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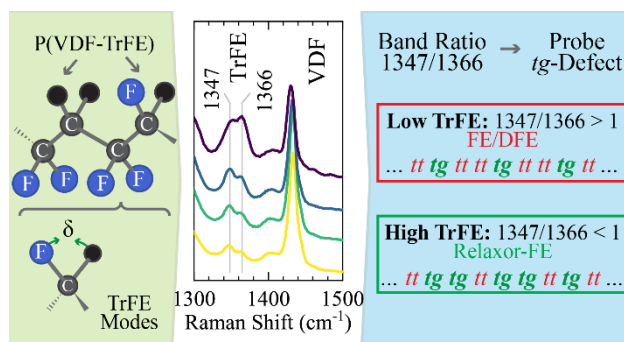
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1 Deciphering TrFE Fingerprints in P(VDF-TrFE) by Raman
2 Spectroscopy: Defect Quantification and Morphotropic Phase
3 Boundary

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6 Keywords: Raman Spectroscopy, P(VDF-TrFE), Chain Conformation, Ferroelectric, Relaxor.



8 ABSTRACT:

9 The electroactive behavior of PVDF-based polymers is tightly related to the macromolecular
10 sequence, chain conformation, and crystallinity. Although β -PVDF is the most attractive phase
11 for applications in organic electronics, PVDF tends to crystallize into other thermodynamically
12 more stable phases. Copolymerization of VDF and TrFE addressed this issue, and has resulted
13 in high ferroelectric content co-polymers. Later on, the insertion of CFE/CTFE units into the
14 P(VDF-TrFE) architecture yielded ter-polymers with relaxor-ferroelectric properties,
15 especially attractive in energy storage and electrocaloric applications. The investigation of the
16 corresponding electroactive phases in these polymers relied mainly on FT-IR and X-ray
17 diffraction techniques, demanding an extensive combination of material characterization and
18 analysis to detect the majority phases and predict material behavior. In this work, we
19 demonstrate a facile and non-invasive approach to assess the relative ratio of defects in TrFE-

20 segments through a detailed analysis of the polymer Raman spectra. By varying the content of
21 TrFE in P(VDF-TrFE) samples, a detailed assignation of the TrFE unit modes (1347 and 1366
22 cm^{-1}) contribution to the polymer Raman spectra was established which was further validated
23 by FT-IR, X-ray diffraction, calorimetry, and dielectric spectroscopy measurements. Based on
24 our findings, we further propose a defect quantification ratio that can be used to predict chain
25 conformation and electroactive behavior.

26

27 INTRODUCTION

28 Poly(vinylidene fluoride)-based (PVDF) polymers have attractive ferroelectric properties,
29 resulting in numerous applications in organic electronics: sensors and transducers (from piezo-
30 and pyroelectricity); FETs for non-volatile memories (from ferroelectricity); energy harvesting
31 from motion and temperature (piezo- and pyroelectricity, and electrocalorics); capacitors for
32 energy storage (from relaxor-ferroelectric); and cooling applications (from electrocalorics).¹⁻¹¹
33 The ferroelectric properties (ferro-, piezo-, pyro-electric and electrocaloric) of these materials
34 are tightly related to their chain structure, and there are numerous reports investigating how
35 these properties evolve as a function of processing and material composition.

36 PVDF is a polymorph that can crystallize into three main distinct phases: α (*tg $\bar{t}g'$*), β (*all-trans*),
37 and γ (*ttg $\bar{t}ttg'$*) phases. The α phase is paraelectric (PE) due to the anti-parallel orientation of
38 adjacent chains (symmetric with respect to the *b* axis), having a net zero dipolar moment. In
39 the β phase, adjacent chains are aligned parallel to each other, creating a non-zero dipolar
40 moment along the *b* axis, at the origin of the ferroelectric (FE) behavior. The *all-trans* chain
41 conformation maximizes the dipolar moment, as all the dipolar moments are aligned in the
42 same direction. Finally, in the γ phase the polymer presents a non-zero dipolar moment, but
43 much weaker than in the previous case. Additional phases are mentioned in the literature, which

44 correspond to variants of the α and γ phases. These phases present the same crystalline
45 structures, but differ in the parallel or anti-parallel orientation of adjacent chains. PVDF
46 predominantly crystallizes into the non-polar α phase requiring additional processing to obtain
47 β phase. Different approaches have been demonstrated to successfully produce high β phase
48 content, such as thermal annealing, material poling, film stretching, blending, or co-
49 polymerization.¹²⁻¹⁶ The last led to the development of co-polymers based on VDF and
50 trifluoroethylene (TrFE) units, that readily crystallize into the β phase. Further research resulted
51 in the observation of relaxor-ferroelectric (RFE) properties in electron-irradiated P(VDF-
52 TrFE), explained by the local disruption of FE domains that softened FE hysteresis and lowered
53 the remnant field.^{17, 18} This is especially attractive for energy storage applications, providing a
54 narrow material hysteresis with lower dielectric losses. RFE behavior was then obtained with
55 P(VDF-TrFE) based ter-polymers by the addition of chlorofluoroethylene (CFE) or
56 chlorotrifluoroethylene (CTFE) units.^{12, 19-22} The presence of CFE or CTFE units disrupted the
57 long all-*trans* chain segments due to the high steric hindrance of the Cl atoms yielding a RFE
58 material. The FE nano-domain model was used to explain the observed RFE behavior in these
59 materials, proposing that the introduction of bulky units, such as CFE and CTFE, greatly
60 disrupted local material ordering (as in electron-irradiated P(VDF-TrFE)), producing small FE
61 domains that softened material hysteresis. However, this interpretation was unable to fully
62 explain the appearance of RFE behavior in P(VDF-TrFE) co-polymers with high TrFE content.
63 Liu and co-workers investigated this system and reported on the presence of a morphotropic
64 phase boundary (MPB) around 50% TrFE molar content, where a competition between the all-
65 *trans* and a 3/1 helix conformation takes place.²³⁻²⁵ Their results showed chain tacticity played
66 a very important role on the polymer FE behavior, and that chain chirality was responsible for
67 the formation of “disordered” helix conformations that lead to RFE behavior.

68 Accordingly, the study of the polymer structure and chain conformation for these systems is of
69 prime importance in order to decipher their functional behaviors. It has been performed mainly
70 by FT-IR and Raman spectroscopies, and X-ray diffraction techniques. FT-IR studies analyzed
71 the vibration spectra for a variety of PVDF-based polymers, attempting to decipher the origin
72 of the different modes both experimentally and through simulation. It was in these works, prior
73 to the 1980s, that researchers managed to detect and differentiate the three commonly observed
74 phases (α , β , and γ). This was especially difficult given the large number of predicted modes
75 for the γ phase, in many cases overlapping with α and β modes. Raman spectroscopy analysis
76 of these polymers became more frequent between the 1980s and the 2000s, offering an easy,
77 non-invasive, and non-destructive approach to study polymer structure and chain conformation
78 under different conditions (such as temperature, stress, or material polarization). Several works
79 investigated structural changes in PVDF and P(VDF-TrFE) with respect to monomer content
80 and temperature. These studies gave important insight into the evolution of the spectra with
81 increasing TrFE content, showing increases in β phase content with increases in TrFE
82 proportion as well as the appearance of TrFE-unit specific modes.^{15, 26-36} Nevertheless, the
83 determination of the polymorphism in PVDF-based polymers has mainly relied on FT-IR
84 spectroscopy combined with X-ray diffraction in the past 20 years. This is particularly true for
85 reports on the FE and RFE properties of PVDF-based ter-polymers. In these systems, it was
86 demonstrated that the introduction of bulky TrFE, CTFE, or CFE units gradually increased the
87 crystalline lamellae interplanar distance, along with the gradual appearance of *tg* defects to the
88 detriment of the all-*trans* conformation. Despite this, the determination of the FE behavior of
89 these materials has relied on an extensive collection of characterization techniques (FT-IR, X-
90 ray diffraction, calorimetry, dielectric spectroscopy, or ferroelectric hysteresis), many of which
91 requiring specific sample preparation that may impact material performance in comparison to
92 real case uses.

