Relaxor Ferroelectric Polymer Exhibits Ultrahigh Electromechanical Coupling at Low Electric Field

One-Sentence Summary: Relaxor ferroelectric polymers exhibit electromechanical coupling and piezo-coefficient exceeding the piezoceramic PZT

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Abstract: The energy conversion between electric and mechanical forms in ferroelectrics, the electromechanical (EM) coupling, has been used for a broad range of applications. Ferroelectric polymers have weak EM coupling that severely limits their usefulness for applications. We introduced a small amount of fluorinated alkyne (FA) monomers (<2 mol%) in relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (PVDF-TrFE-CFE) terpolymer that markedly enhances the polarization change with strong EM coupling while suppressing other polarization changes that do not contribute to it. Under a low DC bias field of 40 MV/m, the relaxor tetrapolymer has the EM coupling factor k_{33} of 88% and the piezoelectric coefficient d_{33} value over 1,000 pm/V. These values make this solution-processed polymer competitive with ceramic oxide piezoelectrics, with the potential for use in distinct applications.

Ferroelectric materials have been widely used in electromechanical (EM) energy conversion such as energy harvesting, acoustic transducers for imaging, fault detection, ship navigation, and sensors and artificial muscles in robots (*1,2*). Due to their high pliability, easy fabrication into complicated shapes, light weight, and low cost, ferroelectric polymers are attractive for these applications (*2-5*). However, the low EM performance of polymers, compared with their inorganic counterparts, severely limits their performance and usefulness in these applications. For example, the EM coupling factor k_{33} of 23% and piezoelectric coefficient d_{33} of -35 pm/V of poly(vinylidene difluoride) (PVDF) based ferroelectric polymers, which have the most attractive performance of ferroelectric polymers in the market, are much smaller than $k_{33} > 70\%$ and $d_{33} > 700$ pm/V of widely used ferroelectric ceramic $Pb(TiZr)O_3$ (PZT) (*1,3-6*). In the past several decades, various efforts have been devoted to improving the EM performance of ferroelectric polymers with limited success (*3,4,7,8*). For example, Ohigashi et al. developed P(VDF-TrFE) (TrFE: trifluoroethylene) single crystals that raised k_{33} to 33% and d_{33} to - 40 pm/V (*7*). More recently, by exploiting the morphotropic phase boundary (MPB) effect in P(VDF-TrFE) copolymers, Liu et al. reported a d_{33} = - 65 pm/V and $k_{33} < 27\%$ for the copolymer compositions near MPB (*8*).

In ferroelectrics, the piezoelectric effect from both the normal ferroelectrics and the electrostrictive effect from the relaxor ferroelectrics has been investigated and utilized for EM applications (*1,4,6,9-11*). Biasing DC electric fields generate piezoelectric states whose EM response can be tuned by varying the DC bias field (see schematic in fig. S1). Relaxor ferroelectric polymers have been developed in the past, and they exhibited relatively high EM responses at high fields such as $k_{33} > 50\%$ at 120 MV/m (*4,12-14*). However, high fields prohibit their applications in practical devices due to easy electric breakdown and failure. For the reliable operation of PVDF polymer-based dielectric devices, the applied field should be lower than 60 MV/m (*15,16*). We report relaxor ferroelectric P(VDF-TrFE-CFE-FA) (CFE: chlorofluoroethylene, FA: fluorinated alkynes) tetrapolymers that generate large electrostriction at low electric fields. Under a low DC bias field of 40 MV/m, the tetrapolymer exhibits k_{33} of 88% and d_{33} of -1050 pm/V.

