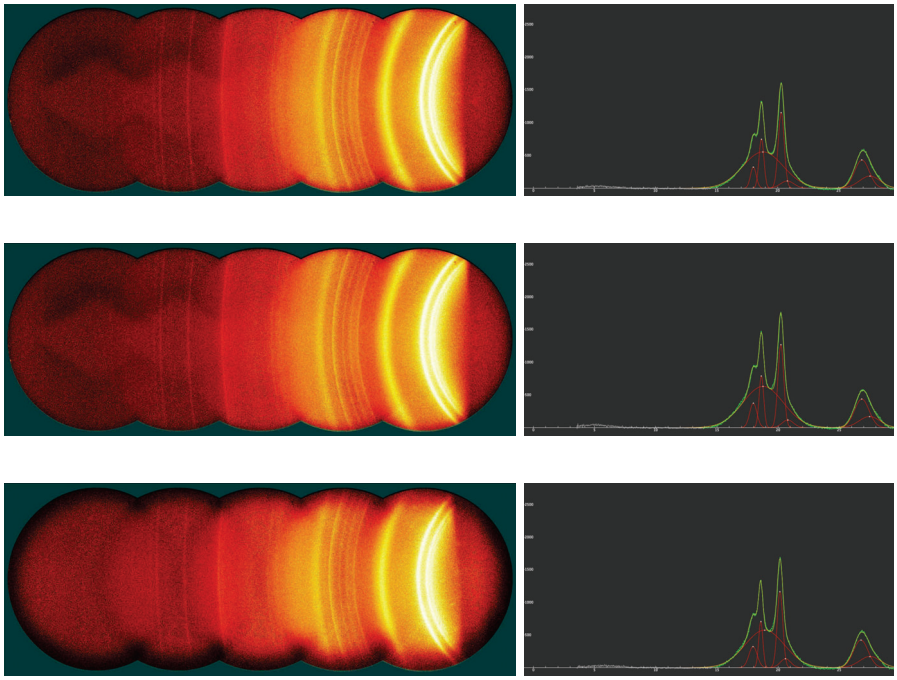


Figure 11:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 110 degrees without Pressure

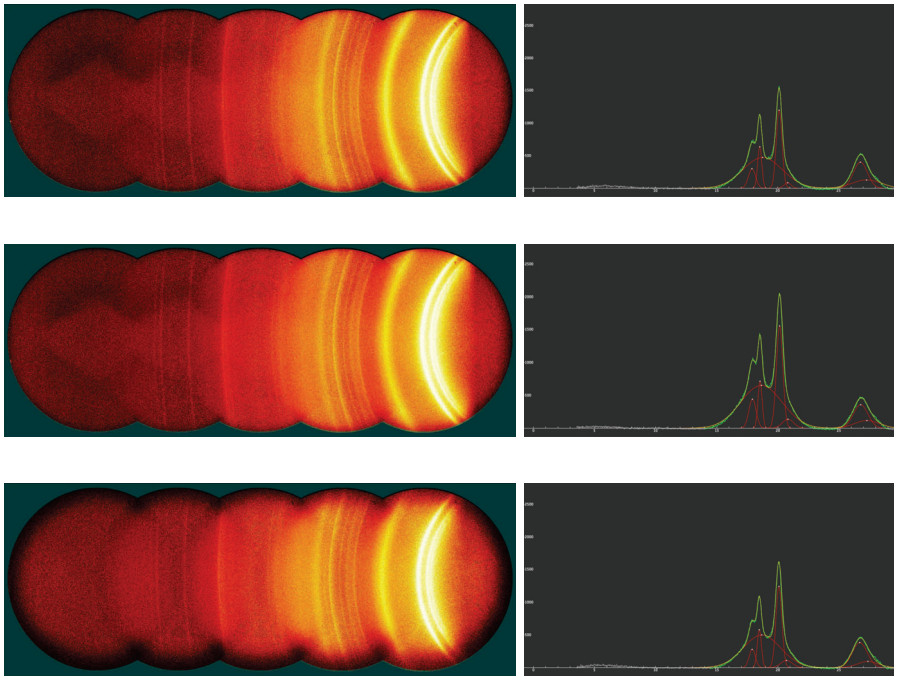


Figure 12:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 130 degrees without Pressure