93 Raman spectroscopy offers a facile and non-invasive approach to probe local polymer chain
94 conformation and chain orientation under a wide range of parameters (temperature, excitation
95 wavelength, or wavenumber range), requiring little to no sample preparation. These aspects
96 make it extremely attractive as a quick and easy-to-implement technique to determine polymer
97 functional behavior, with the possibility to integrate into production line quality control at large
98 scale device fabrication.³⁷ In this work, we utilize Raman spectroscopy to study the evolution
99 in chain conformation of solution-cast P(VDF-TrFE) co-polymers as a function of the TrFE
100 molar content. Raman spectral data are then put into perspective with those from other
101 characterization techniques, including FT-IR spectroscopy, X-ray diffraction (WAXS),
102 calorimetry (DSC), and dielectric spectroscopy (DE), providing a full picture of the underlying
103 chain transformations and consolidating our results. Based on this analysis, we propose a band
104 assignment for the TrFE contributions to the Raman spectra, as well as a defect quantification
105 and chain conformation prediction based on the proposed assignment. These results intend to
106 show the versatility of Raman spectroscopy in the analysis of these ferroelectric materials,
107 potentially predicting their behavior from a straightforward spectral fit and analysis, and
108 expanding this analysis to other PVDF-based co- and ter-polymers.

109

110 MATERIALS AND METHODS

111 **Materials.** The P(VDF-TrFE) co-polymers used in this study were kindly supplied by
112 Piezotech. According to the manufacturer, the four different co-polymers have a TrFE molar
113 content of 20 %, 25 %, 30 %, and 50 %. Additional information is provided in the Supporting
114 Information (SI). Triethyl phosphate (TEP) was purchased from Sigma-Aldrich.

115 **Polymer Thin Films.** Polymer films were made by drop-casting from 15 wt.% solutions in
116 TEP. The solutions were poured onto previously cleaned glass substrates followed by a drying

117 process of 2 hours 20 min, on a hot plate at 90 °C and atmospheric pressure. Before casting,
118 the solutions were stirred for at least 48h at room temperature. The produced films were
119 detached from the glass substrates through immersion in deionized water, wetting the glass and
120 separating the thin films without deformation or stretching.

121 **Raman Spectroscopy.** Raman spectra were recorded with an XploRa spectrometer (Horiba
122 Instruments) coupled with an Olympus microscope, with a linearly polarized laser (Nd:YAG,
123 $\lambda = 532$ nm), at a magnification of $50\times$ (sampling diameter of 10 to 15 μm). No modifications
124 from the laser intensity were observed. The spectra were recorded at ambient conditions after
125 instrument calibration with a Si sample. The spectra were obtained for ranges between 200 and
126 1600 cm^{-1} . Data treatment included spectral peak detection from 2nd derivative, with derivative
127 2nd order Savitsky-Golay smoothing; spectral resizing for multiple sample comparison through
128 standard normal variate analysis; and background removal through fitting of 2nd or 4th order
129 polynomials. Peak fitting was performed with Origin and Fityk software using Gaussian and
130 Voigt profiles.

131 **FT-IR Spectroscopy.** Spectra were recorded with a Nicolet iS5, with an ATR module iD7
132 (diamond-crystal window, diameter of 1.8 mm), between 4000 to 400 cm^{-1} . Software in-built
133 ATR spectral correction was used. No sample modifications were observed from the pressure
134 exerted by the sample holder screw. Data analysis was focused on the 1600 to 400 cm^{-1} range,
135 following the same peak detection procedure used in the Raman spectra analysis.

136 **X-ray Diffraction.** The crystalline structure was analyzed with a wide-angle X-ray scattering
137 (WAXS) system, Xeuss 2.0 from XENOCS, under vacuum and ambient temperature, with a
138 sample-to-detector distance of 151 mm, and $\lambda = 1.54\text{ \AA}$ (Cu $K\alpha$). The diffraction pattern was
139 collecting with a DECTRIS PILATUS-300k detector, for a q range of 0.1 to 3.1 \AA^{-1} (1.4° to

140 46°), followed by azimuthal integration. Data analysis was made with Fityk (software), using
141 Voigt profiles. Additional information on peak fitting is provided in SI.

142 **Calorimetry.** Calorimetric analysis was performed with a Differential Scanning Calorimetry
143 (DSC) system (Mettler Toledo DSC 1, with intra-cooler, and N₂ flux). The thermograms were
144 recorded for a maximum temperature range of -50 to 200 °C, at a heating rate of 10 °C min⁻¹.
145 A total of three curves were recorded, corresponding to the first heating, first cooling, and
146 second heating. Only the first heating curves were considered in this analysis, and related to
147 results obtained from the remaining characterization. The melting and Curie transition
148 temperatures were estimated from the minima of the recorded endotherms.

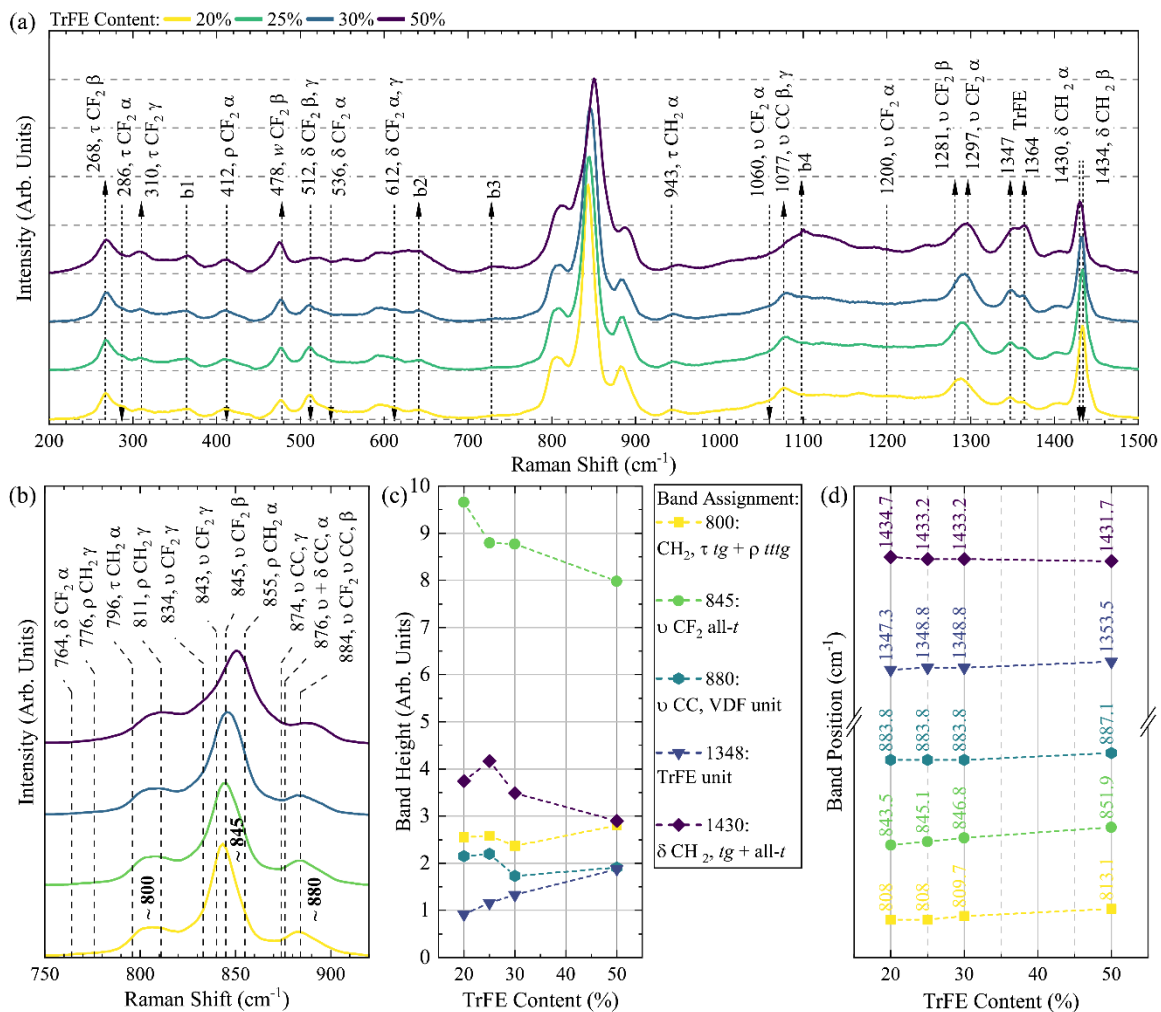
149 **Dielectric Spectroscopy.** Broadband dielectric spectroscopy of metal-polymer-metal devices
150 was performed with a Solartron 1260 A impedance analyzer equipped with a Linkam LTS 350
151 temperature-control system. The measurements were performed with an AC signal of 1 V, at a
152 frequency of 10 Hz, for a maximum temperature range between -60 to 50 °C. The glass
153 transition temperature of the samples was estimated from the loss maximum for the
154 measurements performed at 10 Hz. The device preparation procedure for the dielectric
155 spectroscopy measurements is available in SI.