Phenomenologically, the EM responses of ferroelectric materials can be considered as arising from the electrostriction, e.g., the strain S is proportional to the square of the polarization P (*4,9,10*),

$$S_3 = Q_{33} P^2 \qquad (1)$$

where S_3 is the thickness strain and Q_{33} is the electrostriction coefficient. For piezoelectric coefficient d_{33} (= $\Delta S_3/\Delta E$), $d_{33} = 2 Q_{33} P_b \Delta P/\Delta E$ $(\Delta P/\Delta E = \varepsilon_{33})$, and the associated electromechanical coupling factor k_{33} is

$$k_{33} = d_{33}\sqrt{Y/\varepsilon_{33}} = 2 Q_{33} P_b \sqrt{Y \varepsilon_{33}} \qquad (2)$$

where P_b is the bias polarization, Y is the elastic modulus, and ε_{33} is the dielectric permittivity at constant stress (*17*). $\varepsilon_{33} = K \varepsilon_0$, where K is the dielectric constant at constant stress and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity. In most ferroelectrics, the polarization *P* can arise from many different processes. In inorganic ferroelectrics, *P* originates from single ferroelectric domains and domain wall motions (*6,18*). In polymers such as PVDF-based ferroelectric semicrystalline polymers, in addition to the *P* from the crystalline phase, additional polarization contributions arise from the amorphous phase and crystalline-amorphous interfaces (*3,19,20*). These different polarization processes will contribute to the EM response differently; they will have different *Q* values in Eq. (1). For example, in P(VDF-TrFE) ferroelectric polymers, the polarization switch is primary through successive 60° domain wall motions (*3,21,22*). Due to the pseudo-hexagonal symmetry of the unit cell, these domain wall motions will not generate high strain. The $|Q_{33}|$ of P(VDF-TrFE) ferroelectric copolymers is usually < 3 m^4/C^2, resulting in low k_{33} and d_{33} (*21,23*). Hence, in developing PVDF-based ferroelectric polymers for generating large EM responses, a critical step is to develop a strategy to raise Q_{33} and ε_{33} substantially while maintaining the large polarization or also even enhancing P in the polymers.

We selected the P(VDF-TrFE-CFE) relaxor terpolymer based on these considerations. The relaxor terpolymer exhibits a high dielectric constant K over a broad temperature range ($K > 50$) near room temperature, much higher than P(VDF-TrFE) copolymers and other PVDF-based polymers. In functional ferroelectric materials, a small amount of defects and/or dopants can profoundly affect material performance (*1,3,4,6,18*). In ferroelectric P(VDF-TrFE) copolymers, copolymerizing with CFE that are bulkier than both VDF and TrFE monomers (see fig. S2A for size) and hence expand the interchain spacing as random defects, converts all-trans bonds into trans-gauche bonds (see fig. S2B for conformations in the PVDF polymers) and transforms a ferroelectric into a relaxor ferroelectric at P(VDF-TrFE) compositions < 70/30 VDF/TrFE mol% (*4,24*). As shown by Yong et al. (*25*), CFEs, due to their bulkier size, are excluded from the crystallites and thus do not prevent the transition of the terpolymer from relaxor to ferroelectric phase at high electric fields.

We investigated FA monomer units, which have a smaller size than VDF and TrFE (fig. S2A) as random defects to modify P(VDF-TrFE-CFE) 63/29.7/7.3 mol% terpolymer, with the VDF/TrFE ratio of 68/32 mol%. Earlier studies showed that a minimum of 7 mol% CFE is required to completely convert ferroelectric P(VDF-TrFE) into relaxor ferroelectric (*4,24*). We hypothesize that such smaller-size defects can be at least partially included in the crystalline phase, thus can be effective in controlling the polarization responses in the relaxor polymer. Such FA monomer units can be introduced easily in P(VDF-TrFE-CFE) by de-hydrochlorination of CFEs in the terpolymer (fig. S3). We synthesized and characterized P(VDF-TrFE-CFE-FA) tetrapolymers with different FA contents. The tetrapolymer with the 63/29.7/5.4/1.9 composition displays the highest electroactuation (Fig. 1A). In electroactive polymers, mechanical stretching of polymer films will align the polymer chains and generate morphology changes that can profoundly affect the electroactive responses of the polymers (*3*). For PVDF-based ferroelectric polymers, electromechanical responses perpendicular and parallel to polymer chains have opposite signs, and thus in polymer films with randomly oriented chains, the combination of these competing effects will lower the electromechanical responses. We uniaxially stretched the tetrapolymer film with 1.9 mol% FA to more than 7× stretching ratio. We determined the thickness strain (S_3) as a function of the applied field (unipolar field) for the stretched tetrapolymer P(VDF-TrFE-CFE-FA)