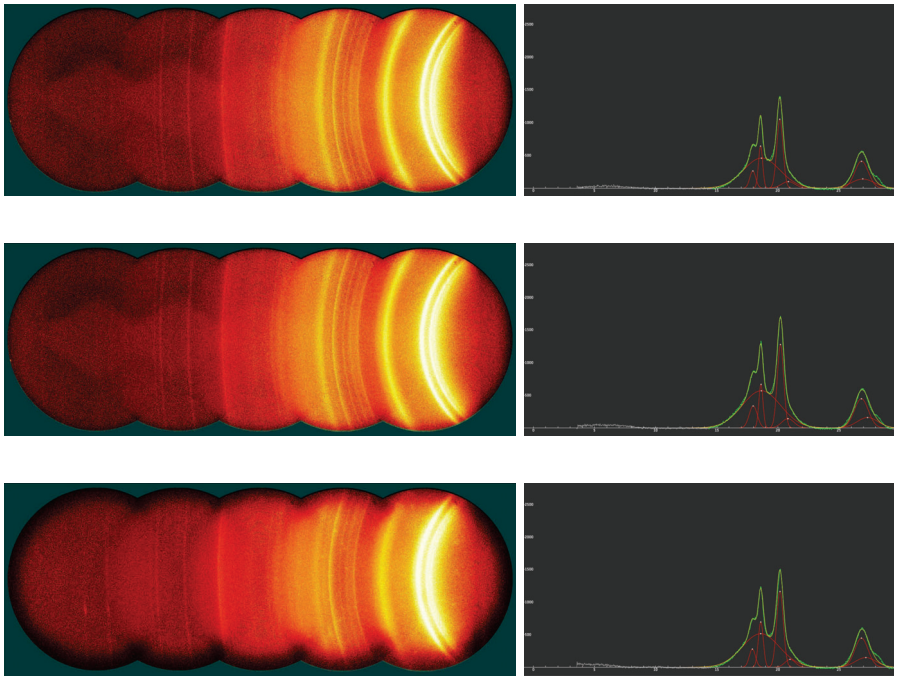


Figure 13:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 150 degrees without Pressure

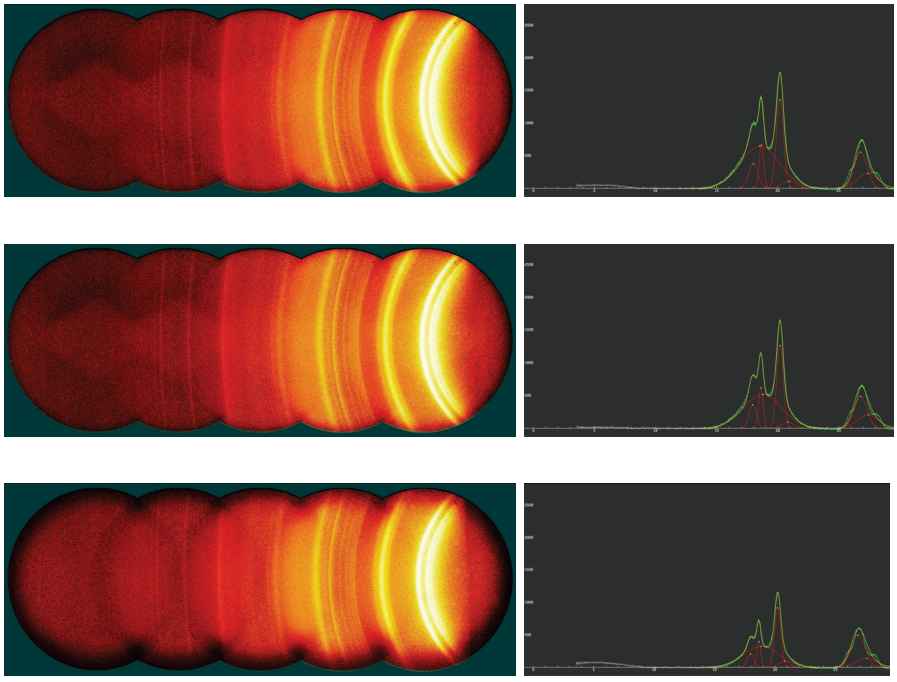


Figure 14:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 170 degrees without Pressure

