



High-temperature electromechanical actuation of relaxor ferroelectric polymers blended with normal ferroelectric polymer

Full-length article

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Soft actuators that can operate at high temperatures are of great interest in emerging research fields such as microfluidics, soft robotics, automotive, aircraft, and bioelectronics. However, most polymer-based flexible actuators suffer from performance degradation at elevated temperatures above 60 °C. In this paper, we present the high-temperature electromechanical actuation of relaxor ferroelectric polymers solution-blended with normal ferroelectric polymers. We conduct a systematic analysis of the electromechanical properties of three unimorph actuators with relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)s [P(VDF-TrFE-CFE)s] containing different amounts of chlorofluoroethylene (CFE) moieties (approximately 1, 3.5, and 9 wt%). In this study, we propose the film stress, given as Young's modulus times strain, as the measure of the electromechanical performance of soft bending actuators under loading, rather than strain or strain energy density. We demonstrate that a relaxor ferroelectric actuator with 1-wt% CFE, which mixes high-modulus ferroelectric crystal domains with an optimized electrostrictive relaxor phase, develops a high film stress of ~3.5 MPa. When blended with the normal ferroelectric P(VDF-TrFE), the actuator exhibits excellent film stress of approximately 3.1 MPa at an elevated temperature of 60 °C comparable with that at 25 °C. The high-modulus ferroelectric crystals in P(VDF-TrFE) reinforce the mechanical properties of the actuator at elevated temperatures,

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generating high-temperature electromechanical actuation with a large strain and strain energy density of approximately 1.6% and 23 mJ/cm², respectively. We also demonstrate successful microfluidic pump operation at 60°C with our actuator using a relaxor ferroelectric polymer blended with an intrinsic ferroelectric polymer.

Introduction

The demand for high-temperature operational soft actuators is increasing for various applications, including microfluidics, robotics, automotive, aircraft, and bioelectronics, owing to harsh operational environments [1–4]. Research on high-temperature operational actuating materials has often focused on piezoelectric responsive ceramic materials such as BaTiO₃, PZT, and (1-x)BiScO₃-xPbTiO₃, which work above ambient temperature with a high Curie temperature [5–7]. However, their rigidity and brittleness limit their versatility and flexibility. By contrast, various soft actuating materials with high flexibility based on ion migration, piezoelectrics, and electrostatics have been developed [8–10]. In most works, degradation of electromechanical properties has been frequently observed at elevated temperatures higher than 60 °C owing to material softening and low phase-transition temperature [11,12]. Therefore, there is a demand to study novel materials suitable for soft actuators capable of operating at elevated temperatures.

Among the most promising materials for addressing the abovementioned issues are relaxor ferroelectric polymers (RFPs) such as poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] and poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] which are superior electronic electroactive polymers that convert electrical energy into mechanical energies and vice versa [13,14]. RFPs can produce a giant electrostrictive strain of ~7% in the thickness direction and ~5% in the transverse direction with an elastic energy density of ~1.1 J/cm³ under an electric field of 150 V/μm [15–18]. In addition, RFPs exhibit fast response time (typically on the order of milliseconds or lower) [19,20], high stability, and reliability [21]. Therefore, RFPs have found wide applications for electrostriction (flexible actuators, artificial muscles, and integrated microelectromechanical systems) [16,22–25], electrical energy storage (capacitors) [26–28], and electrocaloric effect (solid-state cooling systems) [29–32].

To further enhance the electromechanical properties of relaxor ferroelectric (RF) terpolymers, P(VDF-TrFE-CFE) has often been blended with various polymers such as poly(methyl methacrylate) (PMMA) [33], polyvinylidene fluoride (PVDF) [34,35], poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-CTFE)] [36,37], and P(VDF-TrFE) [38–42]. Blending of RF P(VDF-TrFE-CFE) or P(VDF-TrFE-CTFE) with PMMA [33] has been reported to produce high polarization, dielectric constant, and mechanical strength. By blending P(VDF-TrFE-CFE) with a small amount of PMMA (~5 wt%), the elastic modulus of the blends is significantly enhanced while the field-induced strain is rarely influenced. Blends of RFPs with a small amount of (typically less than 30%) P(VDF-CTFE) [36,37], PVDF [34,35], or P(VDF-TrFE) [38–42] efficiently improved electromechanical properties such as polarization response, elastic modulus (i.e., elastic energy density), and breakdown strength. In blends with the P(VDF-TrFE)

copolymer, the coupling between the RF terpolymer and the nano-phase copolymer switches the copolymer to a relaxor, improving the crystallinity and resulting in a higher elastic energy density and electromechanical coupling factor than that of a neat RFP. Further, in blends with the PVDF homopolymer, PVDF reduces the crystallinity of a sample with smaller crystals, leading to a larger polarization response under high electric fields (above 300 MV/m) owing to interfacial polarization. Moreover, blending P(VDF-TrFE-CFE) with PVDF leads to a concomitant enhancement of dielectric permittivity and breakdown strength due to increased modulus of elasticity. In addition, it has been reported that incorporating alkynes group into P(VDF-TrFE-CFE) results in a significantly high electromechanical coupling effect [43]. This group increased all-trans conformation and decreased 3/1 helix and TGTG' conformation. Furthermore, the alkynes group acts as a defect and prevents the conformation transition from relaxor to ferroelectric at an electric field [43]. After all, the tetrapolymer can exhibit high electromechanical properties in a low electric field range compared to the RF terpolymer.

However, most studies on blended RFPs are limited to P(VDF-TrFE-CFE) with specific compositions, and the effect of the compositions of the three monomers on the electromechanical performance of RF terpolymers has not been extensively examined [44]. In particular, terpolymers with low CFE contents exhibiting characteristics of both ferroelectric (FE) and RF are of great interest for high-strength electromechanical applications because of their unique mixed crystalline structures [45,46]. Furthermore, only a few works have examined the strain response of low-CFE terpolymers blended with FE polymers, which is critical for their electromechanical actuator applications at elevated temperatures and is an essential aspect for commercial applications [47,48].

In this study, the electromechanical properties of various terpolymers of P(VDF-TrFE-CFE) with low CFE content are examined along with their blends with a ferroelectric copolymer of P(VDF-TrFE) for use in high-temperature soft actuators (refer to Fig. 1). The composition of VDF and TrFE monomers is known to affect the Curie temperature of the FE P(VDF-TrFE) copolymer [33,49,50]. Therefore, P(VDF-TrFE) copolymers with two compositions (VDF:TrFE = 75:25 and 55:45, designated as Co75 and Co55, respectively) are blended with various P(VDF-TrFE-CFE) terpolymers. The electromechanical characteristics, including the strain response, of the blended RFPs at both room and elevated temperatures, are measured. The film stress, given as Young's modulus times strain, is proposed in this study as the measure of the electromechanical performance of soft bending actuators under loading, rather than strain or strain energy density. Results confirmed that the blended RFP with improved electromechanical properties exhibited ~27% increase in strain energy density and ~29% increase in film stress compared to the pristine FE film at elevated temperatures. We demonstrate that this blended RFP with stable electromechanical properties