63/29.7/5.4/1.9 mol% (s-tetrapolymer) at fields below 80 MV/m. The S_3 is -3.5% at 50 MV/m compared with -1% of the terpolymer, a marked enhancement, Fig. 1B. We obtained the strain-applied electric field loops of s-tetrapolymer along with strain loops of terpolymer and unstretched terpolymer (Fig. 1B, inset and fig. S4A-B). The general rule for dielectric devices such as polymer actuators and capacitors is that the fields should be lower than 20% of the dielectric breakdown strength. We therefore focused on the compositions with high responses below 60 MV/m.

In addition to the electrostriction, Maxwell stress may also generate large electromechanical responses in polymers (*4,26*). For isotropic polymers, the thickness strain S_M from Maxwell stress is

$$S_M = - \tfrac{1}{2}\, \varepsilon\, (1 + 2\, \sigma)\, E^2/Y, \qquad (3)$$

where σ is the Poisson's ratio, and E is the applied electric field. We treat unstretched tetrapolymer as isotropic and take $\sigma \sim 0.3$ for PVDF-based polymers. At 50 MV/m, the tetrapolymer has $\varepsilon = 67\ \varepsilon_0$, yielding a S_M of -0.53%, about 15% of the observed actuation strain (Fig. 1B, fig. S4B). We approximate the actuation strain in the tetrapolymer as occurring from electrostriction.

A DC bias field is often used in electrostrictive materials to induce a piezoelectric state and piezoelectric response (*4,9-11*). We characterized the electroactuation under low DC bias fields, 30 and 40 MV/m, with the AC field amplitude of 10 MV/m. We show the strains and polarizations under the two DC biases for the s-tetrapolymer film (Fig. 1C-D) and the unstretched tetrapolymer (fig. S4C-F) from which d_{33} (= Strain/E_{AC}) and ε_{33} (= $K\varepsilon_0 = \Delta P/E_{AC}$) at DC biased states are obtained (Table 1). We measured the elastic modulus, *Y*, of unstretched tetrapolymer films as 0.224 GPa using dynamic mechanical analysis (DMA). We deduced k_{33} from $d_{33}\sqrt{Y/\varepsilon_{33}}$ at DC-biased states for the tetrapolymer films (Table 1), using *Y*=0.224 GPa for both the unstretched and s-tetrapolymer films. We found high EM performance of P(VDF-TrFE-CFE-FA) s-tetrapolymers, with a k_{33} of 88% and d_{33} of –1050 pm/V even at low electric fields (< 50 MV/m), which exceed the benchmark piezoceramic PZT as well as lead-free piezoceramics, as presented in Fig. 1E and Table S1 (*1,6-8,27*).

We measured the dielectric properties vs. temperature at different frequencies for s-tetrapolymer (Fig. 2A, inset) and terpolymer (fig. S5A) (13). We did not find much of a change in the dielectric dispersion for s-tetrapolymer associated with the relaxor response, whose broad dielectric peak temperature shifts progressively towards lower temperature with frequency (*11-13*), but there is an additional, broad dielectric peak around 40 °C that does not move much with frequency. Differential scanning calorimetry data (fig. S6) also show a weak transition peak at ca 40 ºC. This suggests a diffused ferroelectric transition in the s-tetrapolymer.