156

157 RESULTS AND DISCUSSION

158 Films were prepared through solution casting from four different P(VDF-TrFE) with TrFE
159 molar content ranging from 20 to 50 %. All films were dried for 2 h and 20 min at 90 °C under
160 atmospheric pressure. All the used co-polymers present similar molecular weights around
161 $2 \times 10^5 \text{ kg mol}^{-1}$ (as determined by SEC – see SI), which we expect to have a negligible influence
162 on property variability between co-polymers when compared to changes induced by TrFE
163 molar content. To decipher the evolution of the chain conformation and crystalline structure as

164 a function of the TrFE content, Raman and FT-IR spectroscopies were combined with X-ray
165 scattering, calorimetry, and dielectric spectroscopy. This analysis intends primarily to extract
166 valuable information from the Raman spectra, by providing detailed vibration band labelling
167 and relating the changes observed to the structure with respect to the TrFE content. In the
168 literature, the chain conformation analysis has been predominantly made with FT-IR
169 spectroscopy, with only a handful of works providing in-depth discussions of Raman spectra.^{15,}
170 ^{26-36, 38-53} Several of these works have performed crystalline band labelling based on theoretical
171 spectral simulations. Simulations of Raman and FT-IR spectra identify the lattice modes of an
172 ideal crystal, calculating the contribution of an infinite crystal lattice. This scenario disregards
173 *tg*-defect formation or the presence of head-to-head chain defects. For this reason, these spectra
174 have shown significant shifts from experimental values (that have been independently
175 reproduced in different works), but have nonetheless aided in the assignment of the
176 experimentally detected bands. In the particular case of P(VDF-TrFE) co-polymers, the nature
177 of the detectable TrFE bands is seldom debated, disregarding potential valuable information
178 on the characterization of the material. Indeed, these changes could then be further related with
179 the polymer structural data, drawing relationships between these different techniques.



180
 181 **Figure 1.** Raman spectra with band assignment, height, and Raman shift (position). a) Raman
 182 spectra with band assignment for the different TrFE molar content from 200 to 1500 cm^{-1} . The
 183 dashed arrows indicate the direction of increase in band intensity. The bands marked b1 to b4
 184 correspond to bands with no clear assignment. b) Band modes for the range of 750 to 925 cm^{-1} ,
 185 highlighting the multiple mode contributions to the observed 800, 845, and 880 cm^{-1} bands.
 186 c) Raman band height with band assignment for a selection of bands: 800, 845, 880, 1348, and
 187 1430 cm^{-1} . d) Raman band positions as a function of the TrFE content for the same bands as
 188 shown in c).

189
 190 **Raman Spectroscopy.** The Raman spectra of the different P(VDF-TrFE) films were recorded
 191 in the range 200 to 1600 cm^{-1} . This covers most of the modes for PVDF-based polymers. Figure
 192 1 shows the obtained spectra, with the respective band assignment (with type, molecular group,
 193 and phases), and extracted band height and position for a selection of crystalline bands.
 194 Crystalline band assignment followed several seminal works on Raman and FT-IR

195 spectroscopy of PVDF homopolymer and P(VDF-TrFE) co-polymers.^{36, 38-53} In the literature,
196 bands are typically assigned to specific phases (such as α , β , and γ phases of PVDF), which
197 can lead to misinterpretations. Analysis should focus on the chain conformations associated to
198 the observed modes, in this case, the all-*trans*, *ttg*, and *tg* conformations that are found in the
199 different phases of PVDF-based polymers. Indeed, some bands arising from vibrational modes
200 of *tt*-segments will present overlapping contributions from two distinct phases (in this case, β
201 and γ) and a clear phase attribution cannot be performed. This was addressed by Cai *et al.* as
202 they discussed band assignment and phase determination from FT-IR analysis of PVDF
203 homopolymer through a simple diagram relying on the detection of phase-specific modes.⁴³ A
204 conformation-oriented analysis can provide important information on chain structure with
205 different parameters.

206 The Raman spectra shown in Figure 1a can be divided into five regions: 1) 200 and 750 cm^{-1} ,
207 2) 750 and 900 cm^{-1} , 3) 900 up to 1300 cm^{-1} , 4) 1320 and 1380 cm^{-1} , and 5) above 1380 cm^{-1} .
208 The range between 200 and 750 cm^{-1} (zone 1) covers several torsion (τ), wagging (w), and
209 rocking (ρ) CF_2 modes, with several CF_2 bending (δ) modes after 500 cm^{-1} . The modes at 268,
210 478, and 512 cm^{-1} have been associated to all-*trans* segments and constitute a good evidence
211 for the presence of “all-*trans*-phase” in these PVDF-based co-polymers. The band at 512 cm^{-1}
212 often contains an additional contribution at 514 cm^{-1} associated to *tt*-segments in γ -PVDF, and
213 has been observed in several previous works.^{41-43, 46} A general increase in all-*trans* specific
214 modes can be seen with increasing TrFE molar content. However, several *tg*-associated modes
215 are still present for all spectra, suggesting the presence of *tg* defects for all TrFE contents. A
216 *ttg* (γ) mode at 310 cm^{-1} is observed to increase with TrFE, though no other phase-specific
217 modes are detected in this range. Additional bands are also present, especially for 50% TrFE,
218 labelled as b1, b2, and b3, which do not correspond to any reported band in PVDF-based

219 materials. We can speculate that these bands may be associated to *tg*-containing segments, such
220 as *tttg* or *t₃g*, as their intensity increases with TrFE content.

221 The zone 2 between 750 and 900 cm^{-1} is associated to CH_2 τ and ρ modes (VDF modes), CF_2
222 stretching (ν) modes, and some CC ν modes (associated to VDF). These bands are typically
223 used in the analysis of PVDF phases in Raman and FT-IR studies. A close-up of this region is
224 shown in Figure 1b. The overlapping modes give rise to three main peaks around 800, 845, and
225 880 cm^{-1} . The peak around 800 cm^{-1} has contributions from the α and γ , corresponding to *tg*
226 and *tttg*-segments respectively; the 845 cm^{-1} peak contains largely contributions from all-*trans*
227 segments under the form of a CF_2 ν mode, but several early works point to the presence of
228 additional *tttg*-segment modes, around 833 to 843 cm^{-1} (839 cm^{-1} in FT-IR). More recent
229 simulation works showed these *tttg*-modes are expected to have much lower intensity than the
230 all-*trans* specific mode at around 845 cm^{-1} , even for a pure γ sample (for which the band at 811
231 cm^{-1} appears prominently in the spectra).⁴⁴ Lastly, the 880 peak presents multiple VDF-specific
232 contributions from different modes related to different chain segments (at 874, 876, and 884
233 cm^{-1}). This band is observed to decrease with TrFE content. The most intense peak occurs at
234 around 845 cm^{-1} (ν CF_2) and is associated to β -phase crystallites. As TrFE content increases,
235 the 800 band shifts towards 811 cm^{-1} , which corresponds to a *tttg*-specific mode (ρ CH_2). The
236 main 845 band increases its intensity while also shifting towards higher wavenumbers (increase
237 in all-*trans* segments).