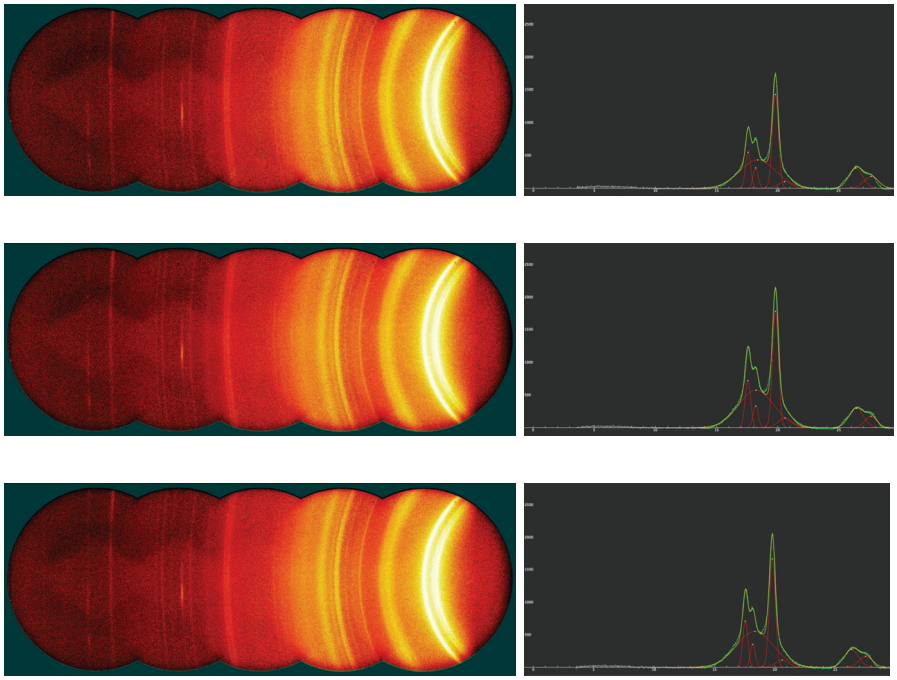


Figure 15:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 190 degrees without Pressure

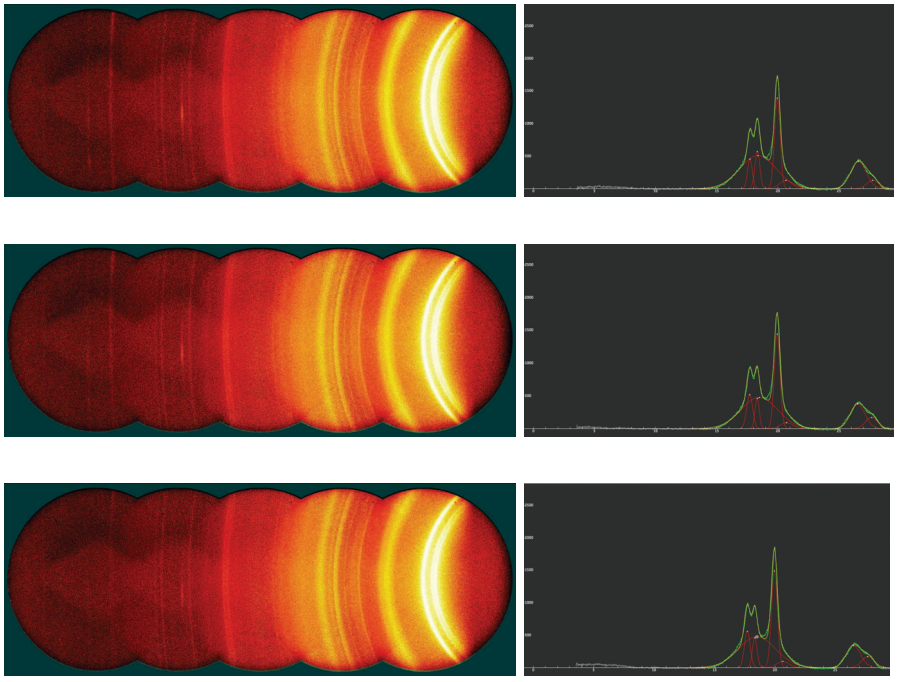
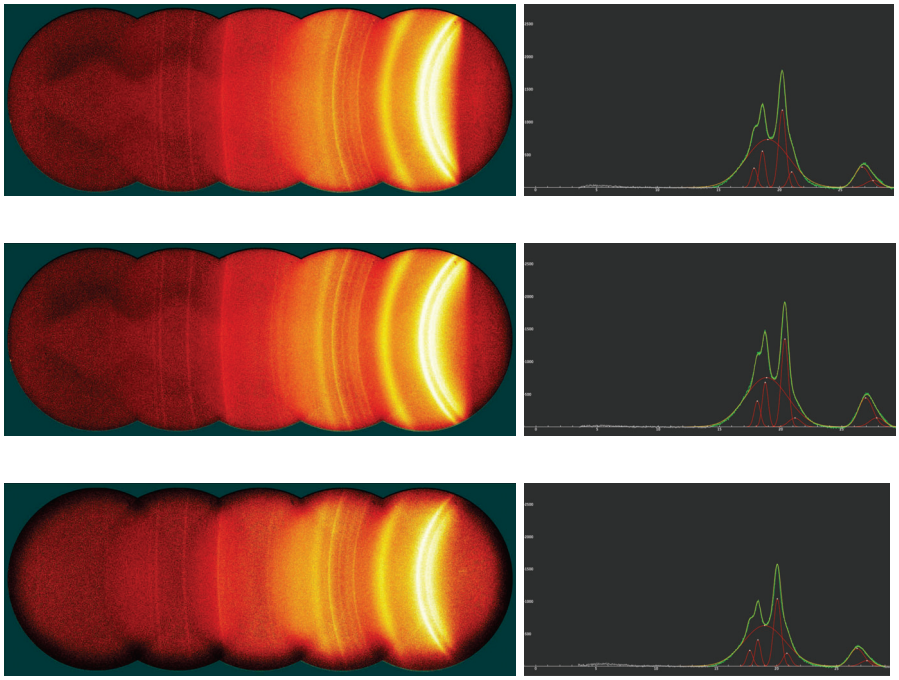