We obtained the polarization response under unipolar and bipolar electric fields for the polymers studied, along with the dielectric properties of the tetrapolymer (Fig. 2A, fig. S5B, C, E). In relaxor ferroelectrics, a critical field, E_c, exists above which the relaxor transitions to a ferroelectric phase (*28*). The large increase in the polarization and polarization hysteresis in the P-E data of terpolymer (Fig. 2A) indicate a transition to ferroelectric at fields around 60 MV/m (*25*), while there is no such transition for the s-tetrapolymer at the experimental fields. To make a quantitative comparison, we plotted the P/E ratio as a function of the applied field [$K= P/(\varepsilon_0 E)$] for the terpolymer and s-tetrapolymer (Fig. 2B). The terpolymer has a lower K and hence lower polarization values than those of the s-tetrapolymer at fields below 60 MV/m. Above 60 MV/m, the field-induced transition to the ferroelectric phase raises the polarization, polarization hysteresis, and K above those of the s-tetrapolymers. In other words, the FA defects in the s-tetrapolymer lower the local polarization switch barriers, which result in higher polarization response at fields below 60 MV/m. At fields higher than that, the FA defects also prevent the transition of the relaxor to the ferroelectric phase. All these are desirable for generating high EM coupling.

From the electro-actuation strains (Fig. 1B) and polarizations (Fig. 2A), we deduced Q_{33} for the s-tetrapolymer from Eq. (1) at different electric fields (Fig. 2C). We also calculated Q_{33} for the terpolymer for comparison. From the elastic and dielectric properties, it is deduced from Eq. (3) that Maxwell stress generates more than 50% of our observed electro-actuation for the terpolymer, and hence the true Q_{33} is only about half that value. Thus, the s-tetrapolymer has more than a four times improvement in Q_{33}. This demonstrates that in PVDF-based ferroelectric polymers, the majority of the polarization changes do not contribute much to the EM performance, thus yielding a low EM coupling factor and small d_{33} (Fig. 1E) (Table S1). In the ferroelectric phase, polarization rotations generate very little electromechanical response. The exceptionally large $|Q_{33}|$ in the relaxor tetrapolymer indicates that FA defects effectively suppress the polarization responses that do not contribute much to the electromechanical response. We also deduce Q_{33} from $d_{33} = 2\, Q_{33}$

$P_b\, \Delta P/\Delta E$ for the s-tetrapolymer films at the two DC bias fields (Fig. 1C, D). Q_{33} of s-tetrapolymer films in the DC-biased state can reach more than 60 m^4/C^2 while the dielectric constant K (~ 40) is lower than that at zero bias field (Fig. 2A, B).

We examined the polymers' molecular and mesoscopic structures related to the large EM coupling in the tetrapolymers. Our X-ray diffraction (XRD) data show the (110/200) reflection of tetrapolymers shifting to higher angles and broadening with FA content (Fig. 3A). These features are indicative of a reduced interchain spacing and reduced coherent crystallization region (from ca. 51 nm to 45 nm) by converting CFE to FA in the relaxor polymers. When comparing the s-tetrapolymer to unstretched tetrapolymer with 1.9 mol% FA (fig. S7), we found no change in the peak position but a large reduction of the coherent crystalline size (from ca. 45 nm to 36 nm). The results suggest that stretching increases the inclusion of FAs in the crystalline phase, generating defect structures that reduce the coherent-scattering crystalline region of the XRD peak. A comparison of Fourier transform infrared (FT-IR) spectra of terpolymer and tetrapolymers (Fig. 3B) reveals that converting CFE into FA causes an increase in the all-trans bonds and a reduction of 3/1 helix bonds (responsible for the relaxor) and *TGTG'* bonds (Fig. S8) (*29,30*). These observations are consistent with the reduced interchain spacing (Fig. 3A). The SAXS spectra of tetrapolymer (1.9 mol% FA) and terpolymer show a slight reduction of lamellar spacing from terpolymer (~ ca. 49.3 nm) to tetrapolymer (~ 40.6 nm) (fig. S9). In contrast to CFEs, which are bulkier than VDF/TrFE and are excluded from the crystalline phase, FAs are at least partially included in the crystalline regions and, as a result, generate a large EM response.