238 The zone 3 spans from around 900 up to 1300 cm^{-1} , comprising several CC and CF_2 ν modes.
239 This region presents high intensity bands in FT-IR spectroscopy, used to estimate chain defects
240 and phase in several PVDF-based co- and ter-polymers. Despite the weaker response in Raman
241 spectroscopy, a few overlapping bands can still be identified around 1060 to 1070 cm^{-1} (from
242 *tg* and *tt* segments); and around 1280 to 1290 cm^{-1} (all-*trans* and *tg* segments, respectively).
243 The band at 1280 cm^{-1} is a good indication of the presence of β -phase crystallites ($t > 4$) in

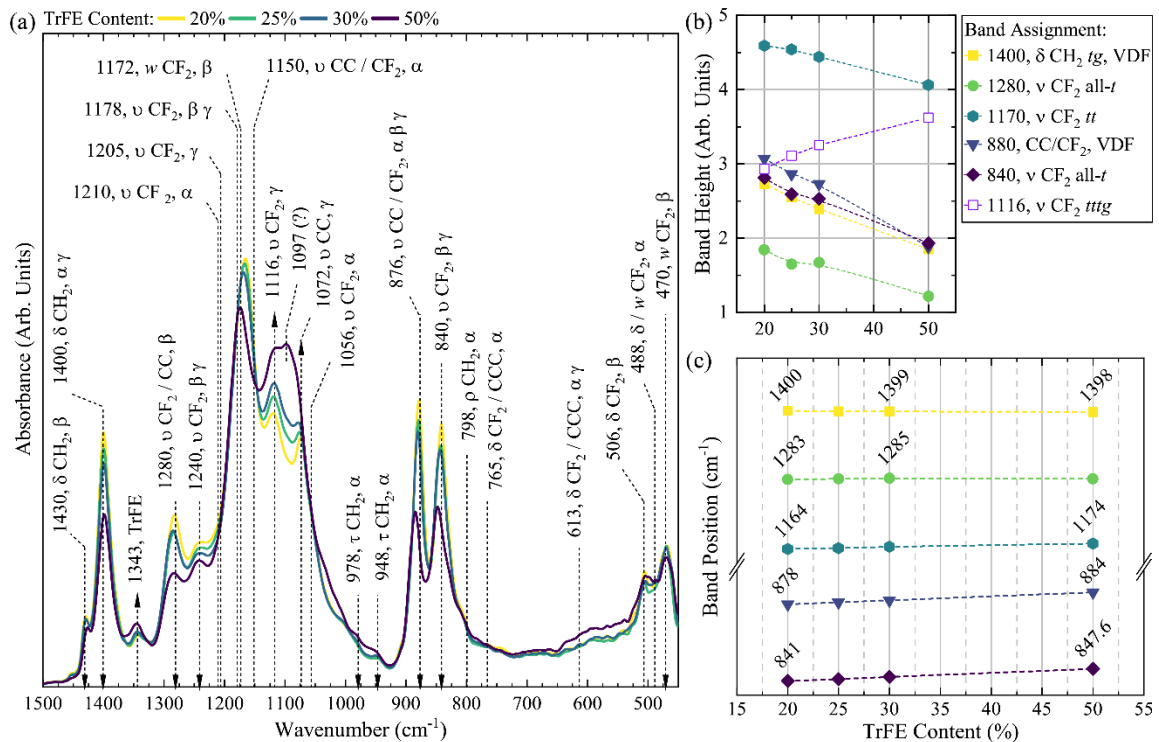
244 PVDF-based materials, often mentioned in FT-IR analysis. Immediately after, zone 4 (1320 to
245 1380 cm^{-1}) contains modes associated to the TrFE units (around 1347 and 1366 cm^{-1}). This
246 assignment has not always been reported in the literature, with works disregarding these bands,
247 performing wrong mode attribution, or acknowledging its relationship with TrFE without
248 further exploration.^{15, 26-36} The neglect is in part due to the low intensity of these bands for low
249 TrFE contents. So far there has not been an exploration of the type of vibration, the associate
250 chain segments, or their relationship with the material behavior or crystallinity, despite reports
251 during the 1980s and 1990s on the synthesis of P(VDF-TrFE) and polytrifluoroethylene
252 (PTrFE) and their IR and Raman spectra.^{15, 26-32} An increase in mode intensity is clearly
253 observed with TrFE molar content. Finally, zone 5 comprises the modes above 1380 cm^{-1} ,
254 which include several VDF specific CH_2 δ modes. In particular, around 1430 cm^{-1} , three modes
255 can be found at approximately 1427 (not shown), 1430, and 1434 cm^{-1} , corresponding to *tttg*,
256 *tgtg*, and all-*trans* segments. For the considered experimental conditions and TrFE molar
257 compositions, a decrease in these bands is observed with TrFE content.

258 The variation in band intensity and band position is plotted in Figure 1c-d, for the bands located
259 at *ca.* 800, 845, 880, 1348, and 1430 cm^{-1} , corresponding to: the 796 + 811 cm^{-1} group (*tg* τ
260 and *tttg* ρ , CH_2); the 843 + 845 cm^{-1} group (*tttg* + all-*trans*, CF_2 ν); the CC ν modes (VDF, all
261 conformations); one of the observed TrFE unit modes; and the 1430 + 1434 cm^{-1} group (*tg* and
262 all-*trans*, CH_2 δ), respectively. Several observations can be made from such a representation.
263 Firstly, the 845 cm^{-1} band is most intense for a TrFE content of 20 %, after which it gradually
264 weakens, consistent with previous reports on the favorable formation of β -phase crystalline
265 domains in P(VDF-TrFE).^{54, 55} Secondly, the 800 cm^{-1} band increases (especially for 50 %
266 TrFE), pointing to an increase in *tg* or *tttg* conformations in VDF-segments and agreeing with
267 other low intensity *tg* and *tttg* modes (*tttg* specific mode at 310 cm^{-1}) observed in the spectra.
268 Lastly, the VDF-specific 880 cm^{-1} band shows a decrease with TrFE, in accordance with the

269 gradual replacement of the VDF units by TrFE. It is interesting to note that the TrFE band at
270 1348 cm^{-1} increases in intensity, but not linearly. The opposite is observed with the VDF band
271 at 1430 cm^{-1} , which decreases with the TrFE content.

272 The shifts in band position, shown in Figure 1d, also proved instructive. These shifts are most
273 significant in the case of the 800 cm^{-1} band, which rises from 808 to 813 cm^{-1} (consistent with
274 an increase in *tttg* segments); and the 845 cm^{-1} band, which initially lies at 843 cm^{-1} and shifts
275 to around 852 cm^{-1} . The observed band position shifts (towards higher energy) can be
276 associated to stress, changing the molecular environment. This behavior will be further
277 discussed in the next sections (*vide infra*). Finally, the 1430 cm^{-1} band initially appears around
278 1434 cm^{-1} , shifting towards 1431 cm^{-1} . As no α -specific modes are clearly observed for a TrFE
279 content of 50%, we can assert that this shift towards 1430 cm^{-1} is due to the observed decrease
280 in band intensity combined to the slow increase in *tttg* modes (in this case, a small
281 overshadowed contribution from the band at 1427 cm^{-1} that shifts the convoluted peak towards
282 low wavenumbers).

283 In summary, the prepared samples are primarily composed of long all-*trans* segments, and
284 should be expected to present high β -phase content (thus a more ferroelectric behavior).
285 Nevertheless, the gradual appearance of defects with TrFE content is clear (especially *tttg*-
286 segments) marked by band position shifts, the persistence of low intensity bands from *tg*-
287 segments (but the absence of α -specific modes), and the appearance of the 310 cm^{-1} band (*tttg*-
288 specific).

