The Pennsylvania State University
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ELECTROCALORIC EFFECT IN RELAXOR FERROELECTRIC MATERIALS

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Xinyu Li

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The dissertation of Xinyu Li was reviewed and approved* by the following:

Qiming Zhang
Distinguished Professor of Electrical Engineering
Dissertation Advisor
Chair of Committee

Zhiwen Liu
Associate Professor of Electrical Engineering

Noel Chris Giebink
Assistant Professor of Electrical Engineering

Christopher D. Rahn
Professor of Mechanical Engineering

Kultegin Aydin
Professor of Electrical Engineering
Head of the Department of Electrical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

Electrocaloric Effect (ECE) refers to the entropy change and/or temperature change in dielectric materials due to electric field induced change of dipole states. ECE may provide an effective means of realizing cooling devices for a broad range of applications in both household appliances as well as industrial facilities. Refrigeration based on ECE has the potential of reaching higher efficiency compared with vapor-compression cycle systems. This dissertation focuses on ECE in relaxor ferroelectric polymers, which exhibit large electrocaloric response over a broad temperature range. Various relaxor ferroelectric polymers have been examined in this work, through theoretical considerations, structural analysis and electrical measurements, to explore general rules to develop material systems with giant ECE.

First, the background and principle of ECE, along with prototypical materials with notable electrocaloric responses are introduced. It is shown that ECE can be generated in various materials including ceramics (bulk and thin film), polymers, polymer composites, polymer/nano-particle composites, dielectric fluids and ionic crystals. Compared with other types of materials, poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE))-based relaxor ferroelectric polymers exhibit superior properties in many ways. ECE cooling device has been discussed to derive critical parameters and requirements for designing electrocaloric materials.

The electrocaloric performance of relaxor ferroelectric polymers can be predicted and understood using theoretical guidelines such as thermodynamic analysis, Landau-Devonshire phenomenological theory, coexisting phases rule near invariant critical points. Based on these considerations, many efforts have been made to tailor material systems in order to generate large ECE response. Specially, defect modifications, such as high energy electron irradiation and copolymerization with monomer with larger size, provide a few facile ways to increase random states and thus improve material properties. To characterize ECE, two different methods, i.e.,
indirect measurement and direct measurement are utilized. It should be noted that indirect method would result in a large deviation when used to deduce ECE in relaxor ferroelectrics, due to the non-ergodic nature of relaxors.

High energy electron irradiated copolymers are then discussed. The impact of high energy electron irradiation, which reduces dipole correlations and thus increases ECE response of P(VDF-TrFE) by introducing defects into the copolymers, is studied in different ferroelectric copolymers. As irradiation dose increases, P(VDF-TrFE) 65/35 mol% copolymer gradually transforms from normal ferroelectric into relaxor ferroelectric material, with dielectric constant peak and ECE response peak shifting from high temperature to room temperature. It is also demonstrated that high energy electron irradiation alleviates hysteresis loss while increases the number of disorder states, therefore, irradiated P(VDF-TrFE) 65/35 mol% copolymer with 20 Mrads shows a large entropy change as high as 130 Jkg⁻¹K⁻¹ and large temperature change of 28 °C. While for P(VDF-TrFE) with high VDF content (>75 mol%), the high energy electron irradiation fails to complete the conversion of these copolymers form normal ferroelectrics to relaxor ferroelectrics. Similarly, for poly(vinylidene chloride) (P(VDF-CTFE)) and poly(vinylidene hexafluoropropylene) (P(VDF-HFP)), the impact of irradiation on electrocaloric effect is also feeble.

Another typical relaxor ferroelectric polymer, the poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CFE)) terpolymer is elaborated in the following chapter. The influence of uniaxial stretching on electrocaloric and other properties of P(VDF-TrFE-CFE) relaxor terpolymer has been investigated to probe how material preparation process may affect its behaviors. Although dielectric constants are almost identical in the non-stretched and stretched samples, it has been found that ECE response varies upon uniaxial stretching. Data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what observed in the normal ferroelectric polymer where ECE
exhibits a sharp peak at ferroelectric-paraelectric phase transition temperature. Around 30 °C, both films show an adiabatic temperature change $\Delta T$ of 15 °C under 150 MVm$^{-1}$. Besides, the directly measured electrocaloric effect and the indirectly measured results P(VDF-TrFE-CFE) terpolymer are compared. The results show that the directly measured $\Delta T$ in the relaxor terpolymer is much larger than that indirectly deduced from Maxwell relation. The large difference between the directly measured $\Delta T$ and that deduced indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers, which are nonergodic (polar-glass) material systems.

Moveover, P(VDF-TrFE-CFE)-based composites, e.g., P(VDF-TrFE-CFE)/P(VDF-TrFE) and P(VDF-TrFE-CFE)/ZrO$_2$, are analyzed. It is shown that the electroactive properties, especially ECE, of PVDF-based ferroelectric polymers can be tailored by blending. When P(VDF-TrFE) copolymer content is low in the terpolymer/copolymer composite (<15 wt%), interfacial coupling between the relaxor terpolymer and the nano-phase copolymer increases the crystallinity of the composite, resulting in an enhanced relaxor polarization response and a significant increase in the electrocaloric effect. At high copolymer content, the blends exhibit mixed structures of the two components and ECE gradually decreases as copolymer becomes more dominant. A larger electrocaloric effect is also observed in relaxor ferroelectric terpolymer (P(VDF-TrFE-CFE))/ZrO$_2$ nanocomposites with modest ZrO$_2$ content. The interface effect between the polymer matrix and nano-fillers increases the polarization response and provides additional electrocaloric entropy changes. Furthermore, the internal bias electric field generated in poled blends of P(VDF-TrFE-CFE)/P(VDF-TrFE) is favorable to obtaining higher polarization and enhanced ECE.

Besides keeping the effort to develop materials with giant ECE response, future works also need to focus on increasing the thermal conductivity of electrocaloric materials and reducing the driving electric field required for generating large ECE.
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Chapter 1

Introduction

1.1 Background

The U.S. anneal electricity consumption is approximately 4000 terawatt hours (TWh), i.e., 4 trillion kilowatt hours (KWh).[1] And according to the data published by Department of Energy shown in Figure 1-1, refrigeration and spacing cooling account for more than a quarter of U.S. primary electricity consumption, which exceeds 1 trillion KWh. [2, 3]

![Figure 1-1 US electricity consumption according to the US Dept. of Energy](image)

Most conventional air conditioners and refrigerators achieve cooling through a mechanical vapor compression cycle (VCC). These systems suffer low efficiency. In order to quantify the efficiency of such system, one figure of merit, the coefficient of performance (COP), is employed, which is defined by COP = Qc/W, where Qc is the heat extracted from the cold end
and W is the work required. Typically, the vapor compression refrigerators (VCR) have a COP of 2 - 4. There does not appear to be any economically viable avenue to markedly improve the efficiency of these VCC systems. Moreover, a related problem with today’s VCC cooling technology is the adverse environmental impact of the refrigerant gases employed. Even though the hydrofluorocarbon (HFC) refrigerants in the current cooling system are relatively safe for the ozone layer, they are still highly undesirable since these refrigerants are strong greenhouse gases.

These factors necessitate a search for new approaches to increase the energy efficiency of these cooling technologies, and at the same time maintain environmentally friendly and low cost. Among various technologies investigated, the electrocaloric effect (ECE) is quite promising for realizing these goals. The electrocaloric effect is the electric-field-induced entropy and/or temperature change in a dielectric material. The combination of low energy loss and giant ECE during the cooling cycle endows certain electrocaloric materials the potential to be used for the development of commercially viable high efficiency cooling applications such as air conditioner and refrigerators.

ECE belongs to a class of caloric effects that generate adiabatic temperature and/or isothermal entropy change in response to external stimuli. These external stimuli, or driving forces, can be electric field, magnetic field, stress/strain and hydrostatic pressure, therefore caloric effects are named as electrocaloric effect (ECE), magnetocaloric effect (MCE), elastocaloric effect (eCE) and Barocaloric effect (BCE), respectively. Historically, elastocaloric effect was first discovered in the late 1850s.[4] It is also believed that both ECE and MCE were predicted based on the inspiration of eCE, where a thermal response due to external stress/strain was generalized and expanded into electric field and magnetic field. The first experimental observation of MCE arguable happened in 1881 [5] by Warburg in room temperature iron while the discovery of ECE in Rochelle salt occurred in the 1930s. However, it is only when the giant MCE was found [6] near the magnetostructural transition in Fe₄₆Rh₅₁ and giant ECE responses
were deduced in the ferroelectric transition in thin-film PbZr$_{0.95}$Ti$_{0.05}$O$_3$ [7] and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer [8] that broad attentions were drawn to these areas among researchers. Giant BCE in Ni–Mn–In magnetic shape-memory alloy was reported in 2010, with a magnitude that is comparable to the giant MCE reported in this class of materials.[9] As electric field or magnetic field is able to induce strain or stress in piezoelectric or piezomagnetic materials, it is possible that multiple caloric effects can be realized within certain types of materials, due to the coupling of electric field or magnetic field and stress/strain. However, up to now there has been no report on the coexistence of both MCE and ECE within unitary component material system.

Compared with eCE and BCE that are induced by mechanical triggers which can only operate under a lower frequency thus limiting the output cooling power, MCE and ECE are more promising for realizing solid state cooling device with large cooling power, since magnetic field and electric field can be easily switched even at a very high frequency. For MCE, isothermal entropy change ($\Delta S$) from MCE is a result of the change of magnetic moment ordering under the application of a magnetic field or removing of a magnetic field at a constant temperature of the surrounding environment. $\Delta S$ is related to the heat Q extracted from the cold end at a temperature T as $Q = T \Delta S$. The adiabatic temperature change ($\Delta T$) is the change of temperature of the material under the application or remove of a magnetic field without exchanging heat from the surrounding environment. Essentially this effect exists in magnetic materials and it has been found that by operating above the ferromagnetic-paramagnetic transition, a phase transition can be induced by applying or removing a magnetic field, which leads to a large MCE ($\Delta T > 10 \, ^\circ C$ and $\Delta S > 30 \, Jkg^{-1}K^{-1}$). [10] Magnetocaloric materials generally contain rare-earth and transitional metal elements such as Gadolinium (Gd), Lanthanum (La) and Rhodium (Rh), which renders the cost of MCE cooling devices prohibitively high compared with that of conventional vapor-compression-based ones. Moreover, MCE requires high magnetic field (>5 Tesla) and it is
extremely difficult, if not impossible, to shrink the size of the source for such high magnetic field, causing a barrier to integrate MCE to chip-scale or micro-scale applications. ECE. On the other hand, can be obtained in various ferroelectric materials and can work within a small area since the generation of electric field is not limited by voltage source size.

Similar to the MCE, ECE is an isothermal entropy change and adiabatic temperature change in a dielectric material when an electrical field is applied or removed. The basic principle of electrocaloric effect is the entropy change associated with the change of polarization ordering in a dielectric material, induced by an external electric field (see schematic illustration Figure 1-2). When materials changing from a non-polar phase to a polar phase or vice versa, there will be accompanying entropy change. Application of an electric field to the material causes partial alignment of dipoles and consequently a reduction of entropy of the dipolar system which releases heat to the surrounding environment as a consequence. In an isothermal condition, the dipolar material rejects heat $Q = T\Delta S$ to the ambient, where $T$ is the temperature and $\Delta S$ is the isothermal entropy change. Or in an adiabatic process, to keep the total entropy of the material constant, the temperature of the dielectric is increased by $\Delta T$, and the adiabatic temperature change which is related to the $Q = c\Delta T$, where $c$ is specific heat capacity of the dielectric. In a reverse process, as the applied electric field is reduced to zero and the dipoles return to the less ordered state (or disordered state), an increase in the entropy of dipolar system occurs and under an isothermal condition, the dielectric will absorb heat $Q$ from the surrounding, which is the key step for electrocaloric materials to be used for cooling applications. Similarly, if in an adiabatic process, the temperature of the material will decrease $\Delta T$, and again the temperature change would be determined by $Q = c\Delta T$. 
In an ideal refrigeration cycle, the working material, in this case ECE material, must absorb heat from the cooling load while the two are in thermal contact. After thermal equilibrium, the material is isolated from the load following a temperature increase due to the application of external field (adiabatic temperature change $\Delta T$). The material is then in thermal contact with the heat sink when heat absorbed from the cooling load is rejected to the heat sink. The working material is again isolated from the heat sink and the temperature is reduced below ambient temperature as the field is removed, which allows the material to absorb heat in the next cycle. As can be seen, the whole process involves both the isothermal entropy changes $\Delta S$ and the adiabatic temperature change $\Delta T$, therefore, both are the key parameters for the ECE of a dielectric material for refrigeration.[11-13]

ECE is attractive because it may provide a very efficient means to realize cooling for a broad range of applications such as on-chip cooling and temperature regulators. Refrigeration based on the ECE approach is more environmentally friendly and hence can also provide an alternative to the existing vapor-compression approach. Besides, cooling device constructed using electrocaloric materials may exhibit high cooling power, high energy efficiency and large
temperature span, which will be discussed in a detailed way in following sections. Compared with MCE, ECE is much more convenient to use and offers much better energy efficiency since it is much easier to apply an electrical field to a dielectric and the ECE materials. Moreover, it is extremely challenging to obtain high magnetic field, especially when the device is size is under certain limit, while electric field for ECE shows no such restriction.