Different applied fields can impact the XRD (110/200) peak, as shown in Fig 3C-D, fig. S10. We found little change in the XRD peak at electric fields ≤ 40 MV/m for the terpolymer, consistent with the low actuation strain at these fields. In contrast, the s-tetrapolymer film already exhibits a broad peak at 19.5°, even at 20 MV/m, in addition to the original peak at ca. 18.4°. This indicates an induced polarization transition that reduces the interchain spacing in the s-tetrapolymer at ultralow fields. The original (110/200) peak broadens with the applied field, showing a decrease in the coherent crystallization region from ca. 36 nm at zero electric field to ca. 23 nm at 40 MV/m. Our XRD results indicate that converting CFEs to FAs at 1.9 mol% substantially reduces the barriers for switching from non-polar (or less polar) bonds to polar bonds locally in the crystalline phase, generating large EM actuations at low electric fields, consistent with the electroactuation results (Fig. 1).

We performed density functional theory (DFT) calculations to determine the local lattice parameters and probe local structure changes due to FA bonds in the polymer (Fig. 3E, table S2). We also performed a DFT calculation of polarization and strain of the ferroelectric phase of P(VDF-TrFE), in which the polarization response is mainly from dipole reorientation under electric fields (fig. S11). Although the polarization rotation can generate a large polarization change, the electro-actuation strain is small (= 1.1 %), causing $Q_{33} < 3\ m^4/C^2$. In a large DFT unit cell, the P(VDF-TrFE) 3/1 helix structure has a lower energy than the polar all-trans structure, both with and without FA defects (table S2). Also, the 3/1 helix has a much smaller polarization than the all-trans. Therefore, as the electric field increases, the all-trans structure becomes energetically more favorable because of the $-\mathbf{E}\cdot\mathbf{P}$ term. The transformation from the helix to the all-trans phase results in substantial negative strain (table S2), in agreement with our experimental observations. We obtained our DFT results for crystalline bulk structures and thin films, but the relaxor polymers we studied experimentally consisted of small crystalline domains embedded in an amorphous matrix. Nevertheless, our calculations confirmed the observed preference for a low-polarization structure. Prior studies of phase transformations in PVDF show that chain transformations in PVDF-structure polymers proceed in a concerted fashion (*31*), in which nearby monomers rotate nearly simultaneously, thereby lowering the transformation barriers. The FA monomers are smaller and thereby present fewer steric constraints for chain transformation. They also partially decouple segments between two FA defects from adjacent segments, allowing for easier segment transformation.

The polarization changes in ferroelectric P(VDF-TrFE) polymers can originate from different processes. Some show strong EM coupling, such as molecular conformation changes between *TG* (*3/1 helix*, *TGTG'*, and T_3GT_3G') and all-trans bonds, while others do not contribute substantially to EM coupling, e.g., polarization reorientations between different crystal directions. Introducing a small amount of FA monomers in relaxor ferroelectric P(VDF-TrFE-CFE) polymers can markedly enhance the polarization changes between *TG* and all-trans bonds at low electric fields while suppressing the polarization reorientations. P(VDF-TrFE-CFE-FA) tetrapolymer with 1.9 mol% FA generates a higher polarization change at fields below 50 MV/m, leading to large electro-actuation. For example, the s-tetrapolymer possesses the electrostriction coefficient $|Q_{33}|$ larger than 40 m^4/C^2, about 4X of that in P(VDF-TrFE-CFE) relaxor polymer. Under a low DC bias field of 40 MV/m, the s-tetrapolymer exhibits k_{33} of 88% and d_{33} of –1050 pm/V, which make them attractive for practical applications such as energy harvesting, sensors and actuators in soft robots and wearable devices, and transducers for imaging.

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Competing Interests: Q.M.Z. and X.C. have filed a provisional patent at Penn State (US Application No. 63/197,275). Otherwise, the authors declare no competing interests.

Data and materials availability: All data are available in the main text or supplementary materials.

Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S13

Tables S1 to S4

References (32 – 37)

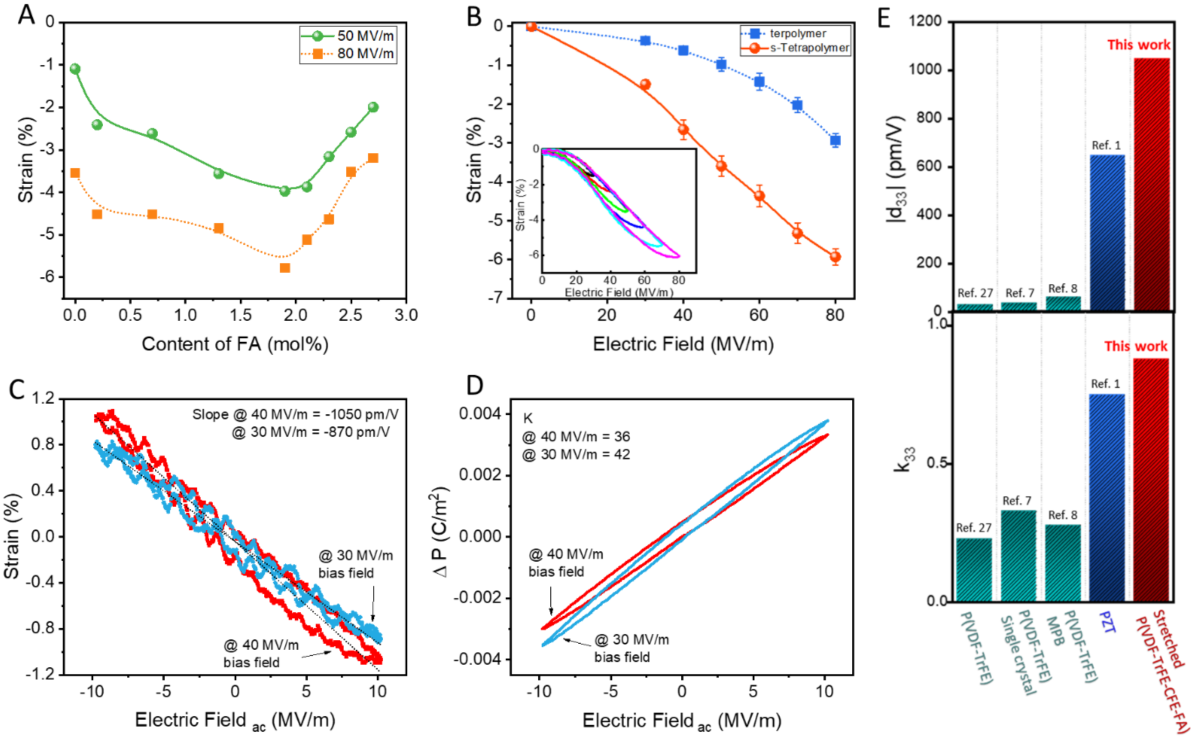

Fig.1 Electromechanical Properties of P(VDF-TrFE-CFE-FA) relaxor polymers. (A) Thickness strain S_3 of P(VDF-TrFE-CFE-FA) with different FA contents at 50 and 80 MV/m unipolar fields at 1 Hz. (B) Thickness strain of terpolymer and 1.9% stretched tetrapolymer at 1 Hz unipolar field vs. electric fields. In (A) and (B), curves are drawn to guide eyes. (C) Strain and (D) polarization at 1 Hz AC field under 30 and 40MV/m bias fields. (E) Comparison of d_{33} and k_{33} of commercial P(VDF-TrFE) copolymer, copolymer single crystal, and copolymer at MPB, $Pb(ZrTi)O_3$ (PZT) piezoceramic, and the relaxor P(VDF-TrFE-CFE-FA) tetrapolymer under 40 MV/m DC bias.

