Multi-stage crystallization mechanism of electroactive phase polyvinylidene fluoride induced by thermal and supercritical carbon dioxide processing

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I. Peak to valley height ratio method

If the β band at 1275 cm^{-1} was present but not the γ band at 1234 cm^{-1}, Equation (S1) was used. This would denote the 763 cm^{-1} band as the α phase and the 840 cm^{-1} electroactive (EA) band as entirely the β phase.

$$F_{EA} = \frac{A_{EA}}{1.26 * A_\alpha + A_{EA}} \times 100\% \qquad (S1)$$

where F_{EA} is the fraction of electroactive crystal phase in PVDF's crystalline region, A_{EA} and A_α are the absorbance bands of the electroactive and α phases, respectively.

If both 1275 and 1234 cm^{-1} bands existed, F_{EA} would be subdivided into fractions of β and γ crystals. Fig. S1 visualizes the definition of ΔH_β and ΔH_γ, the height difference between the peaks at 1275 cm^{-1} and 1234 cm^{-1} to their nearest valleys, respectively. The wavenumbers of the valleys differ depending on the FTIR absorbance curve but they are approximately at 1260 and 1225 cm^{-1} for ΔH_β and ΔH_γ, respectively. The quantification of the fractions of β and γ crystals can be calculated using Equations (S2) and (S3).
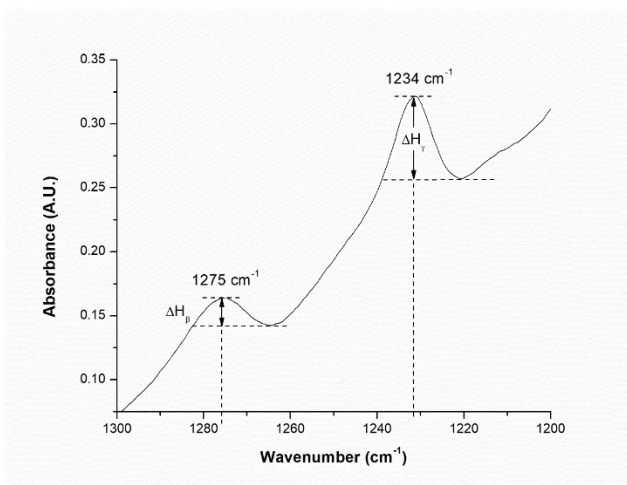
Figure S1. Visual representation of ΔH_β and ΔH_γ for the peak to valley height ratio method

$$F_\beta = F_{EA} \times \left(\frac{\Delta H_\beta}{\Delta H_\beta + \Delta H_\gamma} \right) \times 100\% \qquad (S2)$$

$$F_\gamma = F_{EA} \times \left(\frac{\Delta H_\gamma}{\Delta H_\beta + \Delta H_\gamma} \right) \times 100\% \qquad (S3)$$

where F_β and F_γ are the percentages of the β phase and γ phase, respectively, out of the electroactive crystal phase.

II. Effect of isothermal crystallization time (t_{hold}) on the fractions of β and γ crystal phases in PVDF samples after the completion of phase P2

The samples were heated to T_H of 180 °C and held for t_{hold} of 0, 15, and 300 minutes. After this, the samples were taken out and quenched in an ice bath. Figure S2 illustrates the absence of γ crystals in PVDF processed with no or short t_{hold} (i.e., 15 min). In contrast, γ crystal was found in the PVDF sample processed with t_{hold} increased to 300 minutes.
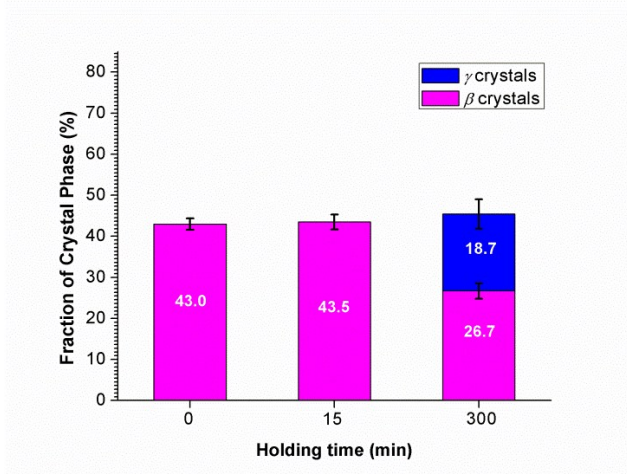