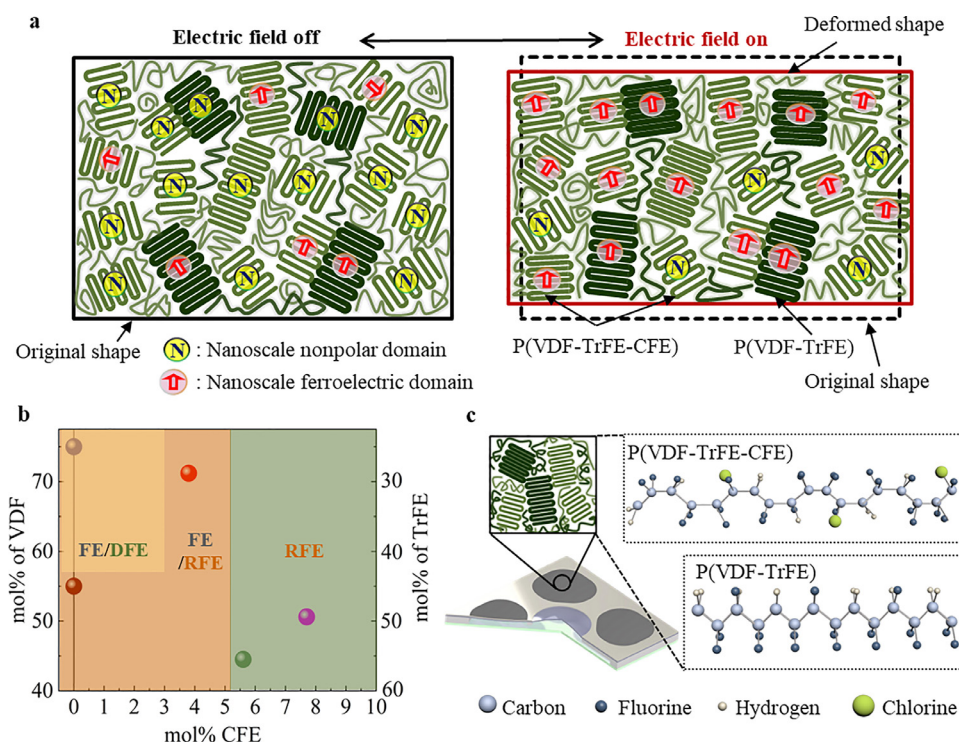


Fig. 1

(a) Schematics of the deformation mechanism of RFP and its blend with a normal FE copolymer P(VDF-TrFE) to generate electrostrictive strain under an external electric field. (b) Composition map of various RFPs, P(VDF-TrFE-CFE), in which FE, DFE, and RFE represent ferroelectric, defective ferroelectric and relaxor ferroelectric, respectively. (c) Schematic of a unimorph actuator composed of RF and FE polymer blends for bending deformation.

can be used as part of a generalized strategy for designing a high-temperature flexible actuator, as evidenced by the stable actuating motion of a microfluidic actuator with this blended RFP at elevated temperatures.

Methods

Synthesis and blending of RFPs

The FE copolymer P(VDF-TrFE), with VDF and TrFE mole fractions of 75:25 and 55:45, respectively, and RF terpolymer P(VDF-TrFE-CFE) having various mole fractions of VDF, TrFE, and CFE monomers were synthesized via a suspension polymerization process [51,52]. The mole fractions of various RF terpolymers are presented in Table 1. Among them, three P(VDF-TrFE-CFE) terpolymers (CFE1, CFE3, and CFE8) were chosen for electromechanical characterization because they have extreme compositions of CFE. Ten grams of each RFP were dissolved in 90 g of methyl isobutyl ketone, and 10 g of P(VDF-TrFE) copolymer was dissolved in 90 g of methyl ethyl ketone. The solutions were stirred for 2 h at 75 °C and then filtered with a polytetrafluoroethylene filter with 5.0-μm pores. An FE P(VDF-TrFE) copolymer solution with a ratio of 10 or 20 wt% was then mixed with the RFP solution. Accordingly, 15 RFP solutions (three neat terpolymers and their 10 and 20 wt% blends with Co75 or Co55), together with two copolymer solutions (Co75 and Co55), were prepared.

Microstructural and electromechanical characterization

The electrical properties of the RFPs were measured using polarization–electric field (P–E) and capacitance–voltage (C–V)

Table 1

Compositions of various relaxor ferroelectric polymers and normal ferroelectric polymers. (Polymers specified with * mark will be used for blending in this study).

Name	VDF	TrFE	CFE
CFE1*	71.2	25.0	3.8
CFE2	63.5	30.8	5.6
CFE3*	44.5	47.8	7.7
CFE4	56.2	36.3	7.7
CFE5	59.8	32.2	8.0
CFE6	62.0	29.9	8.1
CFE7	51.2	39.2	9.6
CFE8*	50.6	35.6	13.8
Co55*	55	45	
Co75*	75	25	

responses, for which a metal–ferroelectric–metal (MFM) structure was fabricated. The thin films of the RFPs were prepared on highly P-doped silicon (bottom electrode) substrates under the same conditions as described above, and a 70-nm-thin Al layer (top electrode) was deposited on the RFP thin films via thermal evaporation. P–E and C–V characterizations were performed using a Precision LC system (Radiant Technology Inc.) and Keithley 4200 semiconductor characterization system (MS TECH), respectively. The response was measured at a voltage frequency of 100 kHz and with an electric field sweep range between –100 and 100 MV/m at room temperature (25 °C). The capacitance is determined by measuring AC current in relation to the AC

impedance and voltage while sweeping the DC voltage across the device, as described by the following equation:

$$C = \frac{I_{DUT}}{2\pi f V_{ac}}$$

Where, the I_{DUT} is AC current from the applied AC voltage (V_{ac}) and the f is a frequency of V_{ac} . When the DC voltage is set to 0 MV/m, an AC voltage of 30 mV is applied to the sample to measure its capacitance. The measured capacitance corresponds to the value obtained with 30 mV AC voltage at an apparent DC voltage of 0 V [53,54]. With this mechanism, the dielectric constant can be also calculated using Johnson's formula:[55]

$$\varepsilon(E) = \frac{\varepsilon(0)}{(1 + \alpha \varepsilon(0) E^2)^{1/3}}$$

Where, $\varepsilon(0)$ is dielectric constant at zero electric field, and α is constant, and E is electric field. The areas of the Al top electrode were measured by optical microscopy (Eclipse LV150N, Nikon), and the thickness of the RFP films was measured by using a surface profiler (DektakXT Stylus Profiler, Burker).

To assess the electromechanical properties of the neat RFPs and blends with FE copolymers, the unimorph actuator shown in Fig. 2a was fabricated as follows. Solutions of various RFPs were prepared as described in the previous section, and their films with a thickness of 3.6 μm were fabricated using the adhesion-mediated film transfer (AMFT) technique [56]. The RFP film was laminated on a Ag nanowires (100 nm) bottom electrode on a polyethylene terephthalate (PET) film (130 μm). A 15-nm-thick gold electrode was then sputtered on top of the RFP film. One end of the unimorph actuator was clamped on a rigid support. The width and length of the unimorph actuator were 5 and 45 mm, respectively. A 110-MV/m and 0.1-Hz sinusoidal electric field was applied to the top and bottom electrodes, and the bending deformation was measured with a laser displacement sensor (LDS) (Keyence, LT-9010). The unimorph actuator was placed in a thermal chamber, which could be precisely controlled to measure the strain response at an elevated temperature, as shown in the experimental setup.

The freestanding films of 15 RFPs and 2 FE polymers with dimensions of 40 $\times$ 6 $\times$ 1 mm were fabricated through the melt-pressing method, followed by annealing at 115 $^{\circ}\text{C}$ for 12 h. Dynamic mechanical analysis (DMA) measurements were performed with the TA Instruments DMA Q800 on the freestanding films in the tensile mode at 1 and 10 Hz in the temperature range of 25 $^{\circ}\text{C}$ –80 $^{\circ}\text{C}$ with a heating rate of 3 $^{\circ}\text{C}/\text{min}$.