1.2 Electrocaoric Materials

To realize large electrocaloric effect, it is necessary to obtain a large entropy change associated with the polarization change in the material. Moreover, the dielectric material should be able to provide large polarization change and the polarization changes can be induced effectively by external field. The latter considerations indicate that it is advantageous to use ferroelectric materials for the ECE and operate the materials at temperatures just above a ferroelectric (polarization ordered)-paraelectric (polarization disordered) phase transition (FE-PE) where the largest electric field induced polarization change in a material can be achieved.

Although the study on the electrocaloric effect (ECE) can be dated back to 1930, when the ECE was measured in Rochelle salt and effect was very small,[14] it is not till the 1960s that more studies to the electrocaloric materials were carried out. However, the small ECE observed in the last half century of 20th century, where the adiabatic temperature change $\Delta T$ was less than 2 °C, makes it not attractive for practical applications. The field has been revived since 2006, when Mischenko et al. reported a giant ECE in ceramic thin films in which $\Delta T$ of 12 °C was observed at 226 °C,[7] and Neese et al. discovered a giant ECE near room temperature in a class of ferroelectric polymer, which exhibits both a large $\Delta T$ (>12 °C) and isothermal entropy change $\Delta S$ (>50 Jkg$^{-1}$K$^{-1}$).[8] Electrocaloric materials with large ECE are promising to realize compact
cooling devices for next-generation refrigeration, temperature regulation and air-conditioning, with high efficiency and environmental friendliness.

Among various ferroelectric materials, P(VDF-TrFE)-based ferroelectric polymers have been regarded as the most promising material for realizing large electrocaloric (EC) responses, due to large temperature change and the scalability in size and shape.[15] Moreover, compared with ferroelectric ceramics, the light weight and fracture tolerance of polymers make them very attractive for practical cooling devices.

1.2.1 P(VDF-TrFE) Copolymer

PVDF (poly(vinylidene-difluoride)) has been used in various piezoelectric and pyroelectric applications, due to its excellent processability, dielectric and mechanical properties, as well as chemical and electrical resistance.[16-23] In PVDF polymers, it has been reported that there exist five crystalline phases.[24, 25] The most interesting one is the ferroelectric β phase, in which, polymer chains adopt all-trans (TTTT) conformation, where all the fluorine atoms are on one side of the chain, forming dipoles perpendicular to the chain direction, as illustrated in Figure 1-3.[24-26] The ferroelectric β phase will undergo a phase transition and turn into α phase consisting of a random sequence of trans-gauche (TG) bonds, such as TGTG’, and T3GT3G’ isomers. Correspondingly, the dipoles in the crystallites also change from an ordered state to a disordered state.
Figure 1-3 Schematic illustration of the two most common crystalline chain conformations in PVDF (a) all-trans conformation and (b) tg+tg- conformation. The arrows indicate the projection of the CF$_2$ dipole directions on planes defined by the carbon backbone.

However, pure PVDF does not experience an F-P transition even when temperature rises up to the melting point, as indicated by the phase diagram in Figure 1-4.[27] Nevertheless, a crossover exists at the composition of 80 mol% VDF and 20 mol% TrFE. As the content of TrFE increases in the copolymer, P(VDF-TrFE) has a varying Curie transition temperature between 50 °C and 150 °C, depending on the composition.

Figure 1-4  P(VDF-TrFE) phase diagram.
Intriguingly, the phase transition in P(VDF-TrFE) copolymer can also be triggered by external electric field. When an electric field applied on the material at the paraelectric phase, the ordered ferroelectric phase can also be induced from the disordered phase as dipoles align along the electric field direction, which is the basic principle of electrocaloric effect. For normal ferroelectric P(VDF-TrFE), the conversion of disordered state into ordered state by electric field is the most efficient when temperature is in the vicinity of its F-P transition. Therefore, the F-P transition temperature, where the electrocaloric effect generally exhibits maximal response, determines the operating temperature of electrocaloric materials.

Phenomenological theory has been widely utilized to illustrate the macroscopic phenomena that occur in the polar materials, e.g. ferroelectric or ferromagnetic materials near their phase transition temperatures. In principle the ECE is one of the characteristics of ferroelectric materials that are associated with the phase transition in terms of the order-disorder transition derived entropy change. Therefore, phenomenological theory can be used to estimate the ECE of ferroelectrics.[28] The entropy will be reduced when the material changes to a polar state from a non-polar state when an external stimulus, e.g. temperature, electric field or stress, is applied. The entropy change and temperature change are associated with the phenomenological coefficient $\beta$ and electric displacement $D$, i.e., proportional to $\beta$ and $D^2$. Both parameters will affect the ECE values of the materials. A material with large $\beta$ and large $D$ will generate large ECE entropy change and temperature change near the FE – PE phase transition temperature. In searching for electrocaloric materials to achieve giant ECE at ambient temperature, one critical question is how to design dielectric materials to significantly enhance the entropy in the polar-disordered state since ECE is directly related to the entropy difference between the polar-disordered and ordered states in a dielectric material. In other words, to design a ferroelectric material to increase $\beta$ while maintaining large $D$.

For ferroelectric P(VDF-TrFE) polymers, phenomenological theory predicts large ECE
values. For example, P(VDF-TrFE) 65/35 mol% copolymer, with $\beta = 3.5 \times 10^{-7}$ Jm (C$^{-2}$K$^{-1}$) and $D = 0.08$ Cm$^{-2}$, will exhibit a $\Delta S = 62$ J kg$^{-1}$K$^{-1}$. Making use of its specific heat capacity $c_E = 1.4 \times 10^3$ Jkg$^{-1}$K$^{-1}$ [29] and Curie temperature $T_c = 102$ °C [30], yields $\Delta T = 16.6$ °C. The large $\Delta S$ and $\Delta T$ values suggest that a large ECE may be achieved in ferroelectric P(VDF-TrFE) copolymers. Furthermore, relaxor ferroelectric polymers based on P(VDF-TrFE) such as P(VDF-TrFE-CFE) (CFE-chlorofluoroethylene) relaxor ferroelectric terpolymers also have potential to reach a large ECE because the $\beta$ and $D$ are still large.

In addition, the heat of FE – PE phase transition can also be used to assess the ECE ($Q = T\Delta S$) in a ferroelectric material at temperatures above the FE – PE transition. For instance, P(VDF-TrFE) 68/32 mol% copolymer shows a heat of FE – PE transition of more than $2.1 \times 10^4$ Jkg$^{-1}$ (or $\Delta S \sim 56.0$ Jkg$^{-1}$K$^{-1}$). [8] This is approximately 10 times larger than its inorganic counterparts. Large ECE in which both large $\Delta S$ and $\Delta T$ can be induced in the ferroelectric P(VDF-TrFE) copolymers. For (P(VDF-TrFE) 65/35 mol% copolymer, the heat of FE-PE transition is more than 16 Jg$^{-1}$ (or $\Delta S \sim 45$ Jkg$^{-1}$K$^{-1}$), which is even larger than the recently reported “giant” magnetocaloric effect. All these considerations and results suggest that ferroelectric P(VDF-TrFE) polymers have potential to realize giant ECE.

P(VDF-TrFE) 55/45 mol% copolymer was also studied as an electrocaloric material because its FE-PE phase transition is continuous. $\Delta S$ and $\Delta T$ at several electric field levels are deduced by indirect measurement. the copolymer exhibits a $\Delta S$ of more than 55 Jkg$^{-1}$K$^{-1}$ and $\Delta T$ of more than 12 °C under an electric field of 209 MVm$^{-1}$ at temperatures around 80 °C, which demonstrates a giant ECE in polymers. However, as temperatures move away from the FE-PE transition, $\Delta T$ drops rapidly. Such a characteristic feature for normal ferroelectric materials makes P(VDF-TrFE) copolymer less attractive for cooling applications such as refrigeration and air-conditioning, which requires operating temperature around room temperature. Besides, the large
hysteresis loss observed in the P(VDF-TrFE) copolymer also diminishes its efficiency, as the hysteresis loss generates heat, which is highly undesirable in a cooling device.

1.2.2 P(VDF-TrFE)-based Relaxor Ferroelectric Polymers

To further improve the material performance, defects modifications to the P(VDF-TrFE) copolymer were introduced as a method of converting the polymer to a relaxor ferroelectric and thus reducing the transition temperature and eliminating the hysteresis.[31] With defect modification such as high energy irradiation or copolymerizing with a third bulky monomer, the details of which are described in Chapters 3 and Chapter 4, the normal ferroelectric polymers can be converted into relaxor ferroelectrics, in which randomly distributed nano-polar regions are embedded in a non-polar matrix. The P(VDF-TrFE)-based ferroelectric relaxor polymers exhibit a large room-temperature dielectric constant, broad dielectric peak range, slim P-E hysteresis loop and disorder dipole states at room temperature. More importantly, besides shifting the operating temperature of the ECE material to around room temperature, defect modifications render relaxor polymers the potential to generate an even larger ECE than the normal ferroelectric P(VDF-TrFE) copolymer. Through thermodynamic consideration and theoretical calculation, which will be shown in Chapter 2, it is predicted that a large ECE around room temperature can be achieved using defect modification to introduce local states and enhance the number of available polar states.

1.2.2.1 Giant Electrocaloric Effect in Irradiated P(VDF-TrFE) Relaxor Copolymers

It has been shown that by employing high energy electron irradiation, the normal ferroelectric P(VDF-TrFE) copolymer can be converted to a relaxor ferroelectric polymer which
displays high dielectric constant, large reversible polarization change, and high electrostriction at room temperature. The dielectric constant of a high energy electron irradiated P(VDF-TrFE) 68/32 mol% copolymer shows a broad dielectric constant peak around room temperature and that peak position moves progressively toward higher temperatures with frequency, a characteristic feature of relaxor ferroelectrics. The high energy electron irradiation breaks up long range polar-correlation in the polymer, which stabilizes dipolar disordered states around room temperature and generates local polar-states that may enhance the ECE. The ECE of the irradiated P(VDF-TrFE) 68/32 mol% copolymer was measured near the broad dielectric peak (33 °C) as a function of electric field. Under a field of 160 MVm⁻¹, an adiabatic temperature change ΔT of 20 °C and isothermal entropy change ΔS of 95 Jkg⁻¹K⁻¹ can be obtained. Moreover, by controlling the irradiation dose, an irradiated copolymer in which multiple intermediate phases coexist can be obtained and this material exhibits extraordinary electrocaloric behavior. At the dielectric peak of 50 °C, an isothermal entropy change ΔS of 160 Jkg⁻¹K⁻¹ and an adiabatic temperature change ΔT of 35 °C can be induced under a 180 MVm⁻¹. The large ΔS observed near the first order FE-PE transition also suggests that there are intermediate states with a large difference in dipolar ordering but a small free energy difference. The mixing of large number of coexisting phases near the first-order FE-PE transition leads to the high ECE observed.

1.2.2.2 ECE in RelaxorFerroelectric P(VDF-TrFE-CFE) Terpolymers

In the P(VDF-TrFE-CFE) relaxor ferroelectric polymers, large ECE has also been observed. ECE of the P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer directly measured at 30 °C showing a very large ΔT ~ 16 °C induced under 160 MVm⁻¹ electric field; besides the large ECE, several relaxor ferroelectric polymers also display a nearly temperature independent ECE. For a P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% relaxor ferroelectric terpolymer, the ECE response
is nearly temperature independent from 0 °C to 45 °C, which is in sharp contrast to that in normal ferroelectrics where the ECE peaks at the FE-PE transition and displays strong temperature dependence. Such a temperature independent ECE over a broad range is attractive for practical cooling device applications, especially for those requiring large temperature spans between cold and hot ends. These results also reveal the intricate roles played by the defects in tailoring the ferroelectric response and its polar nano-structures to generate a large ECE and its temperature response behavior. It is also found that the temperature dependence of the ECE of the terpolymer films depends critically on the film preparation conditions, while the uniaxially stretched terpolymer films show a pronounced temperature dependence on the ECE, the non-stretched films exhibit a nearly temperature independent ECE from 5 °C to 45 °C. At 5 °C and 55 °C, the ΔT of the uniaxially stretched films is more than 15% smaller, compared with that of the non-stretched films. Such a difference is likely caused by the changes in possible polar states and polar-correlation length due to film stretching.

1.2.2.3 P(VDF-TrFE-CFE) Terpolymer-based Blends

It is well known that nano-composites such as polymer blends, which exploit the merits of both the base polymer and the additive polymer, offer a great opportunity to enhance and tailor the material properties. It has been recently reported that the blends of P(VDF-TrFE-CFE) relaxor terpolymer with 10 wt% of P(VDF-TrFE) exhibit a 30% increase in the adiabatic temperature change compared with that of pure terpolymer. Both increased crystallinity in the blends and conversion of the copolymer from a normal ferroelectric to a relaxor lead to an increased relaxor polarization response and an enhanced ECE. Another advantage of the blends over pure terpolymer is that the Young’s modulus of the blends is improved compared to the pure terpolymer.
Therefore P(VDF-TrFE-CFE)/P(VDF-TrFE) blends with modest P(VDF-TrFE) copolymer may be excellent candidates for practical ECE cooling device. Besides giant electrocaloric effect, the stiff nature of these polymer composites reduces the barrier of multilayer fabrications, which is high desired in cooling device configuration. Also, a higher electric breakdown field may be achieved in these composites since stiffer samples tend to be more resistive during each process and result in lower defect amount.