Figure 16:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 210 degrees without Pressure



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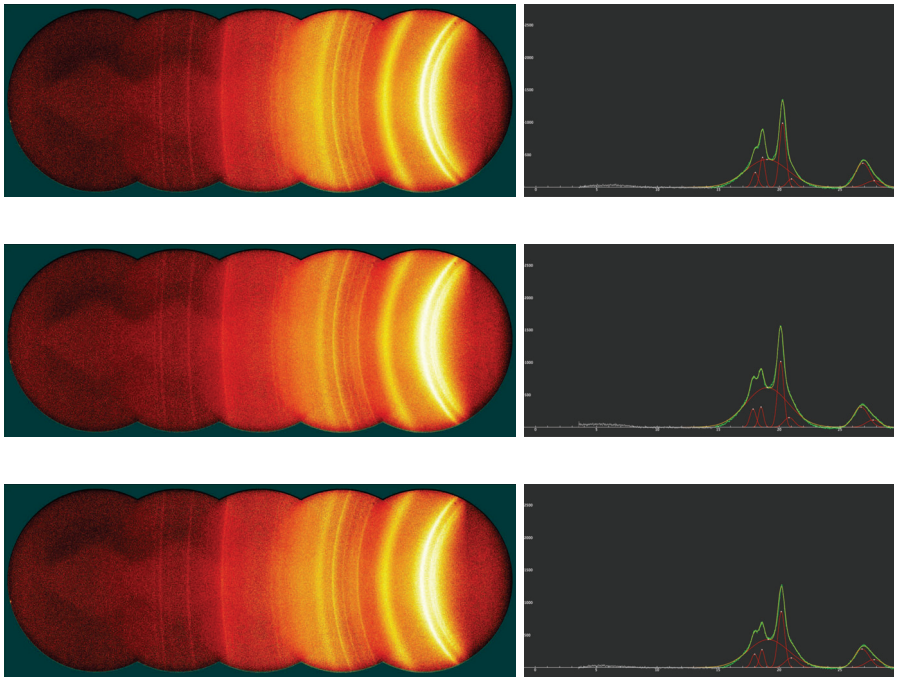


Figure 18:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 50 degrees with Pressure