Figure S2. Effect of t_{hold} at T_H of 180 °C on the fractions of β and γ crystal phases. Processing was completed up until phase P2 and then the PVDF samples were quenched in an ice water bath.

III. Lack of effect of isothermal crystallization time (t_{hold}) on the foam morphologies in PVDF samples

Despite contrasting t_{hold} values, the foam morphologies of the PVDF samples were virtually invariant, causing steady *VER* and β phase contents. Figures S3(a) and (b) illustrate the SEM micrographs of PVDF foams prepared with different t_{hold}.
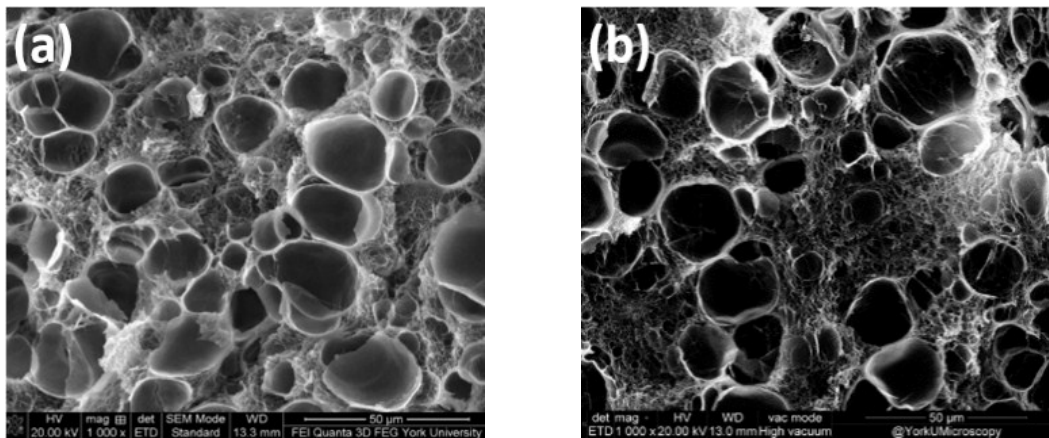

Figure S3. SEM micrographs of PVDF samples at 1000x magnification with t_{hold} of: (a) 0 min; and (b) 1440 mins. [Processing conditions: T_H = 180 °C, T_{sat} = 160 °C, P_{sat} = 2000 psi, *-dP/dt* = 191 MPa/s].

IV. α, β, and γ crystal contents in PVDF samples after being processed in each of the five processing phases involved in the thermal and ScCO$_2$ processing

Equations (3) and (S1-S3) were used to determine the α, β, and γ crystal contents of the processed PVDF samples after each phase. The processing conditions used are: T_H = 180 °C, t_{hold} = 300 mins, T_{sat} = 160 °C, and P_{sat} = 2000 psi. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S1 Raw data for α, β, and γ crystal contents in PVDF samples after each processing phase

Label	Average α content (%)	α Standard deviation (%)	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
Non-processed sample	35.3	2.9	16.6	0.4	0.0	0.0
Phase 1	23.9	0.8	18.2	0.7	0.0	0.0
Phase 2	24.4	1.5	11.5	1.3	8.9	1.9
Phase 3	20.6	2.2	5.3	2.0	20.8	1.8
Phase 4 without ScCO$_2$	19.6	2.4	3.6	0.6	23.5	2.4
Phase 4 with ScCO$_2$	16.0	1.2	12.8	2.6	17.7	1.8

V. Fractions of β and γ crystal contents and volume expansion ratios with varying heating temperatures, T_H

Equations (S1-S3) were used to determine the fraction of β and γ crystal contents and Equation (1) was used to determine the volume expansion ratios (*VER*) of the processed PVDF samples with varying heating temperatures. The processing conditions used are: t_{hold} = 0 min, T_{sat} = 160 °C, P_{sat} = 2000 psi, -*dP/dt* = 191 MPa/s. Each condition used at least three samples to calculate the average polymorph content and the standard deviations.