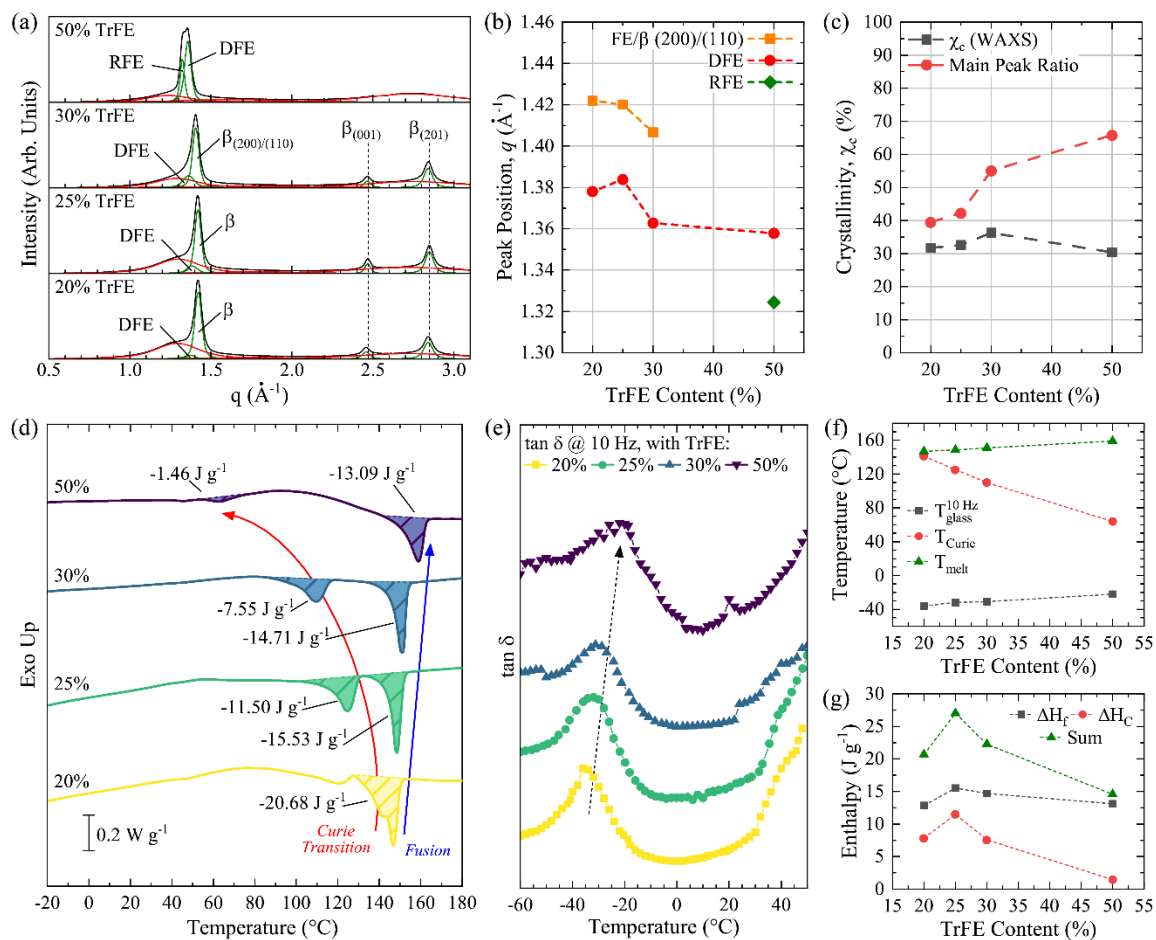


289 **Figure 2.** FT-IR spectra, and band height and shift as a function of TrFE content. a) FT-IR
 290 spectra for samples with different TrFE molar content, with respective band labeling and phase
 291 assignment. Multiple phases can be associated to the same band. b) Band height for a selection
 292 of β -specific (840, 1170, and 1280 cm^{-1}), γ (1116 cm^{-1}), and VDF modes (880 and 1400 cm^{-1})
 293 with TrFE content. c) Band shifts for the same bands shown in b).

295

296 **FT-IR Spectroscopy.** Complementary FT-IR characterization was performed in order to relate
 297 the experimental observations between the two techniques. The FT-IR spectra are plotted in
 298 Figure 2a, with the assignment of several bands to their associated phases and type of vibration.
 299 Several β -specific modes are present for all compositions (470, 506, 840, 1172, 1280, and 1430
 300 cm^{-1}). The range 900-1300 cm^{-1} (zone 3 in Raman) is particularly more active in FT-IR and
 301 provides additional information. A gradual increase in a γ -related mode is observed around
 302 1116 cm^{-1} (arising from *tttg*-segments), as well as other shared modes from *tt* and *tg* segments.
 303 An additional band can also be seen around 1097 cm^{-1} (marked with “?”), the origin of which
 304 is unclear, as previous works have not reported the presence of any band at this location.
 305 Considering its location, it is likely that this mode arises from *tttg* or *tg* segments, as a gradual
 306 increase in these modes is observed with increasing TrFE content. The same band was also

307 detected in the Raman spectra, labelled as b4 (see Figure 1a), albeit with a much lower
308 intensity. The 1343 cm⁻¹ TrFE band is also visible, although it increases only slightly with the
309 TrFE molar content. The 1364 cm⁻¹ TrFE band is overshadowed by the 1400 cm⁻¹ band, which
310 is more active in FT-IR. This shows that Raman spectroscopy is a more suitable technique to
311 analyze changes in this spectral region linked to the TrFE bands. Peak height and position are
312 plotted in Figure 2b and 2c. The same tendencies as those retrieved in Raman spectroscopy are
313 also observed, with maxima in β -specific modes (840, 1170, and 1280 cm⁻¹) occurring for TrFE
314 contents of 20 %. The VDF-specific 880, 1400, and 1430 cm⁻¹ (the latter less active in FT-IR)
315 decrease with TrFE, in line with the Raman spectra. Several band shifts are detected, with β -
316 specific modes shifting towards high wavenumbers. The 1400 cm⁻¹ band presents a shift
317 towards low energy (as the 1430 cm⁻¹ bands in Raman). The presence of these two bands in
318 Raman and FT-IR (with different activity) and arising from different conformations of the VDF
319 units demonstrate that despite the high content of β -phase, there are still several VDF chain
320 segments presenting *tttg* and *tg* conformations in-between long all-*trans* segments. These *tg*-
321 defects may arise from within the crystalline domains but also from the crystalline-to-
322 amorphous boundaries where a certain degree of long range ordering may still exist (oriented
323 amorphous fractions).^{56, 57} The FT-IR spectra agrees very well with the tendencies observed
324 from the Raman spectra. In particular, FT-IR analysis confirmed the increase of defective
325 conformations with TrFE molar content (such as *tttg* and *tg* segments), such as the case of the
326 bands at 1072 and 1116 cm⁻¹.



327
 328 **Figure 3.** X-ray diffraction patterns, calorimetry, and dielectric spectroscopy. a) Diffraction
 329 patterns for the considered samples, with peak labelling. b) Peak position, in q , extracted from
 330 the pattern fitting functions in a). c) Crystallinity and main peak ratio calculated from the
 331 crystalline peak area. d) DSC thermograms, showing the shift in melting temperature (blue
 332 arrow) and Curie transition temperature (red arrow). The areas of the endotherms are also
 333 shown. e) Permittivity loss factor, $\tan \delta$, at 10 Hz, as a function of temperature, showing a shift
 334 of the glass transition temperature (dashed black arrow) towards higher temperatures. f) Plot
 335 of the transition temperatures ($T_{glass}^{10 Hz}$, T_{Curie} , and T_{melt}) estimated from the DSC and DE data
 336 shown in d) and e), respectively. g) Plot of the fusion enthalpy (solid-liquid, ΔH_f), Curie
 337 transition enthalpy (solid-solid, ΔH_C), and their sum, obtained from endotherm integration from
 338 d). The values for 20% TrFE were extrapolated from an endotherm deconvolution (see SI,
 339 Figure 2S).

340

341 **X-ray Structural Analysis.** The structure of the P(VDF-TrFE) films was assessed with wide-
 342 angle X-ray scattering (WAXS). The azimuthally integrated diffraction patterns and the
 343 respective fittings (see SI for additional information) are shown in Figure 3a. Several
 344 diffraction peaks were identified for all compositions: the ferroelectric (FE) β phase with

345 pseudo-hexagonal/orthorhombic unit cell (20 to 30 % TrFE); the defective ferroelectric (DFE)
346 phase (all co-polymers); and the relaxor-ferroelectric (RFE) phase for 50 % TrFE. For the 20
347 to 30 % TrFE, the main detected phase corresponded to the FE β phase, with the most intense
348 reflection associated to the (200)/(110) peak around 1.42 \AA^{-1} . It was already reported that DFE
349 phases can arise in PVDF co- and ter-polymers with TrFE and low amounts of CFE or CTFE
350 due to the increase in the interplanar distance and the incorporation of *tg* defects along the
351 polymer chain, disrupting long-range ferroelectric ordering.^{58, 59} The increase in chain defect
352 occurrence (from the increase of TrFE, CFE, or CTFE) has been linked to the eventual
353 transformation of this DFE phase into a relaxor-ferroelectric (RFE) phase.⁵⁸ This is the case
354 for the sample with 50 % TrFE content, which presents two diffraction peaks associated to a
355 RFE and a DFE phase (at 1.32 and 1.36 \AA^{-1} , respectively), with the disappearance of the FE β
356 phase. The presence of a RFE phase for 50% TrFE is consistent with previous reports on the
357 presence of a morphotropic phase boundary around this TrFE proportion, leading to a
358 competition between FE/DFE and RFE phases, after which the RFE becomes the dominant
359 phase.^{23-25, 60} In addition, no crystalline bands were detected in Raman or FT-IR that correspond
360 to a PE phase (α -specific, *tgtg'*), which further corroborates that the detected diffraction peaks
361 correspond to a RFE and DFE phases. The extracted peak positions (in q) from the fitted data
362 are plotted in Figure 3b for the FE, DFE, and RFE. The positions decrease in q (*i.e.*, an increase
363 in the interplanar distance) due to the incorporation of TrFE units inside the crystalline
364 lamellae. The potential incorporation of *tg* defects inside the crystalline lamellae is also
365 expected to play an important role in the increase of the interplanar distance for high TrFE
366 contents, as backed up by the Raman and FT-IR spectra. The absence of crystalline diffraction
367 peaks at high q (above 2.4 \AA^{-1}) for a 50 % TrFE content suggests a significant disruption in
368 long range chain ordering. The diffraction planes associated to these reflections [(001) and
369 (201)] contain a *c*-axis component (chain axis), and their absence may point to a disruption on