The neat RF terpolymers and their blends with 10% and 20% of FE polymers Co55 and Co75, respectively, were subjected to X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) measurements to understand the crystallographic microstructures and detect local conformational structure changes. The various RFP solutions were coated on silicon substrates with a thickness of 4 μm by the solution-casting method for XRD measurements. In addition, films with a thickness of 4 μm were fabricated with the AMFT technique for FTIR measurements. All films were annealed at 115 $^{\circ}\text{C}$ for 12 h. XRD was measured in the range of 10 $^{\circ}$ –90 $^{\circ}$ with a scan speed of 6 deg/min, 0.02 $^{\circ}$ step width, and Theta/2-Theta scan axis using a SmartLab 9-kW X-ray diffractometer from Rigaku. FTIR was performed by using a Thermo Scientific Nicolet 6700

FTIR spectrometer in the wavelength range of 500–1500 cm^{-1} at a resolution of 2 cm^{-1} .

To characterize surface morphology, the various RFP solutions were spin-coated onto silicon substrates at 1500 rpm for 60 s. After thermal annealing at 115 $^{\circ}\text{C}$ for 2 h, the surfaces of the RFP thin films were analyzed using tapping-mode atomic force microscopy (TM-AFM, Nanoscope Iva Digital Instrument) with a scan size of 2 μm^2 .

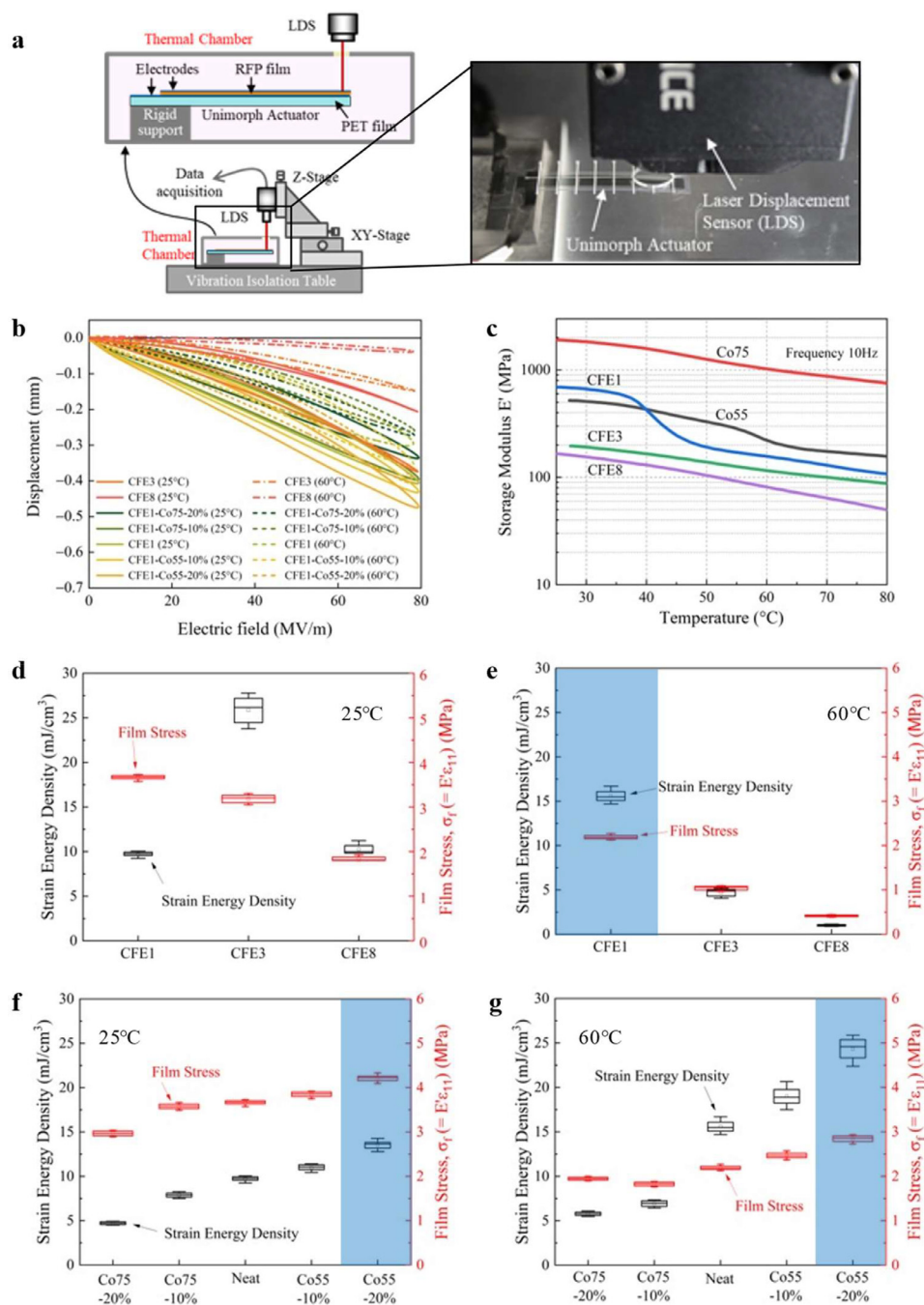
Results and discussion

RF polymer for high-temperature operational actuator

To develop high-temperature operational soft actuators, a blend of P(VDF-TrFE-CFE) as an RFP and P(VDF-TrFE) as an FE polymer was prepared, as shown in Fig. 1a. These blended RFPs exhibit a piezoelectric response due to the large electrostrictive strain originating from various mechanisms, such as field-induced nonpolar-to-polar crystalline phase transformation, reorientation of nano polar regions (all-trans conformations), and Maxwell stress caused by electric coulombic attractions between opposite charges on two electrodes. A series of RFPs with systematically modified chemical compositions in VDF, TrFE, and CFE have been synthesized, as shown in Fig. 1b and Table 1. The DSC analysis revealed a Curie temperature peak of 50.5 $^{\circ}\text{C}$ for CFE1. (Fig.S1) However, distinctive peaks for CFE3 and CFE8 were not detected. Nevertheless, the Curie temperature of P(VDF-TrFE-CFE) with diverse composition has been reported as approximately 50 $^{\circ}\text{C}$. Consequently, by reference [57,58], it can be inferred that CFE3 and CFE8 also have Curie temperatures near 50 $^{\circ}\text{C}$. The electrochemical properties are typically related to the composition between polar regions from P(VDF-TrFE) and nonpolar regions from P(VDF-TrFE-CFE), as shown in Fig. 1c. Furthermore, the ratio between VDF and TrFE affects the polar characteristics, as the gradual increase in VDF composition results in an increase in the average copolymer dipole moment because the dipole moment of a TrFE unit is approximately half that of a VDF unit. Therefore, owing to the composition of CFE, the synthesized series of RFPs have different electromechanical characteristics, such as RF (CFE3 and CFE8) and ferroelectric/relaxor ferroelectric (FE/RF) (CFE1) properties. On the basis of these adjusted characteristics, the RF film was designed to have significantly stable actuating performance at high temperatures, resulting from modulus control, by using the conventional blending process of terpolymer P(VDF-TrFE-CFE) and copolymer P(VDF-TrFE) as depicted in Fig. 1c.