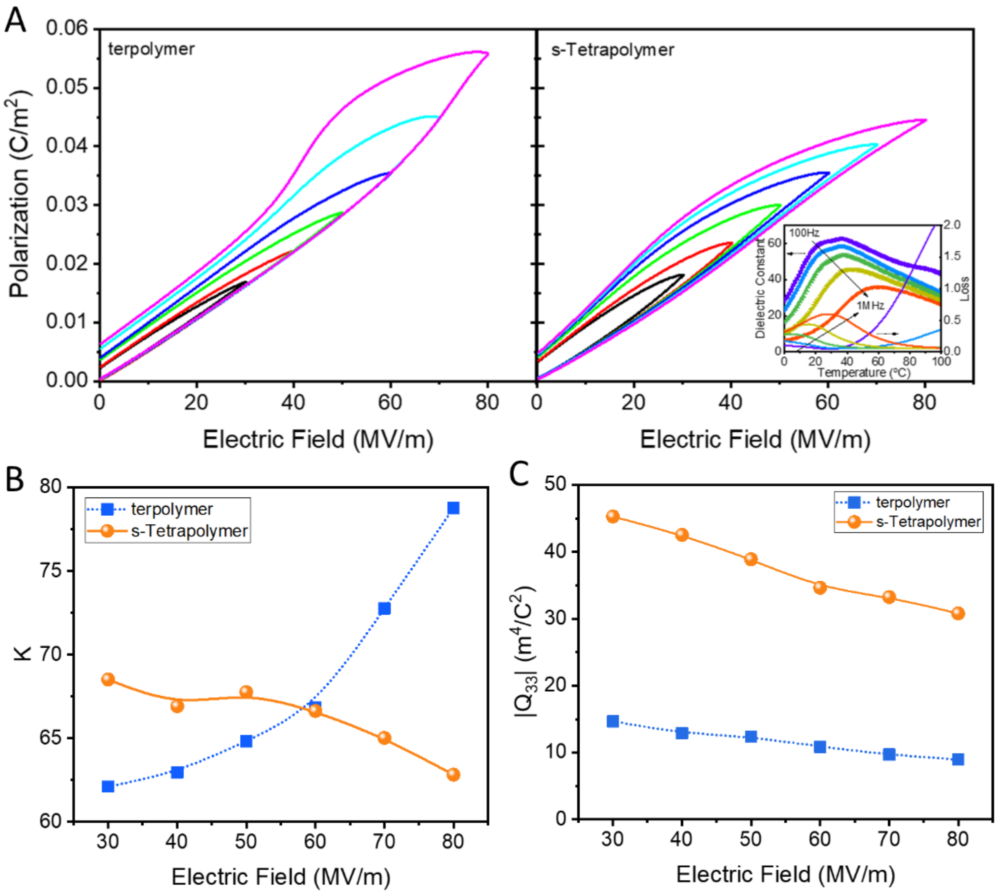

Fig. 2 Polarization data and electrostriction coefficients of P(VDF-TrFE-CFE-FA) relaxor polymers. (A) Polarization vs. electric fields measurement at 1 Hz for terpolymer and s-tetrapolymer, the inset is dielectric properties vs. temperature for s-tetrapolymer. (B) Effective dielectric constant vs. electric fields for terpolymer and s-tetrapolymer. (C) The electrostriction coefficient |Q_{33}| vs. applied electric field for stretched tetrapolymer compared with the terpolymer. In (B) and (C), curves are drawn to guide eyes.

