

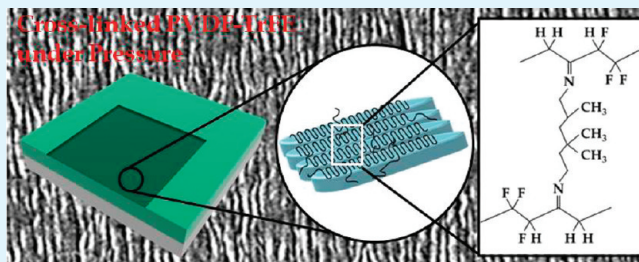
Compression of Cross-Linked Poly(vinylidene fluoride-co-trifluoroethylene) Films for Facile Ferroelectric Polarization

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ABSTRACT: In this study, we demonstrated a facile route for enhancing the ferroelectric polarization of a chemically cross-linked poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) film. Our method is based on thermally induced cross-linking of a PVDF-TrFE film with a 2,2,4-trimethyl-1,6-hexanediamine (THDA) agent under compression. The remanent polarization (P_r) of a metal/ferroelectric/metal capacitor containing a cross-linked PVDF-TrFE film increased with pressure up to a certain value, whereas no change in the P_r value was observed in the absence of THDA. A film cross-linked with 10 wt % THDA with respect to PVDF-TrFE under a pressure of 100 kPa exhibited a P_r of approximately $5.61 \mu\text{C}/\text{cm}^2$, which is 1.6 times higher than that in the absence of pressure. The enhanced ferroelectric polarization was attributed to highly ordered 20-nm-thick edge-on crystalline lamellae whose c -axes are aligned parallel to the substrate. The lamellae were effective for ferroelectric switching of the PVDF-TrFE when a cross-linked film was recrystallized under pressure. Furthermore, compression of a PVDF-TrFE film with a topographically prepatterned poly(dimethyl siloxane) mold gave rise to a chemically cross-linked micropattern in which edge-on crystalline lamellae were globally oriented over a very large area.

KEYWORDS: ferroelectric polymer, 2,2,4-trimethyl-1,6-hexanediamine, PVDF-TrFE, crystal orientation, compression, thermal cross-linking, micropatterning



1. INTRODUCTION

Novel polymeric nonvolatile memories are greatly desired for new mobile, flexible, and ubiquitous computing applications and are being actively investigated, including those based on ferroelectric polymers, which guarantee easy and cost-effective processing as well as mechanical flexibility of devices.^{1–6} Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) (PVDF-TrFE) are representative ferroelectric polymers whose ferroelectricity originates from bistable dipole polarization between hydrogen and fluorine atoms. They have potential beneficial characteristics for memory applications such as good fatigue characteristics, long data retention, and a large remanent polarization.^{1,6–14}

The nonvolatility of information in ferroelectric memory strongly depends upon the remanent polarization (P_r) of PVDF-TrFE and, in particular, is greatly affected by the molecular orientation of polymer crystals and the resulting microstructures.^{15–18} The b axis of PVDF-TrFE crystals aligned parallel to an electric field gives rise to characteristic edge-on crystalline lamellae, allowing the maximization of the ferroelectric polarization of the film.¹⁵ Another issue which should be considered is the feasibility of fabricating both chemically and electrically robust films of PVDF-TrFE using mass production methods based on solution processes which frequently require consecutive solution-based coating processes for a layered structure.¹⁸ For instance, direct spin-coating of another polymer on a PVDF-TrFE film frequently

causes serious mechanical film damage, resulting in poor memory performance.

Chemical cross-linking of a ferroelectric polymer has proven to be an effective way to ensure organic solvent resistance.^{18,19} In a previous work, we demonstrated both chemically and electrically stable PVDF-TrFE films by cross-linking the polymer chains with the thermal cross-linking agent 2,2,4-trimethyl-1,6-hexanediamine (THDA) for nonvolatile memory applications.¹⁸ Although the thermal cross-linking performed at 170 °C, which is above the melting temperature (T_m) of PVDF-TrFE, still produced ferroelectric β crystals upon recrystallization, the P_r of the cross-linked films was remarkably reduced due to the resulting crystal orientation of the PVDF-TrFE film, where the c and b axes were aligned perpendicular and parallel to the substrate, respectively, which is ineffective for ferroelectric switching.^{15–17} The orientation of the b axis perpendicular to the electric field in the metal/ferroelectric/metal (MFM) capacitor geometry gave rise to an approximately 40% reduction in P_r compared to that of a film with characteristic edge-on crystals induced during thermal annealing below the T_m .¹⁸ Therefore, there is need for a method to control the molecular orientation of ferroelectric crystals upon