Highly stable actuation properties of RF blended film at elevated temperatures

The strain response and performance of RFP unimorph actuators were analyzed and evaluated, and the results are presented in Fig. 2, which help to explain not only the electromechanical behavior of various RFPs but also the effect of blending with FE polymers Co55 and Co75. The performance of the unimorph actuator was evaluated by measuring the displacement response under an applied voltage as shown in Fig. 2a. Figs. 2b and S2-3 illustrate the displacement–voltage hysteresis loops of the unimorph actuators made of various types of RFPs blended with 20% Co55 at room temperature (25 $^{\circ}\text{C}$) and at an elevated

**Fig. 2**

(a) Schematics and image of the displacement hysteresis loop characterization system for unimorph actuators made of RFPs and their blends with FE polymer at room temperature (25 °C) and elevated temperature (60 °C). (b) Displacement response of the unimorph actuators made of CFE1, CFE3, CFE8, and their blends with Co55 and Co75 at room temperature (25 °C) and elevated temperature (60 °C). (c) Temperature dependence of storage moduli of RFPs and copolymers from the DMA measurement at 10 Hz. The box plots of strain energy density and film stress of various types of neat RFPs at (d) room temperature (25 °C) and (e) elevated temperature (60 °C). The box plots of strain energy density and film stress of CFE1 blended with FE copolymers at (f) room temperature and (g) elevated temperature.

temperature (60 °C). The displacement of the unimorph actuator strongly depends on the types of RFPs used to fabricate the actuator. Generally, two types of RFPs—CFE1 and CFE3—which produce high deformations at room temperature, have a small amount of CFE in the terpolymer composition as shown in Fig. 2b. The results are consistent with the previous studies of Klein et al.

[59], Capsal et al. [60], and Petchsuk et al. [61]. Fig. 2b shows that the displacement reduction observed with neat RFPs at a high temperature was substantially suppressed in the blended RFPs. Therefore, blending the FE polymer Co55 or Co75 into the neat P(VDF-TrFE-CFE) terpolymers may prevent the reduction in displacement at elevated temperatures.

However, a larger displacement without a load does not necessarily guarantee higher actuation performance, which can be analyzed by calculating the strain, strain energy density, and film stress derived according to the following equations. The longitudinal strain, which is parallel to the applied field direction, can be calculated using the composite beam theory:

$$\varepsilon_{11} = 2d(E'I)_e/l^2 E_p' t_p w_e (t_s + t_p/2 - \eta) \quad (1)$$

where ε_{11} is the strain of the RFP film when it is freely deformed without any constraint under an electric field E , d is the deflection due to the bending deformation, w_e is the width of the upper electrode, E_p' is the storage modulus of the RFP, and t_p is the thickness of the RFP. The position of the neutral axis of the composite structure, η , is calculated as follows:

$$\eta = (E_s' t_s^2 + 2E_p' t_s t_p + \tilde{E}_p' t_p^2) / (E_s' t_s + E_p' t_p) \quad (2)$$

where E_s' and t_s denote the storage modulus and thickness of the substrate, respectively. The effective flexural modulus per unit length of the beam, $(\tilde{E}I)_e$, is given as follows:

$$(\tilde{E}I)_e = \frac{1}{12} E_s' t_s^3 + E_s' t_s \left(\frac{1}{12} t_s - \eta \right)^2 + \frac{1}{12} E_p' t_p^3 + E_p' t_p \left(t_p + \frac{1}{12} t_s - \eta \right)^2 \quad (3)$$

The other two key parameters that give a measure of the strain- and stress-generating capability of an electroactive material are elastic energy density $U_e = 0.5 E_p' \varepsilon_{11}^2$ and film stress $\sigma_f = E_p' \varepsilon_{11}$. Therefore, these two parameters were quantified and analyzed from the above results of displacement response (Fig. 2b) and storage modulus (Fig. 2c) of the RFPs.

In Fig. 2c and Supporting information S3, the storage moduli (E'), loss moduli (E''), and tangent deltas ($\tan \delta = E''/E'$) of three neat terpolymers and two copolymers obtained from the DMA measurement at 10 Hz are plotted. E' is a measure of the energy stored elastically, while E'' represents the energy dissipated owing to viscous behavior. The values of $\tan \delta$ indicate how efficiently the material loses energy to molecular rearrangements and internal friction. As shown in Fig. 2c, the storage moduli of copolymers are generally greater than those of most neat P(VDF-TrFE-CFE) terpolymers. Co75 has the highest storage modulus of ~1906 MPa at 25 °C and 1 Hz because of its higher crystallinity and larger amount of all-trans β phase, while Co55 has a modulus of approximately 519 MPa under the same conditions. The introduction of the third monomer (CFE) reduces the crystallinity and thus reduces the corresponding elastic modulus. Therefore, the moduli of neat terpolymers are usually smaller than those of copolymers. However, there is an exception in the case of CFE1 with a similar VDF content of Co75, whose storage modulus is even higher than that of Co55 for the high VDF content. This may be because the small amount of the third monomer reduces the storage modulus compared to that of Co75 but not by a significant amount, resulting in its storage modulus still being higher than that of Co55. For the neat P(VDF-TrFE-CFE) terpolymers, the moduli can significantly decrease when the CFE fraction in terpolymers increases. For example, the storage modulus of CFE3 with 7.7% CFE (196 MPa at 25 °C) is 3.5 times lower than that of CFE1 with 3.8% CFE (691 MPa at 25 °C).

However, in the case of CFE8 with 13.8% CFE, the storage modulus is 165 MPa at 25 °C, which is further reduced but less significant. The reason for the modulus reduction is the decrease in crystallinity when the CFE content in the neat P(VDF-TrFE-CFE) terpolymers increases, as reported previously [62].

In general, the storage moduli of neat RFPs decrease when the temperature increases. Specifically, in the case of CFE1, the modulus decreases significantly near 42 °C from 691 to 154 MPa (a reduction of ~80%). The dramatic change in the storage modulus of CFE1 is associated with a broad relaxation peak in the $\tan \delta$ signal (Fig. S4), which may correspond to a continuous FE–paraelectric transition. These relaxation peaks reflect high crystalline mobility during these structural transitions. Above 50 °C, the storage modulus still decreases but slightly, which can be attributed to the thermal evolution of paraelectric phases. The other RFPs do not exhibit distinct FE–paraelectric transitions, but their storage moduli gradually decrease as the temperature increases.

Similarly, the storage and loss moduli of the copolymers Co55 and Co75 also gradually decrease with increasing temperature. However, at elevated temperatures (above 60 °C), the decreasing rate of storage moduli of the copolymers becomes slower than those of terpolymers. Thus, the storage moduli of both Co55 and Co75 remain higher than those of all the terpolymers even at 80 °C. As the storage moduli of the copolymers are higher than those of the terpolymers, and the entanglement of the terpolymer and copolymer chains is inevitable in the blend, blending the RF terpolymer with the FE polymer not only improves the mechanical properties at room temperature but also provides greater enhancement at elevated temperatures.