370 chain ordering from the appearance of *tg* segments. This observation is consistent with recent
371 interpretations on the origin of relaxor behavior in the PVDF family of co- and ter-polymers.²³⁻
372 ²⁵ These works highlight the formation of a disordered 3/1 helix structure due to the chirality
373 of the TrFE (or CTFE) monomer, disrupting structural and ferroelectric long-range ordering.

374 The crystallinity (χ_c) was estimated from the diffraction patterns (ratio of crystalline peak area
375 to total pattern area). The values are plotted in Figure 3c, with χ_c increasing up to 38 % for a
376 30 % TrFE content, decreasing to around 30 % for 50 % TrFE. A recent work by María *et al.*
377 reported on the crystallization kinetics of molten bulk P(VDF-TrFE) co-polymers, showing
378 that the inclusion of TrFE inside the PVDF-crystals increased nucleation rate and density.⁶¹
379 This work deals with solution cast and dried thin films, in which solvent-polymer interaction
380 is expected to have an important contribution. In the considered conditions, high TrFE content
381 appears to promote higher crystallinity. The observed decrease for a TrFE content of 50 %
382 could be explained by the absence of high *q* diffraction peaks, reducing χ_c . This may not entail
383 a decrease in sample crystallinity, but rather a disruption in chain long-range ordering
384 (particularly along the *c*-axis). In fact, if we calculate the main peak ratio considering only the
385 contributions between 1.0 to 1.6 Å⁻¹ (also shown in Figure 3c), we observe that it increases
386 constantly with the TrFE content due to the decrease of the amorphous halo around 1.2 to 1.3
387 Å⁻¹.

388

389 **Calorimetry and Dielectric Spectroscopy.** Calorimetry is often used to estimate χ_c in these
390 polymer systems. However, the variation of the enthalpy of fusion (ΔH_f^0) with TrFE in P(VDF-
391 TrFE) is not established, with several works utilizing reported values with variations of 5 to
392 10 % from the experimentally used proportions. ΔH_f^0 of 93 and 67 J g⁻¹ have been reported for
393 PVDF and PTrFE homopolymers, respectively, with more recent works reporting values

394 around 40 J g^{-1} for P(VDF-TrFE) with 20 % TrFE.⁶²⁻⁶⁵ These values show ΔH_f^0 in P(VDF-
395 TrFE) co-polymer systems has a non-linear response, and an extrapolation is not sufficient to
396 properly estimate χ_c for a large array of molar fractions.

397 Nonetheless, calorimetry provides important information on transition temperatures. DSC was
398 performed and the resulting endotherms plotted in Figure 3d, for the first heating scan. The
399 melting (solid-liquid transition, T_{melt}) and Curie (solid-solid transition, T_{Curie}) transition
400 temperatures present opposite tendencies, with the T_{melt} increasing with the TrFE content (blue
401 arrow), while T_{Curie} decreases (red arrow). At 20 % TrFE, T_{Curie} approaches T_{melt} resulting in
402 two overlapping endotherms. The T_{Curie} shift towards low temperature is in line with the
403 observed phases from the X-ray diffraction data, with the increase in TrFE resulting in a loss
404 of dipolar long-range coherence (especially for high TrFE contents). The permittivity loss
405 factor (shown in Figure 3e), $\tan \delta$, as a function of temperature (at 10 Hz) was recorded with
406 dielectric spectroscopy (DE) allowing the estimation of the glass transition temperatures
407 ($T_{\text{glass}}^{10 \text{ Hz}}$). The maxima around $-40 \text{ }^\circ\text{C}$ correspond to $T_{\text{glass}}^{10 \text{ Hz}}$, shifting to higher temperatures with
408 TrFE content. The estimated transition temperatures from DSC and DE ($T_{\text{glass}}^{10 \text{ Hz}}$, T_{Curie} and T_{melt})
409 are plotted in Figure 3f, showing approximately linear tendencies with TrFE, for the considered
410 proportions. The increase in T_{melt} with TrFE content is consistent with previous early works on
411 P(VDF-TrFE) co-polymers that analyzed transition temperatures in this system. The T_{Curie}
412 decrease is also in agreement with the literature, stabilizing at lower temperatures for high TrFE
413 content. This decrease signifies a shift towards a RFE phase.^{63, 66}

414 The enthalpies of fusion and Curie transition (ΔH_f and ΔH_C , respectively) are plotted in Figure
415 3g, along with their sum. The values for 20 % TrFE were extrapolated from the deconvolution
416 of the endotherm by fitting with two Pearson IV functions (see SI, Figure S2). The highest
417 values of ΔH_C are obtained for 25 % TrFE. This would suggest the largest amount of

418 electroactive phases is found for 25 % TrFE despite the fact that this TrFE proportion presents
419 a lower T_{Curie} , a similar χ_c , and less intense all-*trans* modes maxima (Raman and FT-IR) when
420 compared to 20 % TrFE. Another possibility to explain this discrepancy may be related to the
421 solid-solid phase transition enthalpy, which for 25 % TrFE may be higher than for 20 %. As
422 far as the authors know, no systematic study has been performed on potential variations on
423 solid-solid phase transition enthalpy on these co-polymer systems. ΔH_f follows a distinct trend,
424 presenting the lowest values for 20 % TrFE (12.8 J g⁻¹, extracted from fitting), followed by
425 50 % TrFE (at 13.09 J g⁻¹), and retaining values around 15 J g⁻¹ for the remaining TrFE
426 proportions.