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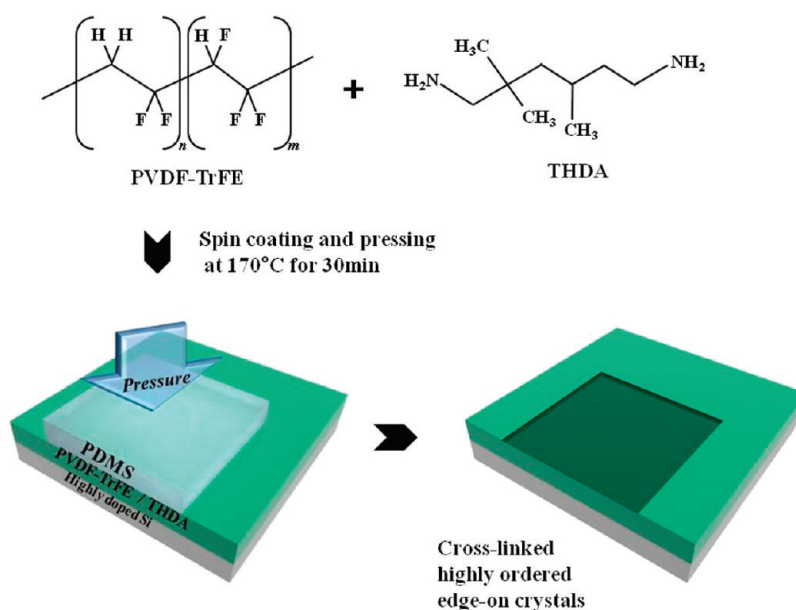


Figure 1. Schematics of the fabrication of a cross-linked PVDF-TrFE film under compression.

thermal cross-linking and subsequent recrystallization, leading to enhanced ferroelectric polarization.

Here, we present a novel route for developing highly ordered edge-on crystalline lamellae in a thin, cross-linked PVDF-TrFE film whose *c*-axis, i.e., chain axis, is oriented parallel to the substrate. Our method relies upon thermal cross-linking of a PVDF-TrFE film with THDA under compression. The P_r of the MFM capacitor with a cross-linked film increased with pressure due to enhanced crystal orientation. A film cross-linked with 10 wt % THDA with respect to the polymer under a pressure of 100 kPa exhibited a P_r of approximately $5.61 \mu\text{C}/\text{cm}^2$, which is 1.6 times higher than that without pressure. Furthermore, compression with a topographically prepatterned poly(dimethyl siloxane) (PDMS) mold allowed us to fabricate a micropatterned, cross-linked ferroelectric film in which edge-on crystalline lamellae were globally ordered over a very large area.

2. EXPERIMENTAL SECTION

Materials and Film Preparation. PVDF-TrFE with 25 wt % TrFE was purchased from MSI Sensors. The cross-linking agent, 2,2,4-trimethyl-1,6-hexanediamine (THDA), and methyl ethyl ketone (MEK) were purchased from Sigma Aldrich, Korea. The melting (T_m) and Curie (T_c) temperatures of the PVDF-TrFE were 160 and 80 °C, respectively, as determined by a differential scanning calorimeter (Perkin-Elmer DSC-7) with heating and cooling rates of 2 °C/min.

The chemical cross-linking of a thin PVDF-TrFE film was performed with THDA as described elsewhere.¹⁸ Briefly, PVDF-TrFE/THDA blend solutions in MEK were spin-coated at 2000 rpm for 60 s onto a highly boron-doped Si substrate by controlling the composition of the THDA from 0 to 10 wt % with respect to the weight of the polymer. The spin-coated films were subsequently cured at 170 °C for 30 min under various pressures ranging from 0 to 200 kPa and were then slowly cooled to room temperature. In our apparatus, a PVDF-TrFE film containing THDA spin coated on a Si wafer was in conformal contact with a few micrometer thick elastomeric PDMS film to ensure uniform pressure applied over the whole film. The bilayered PVDF-TrFE/PDMS sample was in turn pressurized by a metal plate with heater. In our previous

work,¹⁸ we evaluated the degree of cross-linking of a PVDF-TrFE film as a function of amount of THDA by the conventional swelling measurement in which the cross-linking degree was calculated by a relation of $(W_s - W_i)/W_i \times 100$, where W_s and W_i are weights of a PVDF-TrFE film before and after swelling in a solvent, respectively. Although the maximum amount of THDA that can be associated with PVDF-TrFE in our system is approximately 90 wt % of PVDF-TrFE when assumed that only VDF moiety can react with THDA as reported in the previous work,²² we have observed significant macrophase separation between crystalline PVDF-TrFE and amorphous aggregates of PVDF-TrFE and THDA at the amount of THDA greater than 20 wt % with respect to polymer. In the current system, we have found that the maximum amount of THDA for compression was approximately 10 wt % with respect to polymer.

Device Fabrication. For MFM capacitor fabrication, PVDF-TrFE thin films cross-linked with THDA under various pressures were coated onto highly boron-doped Si substrates. Also, Au top electrodes were vacuum-deposited onto cross-linked films through a shadow mask containing holes with diameters of 200 μm under a pressure of 1×10^{-6} mbar and an evaporation rate of 0.1 nm/s.

Micropattern Fabrication. A 300-nm-thick PVDF-TrFE film containing 10 wt % THDA with respect to the weight of the polymer was deposited onto a highly doped Si substrate and was prepared by spin coating with no further thermal curing. A prepatterned poly(dimethyl siloxane) (PDMS) mold was placed in conformal contact with the film. Two PDMS molds with different structural symmetries were used. One mold contained square-shaped mesas with a side width of 5 μm arrayed into a 4 mm symmetry. The other mold had periodic lines with a width and periodicity of 10 and 20 μm , respectively. The PDMS molds were fabricated by casting a PDMS precursor (Sylgard 184, Dow Corning Corp) onto a photoresist master, as described elsewhere.²⁰ Thermal imprinting was performed at 170 °C for 30 min at a pressure of 100 kPa using a custom apparatus.