Table S2 Raw data for fractions of β and γ crystal contents and *VER* of PVDF samples processed with various heating temperatures

Heating Temperature, T_H (°C)	*VER*	*VER* Standard deviation	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
170	3.3	0.3	16.4	1.4	30.6	2.1
180	4.4	0.4	20.8	1.1	51.4	3.3
190	11.6	1.8	29.6	1.4	0.0	0.0
200	12.0	2.1	29.4	1.9	0.0	0.0
220	5.6	1.2	33.7	1.3	0.0	0.0

VI. Fraction of β and γ crystal contents with varying holding times, t_{hold}, processing up to phase 2

Equations (S1-S3) were used to determine the fractions of β and γ crystal contents of PVDF samples processed up to phase 2, with varying holding times at a heating temperature of 180 °C. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S3 Raw data for fractions of β and γ crystal contents of PVDF samples processed up to phase 2 with various holding times

Holding time, t_{hold} (mins)	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
0	43.1	1.5	0.0	0.0
15	43.2	1.8	0.0	0.0
300	26.7	3.0	18.7	3.8

VII. α, β, and γ crystal contents in PVDF polymer with varying holding times, t_{hold}

Equations (S1-S3) were used to determine the α, β, and γ crystal contents of the processed PVDF samples with varying holding times at a heating temperature of 180 °C. The processing conditions used are: T_H = 180 °C, T_{sat} = 160 °C, P_{sat} = 2000 psi, and $-dP/dt$ = 191 MPa/s. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S4 Raw data for α, β, and γ crystal contents in PVDF samples processed with varying holding times

Holding time, t_{hold} (mins)	Average α content (%)	α Standard deviation (%)	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
0	14.5	1.4	10.8	0.5	26.6	1.6
15	13.6	1.3	9.4	1.2	20.6	2.1
45	13.0	1.5	9.3	0.9	20.4	1.0
120	13.8	1.6	12.0	0.9	20.5	2.3
300	16.0	1.2	12.8	2.6	17.7	1.8
1440	17.0	1.2	12.0	2.5	17.3	2.2

VIII. Fractions of β and γ crystal contents of PVDF samples processed with varying saturation temperatures, T_{sat}

Equations (S1-S3) were used to determine the fractions of β and γ crystal contents of PVDF samples processed with varying saturation temperatures. The processing conditions used are: T_H = 180 °C, t_{hold} = 0 min, P_{sat} = 2000 psi, and $-dP/dt$ = 191 MPa/s. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S5 Raw data for fractions of β and γ crystal contents in PVDF samples processed with various saturation temperatures

Saturation Temperature, T_{sat} (°C)	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
120	3.9	1.5	65.6	3.1
140	4.9	0.7	61.6	2.1
160	20.8	1.1	51.4	3.3

IX. Fractions of β and γ crystal contents and volume expansion ratios of PVDF samples processed with varying saturation pressure, P_{sat}

Equations (S1-S3), (1), and (2) were used to determine the fraction of β and γ crystal contents and volume expansion ratios (VER) of the processed PVDF samples, respectively, with varying saturation pressures. The processing conditions used are: T_H = 180 °C, t_{hold} = 0 min, T_{sat} = 160 °C, and $-dP/dt$ = 191 MPa/s. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S6 Raw data for fractions of β and γ crystal contents, VER, and average cell diameter for various saturation pressures