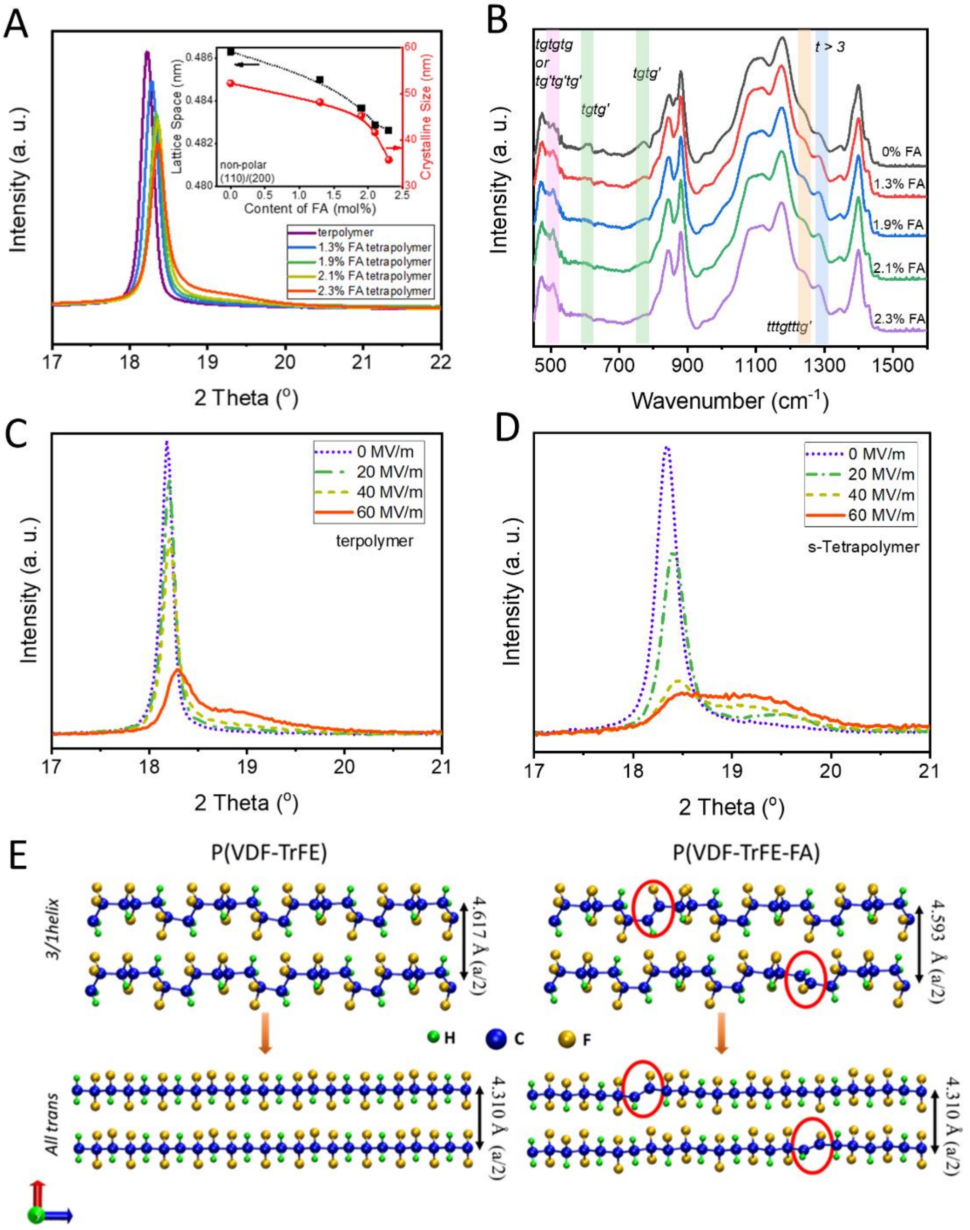

Fig. 3. Structural Analysis of P(VDF-TrFE-CFE-FA) relaxor polymers. (A) X-ray diffraction patterns of tetrapolymers with various contents of FA (X-ray wavelength is 0.154 nm). The inset presents the lattice spacing and crystalline size of the (200/110) diffraction peaks vs. FA content deduced from XRD data. (B) FT-IR spectra for tetrapolymers with various contents of FA. XRD patterns under different electric fields for (C) terpolymer and (D) s-tetrapolymer. (E) DFT calculations on crystal structures of *3/1 helix* and all trans (*tttt*) for P(VDF-TrFE) and P(VDF-TrFE-FA); detailed parameters in Table S2.

Table 1. EM performance for the tetrapolymer at bias fields. Electromechanical and dielectric properties of P(VDF-TrFE-CFE-FA) 63/29.7/5.4/1.9 at DC-biased states.

DC bias	d_{33} (pm/V)	K	k_{33}
30 MV/m (Tetrapolym)	-747	40	59%
30 MV/m (s-Tetrapolym)	-890	42	69 %
40 MV/m (Tetrapolym)	-858	34	74%
40 MV/m (s-Tetrapolym)	-1050	36	88 %