1.2.3 Ceramics

Many early ECE studies were limited to ceramics in the low temperature range of 4 K–15 K, where the ceramics have low specific heat and hence may exhibit a large adiabatic temperature change.[32] The largest ECE was found in SrTiO$_3$,[33, 34] which is not a ferroelectric material yet bears a temperature-dependent dielectric constant. The maximum $\Delta T$ is 0.3 °C from the ECE was observed at 10 K.[34] The ECE at low temperature was also studied in KTaO$_3$ single crystals.[35]

After 1960s, ECE in many perovskite ceramics were studied. It is well known that the properties of these ceramics can be tuned by doping, through which different phases such as normal ferroelectric phase (FE), anti-ferrelectric phase (AFE), and ferroelectric relaxor phase can be obtained, providing excellent models to probe and understand the key factors that may influence the ECE.

Substitution of B-cations in PZT by Sn (PSZT) allows tuning of the temperature and composition ranges of the ferroelectric and anti-ferroelectric phases.[36-38] The largest ECE (i.e., the isothermal entropy change and adiabatic temperature change at the phase transition) appears in compositions where the both the AFE and FE reach their stability limit at high temperature and a first order transition from a PE to FE can be induced electrically. On the other hand, in
compositions where an electric field induced AFE to FE transition is observed, the ECE is much smaller and changes slowly in a wide range of temperature.[39] The largest electrocaloric effect in bulk ceramics, which is 2.6 °C, was measured for PSZT annealed at high temperature. The magnitude of this effect strongly depends on the microstructure of electrocaloric materials. Large grain ceramics with small temperature and field ranges of AFE phase stability yield the largest electrocaloric effect.[40] La doped PZT thick films were also examined and a maximum temperature change of 8.5 °C was observed under a field of 75 MVm$^{-1}$.[41]

In normal ferroelectrics, the sharp FE-PE transition usually leads to a narrow temperature range in which a large ECE exists. However, the ECE can be found in a wider temperature range in ferroelectric relaxors. For example, PMN (Pb(MgNb)TiO$_3$) exhibits a diffused dielectric phase transition around -13 °C, which leads to a relatively large ECE near room temperature, i.e., maintaining a $\Delta T \sim$2.5 °C in temperature range from 16 °C to 67 °C under an electric field of 9 MVm$^{-1}$.[42] PMN-PT (PbTiO$_3$) with different compositions were also investigated in both ceramics and single crystals.[43-48]

In lead scandium niobate (PSN) and its solid solution with lead scandium antalite (PST), the ordering of perovskite heterovalent ions in sublattice B can be tailored either by substitution or thermal treatment.[49, 50] A high degree of long-range order leads to a high ECE maximum ($\Delta T = 1.7$ °C) as well as a high phase transition temperature, while a decreased order causes a lower ECE (which occurs over a broader temperature range) and diffuse phase transitions.

Some lead-free ceramics such as Ba$_{0.73}$Sr$_{0.27}$TiO$_3$, Na$_{0.5}$Bi$_{0.5}$TiO$_3$, and Ba$_{0.3}$Na$_{0.7}$Ti$_{0.3}$Nb$_{0.7}$O$_3$ are also investigated for their ECE.[51-53] Despite the fact that only small electrocaloric responses have been generated, lead-free materials are attractive because of their environmental friendliness.

The ECE reported in all the bulk ceramic samples is below 3 °C, which makes them unimpressive for practical applications. The main reason is the low dielectric strength, i.e., low
breakdown field, of bulk ceramics and the difficult in fabricating bulk ceramic to thin thickness (below 50 µm). By fabricating thick films using an interdigitated multilayer geometry, the film thickness of each layer can be reduced to ~10 µm, which allows for application of high electric fields. Multilayered PbSc$_{0.5}$Ta$_{0.5}$O$_3$[54] BaTiO$_3$[55-58] were also studied.

Ceramic thin films allow for the application of high electric fields (> 10 MVm$^{-1}$) and thus a high ECE may be realized. Here the thin films are referred as to those thinner than 1 µm. Mischenko et al.[7] first reported a temperature change of 12 °C in 350nm PbZr$_{0.95}$Ti$_{0.05}$O$_3$ thin film near Curie temperature of 222 °C. A temperature change of about 11 °C was also observed in a 700 nm PbZrO$_3$ thin film near its phase transition temperature at 235 °C.[59] However, there are a few drawbacks for these electrocaloric ceramics in spite of large temperature changes. First of all, the phase transitions in these thin films are first-order transitions and the high ECE can only exist in a narrow temperature range. Additionally, the phase transition temperatures in these materials are too high for applications near room temperature thus it is difficult for them to be used on cooling devices such as refrigerators and air-conditioners. Moreover, as the specific heat capacity values in these ceramics are smaller compared with those in polymers, the isothermal temperature changes would tend to be smaller, even though the electrocaloric performance may be similar in terms of adiabatic temperature change. To obtain a large ECE at a wide range of temperature near room temperature, La doped PZT thin films, which are relaxor ferroelectrics due to the existence of La atoms, were explored and a $\Delta T \sim 40$ °C was reported under the electric field of 120 MVm$^{-1}$ at 45 °C.[60]

A $\Delta T$ of 9 °C was observed under 72.3 MVm$^{-1}$ in 0.93PMN-0.07PT thin films at the depolarizing temperature of 18 °C instead of the dielectric peak temperature of 35 °C, suggesting a dipolar glass-relaxor phase transition in this system.[61] For 0.9PMN-0.1PT, the maximum $\Delta T$ of 5 °C was observed at 75 °C, where a pseudocubic relaxor ferroelectric transforms to a cubic
paraelectric phase.[62] The PMN-PT with 30%-35% PT are extremely interesting, because of the morphotropic phase boundary (MPB) can contribute additionally to the ECE.[63-66]

Other thin films such as PbSc$_{0.5}$Ta$_{0.5}$O$_3$ relaxor with a wide temperature range of ECE were also investigated. A $\Delta T = 6.2$ °C at 77.4 MVm$^{-1}$ was reported.[67] SrBiTa$_2$O$_9$,[68] a lead-free perovskite-type bismuth layered oxide, was investigated where a $\Delta T$ of 4.93 °C at around 290 °C was reported.

1.2.4 Dielectric Liquids and Ionic Crystals

Compared with solid state ECE materials, a dielectric liquid with large ECE response is even more interesting, due to the fact that electrocaloric liquid may lead to improved device configurations with simpler structures and new cooling cycles. A recent work reported a large ECE can be realized in the liquid crystal (LC) 5CB near its nematic-isotropic (N-I) phase transition. The LC 5CB possesses a large dielectric anisotropy which facilitates the electric field induced large polarization change. As a result, a large ECE, i.e., an isothermal entropy change of more than 23.6 Jkg$^{-1}$K$^{-1}$ was observed just above the N-I transition.[69] The finding in the electrocaloric fluid may open up a new research area in which more liquid state electrocaloric materials with excellent properties could be discovered.

The liquid state electrocaloric materials could be used to simplify cooling device configuration. In conventional cooling devices, a cooling unit generally acts at a heat pump absorbing heat from refrigerant instead of directly from heat load, and the refrigerant is usually fluid-based, which can be cycled and transported easily. And the liquid state electrocaloric materials would be able to replace the cooling unit and the refrigerant at the same time by playing a role of both transferring heat from heat load to heat sink as well as circling around with the cooling device, which is a huge advantage in cooling device design and development.
People have also reported ECE in ionic crystals. Ionic crystals such as Rochelle salt were the research focus in early stages when ferroelectrics were discovered. The ECE in crystals such as Rochelle salt,[70] potassium dihydrogen phosphate (KH$_2$PO$_4$, abbreviated as KDP),[71] triglycine sulphate ((NH$_2$CH$_2$COOH)$_3$•H$_2$SO$_4$, abbreviated as TGS),[72] and some other sulfates like NH$_4$HSO$_4$,[73] Rb$_x$(NH$_4$)$_{1-x}$HSO$_4$[74] were investigated. However, most of these crystals are highly moisture-sensitive. More importantly, their high ionic conduction will lead to easy breakdown at low electric field, which limits further elevation of ECE.[73] Typically the temperature changes in these crystals are smaller than 0.5 °C, far less than the requirement of any practical application.

Another family of ionic crystals exhibiting ECE is doped alkali halides such as KCl or RbCl. Either anionic (OH$, \text{CN}^-$) or cationic (Li$^+$) impurities can generate ordered dipoles in the crystals. Therefore, these dipoles can be controlled by external electric field in the same manner as in the electrocaloric polymers and electrocaloric ceramics. Phase transitions in these ionic crystals can be observed and employed to realize refrigeration at very low temperatures (near 0 K).[75-79] Again, these materials suffer from high ionic conduction which induces large leakage current and energy loss, as well as low electric breakdown field which limits the electrocaloric response can be extracted.

Table 1-1 summarizes ECE properties for some prototypical organic and inorganic materials. For comparison, selected ECE results reported in the literature on inorganic materials, especially inorganic ferroelectric thin films where very high voltage can be applied and large ECE responses have been obtained, are also included. As can be seen, the relaxor ferroelectric polymers, because of their large $\Delta T$ and $\Delta S$, broad operation temperature range and easy scaling up for various sized cooling devices, offer the most attractive ECE properties for practical cooling device applications.

Table 1-1 ECE performance comparison for some organic and inorganic materials
<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>Experiment Temp.(°C)</th>
<th>ΔT (K)</th>
<th>∆S (Jkg⁻¹K⁻¹)</th>
<th>ΔTΔS (Jkg⁻¹)</th>
<th>E (MVm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-TrFE) 55/45[90]</td>
<td>Films</td>
<td>67</td>
<td>12</td>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>P(VDF-TrFE) 70/30[91]</td>
<td>Films</td>
<td>117</td>
<td>21</td>
<td></td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Irradiated P(VDF-TrFE) 65/35</td>
<td>Films</td>
<td>50</td>
<td>35</td>
<td>160</td>
<td>5600</td>
<td>180</td>
</tr>
<tr>
<td>P(VDF-TrFE-CFE) 59.2/33.6/7.2</td>
<td>Films</td>
<td>30</td>
<td>15.7</td>
<td>80</td>
<td>1256</td>
<td>150</td>
</tr>
<tr>
<td>SrTiO₃[33]</td>
<td>Ceramics</td>
<td>-256</td>
<td>0.06</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>SrTiO₃[34]</td>
<td>Single crystal</td>
<td>-262</td>
<td>0.3</td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>KTaO₃[35]</td>
<td>Single crystal</td>
<td>-260</td>
<td>0.25</td>
<td></td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>PbZr₀.₃₅Sn₀.₆₅Ta₀.₆₅O₃[36]</td>
<td>Ceramics</td>
<td>44-55</td>
<td>-1.4</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>PbZr₀.₃₅Sn₀.₆₅Ta₀.₆₅O₃[36]</td>
<td>Ceramics</td>
<td>161</td>
<td>2.6</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Pb₁₋₀.₇₅(Zr₀.₃₅Ta₀.₆₅)O₃[37]</td>
<td>Thick film</td>
<td>1.7</td>
<td>8.5</td>
<td></td>
<td>112(75)</td>
<td></td>
</tr>
<tr>
<td>PMN[42]</td>
<td>Ceramics</td>
<td>16-67</td>
<td>-2.5</td>
<td>2.5</td>
<td>6.25</td>
<td>9</td>
</tr>
<tr>
<td>0.9PMN-0.1PT[43]</td>
<td>Ceramics</td>
<td>50</td>
<td>0.55</td>
<td></td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>0.75PMN-0.25PT[44]</td>
<td>Ceramics</td>
<td>120-130</td>
<td>-0.5</td>
<td></td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>0.87PMN-0.13PT[45]</td>
<td>Ceramics</td>
<td>18</td>
<td>-0.5</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>PbSc₂O₅,Nb₂O₅[46]</td>
<td>Ceramics</td>
<td>92</td>
<td>0.9</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>PbSc₂O₅,Nb₂O₅[46]</td>
<td>Ceramics</td>
<td>-2–10</td>
<td>1–1.7</td>
<td></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Pb(Mg₀.₃₅Zn₀.₆₅)₂O₃[47]</td>
<td>Ceramics</td>
<td>139</td>
<td>0.4</td>
<td></td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Na₀.₂Ba₀.₈TiO₃[52]</td>
<td>Ceramics</td>
<td>140</td>
<td>0.33</td>
<td>0.45</td>
<td>0.1485</td>
<td>5</td>
</tr>
<tr>
<td>Ba₀.₇₅Sr₀.₂₅TiO₃[54]</td>
<td>Ceramics</td>
<td>90</td>
<td>0.45</td>
<td>1.16</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Ba₀.₂₅Na₀.₇₅Ti₀.₇₅Nb₀.₂₅O₃[55]</td>
<td>Ceramics</td>
<td>-13</td>
<td>0.026</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>PST(PhSc₂O₅,Ta₀.₆₅O₃)[54]</td>
<td>Multilayer</td>
<td>2.4</td>
<td>(3.5)</td>
<td></td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>BaTiO₃ (commercial)[52]</td>
<td>Multilayer</td>
<td>80</td>
<td>0.55</td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>PbZr₀.₃₅Sn₀.₆₅Ta₀.₆₅O₃[57]</td>
<td>Thin films</td>
<td>226</td>
<td>12</td>
<td>7.9</td>
<td>94.8</td>
<td>77.6(50)</td>
</tr>
<tr>
<td>Pb₁₋₀.₇₅(Zr₀.₃₅Ta₀.₆₅)O₃[58]</td>
<td>Thin films</td>
<td>45</td>
<td>40</td>
<td>50</td>
<td>2000</td>
<td>120</td>
</tr>
<tr>
<td>PbZr₀.₃₅Ta₁₋₀.₃₅O₃[59]</td>
<td>Thin films</td>
<td>387</td>
<td>11.1</td>
<td>6.17</td>
<td>68.49</td>
<td>57.7</td>
</tr>
<tr>
<td>PbSc₂O₅[60]</td>
<td>Thin films</td>
<td>235</td>
<td>11.4</td>
<td></td>
<td>51(40)</td>
<td></td>
</tr>
<tr>
<td>0.9 PMN-0.1 PT[62]</td>
<td>Thin films</td>
<td>60</td>
<td>5</td>
<td></td>
<td>89.5</td>
<td></td>
</tr>
<tr>
<td>0.93 PMN-0.07 PT[63]</td>
<td>Thin films</td>
<td>25</td>
<td>9</td>
<td></td>
<td>72.3</td>
<td></td>
</tr>
<tr>
<td>0.67 PMN-0.33 PT[64]</td>
<td>Thin films</td>
<td>152</td>
<td>14.5</td>
<td></td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>0.65 PMN-0.35 PT[65]</td>
<td>Thin films</td>
<td>140</td>
<td>31</td>
<td></td>
<td>74.7</td>
<td></td>
</tr>
<tr>
<td>PbSc₂O₅,Ta₁₋₀.₃₅O₃[65]</td>
<td>Thin films</td>
<td>68</td>
<td>6.2</td>
<td>6.3</td>
<td>39.06</td>
<td>77.4</td>
</tr>
<tr>
<td>SrBiTaO₃[66]</td>
<td>Thin films</td>
<td>288</td>
<td>4.93</td>
<td></td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>5CB[69]</td>
<td>Liquid Crystal</td>
<td>39</td>
<td>3.35~ 5.26</td>
<td></td>
<td>23.6</td>
<td></td>
</tr>
</tbody>
</table>
1.3 Cooling Device Based on ECE