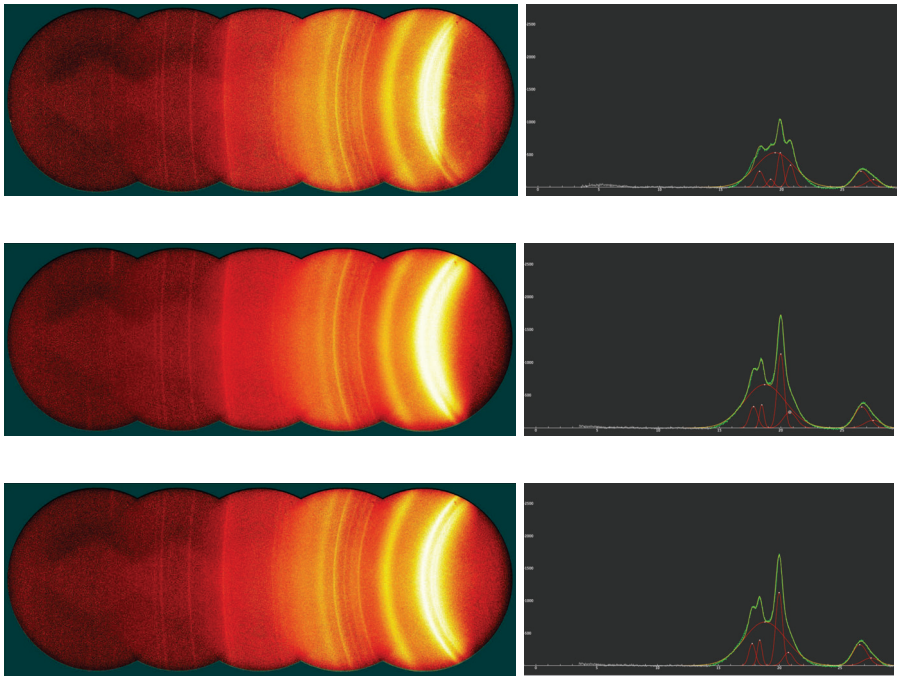


Figure 19:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 70 degrees with Pressure

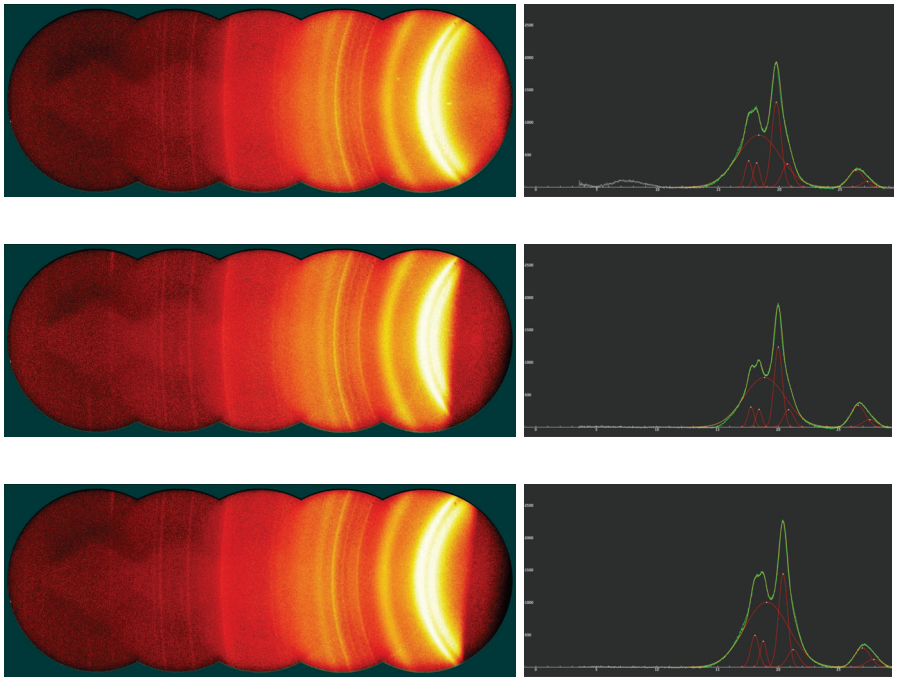
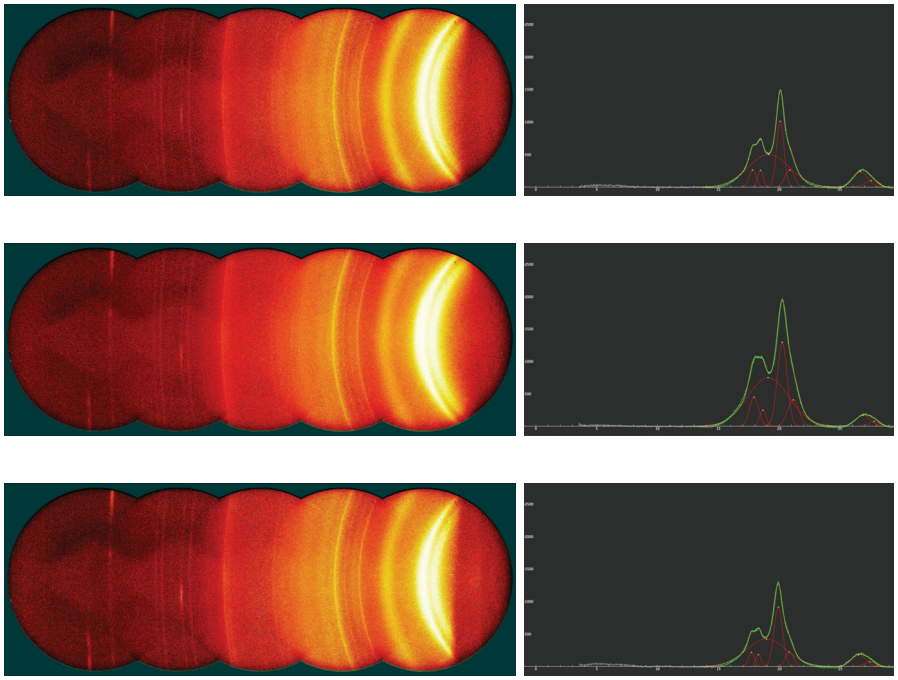