The strain energy density and film stress can be calculated from the storage moduli and displacements at both room and elevated temperatures as shown in Figs. 2d–g and S5. For the neat terpolymers, the electrostrictive strain and elastic energy showed an increasing tendency with an increase in the fraction of CFE but only up to a certain value, which was approximately 7.7% for CFE, the third monomer of RFPs. Specifically, the strain and elastic energy values of CFE1 (3.8% CFE) were 0.53% and 10.04 mJ/cm³, respectively, and the values of CFE3 (7.7% CFE) were approximately 1.68% and 27.76 mJ/cm³. Both values decreased to 1.16% and 11.22 mJ/cm³ when the fraction of CFE was 13.8% for CFE8, as shown in Fig. 2d. Therefore, the CFE fraction in CFE3 can be considered the threshold value that changes the RFP properties such as electrostrictive strain. Similar to the actuator displacement, Figs. 2e and S5 also show that almost all the neat RFPs exhibit a reduced strain and elastic energy density U_e when the temperature increases from 25 °C to 60 °C, except for CFE1, the storage modulus of which decreases considerably more than any others, from 691 MPa at 25 °C to 154 MPa at 60 °C (an ~80% reduction). Meanwhile, the complex behavior of the storage modulus, strain, or strain energy density alone is not well correlated to the actuation performance. In the case of the unimorph actuator, the film stress—given as Young's modulus times strain—could explain the tendency of the actuator displacement more directly because it is related to the electromechanical performance of soft bending actuators under

loading. Fig. 2d and e show the apparent reduction in the film stress when the fraction of CFE in neat RFPs increases at both room and elevated temperatures with the decreased Young's modulus of FE polymer chain [63]. Although the strain increased from CFE1 to CFE3, a significant reduction in the storage modulus was observed, with 691 MPa for CFE1 to 196 MPa for CFE3, leading to the decrease in film stress. These results are also consistent with the displacement response at 25 °C and 60 °C. Therefore, the displacement in a unimorph actuator is better related to the film stress, and CFE1 has properties superior to those of other P(VDF-TrFE-CFE) terpolymers.

In addition, Fig. 2f and g show the elastic energy and film stress of blends of CFE1 and copolymers. At room temperature, the film stress decreased for blends of RFPs with Co75, but it increased for blends of RFPs with Co55. Although blending RFPs with Co55 caused a reduction in strain, the storage modulus of the blends improved. Therefore, the actuation performance, expressed by film stress, still improved. However, this was not the case with blends of Co75, the film stress of which decreased even though Co75 had a higher storage modulus than Co55. Interestingly, the CFE1 terpolymer had the highest modulus but lowest electrostrictive strain at room temperature; however, it produced the highest actuator displacement. Moreover, at room temperature, remarkable results were obtained after blending Co55 and Co75 into CFE1. When blending CFE1 with Co75, the storage modulus increased significantly, but the actuator displacement decreased, while the opposite tendency was observed when blending CFE1 with Co55. Therefore, only the enhanced strain is the reason for the difference between blending RFPs with Co55 and Co75. Co75 has higher crystallinity, larger amount of β phase, and stronger FE interactions than Co55; therefore, at room temperature, Co75 is more resistant to conversion into a relaxor than Co55, resulting in a significant decrease in the strain and no enhancement of the final electrostrictive performance.

From the analyzed actuator displacement results, Fig. 2g shows that although the strain and elastic energy density decrease with increasing temperature, the addition of FE polymer to CFE1 still enables the actuators to produce higher deformation. Therefore, blending CFE1 with FE polymers is the mainly effective method for improving the actuation performance of RFPs at elevated temperatures even when the electrostrictive strain has a decreasing tendency. For RFPs with a high elastic modulus, such as CFE1 (691 MPa), which is only lower than that of Co75 (1904 MPa) and greater than that of Co55 (518 MPa) at room temperature, both the strain and elastic energy density increased from 0.54% to 1.45% and 10.04 to 16.08 mJ/cm³, respectively, as the temperature increased from 25 °C to 60 °C. Notably, Co75 has a larger Curie temperature, ~125°C, which makes its conversion into a relaxor difficult in the temperature range of 25 °C–60 °C. By contrast, Co55 has a Curie temperature of 65 °C, which may contain more paraelectric (nonpolar) phases than Co75, making it advantageous for producing a high electrostrictive strain in CFE1 RFP at elevated temperatures. The above analysis clarifies that blending CFE1 RFP with a copolymer significantly improves mechanical properties such as storage modulus, and even small amounts of copolymer in Co55 can enhance the electrostrictive strain and actuator

performance. These findings are significant and highlight the importance of copolymer blending in improving the performance of RFPs.

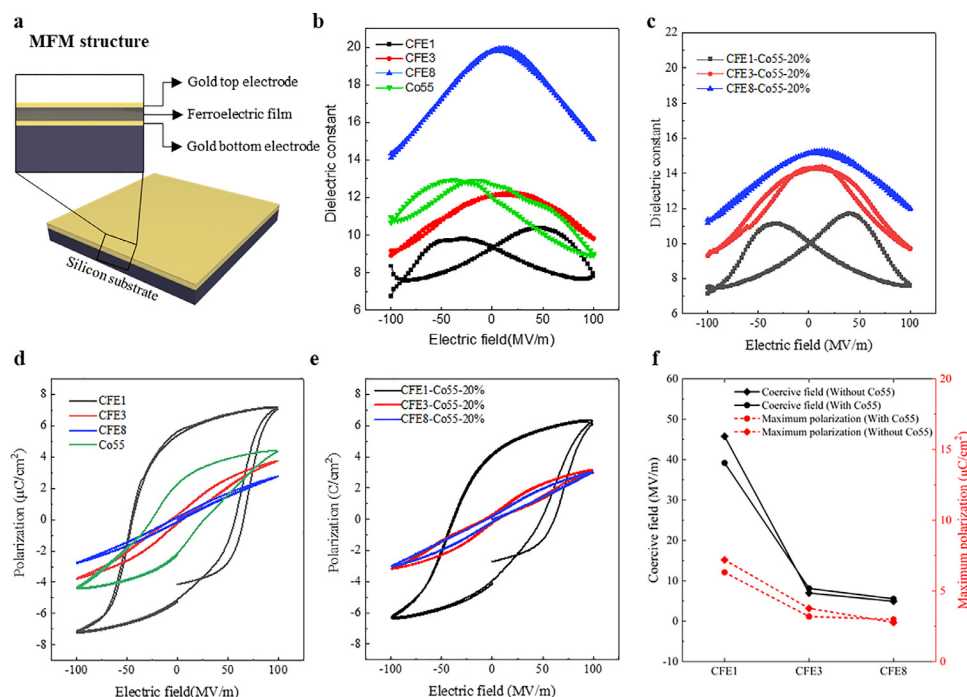
FE properties of RFPs

The dielectric constant–electric field and polarization–electric field characteristics of the CFE RFP series and Co55 were analyzed to confirm the relaxor behavior of CFE polymers and the ferroelectric effect of Co55 in the blended film as shown in Fig. 3a–c. These electrical properties were measured in the MFM structure. The lamellar crystal of Co55 is perpendicularly aligned with respect to the external electric field when an electric field is applied to the RFPs. Further, RFPs have higher dielectric constants due to the exchange coupling effect from entangled chain segments between amorphous and crystalline interfaces compared to FE polymers [64]. The dielectric constant was calculated from the capacitance using the following formula:

$$\varepsilon_r = Ct/(\varepsilon_0 A) \quad (4)$$

where C is the RFP capacitance, ε_r is the RFP dielectric constant, ε_0 is the vacuum dielectric constant, A is the area of the electrode, and t is the thickness of the RFP film. The dielectric and electric field curves of the neat CFE RFPs and Co55 are shown in Fig. 3b. In the case of neat RFPs, the dielectric constant increases and the hysteresis decreases with increasing relaxor characteristics when the proportion of the third monomer increases. Co55 has the maximum dielectric constant, higher than those of CFE1, CFE3, and lower than those of CFE8, which can be a result of the morphotropic phase boundary [65]. Figs. 3c and S6 reveal that the value of the maximum dielectric constants increases in the blends of CFE1 and CFE3 with Co55, while CFE8 shows a reduction in the maximum dielectric values in comparison with the corresponding neat RFPs. Solely CFE1 contains a small amount of the third monomer CFE and shows the dielectric constant–electric field characteristics with a butterfly curve as the FE behavior with two distinct peaks of capacitance during a positive and negative sweep for both neat RFPs and blends with Co55. Dielectric constants at different frequency conditions of CFE1 and CFE1-Co55-20% when using MEK solvent to fabricate thin films are depicted in Fig. S7. Initially, the dielectric constants of CFE1 and CFE1-Co55-20% exhibited similarities under both MIBK and MEK solvent conditions as shown in Fig. S7a and Fig. 3b and c. Furthermore, as the frequency decreases, there is an observable increase in the maximum dielectric constant, as illustrated in Fig. S7b. These measurements were conducted at a high frequency of 100 kHz to align with the conditions of polarization measurements. Therefore, the lower dielectric constant, compared to the reported dielectric constant of CFE, is attributed to the high measurement frequency of 100 kHz. Furthermore, the lower dielectric constant in the CFE polymer is associated with a lower CFE content compared to previous reported CFE polymers in relation to the VDF content.

The polarization responses of the P(VDF-TrFE-CFE) terpolymer and blends with Co55 under a 100-MV/m applied electric field were analyzed through the polarization–electric field measurement as shown in Fig. 3d–f. In the P(VDF-TrFE-CFE) RFPs, the polarization and coercive field were reduced when

**Fig. 3**

(a) Schematics of MFM structures for measuring dielectric constant and polarization–electric field (P–E) characteristics. (b) Dielectric constant–electric field curves of CFE1, CFE3, CFE8, and Co55. (c) Dielectric constant–electric field curves of RFPs blended with Co55. P–E hysteresis loops of (d) neat RFPs and Co55 and (e) RFP-Co55 blends under an electric field of 100 MV/m. (f) Summarized ferroelectric properties (coercive field and maximum polarization) of various RFPs and their blends with Co55.

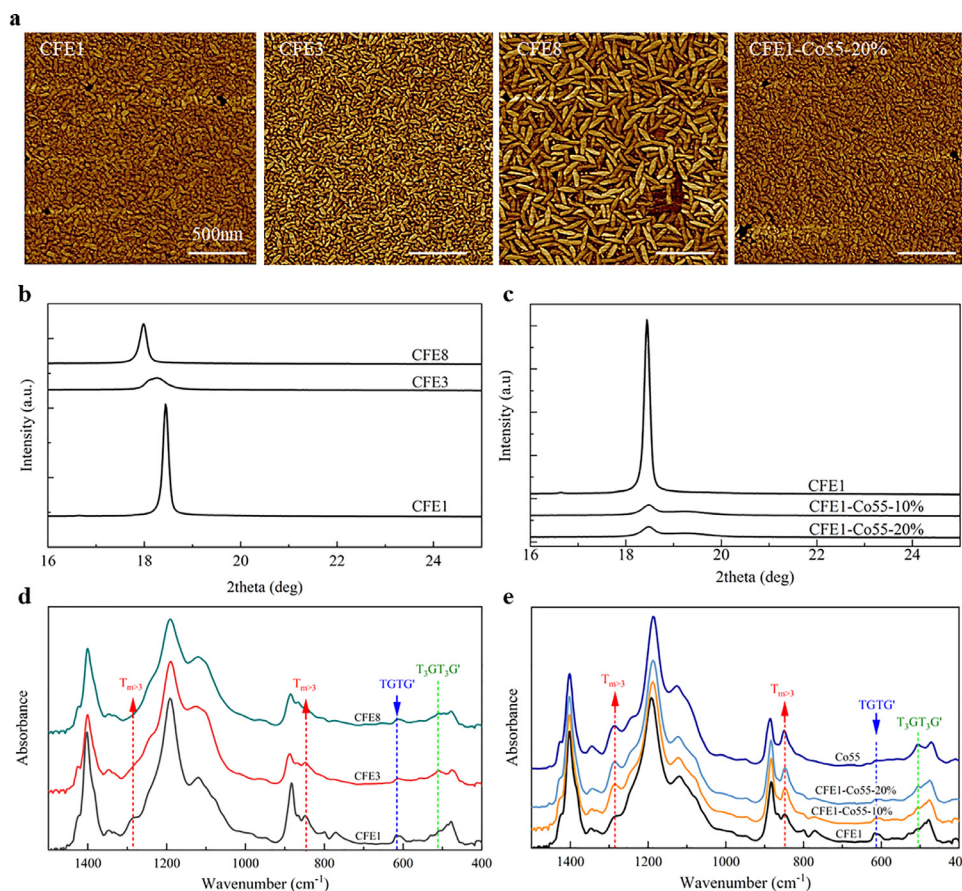
the fraction of the third monomer increased as shown in Figs. 3d and S8. First, CFE1, which possessed a high VDF content compared to other PVDF-TrFE-CFE polymers, exhibited larger polar regions. Consequently, the polarization increased when the area was polarized, necessitating a higher electric field to rotate the polarization direction [66,67]. CFE1 exhibits ferroelectric properties, whereas CFE3 and CFE8 display relaxor ferroelectric behavior. This distinction arises from differences in the composition of VDF and TrFE in the CFE materials. A report on the morphotropic phase of PVDF indicates that the MPB composition typically is between 49% and 55% [63]. The morphotropic phase emerges within this composition range, and PVDF, with a lower VDF content of 49% exhibits antiferroelectric hysteresis. Consequently, CFE1, with a VDF concentration of 71.2%, demonstrates ferroelectric characteristics, while CFE3 (with a VDF concentration of 44.5%) and CFE8 (with a concentration of 50.6%) exhibit relaxor properties. Second, with the increasing amount of the third monomer, the size of FE domains decreased owing to the chlorine atoms acting as defects in the crystal lattice and dividing the FE domains into local nanopolar regions. The electrical properties of the RFPs switch to paraelectric, for which the polarization hysteresis and remnant polarization are reduced [68]. The third monomer also reduced the coercive field because the increased inter-chain distance allows molecular chains to rotate more easily [69,70].

The FE properties of the blends of RFPs with normal FE polymers are summarized in Fig. 3e and f. The graphs in Fig. 3e and f show that blending a small amount of normal FE polymer could enhance polarization and relaxor polarization behavior for certain

RFPs. The RFPs blended with Co55 exhibited a higher polarization level than that of neat RFPs for CFE8, which had low polarizations and low coercive fields, while for CFE1, the neat polymer had a higher polarization. This result indicates that blending normal FE could control the polarization, coercive field of RFPs, and the size of the FE domain. Interestingly, these two measurements showed that CFE1 had FE properties, while the other P(VDF-TrFE-CFE) terpolymers exhibited pristine RF properties. However, the 100 MV/m is not a saturation electric field for the relaxor, and at higher electric fields, the saturation and coercive voltage will change. Therefore, Fig. S9 shows P-E hysteresis at high voltage levels. At the high electric field of 506 MV/m, the CFE1 has the high maximum polarization of $11.31 \mu\text{C}/\text{cm}^2$, greater than those of other CFE terpolymers, and blending with Co55 affects the increase in maximum polarization to $12.85 \mu\text{C}/\text{cm}^2$ with the same coercive field of 113.5 MV/m.