ECE cooling device works as an active heat pump which continuously transfers heat from cold end to hot end thus creates a temperature gradient between the two ends. A schematic illustration of the working cycle for an ECE cooling device is shown in Figure 1-5. The working cycle contains four steps: 1) ECE cooling unit moves from left to right and electric field is applied to the cooling unit when it reaches the right end of the plate, the temperature of the unit rises due to ECE, 2) the ECE unit dissipates heat to the right end of the plate and its temperature returns to ambient temperature, 3) the ECE unit moves back to the left end, and the electric field is removed when it arrives at the left end of the plate, resulting in a temperature decrease in the ECE unit, 4) heat is transferred from the left end of the plate into the ECE cooling unit, which will be pumped to the right end in the next cycle.

![Diagram of ECE cooling device](image)

Figure 1-5 Schematic illustration of work cycle in an ECE cooling device.

It should be noted that the cooling device configuration is not limited within solid state materials. For example, the plate in the previous example can be substituted by gas or fluid, such as shown in Figure 1-6. While the ECE unit stays stationary, gas or fluid can move back and forth, serving as the medium for heat transportation. Similarly, such kind of ECE cooling device also consists of four steps in one working cycle: 1) as gas/fluid moves from left to right, an electric
field is applied to the ECE unit, 2) heat is dumped from ECE unit to the gas/fluid and eventually transferred to the hot end of the device, 3) as gas/fluid moves from right to left, the electric field is removed, 4) the ECE unit absorbs heat from the gas/fluid and thus cools the medium that helps transfer heat from cold end to the ECE unit.

![Schematic illustration of work cycle in an gas/fluid-based ECE cooling device.](image)

Figure 1-6 Schematic illustration of work cycle in an gas/fluid-based ECE cooling device.

Cooling device with large cooling power, large temperature span and high efficiency is highly desired for a broad range of applications in household appliance and microelectronics. Since cooling power is determined by the amount of heat that is transported within unit time, it is therefore beneficial to operate the cooling device at as high frequency as possible.[85] Besides the entropy change and temperature change in ECE materials, two other factors are important in order to achieve high operating frequency, i.e., the field switching speed and thermal conductivity of the materials used in the cooling device (or the efficiency that the heat can be transferred by the cooling device). As mentioned before, ECE and MCE are able to reach high operating frequency since the fast switching speed of electric field and magnetic field, while eCE, BCE as well as other vapor-compression-based cooling devices fail to work under high operating frequency due to the limitation of the mechanical movements in these devices. Therefore the cooling power in ECE device is not limited by the switching speed of electric field, but rather by the low thermal
conductivity of polymer materials used in the ECE cooling device. To be more precise, low thermal conductivity prevents heat from being transferred between ECE unit and heat load, since low thermal conductivity yields a short thermal diffusion length, as presented in the following equation[86]

$$\delta = (2\alpha / \omega),$$  \hspace{1cm} 1.1

where $\omega$ is the angular frequency and $\alpha = k/(\rho c)$ is the thermal diffusivity, $\rho$ representing the density and $c$ representing the thermal conductivity. As can be observed from Equation 1.1, the operating frequency has to remain at a lower value if a material with low thermal conductivity is used in the ECE cooling device in order to achieve reasonably large thermal diffusion value.

While multilayer structure to some extent allows us to maintain the effectiveness of heat transfer between ECE cooling device and heat load, it is essential to develop material with high thermal conductivity to provide more room to raise the operating frequency while allowing the heat to be transported efficiently.

The temperature span of an ECE cooling device, i.e., the difference between hot end temperature ($T_H$) and cold end temperature ($T_C$), is closely related to the temperature change in ECE material. However, as shown in the previous section, the largest temperature change obtained in ECE materials under a reasonable electric field range is around 30 $^\circ$C, therefore it is important to introduce the regenerative process into the working cycle of ECE cooling device to further expand its temperature span ($T_H - T_C$). In fact, the plate in Figure 1-5 serves as a regenerator and allows a regenerative cooling cycle. Let us assume the initial temperature of the plate is $T_0$ and the temperature change due to ECE within one working cycle is $\Delta T$, after one cycle the temperature at the cold end can be expressed by $T_C = T_0 - \Delta T$ and the temperature at the hot end is $T_H = T_0 + \Delta T$. It should be noted that the heat conduction along the plate is ignored. In real case, the heat conduction, which is a function of temperature difference between hot end and cold end, reduces the temperature difference. In the following working cycle, $T_c$ would be $T_0 -$
2\Delta T and \( T_H \) would be = \( T_0 + 2\Delta T \), yielding a temperature span of \( 4\Delta T \), which is larger than the temperature change due to ECE within one working cycle is \( \Delta T \). The temperature span can keep increasing as such regenerative process continues, until the amount of heat transferred by ECE unit is equal to the amount of heat loss due to heat conduction along the plate. It is therefore important to design regenerator within low thermal conductivity in the direction connecting the two ends, on the other hand, a high thermal conductivity in the direction in which the heat is transferred between ECE unit and regenerator is desired, i.e., a regenerator with anisotropic thermal conductivity is crucial for designing ECE cooling device with high cooling power and large temperature span. In this sense, solid state regenerator is advantageous over fluid or gas-based regenerator since it is much easier to fabricate material structure with anisotropic thermal conductivity.

Efficiency in a cooling device is the ratio between the heat that is removed by the device and input electric energy. One way to quantify efficiency is by calculating Coefficient of Performance (COP) using the equation \( \text{COP} = \frac{Q_C}{W} \), where \( Q_C \) is the heat removed and \( W \) is the input energy. As ECE is an electric-field-induced phase transition, from material point of view, the input electric energy required to trigger the phase transition is much smaller than the amount of heat that is released or absorbed by the phase transition. Therefore, in order to achieve large COP, electrocaloric materials with excellent performance (giant temperature change and entropy change) are necessary.

Another way to compare the efficiency among various cooling cycles is using Carnot Cycle as a standard. The efficiency in a Carnot Cycle is proven to be the highest in different working cycles.\cite{86} The Carnot Cycle consists of the following four steps: 1) reversible isothermal heat absorption, 2) reversible adiabatic temperature increase, 3) reversible isothermal heat release and 4) reversible adiabatic temperature decrease. Theoretically, the working cycle of an ECE cooling device is able to be separated into the four steps as in Carnot Cycle. An
demonstration of a “Carnot-like” working cycle of an ECE cooling device is shown in Figure 1-7. It can be observed that in ideal case, the working cycle is a Carnot Cycle, thus its efficiency is equal to the Carnot efficiency.

![Graph showing Carnot cycle and efficiency](image.png)

Figure 1-7 Demonstration of a “Carnot-like” working cycle of an ECE cooling device.

In real device situation, since regenerator is adopted to increase the temperature span, the working cycle of an ECE cooling device would be a combination of multiple Carnot cycles, as presented in Figure 1-8. It should be noted that the entropy change within each single Carnot cycle should be equal in order to achieve large efficiency. And since for each single Carnot cycle the operating temperature is different, therefore electrocaloric materials with weak temperature dependence are highly desired. Relaxor ferroelectric P(VDF-TrFE-CFE) terpolymers and P(VDF-TrFE-CFE)/P(VDF-TrFE) blends show large ECE properties with little temperature dependence, making them excellent candidates in constructing ECE cooling device with high efficiency.
Based on the requirement for developing ECE cooling device with large temperature span, high cooling power and high COP, several criteria should be met from materials point of view. First, giant temperature change and entropy change are essential for high cooling power and high COP. In irradiated P(VDF-TrFE) 65/35 mol% copolymers, large $\Delta T$ and $\Delta S$ are observed, making these materials promising for device design. Second, large ECE over a broad temperature range benefits both temperature span and COP, therefore materials such as P(VDF-TrFE-CFE) terpolymer and P(VDF-TrFE-CFE)/P(VDF-TrFE) blends poise advantages due to the weak temperature dependence of their ECE properties. Also, high thermal conductivity is required to guarantee a reasonably high operating frequency and thus a high cooling power. P(VDF-TrFE-CFE)/nano-particle composite provides a new material system which is able to show both large ECE and high thermal conductivity. Moreover, since most ECE cooling device involves mechanical movement at the present stage, the mechanical strength of the materials needs to be considered as well. To give an ideal material example, the polymer/nano-particle composites can be very promising for device applications, due to the enhancement in both electrocaloric properties and thermal conductivity, as well as weak temperature dependence of ECE properties,
which are equally important from cooling device application point of view. In developing materials with large ECE, one should also pay special attention to the possibility of these materials and phenomena for practical applications.

1.4 Research Objectives

The goal of this dissertation is,

(1) to obtain a comprehensive understanding on the structure-property relationship in electrocaloric materials.

(2) to develop electrocaloric materials, especially electrocaloric polymers, with desirable responses meeting the demand for practical cooling applications through systematic processing, e.g., defect modification or polymer blending.

(3) to introduce theoretical considerations and general rules predicting the performance of electrocaloric materials

(4) to compare different characterization methods for electrocaloric effect and provide insight on the scope and limitation of each characterization methods.

Based on the goal, this dissertation is organized as follows:

- In Chapter 2, several thermodynamic frameworks are presented, including Landau-Devonshire Phenomenological Theory, Multiphase Coexistence Theory, and Defect-enhanced Random States Theory. These theoretical discussions connect physical parameters with material properties, thus providing guidance for both fundamental studies and material development. Different methods for measuring electrocaloric effect, i.e., indirect method which derives $\Delta S$ and $\Delta T$ using Maxwell Relation and direct method which directly detects temperature signal or heat flux signal, are compared and evaluated.
In Chapter 3, the main focus is on one of the most promising electrocaloric materials, high-energy-electron irradiated P(VDF-TrFE) 65/35 mol% copolymers. Dielectric permittivity, differential scanning calorimetry and hysteresis loop analysis are conducted to quantify the impact of high-energy-electron irradiation on the P(VDF-TrFE) 65/35 mol% copolymers. More importantly, ECE data in irradiated P(VDF-TrFE) 65/35 mol% copolymers with different dosages are presented. Phenomena such as temperature dependence and cycle impact are explored. Besides, other irradiated copolymers, e.g., P(VDF-TrFE) 75/25 mol%, P(VDF-CTFE) and P(VDF-HFP), are also characterized. Through the comparison of the behaviors among different irradiated copolymers, a tentative conclusion on the irradiation impact is drawn.

In Chapter 4, structure-property relationship in relaxor ferroelectric P(VDF-TrFE-CFE) terpolymers is discussed, from dielectric and electrocaloric properties, to terpolymer microstructure analysis using various characterization methods. Influence of polymer process conditions such as uniaxial stretching on properties of terpolymers is also elaborated. Finally a comparison between direct and indirect results using terpolymer as an example is presented to further explore the limitation of the indirect method.