Characterization. The microstructures of the PVDF-TrFE films cross-linked with THDA under pressure were analyzed with a scanning electron microscope (SEM, JEOL JSM-600F) and atomic force microscope in tapping mode (AFM, Digital Instruments NanoScope 3100). The crystalline structures of the PVDF-TrFE films were characterized by 2-dimensional (2D) grazing incidence X-ray diffraction (GIXD) analysis.

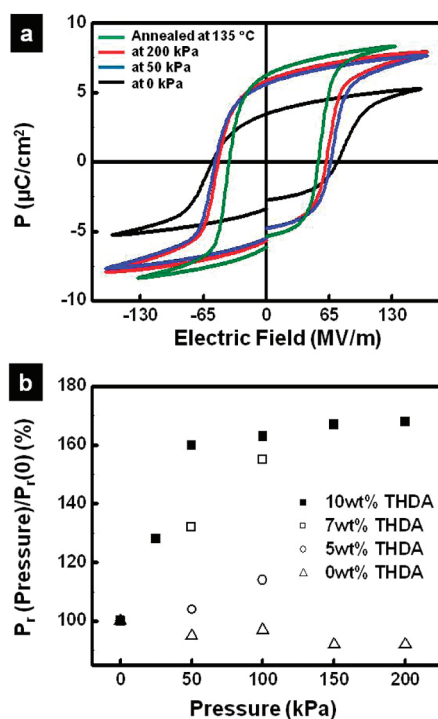


Figure 2. (a) Polarization P vs E hysteresis loops of metal/ferroelectric/metal capacitors containing PVDF-TrFE films under different conditions: annealing at 135 °C for 2 h without pressure (green), annealing at 170 °C for 30 min containing 10 wt % THDA without pressure (black), at 50 kPa (red), and at 200 kPa (blue). (b) Degree of the enhanced remanent polarization calculated as the ratio of $P_r(\text{pressure})/P_r(0) \times 100$, where $P_r(\text{pressure})$ and $P_r(0)$ are the polarization values of the samples under the specific pressure and 0 kPa, respectively, as a function of the pressure applied on PVDF-TrFE films annealed at 170 °C for 30 min with 10 wt % (solid square), 7 wt % (open square), 5 wt % (circle), and 0 wt % THDA (triangle).

GIXD was performed on the 4C2 beamline at the Pohang Accelerator Laboratory in Korea (incidence angle of 0.15°). The scattered beam intensity was recorded using an SCX 4300–165/2 CCD detector (Princeton Instruments). 2D GIXD patterns were obtained in the ranges of $0 < q_z < 2.33 \text{ \AA}^{-1}$ and $0 < q_{xy} < 2.33 \text{ \AA}^{-1}$ ($q = 4\pi \sin \theta / \lambda$, with Z perpendicular to X and Y and parallel to the substrate) with the monochromatized X-rays ($\lambda = 0.1608 \text{ nm}$) under vacuum. Azimuthal intensity plots of the 2D GIXD patterns were obtained using FIT 2D software provided by the European Synchrotron Radiation Facility. The ferroelectric properties were determined using a virtual ground circuit (Radiant Technologies Precision LC units). All measurements were performed in a metallic shielded box at room temperature under ambient conditions.

3. RESULTS AND DISCUSSION

Figure 1 shows the schematic of the fabrication of the thin cross-linked PVDF-TrFE film with THDA under compression. As described in detail in our previous work,¹⁸ chemical cross-linking between PVDF-TrFE and THDA arises from the good basicity of diamine in THDA enabling dehydrofluorination of a fluorinated polymer, leading to a double bond between the carbon atoms in PVDF-TrFE and nitrogen atoms of THDA. The cross-linking of PVDF-TrFE previously confirmed by dissolution and swelling experiments vigorously occurs at temperatures above 160 °C.¹⁸ Greatly motivated by a hypothesis presented in a

previous work by Taguet et al. in which the application of an appropriate pressure activates the cross-linking reaction of fluorinated polymers such as poly(vinylidene fluoride-*co*-hexafluoropropylene) and PVDF and thus results in improved thermal properties,¹⁹ we employed compression during the cross-linking reaction at 170 °C in our system. An approximately 300-nm-thick PVDF-TrFE film spin-coated onto a Si substrate and subsequently covered with a thin PDMS pad was pressurized at 170 °C for 30 min under pressures ranging from approximately 25 to 200 kPa. After the cross-linking under pressure, the sample slowly cooled to room temperature and was subject to various ferroelectric and microstructural property analyses.

The ferroelectric polarization behavior of a cross-linked PVDF-TrFE film containing 10 wt % THDA with respect to the weight of polymer was characterized using polarization-applied electric field (P – E) hysteresis loops under different pressure conditions, as shown in Figure 2a. It is noted that there should be some thickness change of a PVDF-TrFE film upon compression. We carefully measured the thickness variation of the films pressurized with different pressure by examining the edge step between pressed and nonpressed regions by AFM in height contrast. At the maximum pressure we applied, approximately 20% thickness variation was observed in both films with THDA. The plots in Figure 2a were obtained after normalizing the applied voltage with film thickness.