RFP crystal analysis

To investigate the morphology and crystallization effect of Co55 in blended polymers, atomic force microscopy (AFM), XRD patterns, and Fourier transform infrared spectroscopy (FTIR) were used to analyze the neat RFPs and the blend of RFPs with Co55, as shown in Fig. 4. The mechanical and aggregation characteristics of the polymer changed when the different crystalline phases were formed, resulting in different surface morphologies as shown in Figs. 4a and S10. The crystalline structure of P(VDF-TrFE-CFE) usually forms needle-like grains, which are attributed to steric hindrance by TrFE monomers in lamellar structures as the beta phase crystallinity of VDF monomer chains. The beta phase has

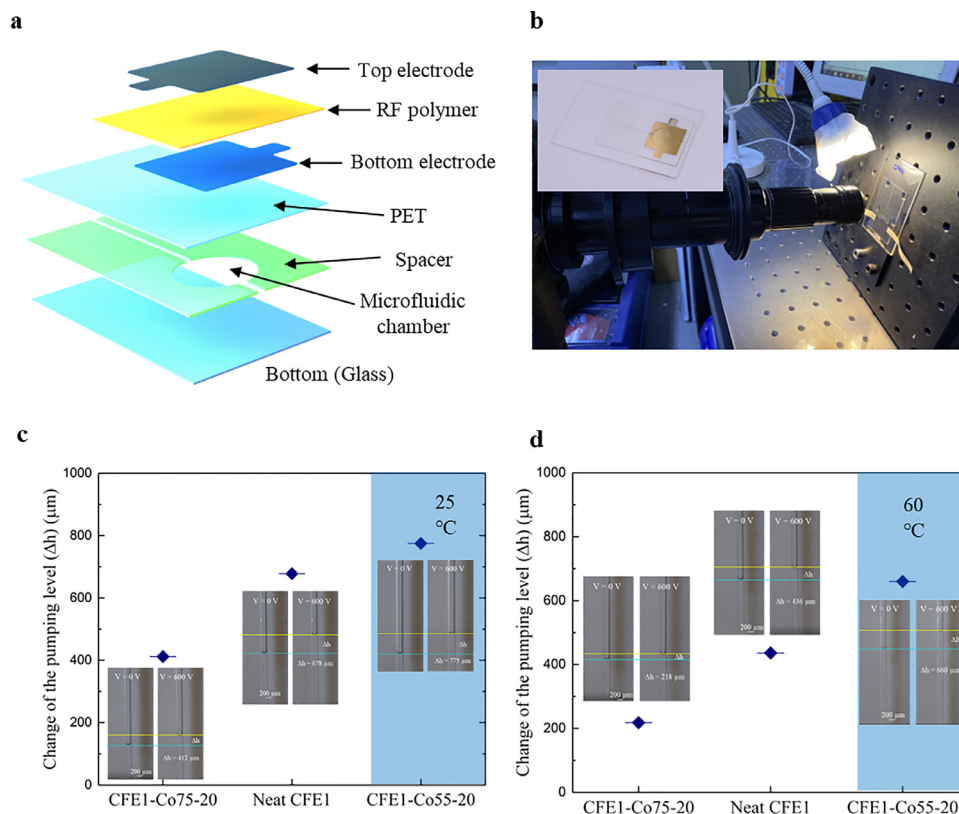
**Fig. 4**

(a) Phase-contrast TM-AFM images of various P(VDF-TrFE-CFE) RFP thin films and a CFE1-Co55 blend film on silicon substrates in the range of $2 \mu\text{m}^2$. XRD result of (b) various RFPs, CFE1, CFE3, and CFE8, and (c) CFE1-Co55 blends. FTIR results of (d) various RFPs, CFE1, CFE3, and CFE8, and (e) CFE1-Co55 blends.

FE properties with the H-F dipole aligned in a specific direction as a T(Trans)TTT conformation [60]. The AFM images of CFE1, CFE3, and CFE8 showed different domain sizes and morphologies with grains having average lengths of approximately 66, 72, and 160 nm, respectively. Results showed that the CFE monomer induced larger grains of P(VDF-TrFE-CFE) terpolymers, and the grain size slightly decreased when blending the terpolymers with Co55, which could be due to the decreased amount of CFE monomer. The CFE monomer has a larger molecular size with chlorine atoms compared to the TrFE monomer, which creates a higher steric hindrance and induces a large grain size [37,69].

Furthermore, the XRD analyses in Fig. 4b and c and Supporting information S8 show that the P(VDF-TrFE-CFE) terpolymers with the inter-chain lattice space of $4.86 \text{ \AA}$ exhibit one narrow peak in the range of 18.0° – 18.4° . By contrast, the P(VDF-TrFE) copolymer exhibits a wide peak at 19.0° , reflecting inter-chain lattice spaces of 4.7 and $4.6 \text{ \AA}$ corresponding to (110) and (200) reflections, respectively [65]. Because of the increment in the lattice space, which is caused by the third monomer CFE, the terpolymer peaks are higher and narrower than the copolymer peaks with the same (110) and (200) reflections. Fig. 4b and c show that the neat P(VDF-TrFE-CFE) terpolymer with a small amount of CFE, i.e., CFE1 (3.8%), exhibits one peak at 18.4° , while with a larger amount of CFE, i.e., CFE3 (7.7%) and CFE8 (13.8%), it

exhibits one sharp peak around 18° – 18.2° . Increasing the fraction of the third monomer from 3.8% of CFE1 to 7.7% of CFE3 and 13.8% of CFE8 not only caused a reduction in crystallinity, which was indicated by the reduction in the peak intensity, but also induced a shift of the peak position from 18.4° of CFE1 to 18.2° of CFE3 and 18° of CFE8. In addition, increasing the VDF content shifted the XRD peak corresponding to the all-trans structure to the right by $\sim 19.5^\circ$ – 20° when the VDF content was increased from 50% to 80% [65]. Therefore, compared to CFE3 and CFE8, CFE1 with a high VDF content similar to Co55 had a rightward-shifted peak. These results also help in explaining the reduction of the storage modulus of RFPs when the fraction of the third monomer increases. The XRD results of RFPs blended with low Co55 contents (10% and 20%) are plotted in Figs. 4c and S11. No noticeable microstructural changes were observed in the terpolymer-rich blends. The peak positions for the terpolymer component in the blends remained unchanged compared to the neat terpolymer. Blends of P(VDF-TrFE-CFE) RFPs with Co55 exhibited not only weakened peaks at almost the same initial positions but also other rising broad peaks at 19.3° corresponding to the reflection of the (200) crystal plane of the FE phase in Co55. In addition, the peak intensity of XRD significantly represents the mechanical and electrical properties of the relaxor. By blending the Co55 with CFE1, the XRD peak of 18.4° ascribed

**Fig. 5**

(a) Design of the microfluidic pump operated by a unimorph RFP actuator. (b) Experimental setup for evaluating the performance of the microfluidic pump made of RFPs and their blends with FE copolymers. Changes in the pumping level (Δh) of the silicone oil in the drain produced by the microfluidic pump and their optical microscope images at (c) room temperature (25 °C) and (d) elevated temperature (60 °C).

to the overlapping (110) and (200) reflection of the alpha phase as paraelectric decrease [71]. It means that the Co55 blending induces a decreased alpha phase. Furthermore, the crystal size (L) of the terpolymers can be estimated by the Scherrer formula.

$$L = 0.9\lambda / (B \cos \theta)$$

λ is the x-ray wavelength, B is the full width at half the maximum of the peak, and θ is the Bragg angle. The crystals of blended terpolymer smaller than those of neat polymer could lower the energy barrier for the dipole orientation under specific electric field [72]. Furthermore, the decreased crystallinity of the blending Co55 reflects the decrease in Young's modulus [73]. Although the intensity of the peak corresponding to crystalline β phases is very small compared to others, it proves the coexistence of both copolymer and terpolymer crystal structures. Interestingly, blends of CFE1 (with a small amount of CFE) with Co55 exhibited this phenomenon more clearly than others.