In Chapter 5, several series of blends, including P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends and P(VDF-TrFE-CFE) terpolymer/nano-particle blends, are presented. These relaxor ferroelectric composites exhibit enhanced polarization and improved electrocaloric effect. P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends exhibit interfacial effect, which enhances crystallinity as well as converts the normal ferroelectric P(VDF-TrFE) copolymer into relaxor ferroelectric phase when the content of
copolymers in the blends. Similarly, the interface effect between the polymer matrix and nano-fillers enhances the polarization response and provides additional electrocaloric entropy changes. As a consequence, the nanocomposites exhibit a larger ECE than that of the neat terpolymer. Moreover, poling effect, which induces internal bias electric field to increase ECE, is detailed as a facile way to generate large ECE using relatively low electric field.

- In chapter 6, conclusion and future works are presented. Further improvement of ECE in relaxor ferroelectric materials is proposed in three aspects.
Chapter 2

Basic Considerations and Measurement Methods of ECE

2.1 General consideration

2.1.1 Thermodynamic Analysis

In general, the Gibbs free energy $G$ for a dielectric material could be expressed as a function of temperature $T$, entropy $S$, stress $X$, strain $x$, electric field $E$ and electric displacement $D$ in the form

$$G = U - TS - X_i x_i - E_j D_j,$$  \hspace{1cm} (2.1)

where $U$ is the internal energy of the system, the stress and field terms are written using Einstein notation where $i$ runs from 1 to 6 and $j$ is from 1 to 3. The differential form of Equation 2.1 is

$$dG = -SdT - x_i dx_i - D_j dE_j$$  \hspace{1cm} (2.2)

Hence the entropy $S$ and electric displacement $D_j$ are expressed as,

$$S = - \left( \frac{\partial G}{\partial T} \right)_{x,E}, \quad D_j = \left( \frac{\partial G}{\partial E_j} \right)_{T,X}$$  \hspace{1cm} (2.3)

Equation 2.3 leads to the Maxwell relation, linking the electrocaloric effect to the pyroelectric effect for a thermodynamically reversible system,[28]

$$\left( \frac{\partial S}{\partial E} \right)_{T,X} = \left( \frac{\partial D}{\partial T} \right)_{E,X},$$  \hspace{1cm} (2.4)

and
where $c_E$ is the heat capacity. Under a constant stress $X$, the isothermal entropy change $\Delta S$ and adiabatic temperature change $\Delta T$ of an ECE material as the $E$ is changed from $E_1$ to $E_2$ can be expressed as[28]

$$\Delta S = \int_{E_1}^{E_2} \left( \frac{\partial D}{\partial T} \right)_E dE$$  \hspace{1cm} \text{(2.6)}$$

$$\Delta T = -T \int_{E_1}^{E_2} \frac{1}{c_E} \left( \frac{\partial D}{\partial T} \right)_E dE$$  \hspace{1cm} \text{(2.7)}$$

Equations 2.4 through 2.7 indicate that in order to achieve a large $\Delta S$ and $\Delta T$, the dielectric materials should possess a large pyroelectric coefficient, i.e., $\frac{\partial D}{\partial T}$ value, over a broad electric field range. For ferroelectric materials, a large pyroelectric effect exists near the ferroelectric (FE) – paraelectric (PE) phase transition, as a result it can be predicted that a large electrocaloric effect may also exist near the FE-PE phase transition, as discussed earlier in Chapter 1. It should be noted that a large $\Delta T$ may still be achieved, even if $\Delta S$ is small, provided $c_E$ of a dielectric material is small. However, an ECE material should possess both a large $\Delta S$ and $\Delta T$ for practical refrigeration applications, since it is the cooling power, or the heat transferred by ECE material within certain amount of time, that is important for device operations, and the heat $Q$ is related to both $\Delta S$ and $\Delta T$, as shown in Equation 2.8.

$$Q = C_E \Delta T = T \Delta S$$  \hspace{1cm} \text{(2.8)}$$

If the temperature region including a first-order FE-PE transition, Equation 2.6 should be modified by taking into account the discontinuous change of the polarization $\Delta P$ (in most cases, $\Delta P = \Delta D$) at the transition temperature, i.e.,
\[ \Delta S = \int_{0}^{E} \left( \frac{\partial D}{\partial T} \right) dE - \Delta D \left( \frac{\partial E}{\partial T} \right) \]  \hspace{1cm} \text{(2.9)}

As in the early stage of ECE research, only small \( \Delta T \) and \( \Delta S \) were generated, it was very difficult, if not impossible, to direct measure the signal changes using temperature sensors or heat flux sensors. Therefore it was practical for people to deduce \( \Delta S \) and \( \Delta T \) through Maxwell Relation (Equations 2.6 and 2.7). Maxwell relation is also the most commonly used method to characterize ECE to date. However, it should be emphasized that one should be cautious in using the Maxwell relation to deduce the ECE near first order FE-PE transitions. The hysteresis associated with first order FE-PE transition means the process is not thermodynamically reversible while the Maxwell relation is derived based on reversible thermodynamic process. Such a divergence may lead to error when one tries to predict the electrocaloric effect in non-ergodic material systems such as relaxor ferroelectrics

### 2.1.2 ECE Derived from the Landau-Devonshire Phenomenological Theory

The Landau-Devonshire (L-D) phenomenological theory has been widely utilized to describe the macroscopic phenomena that occur in the polar materials, e.g. ferroelectric or ferromagnetic materials near their phase transitions. As has been discussed earlier, the ECE is related to the order-disorder transition in polar materials, thus the L-D phenomenological theory is employed to estimate the ECE of ferroelectrics. From the L-D theory, the Gibbs free energy of a ferroelectric material can be written as an expansion of the polarization \( P \) (for most ferroelectrics, \( P \approx D \)) as[28]

\[ G = \frac{1}{2} \alpha P^2 + \frac{1}{4} \xi P^4 + \frac{1}{6} \zeta P^6 - EP, \]  \hspace{1cm} \text{(2.10)}

where \( \alpha = \beta(T-T_0) \), and \( \beta \), \( \xi \) and \( \zeta \) are temperature-independent phenomenological coefficients.
From $\left( \frac{\partial G}{\partial T} \right)_E = -\Delta S$ and at temperatures above FE-PE transition where a single $P$ value exists under an applied field $E$, we can obtain,

$$\Delta S = -\frac{1}{2} \beta P^2,$$

and the adiabatic temperature change $\Delta T \left( = -T \Delta S / c_E \right)$ can be obtained, i.e.,

$$\Delta T = \frac{1}{2c_E} \beta TP^2$$

Equation 2.11 indicates that the entropy will be reduced when the material increases its polarization or changes to a polar state from a non-polar state when an external action, e.g. temperature, electric field or stress, is applied. The entropy change and temperature change are associated with the phenomenological coefficient $\beta$ and polarization, viz. proportional to $\beta$ and $P^2$. Both parameters will affect the ECE values of the materials. A material with a large $\beta$ and a large $P$ will generate a large ECE entropy change and temperature change near the FE-PE phase transition temperature.

As an example, the L-D phenomenological theory predicts large ECE values in ferroelectric P(VDF-TrFE) polymers. P(VDF-TrFE) 65/35 mol% copolymer, with $\beta = 3.5 \times 10^7$ Jm$^{-2}$K$^{-1}$ and $D = 0.08$ Cm$^{-2}$,[30] will exhibit a $\Delta S = 62$ Jkg$^{-1}$K$^{-1}$. With specific heat capacity $c_E = 1.4 \times 10^3$ Jkg$^{-1}$K$^{-1}$,[29] and Curie temperature $T_c = 102$ °C,[30] a $\Delta T = 16.6$ °C can be derived through calculation using Equation 2.12. The large $\Delta S$ and $\Delta T$ values suggest that a large ECE may be achieved in ferroelectric P(VDF-TrFE) copolymers.

In addition, the heat of FE-PE phase transition can also be used to assess the ECE ($Q = T \Delta S$) in a ferroelectric material at temperatures above the FE-PE transition. For example, P(VDF-TrFE) 68/32 mol% copolymer shows a heat associated to the FE-PE transition is larger than $2.1 \times 10^4$ Jkg$^{-1}$, yielding an entropy change $\Delta S = 56.0$ Jkg$^{-1}$K$^{-1}$, which is consistent with the prediction.
based on the phenomenological theory that a large ECE can be obtained in P(VDF-TrFE) ferroelectric polymers.[8, 13, 87]

### 2.1.3 Contribution of Secondary Pyroelectricity to ECE

For polymeric materials, the secondary pyroelectric effect, i.e., $\frac{\partial D}{\partial T}$ caused by the thermal expansion, can be significant. Therefore, to derive the thermodynamic relations correctly, the secondary effect should be included in the considerations. In a real experimental situation, it is the force $F$, displacement $R$, voltage $V$, charge $Q$, temperature $T$, and the total entropy $S$ of the sample that are directly measured. It should be noted that the black font for force and displacement represents they are vectors with both magnitude and direction. The general form of the elastic Gibbs energy, hence, can be written as[88]

$$dG = -SdT - R \cdot dF - QdV,$$

which yields a general form of the Maxwell relation,

$$\left(\frac{\partial Q}{\partial T}\right)_{V, F} = \left(\frac{\partial S}{\partial V}\right)_{T, F}$$

When the dimensional change is small, Equation 2.14 is reduced to Equation 2.4.

Assuming the ECE film has a volume $\Omega$, an area $A_z$ in XY plane (perpendicular to the film thickness and the applied electric field), the electric field is along the $z$ direction, and also let $D = P$, which is reasonable for ferroelectric polymers, then $dQ$ should be written as

$$dQ = A_z dP + P dA_z,$$

if $dA_z$, the dimensional change, is not negligibly small.

So the unit volume entropy $\Delta s = \Delta S/\Omega$ is,

$$\Delta s = \int_{E_1}^{E_2} \left(\frac{\partial Q}{\partial T}\right)_{E, X} / A_z dE$$

2.16
On the device side, the total dipole moment \( M \) of the sample is related to the measured charge \( Q \) and polarization \( P \) as\[88, 89\]
\[
Q = AP = M/d
\] 
2.17

Making use of \[ \frac{1}{d} \left( \frac{\partial M}{\partial T} \right)_V = A \left( \frac{\partial P}{\partial T} \right)_V \] and Equation 2.11, we have
\[
\Delta s = -\left( \frac{1}{2} \beta P^2 + \int_{V_1}^{V_2} \left[ \frac{P}{d} \left( \frac{\partial d}{\partial T} \right)_V \right] dV \right)
\]
2.18

For freestanding films, the mechanical boundary conditions are \( X_i = 0 \) (\( I = 1, 2, \) and 3). Then the entropy change per unit volume \( \Delta s \) in Equation 2.18 has the form\[90\]
\[
\Delta s = -\left( \frac{1}{2} \beta P^2 + \int_{E_1}^{E_2} \left[ \frac{P}{d} \left( \frac{\partial d}{\partial T} \right)_E \right] dE \right)
\]
2.19

Using \( (\partial d/d)/\partial T=\alpha \) and equation \( E = \beta(T - T_c)P + \gamma P^3 \) for a 2\textsuperscript{nd} order phase transition, \( \Delta s \) becomes
\[
\Delta s = -\frac{1}{2} \beta P^2 - \frac{1}{2} \alpha PE - \frac{1}{4} \alpha \gamma P^4
\]
2.20

Taking the typical data of \( \beta = 2.4 \times 10^7 \text{ Jm}^{-2}\text{K}^{-1} \),\[88, 89\] \( \alpha = 2 \times 10^{-3} \text{ K}^{-1} \) (in the phase transition regime),\[91\] and \( \gamma = 8.3 \times 10^{11} \text{ Jm}^5\text{C}^{-4} \),\[92\] for a P(VDF-TrFE) 55/45 mol\% copolymer, it can be estimated that \( \frac{1}{2} \beta P^2 = 5.88 \times 10^4 \text{ Jm}^{-3}\text{K}^{-1} \), the sum of the last two terms on the right side of Equation 2.20 is \( 2.05 \times 10^4 \text{ Jm}^{-3}\text{K}^{-1} \), where \( P = 0.07 \text{ Cm}^{-2} \) and \( E = 150 \text{ MVm}^{-1} \) are used. The contribution of secondary pyroelectricity to the ECE is 26\%. The results indicate that for polymers, the thermal expansion has a significant impact on the ECE entropy change through the interaction among the thermal expansion, electric field, and polarization.