A capacitor of the PVDF-TrFE film spin-coated and annealed at 135 °C for 2 h on a highly boron-doped Si electrode without THDA showed a typical hysteresis loop, resulting in a remanent polarization, P_r , of approximately 5.56 $\mu\text{C}/\text{cm}^2$ and a coercive voltage, E_c , of approximately 50 MV/m, as shown in Figure 2a (green line). As observed in our previous work, the P_r of the heat-treated sample above its T_m without pressure decreased by approximately 30% along with an increase in E_c (black line) compared to that of the PVDF-TrFE film annealed at 135 °C for 2 h. Our previous study has shown that coercive field of a PVDF-TrFE film recrystallized from a molten state was approximately 63 MV/m and the value increased with 10 wt % THDA to approximately 70 MV/m.¹⁸ The preferred crystal orientation of the chain axis (c -axis) normal to the substrate was attributed to a reduction in polarization in the PVDF-TrFE film annealed above the T_m .^{15,18} Interestingly, ferroelectric polarization was enhanced with the pressure applied during cross-linking at 170 °C, as shown in Figure 2a. For instance, the P_r values of films pressurized at 50 and 200 kPa were very similar to the P_r of the sample annealed at 135 °C (blue and red lines). Figure 2a apparently exhibits the coercive field of a cross-linked film under compression smaller than that of a film recrystallized from molten state without THDA.

To gain further insight into the enhanced polarization of a cross-linked film under pressure, we investigated the effect of pressure on a cross-linked PVDF-TrFE film with 10 wt % THDA. As shown in Figure 2b, P_r increased nearly linearly with increasing pressure and became saturated at approximately 50 kPa. The degree of enhanced polarization was quantified by the ratio of $P_r(\text{pressure})/P_r(0) \times 100$, where $P_r(\text{pressure})$ and $P_r(0)$ are the remanent polarization values of the samples under the specific pressure and 0 kPa, respectively. The maximum change in polarization was approximately 160%, which is comparable to the value of the sample annealed at 135 °C.

Combined with the pressure, the chemical cross-linking with THDA was an additional essential step for the enhancement of ferroelectric polarization. Almost no change in the P_r value was observed in the samples without THDA, regardless of the

pressure, as shown in Figure 2b (triangles). It is apparent that the P_r value increases as the amount of THDA increases. For instance, at a constant pressure of 50 kPa, the P_r value of the sample without THDA was approximately $4.4 \mu\text{C}/\text{cm}^2$, and it continuously increased with THDA content, reaching approximately $5.5 \mu\text{C}/\text{cm}^2$. Our results clearly suggest that the enhanced polarization arises from the combination of chemical cross-linking and pressure. The ferroelectric properties of the PVDF-TrFE films with various amounts of THDA and pressures are summarized in Table 1.

Table 1. Remanent Polarization ($\mu\text{C}/\text{cm}^2$) of MFM Capacitors Containing PVDF-TrFE Films with Various THDA Content under Different Pressure

pressure (kPa)	THDA (wt%)			
	0	5	7	10
0 ^a	4.66	4.50	4.59	3.45
25				4.43
50	4.44	4.68	6.05	5.55
100	4.5	5.11	6.26	5.61
150	4.3			5.76
200	4.28			5.79

^a All ferroelectric properties are averaged out of 10 MFM cells. V.

To understand how pressure affects the molecular structure and microstructure of a thin crystalline PVDF-TrFE film cross-linked with THDA, we performed surface probe, electron microscope, and X-ray diffraction analyses. The surface of the PVDF-TrFE film thermally annealed at 170°C for 30 min shown in Figure 3a was relatively smooth, with no distinctive crystalline microstructure resulting from the in-plane lamellar structure where the chain axis (*c*-axis) was dominantly normal to the substrate, as described in detail in our previous works.^{15,16} As mentioned previously, the low P_r value of the sample is attributed to the ineffective crystal orientation for ferroelectric dipole switching. The pressurized PVDF-TrFE film without THDA also had a similar flat surface, as shown in Figure 3b, which explains the previous polarization behavior of no change in P_r value, as shown in Figure 2b. Furthermore, the cross-linked PVDF-TrFE film without pressure gave rise to a characteristic bumpy surface with in-plane crystalline lamellae, as shown in Figure 3c, similar to the observation in our previous work.¹⁸ The bumps on the film result from the residual THDA segregated on the film. A sample cross-linked with 10 wt % THDA under a pressure of 100 kPa exhibits a completely different surface morphology in which edge-on crystalline lamellae with a thickness of approximately 20 nm are well organized, as shown in Figure 3d.