Figure 20:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 90 degrees with Pressure



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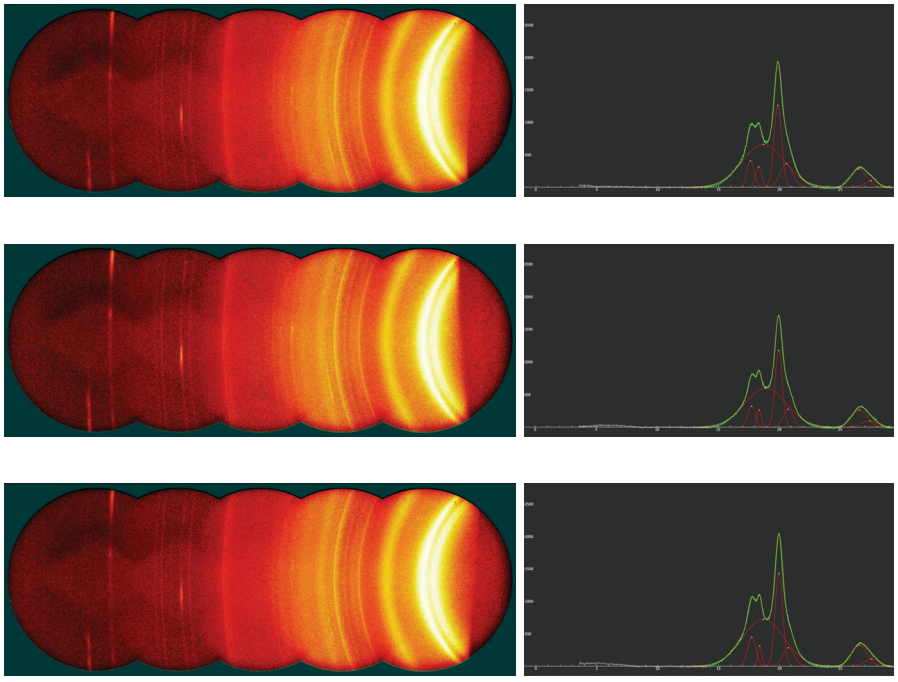