Now if the polymer films are fixed to an inorganic substrate, the boundary conditions become \( \alpha_1 = \alpha_2, x_1 = x_2 = 0, X_1 = X_2 \neq 0 \) (the film surface is along the XY plane and Z is the film thickness direction). Using the electrostriction instead of piezoelectricity,\[88, 89\] near the phase transition temperature, the elastic Gibbs free energy can be written as
\[ G = \frac{1}{2} \beta (T - T_0) P^2 + \frac{1}{4} \gamma P^4 - EP - (X_1 + X_2) Q_{13} P^2 - \frac{1}{2} s_{11} (X_1^2 + X_2^2) - s_{12} X_1 X_2 \]  \hspace{1cm} (2.21)

The equations of state could be expressed as:\[93\]
\[ dx_1 = dx_2 = \left( s_{11}^{ET} + s_{12}^{ET} \right) dx_1 + 2Q_{13}^{ET} P_3 dP_3 = 0, \]  \hspace{1cm} (2.22)

and it can be deduced,
\[ -\Delta S = \frac{1}{2} \beta p^2 + \frac{2a_1 s_1 + 2a_2 T}{s_{11} + s_{12}} \]  \hspace{1cm} (2.23)

Equation 2.23 indicates that the clamping effect of substrate can change the ECE of polymer films. Since for P(VDF-TrFE) based polymers, the strain \( S_1 = Q_{13} P^2 > 0 \), the second term of the right hand side of Equation 2.23 will enhance the ECE entropy change in the clamped situation in addition to the contribution of the field induced phase transition.\[90\]

### 2.2 Coexisting Phases Rule Near Invariant Critical Points for Giant Electrocaloric Responses

One critical issue in the ECE research field is to design and tailor ferroelectric materials to achieve high responses, i.e., adiabatic temperature change \( \Delta T \) and isothermal entropy change \( \Delta S \). Generally it is believed that large response can be realized by operating near phase transitions of both electrocaloric (EC) and electromechanical (EM) materials. Moreover, it has been shown that the giant electromechanical response in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT) is a manifestation of two-phase critical points that define a line of critical end points (LCEP) in the electric-field–temperature–composition \((E - T - x_{PT})\) phase diagram of this system. Near the LCEP, the energy barrier for the phase transition could be significantly reduced, thus leading to the giant EM response.\[95, 96\] In these studies, the field-induced reversible phase change between the two coexisting phases with low transition barrier results in the giant EC or EM response.\[95, 96\] Inspired by these works, a theoretical framework is proposed for improving existing ferroelectric materials and developing new ferroelectric materials with better EC
responses. Specifically, it has been pointed out that the number of coexisting phases can be maximized near invariant critical points (ICP), which are important for one to explore material system with giant EC response.

Through a very detailed thermodynamic derivation, it is found that multiple phases can coexist within one material system, by tuning factors such as temperature, electric field, composition and stress. A material within coexisting phases has great potential to realize large ECE since the energy barrier among different phases is minimized therefore a small electric field would be able to trigger phase transition and generate large entropy change, i.e., large ECE.

It should be pointed out that there are many other effects that exist in thin films which can also cause change and enhancement in the EC and ME effects.[97-99] For example, an applied electric field in thin films can cause changes in the stress level, which in turn can contribute to EC and EM responses. Moreover, in multi-domain thin films, the field induced stress change may also change the domain configurations which again can contribute to EC and EM responses. These additional effects may further enhance the EC and EM responses besides the ICP effect. The ICP enhancement is due to the entropy increase purely from phase mixing. As shown in this letter, by engineering the material system so that it can be operated near the ICP to maximize the number of coexisting phases, a very large EC and EM may be realized.

2.3 Defect Modification to Increase Random States

Defects modification can disrupt the macroscopic polarization in P(VDF-TrFE) copolymers, and with proper defect modification, the dipolar disordered state can become stable at room temperature and the polymer is converted into a relaxor ferroelectric.[8] Moreover, the defect modification eliminates the polarization hysteresis associated with the change of polarization and also shifts the dielectric constant peak to room temperature and eliminates the
thermal hysteresis in the original copolymer. On microstructure scale, the defect generally has a large size compared with VDF or TrFE, thus the introduction of defects into the P(VDF-TrFE) will expand the unit cell and increase the interchain distance between polymer chains. Such an increase in the interchain distance allows dipoles to move more freely and as a result, the friction between dipoles when they rotate and realign is reduced, i.e., the hysteresis decreases in defect-modified materials. On the other hand, from domain level, the defects reduce correlation length, i.e., break large ferroelectric domains into multiple small domains, therefore increase the number of random states. By using high energy electron irradiation or copolymerization with a large size monomer, the material can be converted from normal ferroelectrics into relaxor ferroelectrics. The mechanism of defect modification will be discussed in a more detailed manner in Chapter 3 and Chapter 4.

More importantly, the defect modification might be able to improve the ECE. From the thermodynamic and statistic perspective in polar-dielectrics, as the electric field is increased from 0 to E, the isothermal entropy change $\Delta S$ and adiabatic temperature change $\Delta T$ can be expressed as,

$$\Delta S = S(E,T) - S(0,T),$$  \hspace{1cm} 2.24

where $c_e$ is the specific heat and $S(E,T)$ is the total entropy at a temperature T and electric field E. Since the lattice entropy is field independent, $\Delta S$ is determined by the dipolar entropy $S_{dp}$. In order to maximize $\Delta S$, it is necessary to maximize the entropy $S_{dp}(0,T)$ at $E=0$ and minimize $S_{dp}(E,T)$, occurring in a field E sufficiently large to induce polarization saturation. As shown in a recent thermodynamic and statistical analysis, for a system of N dipolar entities, each having $\Omega$ discrete equilibrium orientations, the maximum entropy corresponds to the case where all
directions i are equally populated or $N_i = N/\Omega$, where $N_i$ is the number of dipoles along symmetry direction i with the condition $\sum_i N_i = N$, where $\Theta$ is the Curie constant in the asymptotic behavior of the linear dielectric susceptibility, $\chi = \Theta/(T - T_0)$, and $T_0$ the Curie-Weiss temperature for a ferroelectric, $\varepsilon_0$ is the vacuum permittivity.

In deriving Equation 2.25, it was assumed that $S_{dip}(E,T) = 0$, corresponding to the minimum of entropy occurring when all dipoles are aligned along the field $E$.[100] For normal ferroelectrics such as a tetragonal ferroelectric phase, $\Omega = 6$ due to 6 possible polarization directions, as shown in Figure 2-1. Therefore, a dipole system with a larger number of dipole entities $\Omega$ and small dipole correlation (small $\Theta$) will have the potential to realize very large ECE. This is analogous to that of the magnetocaoric effect where a larger number of angular momentum states lead to higher magnetic entropy in the disordered state.[101, 102] Compared to other ceramic materials which also exhibit large ECE as well as MCE,[11, 65] the defect-modified P(VDF-TrFE) based relaxor polymers are regarded as the most promising commercial material due to its large temperature cooling per volt and to its scalability in size and shape.[15]

Figure 2-1 Schematic of 6 possible polarization directions in a tetragonal ferroelectric phase.
2.4 Measurement Methods for Electrocaloric Effect

Generally, ECE measurement can be categorized into two groups: indirect method and direct method. Indirect method measures polarization change as a function of temperature under constant electric field, then deduce entropy change $\Delta S$ and temperature change $\Delta T$ using Maxwell’s relation; While in direct method, temperature signal or heat flux signal from electrocaloric material samples is acquired by temperature sensor such as infrared sensor or heat flux sensor, and $\Delta S$ and/or $\Delta T$ are calculated from the equation $T\Delta S = c_p\Delta T$, where $T$ is the measuring temperature or the temperature of thermal bath, and $c_p$ is the specific heat of the sample. It should noted that $c_p$ might show temperature dependent, especially when measurement is conducted around phase transition temperature, thus a more accurate form of the previous equation should be written as

$$T\Delta S = \int_{T}^{T\pm\Delta T} c_p(T)\,dT \quad 2.26$$

2.4.1 Indirect Measurement

The indirect method, instead of measuring the temperature change associated with ECE, records polarization as a function of temperature under a series of electric field. It is based on the Maxwell relation, shown in Equation 2.4, from which the $\Delta S$ and $\Delta T$ of the ECE as the electric field changes from $E_1$ to $E_2$ can be deduced, i.e., Equation 2.5 to Equation 2.6. The indirect method has been widely used to characterize the ECE since 1960s,[37] due to the fact that in early stage of ECE study, the temperature change signal was weak and often had large noise from environment, while the apparatus that measure the polarization as a function of temperature is
quite universal and relatively convenient to use. This dissertation would not talk about the details on the indirect measurement method, since it has been explained explicitly elsewhere[8, 15] and also the majority of ECE data in this dissertation are measured using the direct method. However, It should be noted that since the Maxwell relation is derived for ergodic systems, it should be used with caution when one uses the indirect method to deduce the ECE in material systems that are not thermodynamically reversible such as the relaxor ferroelectric polymers.[80] The comparison of direct and indirect ECE measurement in relaxor ferroelectric terpolymers as well as the limitation of indirect method will be presented in Chapter 4.

2.4.2 Direct Measurement

The direct method measuring temperature change or entropy change directly from ECE samples can be further divided into two subgroups, i.e., direct method that detects temperature signal using sensors such as infrared temperature sensor or thermal couple temperature sensor, and direct method that measures heat flux signal using differential scanning calorimeter (DSC) or heat flux sensor. Since up to now there is no standard commercial equipment for measuring ECE (Commercial DSC system can be modified so that electric fields can be applied to the sample, and the heat absorbed or ejected by the sample is simultaneously recorded [103], various calorimeters have been developed by several research groups.

A calorimeter using infrared temperature signal sensor was developed at Penn State, as shown in Figure 2-2, where the temperature change generated by the ECE of the sample is calibrated using the temperature change generated by a standard reference resistor R, from which \( \Delta S \) is determined.
The principle of direct ECE measurement setup using the infrared temperature sensor is explained in the following context. In this calorimeter, the heat generated by the ECE sample is calibrated by the heat generated by a reference resistor $R$, from which $\Delta S$ is determined. When a voltage, $V$, with a pulse time duration, $t$, is applied to the resistor heater, it will produce a joule heat $Q_h$ expressed by

$$Q_h = \frac{V^2}{R} t \quad (2.27)$$

The heat will generate a temperature change in the sample system and this temperature change is detected by an infrared temperature sensor. Now if the ECE sample under an applied electric field also generates the same value of temperature change, then the effective heat $Q_{ECE}$ from the ECE material is equal to $Q_h$: $Q_{ECE} = T\Delta S$, where $\Delta S$ is the isothermal entropy change. If the ECE material has a heat capacity of $c_E$, a density $\rho$, and a volume of $U$, then the adiabatic temperature change can be obtained through calculation using the equation

Figure 2-2 Specially designed electrocaloric measurement calorimeter using infrared temperature sensor.
\[ T_{\text{ECE}} = \frac{Q_{\text{ECE}}}{c_e \rho U} \]

2.28

Figure 2-3 shows the schematic of the sample configuration. For thermal insulation, the film sample is placed between two netted plastic frames. A thin aluminum layer was deposited on the Kapton film to form a resistor heater, which is used to produce a reference heat signal for the ECE measurement. A commercial infrared (IR) temperature sensor is used to detect the temperature change produced by the Al resistor heater as well as the ECE materials, which output signal is recorded by an oscilloscope and computers.

![Sample system configuration for direct ECE measurement using infrared temperature sensor.](image)

Figure 2-3 Sample system configuration for direct ECE measurement using infrared temperature sensor.

The temperature signal measured in relaxor ferroelectric polymer using infrared sensor is presented in Figure 2-4. The base line of sensor signal has been shifted to zero for the sake of simplicity. As electric field is applied, the sample temperature increases generating an upward peak. Within a few seconds the signal returns to ambient temperature, which means the sample achieved thermal equilibrium with surrounding environment. Then as electric field is removed, the sample temperature drops sharply and climbs back to base line within approximately 2 seconds.
By substituting the infrared sensor with a heat flux sensor or thermal couple, the adiabatic temperature change can be obtained using the same calorimeter. Similar to the measurement setup described above, the ECE can also be directly measured using heat flux sensor, as shown in Figure 2-5.

Again the heat generated by the ECE sample was compared with the heat generated by a standard reference resistor $R$, from which $\Delta S$ is determined. When a voltage, $V$, with a pulse time duration, $t$, applies to the resistor heater, it would produce a joule heat $Q_h = (V^2/R)t$. The heat generated is detected by a heat flux sensor directly attached to the sample surface. Now if the
ECE film under an applied electric field also generates the same amount of heat as detected by the same flux sensor, then the heat $Q_{ECE}$ from the ECE material is equal to $Q_h$. From $Q_h = Q_{ECE} = T\Delta S$, thus $\Delta S$ can be obtained. If the ECE material has a heat capacity of $c_E$, a density $\rho$, and a volume of $U$, then the adiabatic temperature change can be obtained, $T_{ECE} = Q_{ECE}/(c_E\rho U)$. ECE as function of both temperature and applied electric field $E$ were characterized. Presented in Figure 2-6 are typical ECE signals from a terpolymer film measured by the heat flux sensor in which both heat generation and absorption, corresponding to the field increase and decrease, were recorded. Specially, the impact of step voltage direction is tested. And as can be seen from Figure 2-6, the step voltage direction shows no influence on ECE, and only the magnitude of the step voltage is important to ECE in this case.

![Figure 2-6](image.png)

Figure 2-6 Heat flux sensor signals when a step voltage is applied to a relaxor polymer film, causing an upward heat flux peak and when a step voltage is turned off from a relaxor polymer film, causing a downward heat flux peak.

Special attention needs to be paid when one analyzes the direct measurement data when the specific heat of sample is temperature dependent. For example, the specific heat $c_E$ in P(VDF-
TrFE) copolymer shows a strong temperature dependence, especially around the F-P transition temperature of 85 °C as shown in Figure 2-7.