The crystalline microstructure of the cross-linked PVDF-TrFE film compressed at the lower pressure of 10 kPa also clearly shows a mixture of edge-on and in-plane lamellae, while

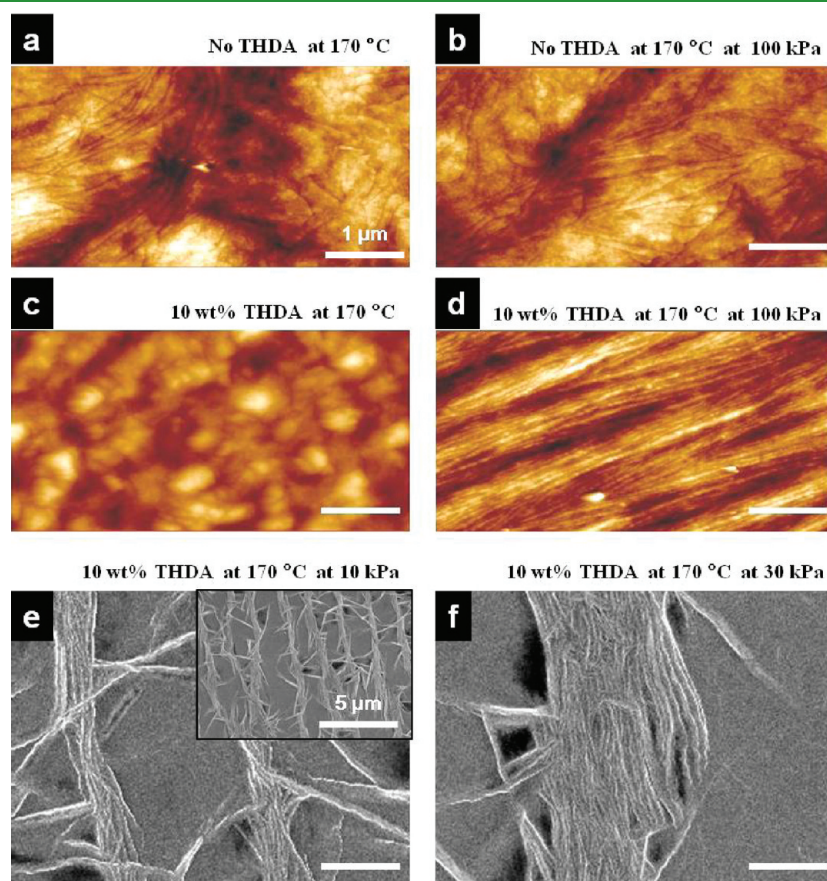


Figure 3. Height contrast (a-d) TM-AFM and (e, f) SEM images of approximately 300-nm-thick PVDF-TrFE films obtained under different conditions. The films exhibit a characteristic in-plane crystalline surface when annealed at 170°C for 30 min (a) with no THDA at 0 kPa, (b) with no THDA at 100 kPa, and (c) with 10 wt % THDA without pressure. Surface morphologies of PVDF-TrFE films annealed at 170°C for 30 min with 10 wt % THDA (d) at 100 kPa, (e) at 10 kPa, and (f) at 30 kPa. Well-ordered edge-on crystalline lamellae are observed in (d). A low-magnification image of e is shown in the inset.

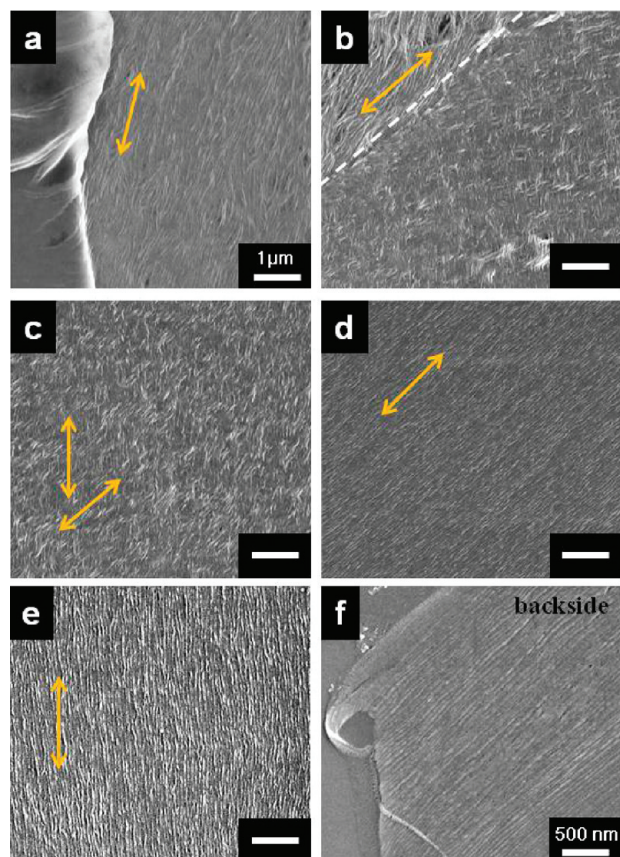


Figure 4. SEM images of a PVDF-TrFE film annealed at 170 °C for 30 min with 10 wt % THDA at a pressure of 100 kPa. Several parts of the film were examined from (a) the borderline between pressurized and nonpressurized regions to (b–e) the inner regions of the film. Various crystalline grains are visible with different lamellae textures in b–e. (f) Backside of the film, exhibiting highly ordered edge-on crystalline lamellae.

the surface coverage of the edge-on crystals is quite low, as shown in Figure 3e. It should be noted that the low magnification image in the inset of Figure 3e exhibits anisotropic grain growth of the edge-on crystals, resulting in oriented bundles of the edge-on lamellae. The area density of the edge-on lamellae further increased at a pressure of 30 kPa with the thicker bundles forming agglomerations, as shown in Figure 2f.