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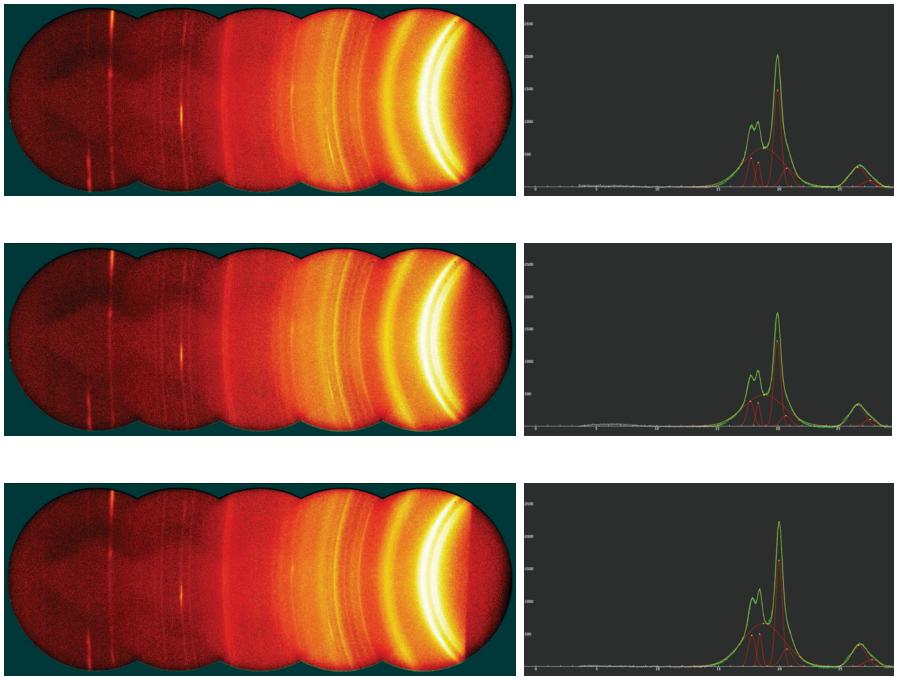


Figure 23:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 150 degrees with Pressure

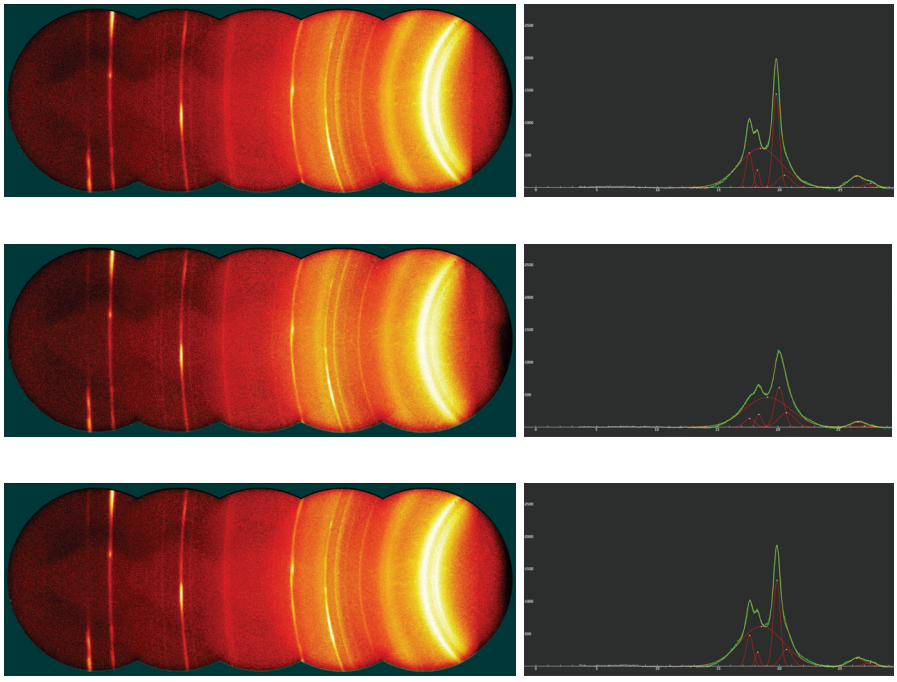
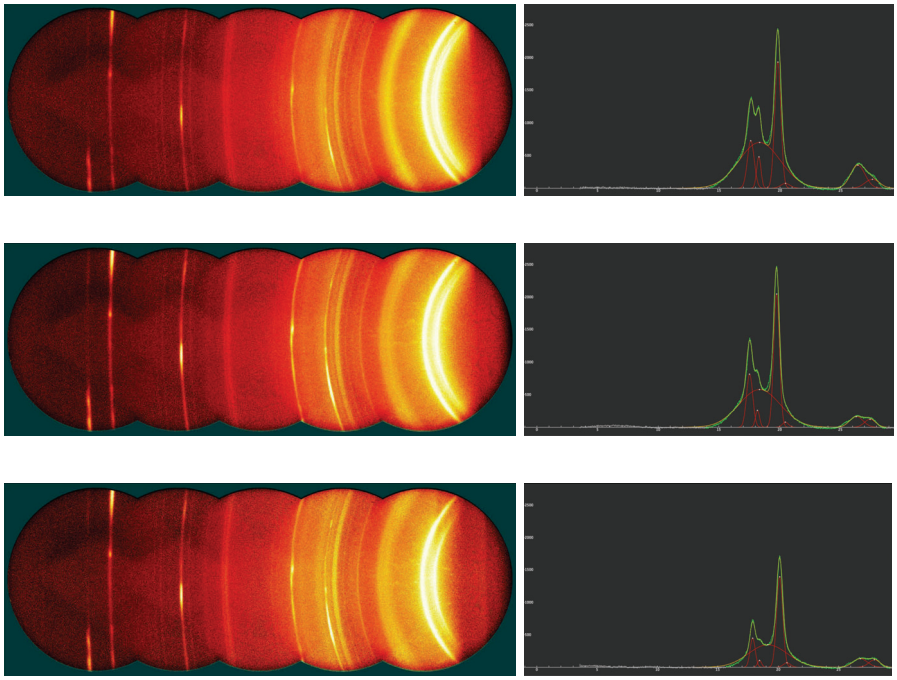