To further understand the local conformational structure changes in RFP blends, FTIR was performed; the results are shown Fig. 4d and e and Fig. S12. Neat P(VDF-TrFE-CFE) terpolymers exhibit several chain conformations comprising trans and gauche bonds, namely, T_3GT_3G' (504 cm^{-1}), TGTG' (613 cm^{-1}), and $T_{m>3}$ (850 and 1285 cm^{-1}) conformations. Both $T_{m>3}$ and T_3GT_3G' bonds are polar conformations that are related to the FE properties of polymers, while the TGTG' bond is a nonpolar conformation that results in the RF properties of polymers. The characteristic

peaks from FTIR spectroscopy showed the influence of the FE phases in the RFP matrix, where a clear transition was observed in the entire spectrum. The crystal bands at 504 and 613 cm^{-1} slowly increased and decreased, respectively, as the content of the third monomer CFE increased, while adding CFE gradually reduced all-trans ($T_{m>3}$) conformations corresponding to the crystalline β phase. In particular, CFE1 (3.8%) showed a more obvious and substantial increase in $T_{m>3}$ conformations compared to CFE3 (7.7%) and CFE8 (13.8%). These results are consistent with the XRD results. The tendencies of the blends with both 10% and 20% Co55 were very similar, where the crystal bands at 504 and 613 cm^{-1} slowly increased and decreased, respectively, in the blends with Co55, while the blending gradually increased all-trans ($T_{m>3}$) conformations. Thus, these crystal analyses reveal that the Co55 added into RFPs still maintains its own crystal structure at both 10% and 20% copolymer concentrations. The increase in the T_3GT_3G' (504 cm^{-1}) and $T_{m>3}$ (850 and 1285 cm^{-1}) conformations indicates that the copolymers adopt a mixed structure consisting of three conformations only as RFPs. The fraction of beta(TTT) and gamma(T_3GT_3G) compared to alpha (TGTG) phase can be calculated using the following formula [74]:

$$F_{\text{beta+gamma}} = \frac{I_{840}}{\left(\frac{K_{840}}{K_{763}}\right)I_{763} + I_{840}}$$

Where, the absorbencies at 840 and 763nm are I_{840} and I_{763} are. K_{840} is $7.7 \times 10^4 \text{ cm}^2/\text{m}$ and K_{763} is $6.1 \times 10^4 \text{ cm}^2/\text{mol}$ as the absorption coefficient at the respective wave number.

Furthermore, the beta and gamma phase can be also calculated with the following equations:

$$F(\gamma) = F_{\beta+\gamma} \times \left(\frac{H_\gamma}{H_\beta + H_\gamma} \right) \times 100\%$$

$$F(\beta) = F_{\beta+\gamma} \times \left(\frac{H_\beta}{H_\beta + H_\gamma} \right) \times 100\%$$

Where the H_γ and H_β peak differences between around 1275 cm^{-1} and 1260 cm^{-1} , and around 1234 cm^{-1} and 1225 cm^{-1} . as Co55(alpha:24%, beta: 55%, gamma:20%), CFE1(alpha:39 beta: 31%, gamma:30%), CFE1-Co55-10%(alpha:27%, beta: 54%, gamma:19%), and CFE1-Co55-20%(alpha:25%, beta: 57%, gamma:18%). These results confirm the decrease in RF crystallinity and increase in the crystalline β phase of blended RFPs, which can help explain the reduced elastic moduli of both neat and blended RFPs when the fraction of the third monomer increases, and also support the high storage modulus of the CFE1 terpolymer.

Applications

An essential requirement for the commercialization of soft actuators, particularly those based on electroactive polymers, is high performance at elevated temperatures. To demonstrate the applicability of the RF bending actuators at elevated temperatures, microfluidic pumps were developed as shown in Fig. 5. These RF polymer membrane actuators can push fluid in a microfluidic chamber into a microfluidic channel. Microfluidic pumps have potential applications in micro-optical systems such as variable-focus lens [75], lab-on-a-chip [76], and micro total-analysis systems [77]. The MFM actuator, composed of gold/RFP/gold, was formed on a PET film as illustrated in Fig. 5a, such that the MFM actuator and PET film formed a unimorph actuator to push the silicone oil in the microfluidic chamber by bending deflection. The CFE1 terpolymer and two blends with 20% Co55 and 20% Co75 were used for comparison. A sinusoidal voltage with a maximum of 600 V and 0.5 Hz was applied. The viscous silicone oil dramatically retarded the response of the soft microfluidic pump; however, the pumping level changes (h) between minimum and maximum could be easily evaluated with an optical microscope as shown in Fig. 5b. Fig. 5c and d present the actuation performance at room temperature (25 °C) and elevated temperature (60 °C), respectively. As expected, the soft microfluidic pump composed of CFE1-Co55-20% showed the best performance at room as well as elevated temperatures. Further, the pumping performance of CFE1-Co55-20% decreased by only 15% at 60 °C compared to that at room temperature. Thus, these results confirm the findings presented in the previous sections.

Conclusion

In conclusion, uniquely designed RFPs are introduced as a promising material for designing high-temperature operational flexible actuators. The study shows that the electromechanical responses of RFPs highly depend on the composition of three monomers, particularly the fraction of the third monomer CFE.

The analysis of strain energy density and film stress has confirmed that CFE1 has approximately four times higher film stress and around eight times higher strain energy density than CFE8 at elevated temperatures. Further, we investigated the influence of blending RFP terpolymers with a normal FE polymer. Blending a small amount (less than 20%) of Co55 into the RFPs resulted in enhanced actuation performance at both room and elevated temperatures. Moreover, the formation of distinct crystalline phases in the blends by both components could completely produce a relaxor because the interfacial couplings to the bulky defects in the terpolymer converted the normal FE polymer into a relaxor. At elevated temperatures, all the storage moduli of the polymers decrease significantly, while the moduli of the copolymers are mostly higher than those of any RFPs. Therefore, blending RFPs, especially CFE1, with FE Co55 not only improves the mechanical properties at room temperature but also affords greater enhancement at elevated temperatures. Although blending RFPs with Co55 causes the reduction of strain, the storage modulus of the blends improves, and the actuation performance, which is expressed in terms of film stress, is still enhanced, particularly at elevated temperatures. Therefore, blending the RFP terpolymer with FE Co55 is an effective method for improving the actuation performance of RFPs at higher temperatures even when the electrostrictive strain has a decreasing tendency. Finally, the study demonstrated the stable actuation performance of microfluidic pump applications using CFE1-Co55-20% at high temperatures and verified the versatile usage of the RFP in various areas.

Declaration of generative AI and AI-assisted technologies in the writing Process

During the preparation of this work the author(s) used ChatGPT in order to grammar confirming. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.giant.2023.100208](https://doi.org/10.1016/j.giant.2023.100208).

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