At a pressure greater than 50 kPa, oriented edge-on crystalline lamellae were developed over a large area, as shown in Figure 4. To examine how the grains of the oriented crystalline lamellae were developed in a pressured film, we scanned several parts of the film from the boundary between the pressurized and nonpressurized regions to the center of the film. The scanned film shows crystalline grains with various lamellae orientations, as shown in Figure 4. The crystalline lamellae tend to grow parallel to the borderline between the pressurized and nonpressurized regions, as shown in Figure 4a. The grain containing the lamellae parallel to the borderline extends over an area of tens of square micrometers and meets with another grain with a different crystal orientation, leading to a clearly visible grain boundary, as shown in Figure 4b. Mixed lamellae with two different orientations, i.e., cross-hatched lamellae, were developed over an area of tens of square micrometers, as shown in Figure 4c. In addition, inside the sample, we observed other grains with distinctive lamellar

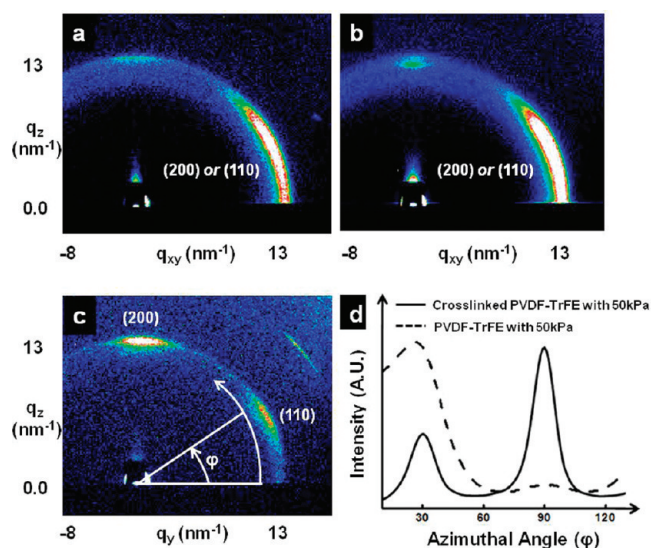


Figure 5. 2D GIXD patterns of PVDF-TrFE films annealed at 170 °C for 30 min (a) without THDA at 0 kPa, (b) without THDA at 50 kPa, and (c) with 10 wt % THDA at 50 kPa. Although non-cross-linked films show an intensified reflection on the equator, the cross-linked film displays two distinguishable peaks at 13.5 nm^{-1} on the meridian and 60° from the meridian. (d) Equatorial azimuthal intensity profile as a function of the scanning azimuthal angle (φ) obtained from the diffraction patterns of b and c.

orientations, as shown in Figure 4d,e. To confirm the presence edge-on lamellae grown from the bottom to top surface of the PVDF-TrFE films, we also investigated the backside of a pressured film by detaching the film from the Si substrate using poly(acrylic acid) according to a process described elsewhere.²³ Figure 4f clearly exhibits similar globally oriented edge-on lamellae. It is noteworthy that in our experimental conditions, no significant difference in microstructure was observed with the cooling rate of a sample.

The detailed molecular orientation of thin cross-linked and pressured PVDF-TrFE films was revealed with grazing incident X-ray diffraction (GIXD) experiments. For comparison, a PVDF-TrFE film spin-coated and thermally annealed at 170 °C for 30 min without THDA showed the preferred orientation of the {110} and {200} reflections apparent near the equator, as shown in Figure 5a. These results imply that the *c* chain axis is preferentially aligned perpendicular to the substrate surface, with both *a* and *b* axes parallel to the substrate.¹⁵ The application of 50 kPa to the sample thermally treated at 170 °C without THDA also resulted in a diffraction pattern similar to that without pressure, as shown in Figure 5b. A thin PVDF-TrFE film cross-linked with 10 wt % THDA under a pressure of 50 kPa displayed a different diffraction pattern, as shown in Figure 5c, where two distinguishable diffraction peaks at 13.5 nm^{-1} (i.e., $\sim 4.6 \text{ \AA}$) were apparent on the meridian of the diffraction pattern and 60° from the meridian.

As described in detail in our previous works,^{15,18,24,25} although it is difficult to unambiguously index the meridional and off-meridional reflections due to the orthorhombic PVDF-TrFE crystal lattice characterized by a $\sqrt{3}/2$ ratio of its *a* and *b* axes and with nearly equal (200) and (110) spacings, the diffraction pattern clearly implies that the *ab* plane of the PVDF-TrFE crystals is perpendicular to the X-ray direction. In other words, the *c*-axis of the crystals is predominantly parallel to the substrate.