Figure 24:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 170 degrees with Pressure



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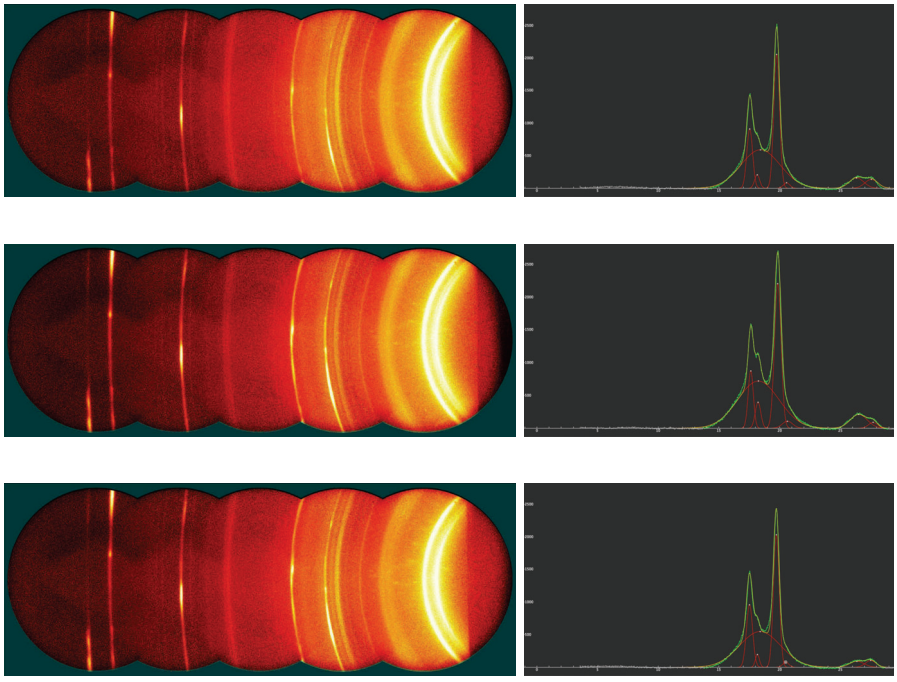

Figure 26:X-Ray Diffraction Triplicate Data of Polyvinylidene fluoride 210 degrees with Pressure