As pointed out earlier, when $c_E$ is dependent on temperature, the equation $T\Delta S = c_E\Delta T$ should not be used. Instead, Equation 2.30 yields more accurate data. When calculating the temperature change upon applying the electric field, one should use

$$T\Delta S = \int_{T}^{T+\Delta T} c_E(T) dT,$$

and when calculating the temperature change upon removing the electric field, the equation should be rewritten as following

$$T\Delta S = \int_{T}^{T-\Delta T} c_E(T) dT$$

Factors that may influence the accuracy of a direct ECE measurement include the sensitivity and response time of the thermal sensor, the stability of temperature control, and the ability of the system to prevent undesired heat dissipation.

Figure 2-7 Specific heat for P(VDF-TrFE) 65/35 mol% copolymer, which exhibits strong temperature dependence.
Chapter 3
ECE in Irradiated PVDF-based Copolymer

3.1 Introduction

By introducing certain defects into PVDF-based copolymers, one can modify and tailor the properties of these materials. It has been shown that an exceptionally high electrostrictive response of 4% was observed in electron-irradiated P(VDF-TrFE) copolymer.[31] The material exhibits typical relaxor ferroelectric behavior, suggesting that the high energy electron irradiation breaks up the coherent polarization domain in normal ferroelectric P(VDF-TrFE) copolymer into nanopolar regions that transform the material into a relaxor ferroelectric generating the large electrostrictive response. In other words, the irradiation breaks dipole correlation and therefore may be able to enhance ECE as discussed in Chapter 2. On the fundamental side, weakened dipole correlation yields less hysteresis loss which is advantageous from ECE perspective. Besides, according to Equation 2.25, the large number of disordered fluctuating polarization entities $\Omega$ in relaxor ferroelectrics could lead to large electrocaloric response. On the experimental side, a large electrocaloric effect with $\Delta T = 20^\circ C$ has been observed in irradiated P(VDF-TrFE) 68/32 mol% copolymer with high energy electron irradiation.[104]

While most of investigations have focused on either normal ferroelectric polymers or polymers that are completely transformed into a relaxor, e.g., irradiated P(VDF–TrFE) copolymer with a low VDF content and a high irradiation dose, only a few studies on the influence of irradiation dose on the structure and properties have been conducted. In this chapter, a series of dielectric, thermal, and specially electrocaloric investigations of P(VDF–TrFE) 65/35 mol% copolymer irradiated with varying doses of high-energy electrons are systematically presented.
By employing the high energy electron irradiation, with large amount of irradiation dose, the normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer can be converted to a relaxor ferroelectric polymer which displays high dielectric constant and large reversible polarization change around room temperature range. On the other hand, at lower irradiation doses it has been found that ferroelectric and relaxor states coexist in the P(VDF–TrFE) 65/35 mol% copolymer. The coexistence of normal ferroelectric and relaxor ferroelectric states strongly influences certain properties of these materials, particularly the electrocaloric response. It is shown that the irradiation process, by creating crosslinking and pinning on the polymer chain level, expands the inter-chain distance between polymer chains and thus reduces hysteresis loss, since dipoles are able to rotate more freely. Interestingly, giant ECE response is acquired in irradiated P(VDF–TrFE) 65/35 mol% copolymer with moderate irradiation dose, rather than in relaxor ferroelectric samples prepared with higher irradiation dose. It is demonstrated that in irradiated P(VDF-TrFE) 65/35 mol% with 20 Mrads, an entropy change as high as 130 Jkg\(^{-1}\)K\(^{-1}\) and a temperature change of 28 °C can be obtained. As irradiation dose increases, the peak value of ECE is gradually dampened, which may be attributed to a reduction in crystallinity as well as polarization. Moreover, the dependence of ECE on the times of measurement has been discussed, which is important for exploring materials performance under practical operating condition of ECE cooling device. It appears counter-intuitive the fact that ECE is enhanced as measurement cycle increases, yet the phenomenon is understandable after a detailed analysis on the electrocaloric signals. Finally, the impact of high energy electron irradiation on P(VDF-TrFE) 75/25 mol%, P(VDF-CTFE) and P(VDF-HFP) is also explored. These series of materials with strong ferroelectricity are more resistant to high energy electron irradiation, therefore the impact is feeble, especially on electrocaloric effect, which is in a clear contrast to what has been observed in the irradiated P(VDF-TrFE) 65/35 mol% case.
3.2 Irradiated P(VDF-TrFE) 65/35 mol% Copolymer

3.2.1 Experimental

P(VDF-TrFE) 65/35 mol% copolymer powders were purchased from Solvay and Cie (Bruxelles, Belgium). Solution casting method was employed to prepare the copolymer films. The copolymer powders were dissolved in dimethylformamide (DMF) and then the solution was cast on a flat glass plate and dried in an oven. The temperature of the oven was intentionally set at a low value around 60 °C, which prevented high crystallinity in the copolymer films. Two types of films were used in this investigation: the uniaxially stretched and non-stretched. In stretched films, films made from solution cast were uniaxially stretched by a factor of 5 using zone stretching method. Both stretched and non-stretched films were annealed at 140 °C for a period between 16-20 hours in order to increase the crystallinity. To prevent shrinkage during the annealing for the stretched films, the two ends of the films were mechanically fixed during annealing. The thickness for both stretched and non-stretched films was in the range of 10 to 15 µm.

The irradiation was carried out using the facility at National Institute of Standards and Technology, in a controlled atmosphere (Ar or N₂ gas) to avoid oxidation of the polymers in the irradiation. The specially designed setup allowed heating which provided high temperature above the phase transition of P(VDF-TrFE) 65/35 mol%. The electron energy about 1.2 MeV was used for the irradiation. The high energy electrons have large penetration depth so that many P(VDF-TrFE) copolymer layers (up to 0.5 mm in total thickness) can be irradiated at once. To avoid possible overheating of the polymer films in the irradiation process, the irradiation rate is maintained at 1 Mrad per minute. For a copolymer 65/35 mol% irradiated at above FE-PE
transition temperature (~ 100 °C). In this study, the irradiation doses at 20, 40, 60, 75 Mrads had been used to vary the defects concentration in the copolymer.

The dielectric constant measurement was conducted using the facility at Dielectric Lab of Materials Research Institute. Dielectric constant for P(VDF-TrFE) 65/35 wt% copolymers with different irradiate dose were measured as a function of temperature during the heating process, under a low AC voltage with the frequency of 1 KHz. The Hysteresis Loop (P-E Loop) was conducted using the Sawyer-Tower Circuit built in Dielectric Lab of Materials Research Laboratory. Polarization and hysteresis information have been obtained from the P-E Loop measured under a constant electric field of 100 MVm⁻¹ and a frequency of 10 Hz during heating process. Modulated DSC was measured using TA Q100 as a function of temperature. Electrocaloric effect was directly measured using specially designed calorimeter at Pennsylvania State University with heat flux sensor. The ECE response (temperature change) for irradiated copolymer with different doses was directly measured as a function of temperature in the way described in Chapter 2, under a constant electric field of 100 MVm⁻¹. The dielectric constant measurement was conducted using the facility at Dielectric Lab of Materials Research Institute. Dielectric constant for P(VDF-TrFE) 65/35 wt% copolymers with different irradiate dose were measured as a function of temperature during the heating process, under a low AC voltage with the frequency of 1 KHz.

3.2.2 Dielectric Analysis

As can be seen from Figure 3-1(a), the dielectric constant peak shifts from high temperature to room temperature and peak value decreases as irradiation dose increases, indicating the reduction of correlation length in P(VDF-TrFE) copolymer samples, which is caused by the high-energy-electron irradiation breaking the long chains of P(VDF-TrFE) into
shorter units. For copolymer films without irradiation, the dielectric constant peak appears around 90 °C when measured during cooling process, while after 20 Mrads irradiation, the dielectric constant peaked at 50 °C but at the same time the peak value still maintained to a large value. When irradiation dose increased to 60 Mrads, the peak barely shifted yet its value dropped significantly, showing abrupt reduction of correlation length in the P(VDF-TrFE) copolymer.

Films with irradiation of 40 Mrads is a proper candidate for exhibiting large ECE around room temperature, since its dielectric constant peaks around 35 °C and at the same time still maintains a value close to 65. By comparing Figure 3-1(b) and Figure 3-1(c), it can be seen that when irradiation dose reaches 40 Mrads, the temperature of dielectric peak acquired during heating process and that acquired during cooling process are the same, thus the hysteresis in irradiated copolymer with 40 Mrads has been mostly eliminated, or can be neglected.

It should also be noted that the uniaxial stretching process has little impact on the dielectric constant, as observed in Figure 3-1(a) and Figure 3-1(b). This can be understood in a sense that while uniaxial stretching may align dipoles, increase crystallinity and change crystallite size, the sequential high-energy electron irradiation partially melts the copolymer and reorganizes its structure on the domain scale, by creating crosslinking that expands interchain distance as well as reduces crystallinity. Therefore, in a simple way, the high-energy electron irradiation plays a more dominant role in modifying the P(VDF-TrFE) copolymer structure and property compared with uniaxial stretching, and the impact of uniaxial stretching on P(VDF-TrFE) copolymer has been eliminated by the following high-energy electron irradiation.
Figure 3-1 (a) Dielectric constant for non-stretched irradiated P(VDF-TrFE) 65/35 mol% copolymer films as a function of temperature at 1 KHz during heating process; (b) Dielectric constant for stretched irradiated P(VDF-TrFE) 65/35 mol% copolymer films as a function of temperature at 1 KHz during heating process. (c) Dielectric constant for stretched irradiated P(VDF-TrFE) 65/35 mol% copolymer films as a function of temperature at 1 KHz during cooling process.
Figure 3-2 shows the temperature dependences of the real, \( \varepsilon' \) and imaginary, \( \varepsilon'' \), parts of the complex linear dielectric constant, measured at various frequencies in the ferroelectric P(VDF–TrFE) copolymers with irradiation doses of 0, 20, 40, and 60 Mrads. In 0 Mrad sample, both \( \varepsilon' \) and \( \varepsilon'' \) reach maximum values at the temperature of the paraelectric-ferroelectric phase transition of \( T_c = 341 \) K (the absolute temperature in the unit of Kelvin is used here for the sake of convenience as the Vogel – Fulcher law will be explored in the following context), regardless of the measuring frequency. As irradiation dose increases, the dielectric maximum broadens and peak position becomes frequency dependence. For example, in 60 Mrads sample the maximum temperature is fully frequency dependent in the complete frequency range. Such a broad dispersive dielectric maximum is a typical characteristic for relaxor systems [105], meaning that the irradiated copolymer is gradually converted into relaxor ferroelectric phase as irradiation dose increases. It should be noted that, similar to dipolar glasses [106], the peak observed in the relaxor ferroelectric irradiated copolymer does not represent any phase transition, but rather a solely dynamic property arising from the freezing of polar clusters. Another altered feature of the dielectric constant is the reduction of the peak value, i.e., the peak value decreases as irradiation dose increases. Such a phenomenon is likely to be cause by the fact that high-energy electron irradiation reduces both the correlation length and crystallinity in copolymer samples.
Figure 3-2 Temperature dependences of the real part $\varepsilon'$ and imaginary part $\varepsilon''$ of the complex linear dielectric constant, detected at various frequencies in the ferroelectric and irradiated P(VDF–TrFE) copolymer samples.

The broadening of the dielectric maximum, i.e., of the dielectric relaxation spectrum, is emphasized in Figure 3.3, which presents the temperature dependences of the characteristic relaxation frequencies, determined from $\varepsilon''(T)$ peaks. The data are also fit using Vogel–Fulcher law.

As discussed earlier, the irradiated copolymer with higher irradiation dose shows stronger frequency dependence. It has been shown that in relaxor ferroelectric materials, the frequency-peak temperature data follow the Vogel–Fulcher law

$$v = v_0 \exp\left[-\frac{E}{k(T - T_0)}\right],$$

where $v_0$ is the attempt frequency, $E$ is the activation energy, and $T_0$ is the Vogel–Fulcher freezing temperature of the characteristic relaxation time. [107] Intriguingly, the data for 60 Mrads sample can be perfect fit by the Vogel–Fulcher law. The obtained values of parameters $v_0 = (2.1 \pm 0.5) \times 10^{10}$ Hz, $E/k = 1080 \pm 120$ K, and $T_0 = 214 \pm 4$ K are similar to those obtained in relaxor
P(VDF–TrFE–CFE) terpolymer where instead of using electron irradiation, the long-range polar ordering of chains is prevented by additional monomer that contains chlorine atom.[105] While in 20 and 40 Mrads samples, the temperature dependence of the characteristic relaxation frequency is a combination of the ferroelectric and relaxor behavior. This is associated with the evolution of the polymer system from the normal ferroelectric which has a long-range polar order to relaxor which has a short-range order system. Similar to the inorganic lanthanum-modified lead zirconate titanate ceramics (PLZT), where increasing of the La content transforms a ferroelectric PZT into a relaxor system such as 9/65/35 PLZT, via intermediate ferroelectric-relaxor compound such as 6.5/65/35 PLZT, where relaxor glasslike and ferroelectric order-dominated regions coexist.[108] Here the irradiation with high-energy electrons, which breaks the polar all-trans configurations, also transforms a ferroelectric P(VDF–TrFE) into a complete relaxor system via intermediate systems, where both phases coexist.