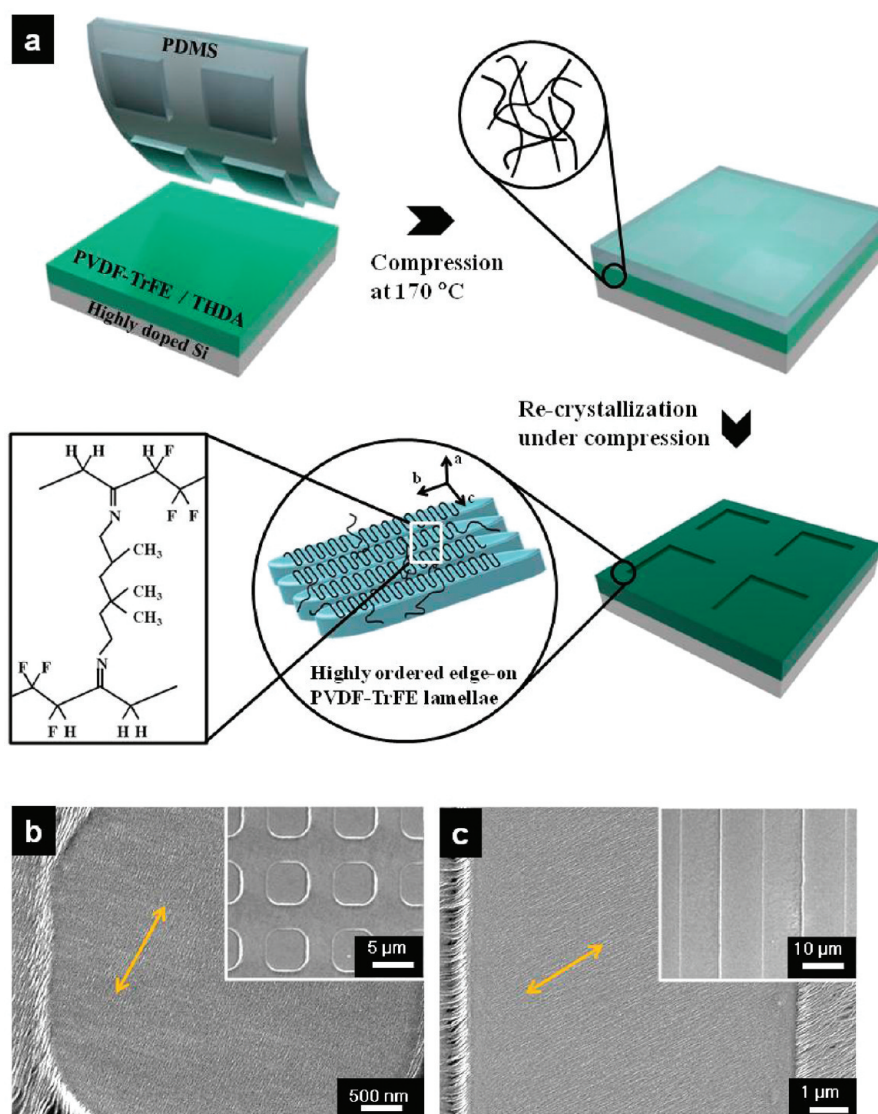


Figure 6. (a) Schematic illustration of the fabrication of micropatterns of a chemically cross-linked PVDF-TrFE film under pressure with highly ordered edge-on crystalline lamellae. SEM images of PVDF-TrFE films containing 10 wt % THDA imprinted with topographically prepatterned PDMS molds consisting of (b) periodic squares with a side width of 5 μm and (c) periodic 10 μm lines. Highly ordered edge-on lamellae were developed in individual patterned domains with a nearly single-crystal-like texture.

In addition, the equatorial azimuthal intensity distribution profile as a function of the scanning azimuthal angle (φ) shown in Figure 5d reveals two reflections separated by 60° , indicative of a 6-fold hexagonal structure. It should be noted that the portion of β crystals with respect to γ ones evaluated from IR spectra was approximately 0.5 for all the samples, irrespective of THDA, which implies that the ferroelectric β crystal phase is well-maintained, even after chain cross-linking.¹⁸ It is also important to note that the degree of crystallization was not significantly affected at the low content of THDA up to approximately 10 wt % with respect to PVDF-TrFE. When THDA increased in a sample, for instance, to 50 wt %, macrophase separation occurred between crystalline PVDF-TrFE and amorphous aggregates of unreacted, residual THDA and PVDF-TrFE, giving rise to the reduction of degree of crystallization.¹⁸

Both the microstructure and molecular orientation results of the thin cross-linked PVDF-TrFE film under pressure explain the enhanced ferroelectric polarization of the film in the MFM

capacitor. Globally ordered edge-on crystalline lamellae with the c -axis aligned parallel to the substrate were much more effective for facile polarization switching than were in-plane lamellae obtained from the samples heat-treated at 170 $^\circ\text{C}$ with or without THDA, giving rise to a P_r value almost 60% greater than that obtained without pressure. Considering that edge-on crystalline lamellae were well developed in the PVDF-TrFE film spin-coated and subsequently annealed at 135 $^\circ\text{C}$,^{15,25} it is also obvious that the P_r value of the pressurized and cross-linked film was very similar to that of the film annealed at 135 $^\circ\text{C}$ shown in Figure 2.