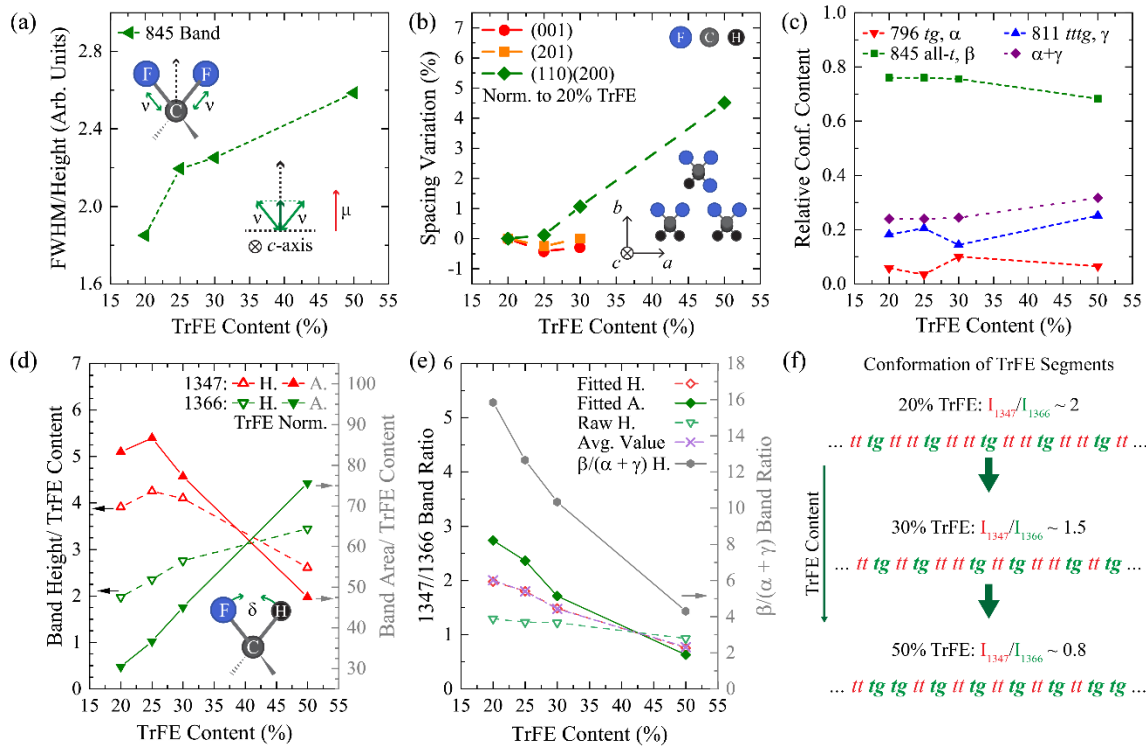
427

428 **Deciphering the Effects of TrFE on Raman Spectra.** Following the additional analysis with
429 WAXS, DSC, and DE, we can now address the band broadening and shifting observed in the
430 Raman (and FT-IR) spectra. Signal broadening is associated to loss in vibration coherence,
431 while band shifts are associated to vibration energy shifts induced by changes in molecular
432 interactions or bond compressive/tensile stresses. In the spectra in Figure 1a-b, we can see a
433 gradual broadening of the 845 cm⁻¹ band, corresponding to an all-*trans* CF₂ v mode. We can
434 quantify the degree of broadening by performing a non-linear multi-peak fitting (see SI for
435 details) for the bands located in this range (*ca.* 750 to 920 cm⁻¹) and extracting the height and
436 breadth of the 845 cm⁻¹ band. As material crystallinity and the relative amount of all-*trans*
437 segments directly impact the intensity of this band, we can attempt to remove these
438 contributions by calculating the ratio between peak FWHM and height. This ratio is plotted in
439 Figure 4a, where it shows a minimum for 20 % TrFE, after which it increases steadily. The
440 curve suggests that this vibration mode presents high coherence for 20 % TrFE (*i.e.*, the highest
441 all-*trans* content). The vibration coherence then decreases as the TrFE molar content increases.
442 The all-*trans* CF₂ v mode is of particular importance given the direction of the vibration with

443 respect to the chain backbone, *i.e.*, having a perpendicular projection to the chain, as illustrated
444 in Figure 4a. This component is also parallel to the monomer dipolar moment (μ , which is
445 perpendicular to the polymer backbone, or *c*-axis), and may serve as an indicator for dipolar
446 long-range ordering. This is consistent with the variation of the T_{Curie} extracted from the DSC
447 data (Figure 3d and 3f). The highest T_{Curie} was obtained for 20 % TrFE, entailing long-range
448 dipolar ordering, after which it decreases due to a decrease in dipolar ordering from the increase
449 in inter-chain spacing (as attested by the X-ray data). It is also important to mention that phonon
450 confinement effects can also play an important role on the observed band broadening.⁶⁷ This
451 confinement effect originates from the gradual formation of *tg*-defects along all-*trans*
452 segments, producing an asymmetrical band broadening. However, the complex band
453 contribution in this region hinders the proper detection of a biased broadening effect.

454 The band shifts can be analyzed considering the effects of the TrFE units and defect
455 incorporation into the polymer structure. Considering the diffraction peaks at high *q* values
456 (see Figure 3a), we can express the relative spacing variation with respect to the peak positions
457 for 20 % TrFE. This is plotted in Figure 4b, for the diffraction peaks associated to the (001),
458 (201), and (110)/(200) planes. The (001) and (201) planes containing the *a* and *c*-axis of the
459 unit cell present negligible relative variations, lower than 1 %; while the (110)/(200) plane
460 increases its relative spacing, reaching almost 5 % for the DFE-phase at 50 % TrFE. As the
461 (201) plane includes an *a*-axis component and presents minor variations, we can conclude that
462 the unit cell expands non-uniformly in the *b*-axis, experiencing compressive stress along the *a*
463 and *c*-axis as more TrFE units are incorporated into the polymer chain. This anisotropic unit
464 cell expansion is likely responsible for the band shift observed in both Raman and FT-IR
465 spectroscopy.

466



467

468 **Figure 4.** Band broadening, shifting, and ratios from X-ray and Raman data. a) 845 cm⁻¹ all-

469 *trans* CF₂ v mode band broadening normalized to peak height vs. TrFE content, with illustration

470 of the vibration geometry relative to the chain *c*-axis and dipolar moment, μ . b) Relative unit

471 cell diffraction plane spacing variation (with respect to 20 % TrFE) for the (001), (201), and

472 (110)/(200) diffraction planes as a function of the TrFE content. An illustration of the all-*trans*

473 orthorhombic unit cell is also shown, seen from the direction of the *c*-axis. c) Relative

474 conformation content vs. TrFE molar content, calculated from the height of the 796, 811, and

475 845 cm⁻¹ fitted Raman bands. d) Evolution of the band height and area of the 1347 and 1366

476 cm⁻¹ TrFE bands, extracted from spectral fitting, and normalized to the TrFE content. An

477 illustration of the vibration mode is also shown. e) Band height and band area ratios for the

478 1347 cm⁻¹ *tt* and 1366 cm⁻¹ *tg* TrFE bands, extracted from the fitted data (Fitted H. and Fitted

479 A.) and the raw data (denoted as Raw H.), and the calculated average value (Avg. Value) from

480 all the data sets. The calculated average coincides with the fitted band height values. The β (all-

481 *trans*) to $\alpha+\gamma$ (*tg* + *tttg*) band height ratios (in gray, left axis) are also plotted, extracted from

482 the same fitted data utilized in c). f) Illustration of the chain conformation within the TrFE

483 segments, with decrease of the number of *tt*-segments between each *tg*-segment with increases

484 in TrFE content. The ratios I_{1347}/I_{1366} represent the band intensity [height or area, plotted in e)]

485 ratios between the bands 1347 and 1366 cm⁻¹.

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489

TrFE-specific Raman Bands and Defect Quantification. The different characterization

techniques reveal important information on the evolution of the chain conformation with TrFE

content. We start by addressing the origin of the TrFE vibration bands, especially clear in

490 Raman spectroscopy. The inverse relationship between the 1347 and 1430 cm^{-1} bands (Figure
491 1a and 1c) is a good indication of their nature. Based on well-established spectroscopic data of
492 high polymers^{28, 68} combined with the observed behavior in the recorded spectra, we are able
493 to infer the mechanism behind the evolution of the 1347 and 1366 cm^{-1} TrFE bands. It is well-
494 known that the CH_2 deformation in PVDF is shifted towards low wavenumbers in comparison
495 to polyalkenes, such as polyethylene or polypropylene, due to the presence of the F atoms that
496 reduce the vibration frequency of the δCH_2 modes.⁶⁸ The addition of another F atom, as is the
497 case of the TrFE unit, should further shift the vibration frequency of this mode towards lower
498 energies, having a vibration dampening effect. Considering the decrease in the 1430 cm^{-1} δ
499 CH_2 mode, we can associate the 1347 and 1366 cm^{-1} bands as arising from CHF deformation
500 modes (δCHF) in the TrFE units.

501 On the basis of this hypothesis, we can further explore the chain conformation related to these
502 two bands by gathering evidence from the characterizations carried out. Firstly, we can use the
503 data obtained from the 845 cm^{-1} band fitting (as discussed above; see SI, Figure S3) to infer
504 the overall relative conformation content based on the intensity of the fitted peaks for the 796,
505 811 and 845 cm^{-1} bands. This is plotted in Figure 4c, with the highest relative all-*trans* content
506 obtained for TrFE contents of 20 % up to 30 %. An increase in the *tttg* conformation is then
507 seen for 50 % TrFE, in line with the appearance of other *tttg* related bands in other zones of the
508 Raman and FT-IR spectra. This is also validated by the presence of the RFE phase in the X-
509 ray diffraction pattern, as well as the decrease in the magnitude of T_{Curie} and ΔH_C in the DSC
510 data. We can apply the same analysis to the two TrFE bands at 1347 and 1366 cm^{-1} and perform
511 a multi-peak fitting with several Gaussian and Voigt profiles between the range of 1270 and
512 1500 cm^{-1} (see SI, Figure S4), extracting the height and the area of these bands. As the intensity
513 is also proportional to the amount of TrFE, we should normalize the extracted data by the TrFE
514 molar content. The normalized peak height and area for the two bands is plotted in Figure 4d

515 for the considered TrFE molar contents. These two bands present approximately mirrored
516 behaviors with similar tendencies as those observed in Figure 4c. This suggests that these two
517 bands arise from different chain conformations, and a clear shift is detected with the variation
518 of the TrFE molar content. Considering these observations and the overall increase in *tg* chain
519 defects supported by the different characterization techniques, we propose that the two TrFE
520 bands at 1347 and 1366 cm^{-1} are associated to δ CHF modes arising from two different chain
521 conformations, namely, a *tt* and *tg* conformation, respectively.