Saturation Pressure, P_{sat} (psi)	VER	VER Standard deviation	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
1200	2.3	0.1	8.2	2.4	63.3	1.9
2000	4.4	0.4	20.8	1.1	51.4	3.3
2500	9.3	1.3	28.5	2.7	37.0	3.5

X. Fractions of β and γ crystal contents and volume expansion ratio of PVDF samples processed with varying pressure drop rates, -*dP/dt*

Equations (S1-S3) were used to determine the fractions of β and γ crystal contents and equation (1) was used to determine the volume expansion ratios (*VER*) of the PVDF samples processed with varying pressure drop rates. The processing conditions used are: T_H = 180 °C, t_{hold} = 0 min, T_{sat} = 160 °C, and P_{sat} = 2000 psi. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S7 Raw data for fractions of β and γ crystal contents and *VER* in PVDF samples processed in various pressure drop rates

Pressure drop rate, -*dP/dt* (MPa/s)	*VER*	*VER* Standard deviation	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard deviation (%)
48	1.8	0.2	8.8	1.7	57.0	2.5
55	2.9	0.4	12.3	2.3	60.0	2.0
123	3.9	1.5	21.3	2.1	50.5	2.5
164	4.1	0.1	19.3	1.9	51.5	2.6
191	4.4	0.4	20.8	1.1	51.4	3.3

XI. Fractions of β and γ crystal contents and volume expansion ratios of processed PVDF samples processed using two different processing conditions

Equations (S1-3), (1), and (2) were used to determine the fractions of β and γ crystal contents and volume expansion ratios (*VER*) of PVDF samples, respectively, processed with the following 2 processing conditions.
Condition 1. T_H = 180 °C, t_{hold} = 0 min, T_{sat} = 160 °C, P_{sat} = 2000 psi.
Condition 2. T_H = 220 °C, t_{hold} = 0 min, T_{sat} = 160 °C, P_{sat} = 2500 psi.
Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S8 Raw data for fraction of β and γ crystal content, and *VER* in PVDF samples processed with different processing conditions

Condition	*VER*	*VER* Standard deviation	Average β content (%)	β Standard deviation (%)	Average γ content (%)	γ Standard dDeviation (%)
1	4.4	0.4	20.8	1.1	51.4	3.3
2	4.8	0.1	30.1	1.8	0	0

XII. Fractions of β and γ crystal content and volume expansion ratios of PVDF samples prepared using uniaxial mechanical stretching

Equations (S1) was used to determine the α, β, and γ crystal contents of the PVDF samples processed by uniaxial mechanical stretching. Each condition used at least three samples to calculate the average polymorph contents and the standard deviations.

Table S9 Raw data for α, β, and γ crystal contents in PVDF polymer processed by uniaxial mechanical stretching

Stretch ratio (%)	Stretching Temperature (°C)	Stretching speed (mm/s)	Thickness (μm)	Avgerage β content (%)	β Standard deviation (%)
0	90	0.1	100	31.0	0.88
200	90	0.1	100	37.4	2.0
300	90	0.1	100	68.4	1.9

XIII. Dielectric constants of PVDF solid and foam samples with different volume expansion ratios

The dielectric constants (at 100,000 Hz) of the as molded PVDF sample and PVDF foam samples with differnet volume expansion ratios were measured and the data are summarized in Table S10.

Table S10 Crystal contents and dielectric constants of as-molded PVDF samples and PVDF foams with maximum fractions of β, γ, and electroactive phases

T_H (°C)	T_{sat} (°C)	P_{sat} (psi)	β phase (%)	γ phase (%)	Electroactive phase (%)	Volume Expansion Ratio	Dielectric Constant
220	160	2000	**33.7 ± 1.3**	-	33.7	5.6	2.0
180	120	2000	3.9	**65.6 ± 3.2**	69.5	4.4	8.7
180	160	2000	20.8	51.4	**72.2 ± 2.9**	1.0	2.2
	As-molded PVDF		32.0	0	**32.0**	1.0	8.2