Although we observed that the enhanced ferroelectric polarization arising from the oriented edge-on crystalline lamellae requires both cross-linking and pressure, its detailed mechanism still remains unclear. Applied compression in a polymer molten state can preferentially result in polymer chains oriented parallel to the substrate surface. The chemical cross-linking reaction occurring in the molten state can maintain the preferential chain

conformation. The subsequent crystallization upon cooling of the sample under pressure likely induces the observed edge-on crystalline lamellae. Our speculation is partially supported by the fact that the edge-on crystals became increasingly dominant with increasing applied pressure, as shown in Figure 3e,f. On the other hand, in the case of the sample pressurized without THDA, the preferential chain conformation developed parallel to the substrate appears to be completely destroyed during crystallization because of the preferential crystal surface interaction, as reported in our previous works.^{15,16} The edge-on lamellae were also formed upon cross-linking at a temperature higher than 170 °C with compression. In addition, a subsequent melt and recrystallization of the cross-linked edge-on crystals in the absence of pressure gave rise to in-plane lamellae, which again implies that compression is an essential step for the crystal orientation.

The globally ordered edge-on lamellae with large grain size may be attributed to polymorphic crystal-to-crystal phase transition of PVDF-TrFE. There are three different crystalline phases reported of PVDF-TrFEs: (1) the ferroelectric low-temperature (LT) phase, (2) the paraelectric high-temperature (HT) phase, and (3) the cooled phase (CP).^{25–27} The ferroelectric LT phase consists of planar zigzag chains with the lattice constants as follows: $a = 9.12 \text{ \AA}$, $b = 5.25 \text{ \AA}$, $c = 2.55 \text{ \AA}$ ($\beta = 93^\circ$). The HT phase, which appears above the phase transition temperature, Curie temperature, T_C , has hexagonal crystal packing ($a = b = 5.63 \text{ \AA}$, $c = 4.60 \text{ \AA}$) with the molecular chains of a disordered conformation, $T_3GT_3\bar{C}$, $T\bar{C}$, leading to the nonpolar characteristic. The crystal structure of CP phase ($a = 9.16 \text{ \AA}$, $b = 5.43 \text{ \AA}$, $c = 2.53 \text{ \AA}$, $\beta = 93^\circ$) is similar to that of LT phase, but the zigzag chains tilt by about 18° . Due to high VDF molar ratio of approximately 72% of our PVDF-TrFE, only LP phase appears below Curie temperature. In the current system, edge-on crystals were first developed in paraelectric regime from the combination of cross-linking and compression when a sample was cooled down below its crystallization temperature. Upon further cooling of the sample below its T_C , polymorphic crystal phase transition from HT to LT occurred with large and anisotropic volume change in the sample due to the difference in crystal lattices of the two phases. The significant volume change could give rise to very large crystal grains in which highly ordered edge-on lamellae were developed. In the case of a sample spin-coated and subsequently annealed at 135 °C in paraelectric phase, however, anisotropic crystal growth with large grains would be hardly obtained because grain growth was strictly limited from very small grains with edge-on crystals which had been formed during spin coating even upon thermal annealing.

From a technological point of view, the pressure-induced modification of crystal orientation of cross-linked PVDF-TrFE films can be readily combined with conventional micro imprinting to fabricate facile micropatterns.^{17,28,29} We employed topographic PDMS molds with periodic squares and lines for a PVDF-TrFE film containing 10 wt % THDA pressurized at 170 °C for 30 min, as schematically illustrated in Figure 6a. As noted, nearly single crystal-like textures of the oriented edge-on lamellae were obtained in both the pressurized squares and lines, as shown in images b and c in Figure 6, respectively. In the experiments, the PVDF-TrFE films were in contact with the entire surfaces of the topographic molds during pressurization, as illustrated in Figure 6a, leading to highly ordered crystalline lamellae not only in the dented regions but also in the elevated regions, as shown in images b and c in Figure 6. Because the ordered lamellae produced over the entire topography of the

PVDF-TrFE films cross-linked under pressure, there is no specific effect of pattern boundary on crystal orientation. Instead, the crystal orientations indicated by the arrows in Figures 6b and 6c are preserved in both the elevated and dented regions. It is noteworthy that considering that maximum amount of THDA which can be associated with PVDF-TrFE in our system is approximately 90 wt % of PVDF-TrFE as described in the experimental parts, our samples with 10 wt % THDA seem lightly cross-linked without any technical difficulty for imprinting. Further micropatterning studies are currently being conducted to investigate selective pressurization and the effects of pattern geometry and size on crystal confinement and orientation.

4. CONCLUSIONS

We observed the enhancement of ferroelectric polarization in a thin PVDF-TrFE film cross-linked with THDA under pressure. The remanent polarization of a MFM capacitor containing a cross-linked PVDF-TrFE film increased up to a certain pressure, above which the value was saturated. At the optimal conditions, a maximum P_r increase of approximately 60% was achieved compared to the value obtained in the absence of pressure. We demonstrated that the pressure-induced P_r enhancement of a chemically cross-linked PVDF-TrFE film arose from globally ordered edge-on crystalline lamellae during cooling. The preferential orientation of the crystal c -axis parallel to the substrate in the edge-on lamellae was effective for ferroelectric switching, leading to the enhanced P_r . Furthermore, we demonstrated the micropatterns of a cross-linked PVDF-TrFE film based on an imprinting technique in which edge-on crystalline lamellae were globally ordered with single crystal-like textures in individual patterned areas. The results clearly suggest that the chemical reaction networking ferroelectric polymer chains with each other when combined with mechanical compression effectively controlled molecular assembly during crystallization, leading to a thin cross-linked film with the preferential crystal ordering favorable for ferroelectric switching.

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