522 This band assignment opens the possibility for defect quantification in P(VDF-TrFE) co-
523 polymers by measuring and fitting these two bands from Raman spectroscopy data. In
524 particular, it offers a way to quantify TrFE *tg* defect occurrence along the polymer chain by
525 focusing on the height or area ratio of the 1347 and 1366 cm^{-1} bands. This is shown in Figure
526 4e, where the 1347 and 1366 band height and area ratios are plotted from the fitted (Fitted H.
527 and Fitted A.) and raw data (Raw H.), along with the ratio average value (Avg. Value). The
528 $\beta/(\alpha+\gamma)$ [alternatively, $tttt/(tg + tttg)$] band height ratio is also shown, obtained from the fitted
529 data (796, 811, and 845 cm^{-1}) used in the calculation of the relative conformation content
530 (Figure 4c). All the plotted data present the same tendencies with increasing TrFE content,
531 indicating an increase in the amount of *tg* defects along the polymer chain. The $\beta/(\alpha+\gamma)$ ratio
532 presents values above the 1347/1366 ratio, suggesting the VDF segments present higher
533 amounts of all-*trans* sequences in relation to *tg* sequences. It is very important to note that the
534 bands at 796 and 811 cm^{-1} , commonly used to estimate phase proportion in PVDF-based co-
535 polymers, arise from VDF-specific segments corresponding to CH_2 vibration modes. Our
536 relative conformation estimation does not account for the mode intensity loss from the
537 reduction in VDF segments with TrFE content, meaning the $\beta/(\alpha+\gamma)$ ratio may be
538 overestimated, and the VDF units may present a higher defect content than previously
539 suggested. This is also an aspect that has not been addressed in previous works, many of which

540 have relied on band intensity to estimate phase proportion in different processing and
541 composition studies. Interestingly, the 1347/1366 ratio also suggests that TrFE containing
542 chain segments already present *tg* defects even for low TrFE content. These *tg* defects may be
543 incorporated into the polymer crystallites and be responsible for the increase in unit cell volume
544 along with the incorporation of TrFE units, resulting in the observed DFE phases. The larger
545 value discrepancy between the ratios calculated from fitted height and area for low TrFE
546 contents can be explained by the error associated with multi-peak fitting for low intensity bands
547 that are easily overshadowed by other more intense contributions.

548 Recent literature has highlighted the importance of *tg* defects along the polymer chain, being
549 responsible for the appearance of RFE behavior.²³⁻²⁵ In 2020, Liu *et al.* reported on this effect,
550 and demonstrated how the chiral nature of the TrFE monomer leads to the formation of a
551 disordered 3/1 helix chain, with a (*tg*)₃ conformation.²⁴ Following the results discussed in this
552 article, we should expect to observe an intense vibration band around 1366 cm⁻¹ for a 3/1 helix
553 structure with (*tg*)₃, corresponding to the *tg* δ CHF, with a very small to negligible contribution
554 at 1347 cm⁻¹. This trend is indeed observed with the gradual increase of TrFE reducing the
555 contribution of the 1347 in favor of 1366 cm⁻¹, pointing to an increase in *tg* defects within the
556 TrFE segments. The ratio of these two bands may constitute a probe into the conformation of
557 the TrFE segments, with ratios above 1 and below 1 signifying a majority of *tt*-segments or a
558 dominance by *tg*-segments, respectively. We can note from Figure 4e, that the 1347/1366 ratio
559 drops continuously, from around 2 to a value around 0.8 for 50 % TrFE. An illustration of the
560 chain structure based on the 1347/1366 ratio (I_{1347}/I_{1366}) is depicted in Figure 4f, where the
561 chain conformation is represented for different contents of TrFE. The gradual increase of TrFE
562 decreases the length of the all-*trans* segments, with the ratio I_{1347}/I_{1366} representing the
563 approximate total number of *tt*-segments periodically separated by *tg* defects within the TrFE
564 segments of the polymer chain. A RFE phase is detected in this work for 50 % TrFE, for which

565 $I_{1347}/I_{1366} < 1$, *i.e.*, a *tg*-dominated chain structure that gradually approaches the 3/1 helix
566 structure. From the extrapolation of the calculated data, it can be seen that $I_{1347}/I_{1366} < 1$ occurs
567 around 45 % TrFE, the same proportion where the 1347 and 1366 bands height (area) inversion
568 takes place (Figure 4d). This proportion has previously been linked to the start of the
569 morphotropic phase boundary (around 45 % to 55 % TrFE) in P(VDF-TrFE) co-polymers. As
570 a result, a quantitative relationship has been established between specific band ratios and the
571 occurrence of *tg* defect in PVDF-based polymers, in good agreement with recent literature on
572 the structure and FE behavior of P(VDF-TrFE) co-polymers.²³⁻²⁵

573

574 CONCLUSION

575 In this work, we have analyzed the Raman spectra of P(VDF-TrFE) co-polymers for various
576 TrFE proportions. Under the considered conditions (solution-cast, no thermal annealing), the
577 co-polymers presented β phase (*all-trans*) specific vibration modes, with an increase in
578 defective modes (*tg* and *tttg* containing modes) for higher TrFE molar content. TrFE-specific
579 modes, whose intensity increases with TrFE content, were detected at 1347 and 1366 cm^{-1} , and
580 show opposite evolution to the surrounding VDF modes at 1430 cm^{-1} . Complementary FT-IR
581 analysis confirms these observations, with the highest intensity of *all-trans* modes found for
582 20 % TrFE, and with several *tttg*-specific modes appearing for higher TrFE contents (at 1056
583 and 1116 cm^{-1}). X-ray diffraction showed that the majority phase corresponded to the FE β
584 phase, with traces of a minor DFE phase. For 50 % TrFE, a RFE phase was observed with DFE
585 as the majority phase. Material crystallinity for the solution-cast films increased with TrFE
586 content, but was observed to decrease for 50 % TrFE, suggesting enhanced nucleation for
587 proportions around 30 %. DSC and DE showed an increase in the melting and glass
588 temperatures (T_{melt} and $T_{\text{glass}}^{10\text{ Hz}}$) and a decrease of the Curie transition temperature (T_{Curie}).

589 Following these results, we have proposed that the two detected TrFE bands at 1347 and 1366
590 cm^{-1} are associated to δ CHF modes arising from a *tt* and *tg* conformation, respectively.
591 Monitoring of the 1347/1366 intensity ratio (I_{1347}/I_{1366}) was proposed as a potential probe into
592 the structure of the TrFE-segments: ratios above 1 represent a majority of *tt*-segments, while
593 ratios below 1 represent a dominance by *tg*-segments. The extrapolated inversion in the 1347
594 and 1366 cm^{-1} bands intensity also takes place for TrFE molar fractions corresponding to the
595 reported morphotropic phase boundary for P(VDF-TrFE). Accordingly, a quantitative
596 relationship has been drawn for the first time between specific band ratios and *tg* defect
597 occurrence in PVDF-based polymers. We expect this method to also be applicable to other
598 PVDF co- and ter-polymers containing chiral monomers (like CTFE or CFE).

599

600 ASSOCIATED CONTENT

601 **Supporting Information**

602 The Supporting Information is available free of charge at.

603 Additional information on polymer molecular weight from SEC. Polymer thin film
604 fabrication for dielectric spectroscopy. Multi-peak non-linear fitting of the X-ray diffraction
605 patterns. Multi-peak non-linear fitting of the DSC endotherm for 20% TrFE. Multi-peak non-
606 linear fitting of the Raman spectra.

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619

620 **Notes**

621 The authors declare no conflicts of interest.

622

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