Since P(VDF-TrFE) copolymers are well known as semicrystalline materials that comprise in amorphous and crystalline phases, it should be pointed out that the ferroelectric phase transition and the transformation into a relaxor take place only in the crystalline part of the system. During heating process, while the crystalline region adopted ferroelectric phase undergoes a transition into a paraelectric phase and finally melts, the amorphous region undergoes a transition from glassy to a rubbery state below room temperature.[109] This glass transition is dynamically manifested as an additional dielectric relaxation in the temperature region of 250–300 K, which is more pronounced in our irradiated samples and is fully noticeable in the 60 Mrads sample spectra in Figure 3-2. This indicates that high-energy electron irradiation increases the amount of amorphous phase, as has ultimately been confirmed by DSC experiments, as shown in the following section. Figures 3-2 and 3-3 furthermore demonstrate that the Curie temperature of the ferroelectric phase transition (e.g., the temperature of the frequency-independent peaks in ε”(T)) decrease on increasing irradiation dose, as the consequence of the random electric fields
introduced in the form of irradiation-induced defects. Finally, it should be stressed that the electrical conductivity of P(VDF–TrFE) samples does not significantly increase after irradiation, as can be deduced by comparing the $\varepsilon'(T)$ and $\varepsilon''(T)$ data, obtained at the lowest frequencies and the highest measured temperatures, in Figure 3-2.

### 3.2.3 Differential Scanning Calorimetry Results

The Differential Scanning Calorimetry (DSC) study is of importance to probe the micro-scale structure such as crystallite size and crystallinity as well as dynamic processes of ferroelectric-paraelectric phase transition and glass transition. The DSC results for irradiated P(VDF–TrFE) copolymer samples are presented in Figure 3-4. It can be observed from the DSC data that as the irradiation dose increases, the melting peak gradually shifts to lower temperature, indicating the crystallite size, or ferroelectric domain, decreases, which further proves that high-energy irradiation breaks long correlation between dipoles and turns large ferroelectric domains into small ones. Again, in irradiated copolymer with low or moderate doses, the normal ferroelectric states still persist and coexist with relaxor states. The inset to Figure 3-4 clearly reveals that, in addition to the melting peak at 415 K, an additional ferroelectric-paraelectric phase transition occurs at 315 K, which is exactly the Curie temperature where the frequency independent $\varepsilon''(T)$ peaks occur.
The crystallinity of investigated samples has been deduced by assuming that the enthalpy of the melting is directly proportional to the crystallinity in the sample, while the crystallinity of the ferroelectric copolymer has been estimated to 80%. Table 3-1 exhibits the Total enthalpy change of the melting peaks, DSC melting peak temperatures, and the crystallinity of the ferroelectric and irradiated P(VDF–TrFE) copolymer system. For irradiated copolymer with 60 Mrads, the crystallinity is approximately 55% along with the melting temperature at 390.1 K. It can be clearly concluded from the DSC data that not only the irradiation-induced defects and increased crosslinking decrease the ferroelectric transition temperature but also high-energy electron irradiation also significantly lowers the melting point and reduces the crystallinity of P(VDF–TrFE) samples. Since ECE can only be generated in crystalline phase, the irradiation dose should be controlled within a modest range to avoid significant crystallinity decrease that limits ECE response.

Table 3-1 Total enthalpy change of the melting peaks, DSC melting peak temperatures, and the crystallinity of the ferroelectric and irradiated P(VDF–TrFE) copolymer system.
Irradiated Copolymer | ΔH (J/g) | Tm (K) | Xc (%)  
---|---|---|---
0 Mrad  | -26.6 | 425.6 | 80  
20 Mrads  | -25.6 | 411.5 | 77  
40 Mrads  | -20.8 | 400.6 | 62  
60 Mrads  | -18.4 | 390.1 | 55  

### 3.2.4 Hysteresis Loops

As presented in Figure 3-5(a) and Figure 3-5(b), the copolymer films with irradiation dose of 20 Mrads exhibit moderate hysteresis at 30 °C, while other films with more irradiation dose behave as relaxor ferroelectric, with slim polarization vs. electric (P-E) hysteresis loops and small ferroelectric loss. The uniaxially stretched films and non-stretched films show a similar response so in the following context they will not be distinguished for convenience. Figure 3-5(a) shows the hysteresis loop for copolymers films with different irradiation dose at 30 °C. The copolymer films with irradiation dose of 20 Mrads exhibit moderate hysteresis at 30 °C, while other films with more irradiation dose behave as relaxor ferroelectric, with slim P-E Loops and small ferroelectric hysteresis. The results also prove that high energy-electron irradiation converts normal ferroelectric into relaxor ferroelectric by reducing the correlation length of the copolymers. However, as the correlation length decreases, the polarization under same electric field also drops, especially for samples with higher irradiation doses at and above 60 Mrads. It can be estimated that the decrease of polarization would lead to a small ECE-related entropy change, as ECE is proportional to the square of polarization change, according to Equation 2.25.[100]
For each film the P-E loop has a different transition temperature, at which point there is a phase change from the ferroelectric state to paraelectric state (P-E Loop becomes slim and polarization value starts to drop). In the case of irradiated copolymer with irradiation dose of 20 Mrads in Figure 3-6(a), the transition temperature is around 50 °C, which is consistent with the dielectric constant data. With more irradiation dose, slim P-E loop is observed over the whole temperature range, as presented in Figure 3-6(b), indicating that the irradiated copolymer with 40 Mrads is in the relaxor ferroelectric state rather than the normal ferroelectric state.

Figure 3-5 (a) Hysteresis loop measured at 30 °C for non-stretched irradiated P(VDF-TrFE) 65/35 mol% copolymer films with different dosages (b) hysteresis loop measured at 30 °C for stretched irradiated P(VDF-TrFE) 65/35 mol% copolymer films with different dosages.

Figure 3-6 (a) Hysteresis Loop measured in Irradiated P(VDF-TrFE) 65/35 mol% Copolymer Films with irradiation dose of 20 Mrads, as a function of temperature (b) Hysteresis Loop measured in Irradiated P(VDF-TrFE) 65/35 mol% Copolymer Films with irradiation dose of 40 Mrads, as a function of temperature.
Figure 3-7 shows polarization value measured during unipolar process in various irradiated copolymers. It should be noted that the unipolar process data rather than bipolar process data are selected due to the fact that in electrocaloric effect measurement, electric field is applied and removed along the same direction, similar to the conduction of unipolar process. Thus the unipolar polarization value represents the polarization change in electrocaloric materials when ECE is measured. In Figure 3-7, the largest polarization change in irradiated copolymer with 20 Mrads is observed at 50 °C, corresponding to the dielectric peak position. Irradiation broadens polarization peak, shifts peak to room temperature yet reduces the polarization value. Therefore a moderate irradiation dose should be selected in order to maximize the polarization value, i.e., the ECE in irradiated copolymers. It should be noted that the conduction loss, which is half of the remanent polarization value, has been deducted to reveal the true response from the dipoles.

Figure 3-7 Polarization value based on the unipolar P-E Loop presented the polarization value of irradiated copolymer films with different irradiation dose, under a constant electric field of 100 MVm⁻¹, as a function of temperature.
3.2.5 ECE in Irradiated P(VDF-TrFE) 65/35 Copolymer

As presented in Figure 3-8(a), Film with the irradiation dose of 20 Mrads exhibits large temperature change of 13 °C when measured at 50 °C. As irradiation dose increases, the ECE response peak shifts from high temperature to room temperature, with is consistent with the results of dielectric constant and P-E Loop. Around room temperature, the copolymer films with irradiation dose of 40 Mrads exhibit largest ECE response compared with other films. It should be noted that for samples with moderate irradiation dose, there is large ECE response (>12 °C) within a narrow temperature range (45 - 60 °C), while as the irradiation dose increased, the ECE response decreased yet maintained a relatively large value over a broad temperature range. In other words, there is a tradeoff between maximum ECE response and the range of allowed operating temperature. Again, there is little difference in terms of ECE properties considering the error of measured data. The beta values, where $\Delta S = \beta P^2$, in different irradiated copolymers are compared in Figure 3-8(b). In room temperature range, irradiated copolymer with 60 Mrads shows largest $\beta$ value of approximately $2.8 \times 10^7 \text{ Jm}^{-1}\text{K}^{-2}$ while irradiated copolymer with 20 Mrads yields a low $\beta$ value, which is consistent with what can be observed from the ECE response data in Figure 3-8(a).

Intriguingly, the optimal irradiation doses are different in terms of $\beta$ value and ECE performance. For $\beta$ value, irradiation dose of 60 Mrads yields highest data, since the amount of irradiation completely converts P(VDF-TrFE) 65/35 mol% copolymer into relaxor ferroelectric material and the correlation between dipoles is significantly reduced, which generates high $\beta$ value. While for ECE, beside $\beta$ value, polarization level also plays an important role. Since irradiation reduces crystallinity thus rendering a lower polarization, the irradiated copolymer with 40 Mrads exhibit best ECE performance around room temperature. Therefore, one has to bear such difference in mind when determining the irradiation dose to tune material properties.
Figure 3-8 (a) ECE ($\Delta T$) vs $T$ measured under a constant electric field of 100 MVm$^{-1}$ during heating process (b) beta value for irradiated copolymer with different irradiation dose.

Meanwhile, the ECE response as a function of electric field was conducted on P(VDF-TrFE) copolymer samples with irradiation dose of 20 Mrads around its F-P transition temperature, i.e., 50 °C. Under the E-field of 180 MVm$^{-1}$, there is a temperature change as large as 28 °C which is presented in Figure 3-9, the largest by far in the polymer-based materials. Such a large ECE response can be attributed to the fact that multiple phases with minimal energy barrier
coexist in the modestly irradiated copolymer, which will be analyzed in a more detailed way in the following section. The giant ECE response would provide a huge cooling power to make it very attractive for compact cooling device with ultrahigh efficiency.

![Figure 3-9](image)

**Figure 3-9** Temperature change caused by electrocaloric effect as a function of electric field at 50 °C in irradiated copolymer with 20 Mrads.

Besides the giant ECE observed in the irradiated copolymer, the impact of the two half cycles (the heating half-cycle, in which an electric field is applied to the polymer film to cause reduction of entropy in and rejection of heat from the polymer films, and the cooling half-cycle in which the field is removed to cause an increase in entropy in and absorbing heat by the polymer films) on the ECE is also probed. The results reveal that there is a large difference between the isothermal entropy changes in the two half cycles (ΔS_h in the heating half-cycle can be much larger than ΔS_c in the cooling half-cycle), and that this might be caused by the presence of intermediate phases.

The typical ECE signals thus obtained, at temperatures below, near, and above the dielectric constant maximum (~ 90 °C), from the heat flux sensor during the heating run under a unipolar single pulse of 100 MVm⁻¹ electric field are presented in Figure 3-10(a), where the
A positive voltage signal is from the heating half-cycle and the negative voltage signal is from the cooling half-cycle. It is apparent that there is a large difference between signals in the positive (heating) and negative (cooling) half-cycles and the signals from the positive half-cycle is larger than that of the negative half-cycle. Figure 3-10(b) presents the ECE signal acquired at 90 °C under 50 MVm⁻¹, which shows that the difference between the two half-cycles becomes much small. This is understandable since phase transition is nonlinear with applied electric field.

![Graph](image)

Figure 3-10 Directly recorded ECE signal from the flux sensor when the P(VDF-TrFE) 65/35 mol% films under an uni-polar electric field pulse of (a) 100 MVm⁻¹ with pulse width larger than 10 seconds measured at 60 °C, 90 °C, and 100 °C; and (b) 50 MVm⁻¹ at 90 °C. The positive signals correspond to the heat ejection from the film as the field is applied and the negative signals are when the field is removed (film absorbs heat). The integrated area corresponds to the heat ejected (positive signal) or absorbed (negative signal).

Figure 3-11 presents a full set of ECE signals at various temperature points in P(VDF-TrFE) 65/35 mol% copolymer, irradiated P(VDF-TrFE) 65/35 mol% copolymer with 20 Mrads irradiation dose and irradiated P(VDF-TrFE) 65/35 mol% copolymer with 40 Mrads irradiation dose. The trend is identical to that in Figure 3-10, which shows that as irradiation dose increases,
the difference between heating cycle and cooling cycle becomes smaller and in each set of samples, the difference increases as temperature falls in the vicinity of F-P phase transition temperature range.

Figure 3-11 ECE signals (both when applying electric field and removing electric field) at various temperature points in (a) P(VDF-TrFE) 65/35 copolymer; (b) irradiated P(VDF-TrFE) 65/35 copolymer with 20 Mrads; (c) irradiated P(VDF-TrFE) 65/35 copolymer with 40 Mrads.
ΔS_h and ΔS_c deduced from the data in the two half-cycles at various temperatures are presented in Figure 3-12(a). In the data presented, the heating due to conduction loss which is a constant when the film is under constant electric field has been subtracted. At 85°C, near the first order FE-PE transition, ΔS_h acquired from several films under 100 MVm⁻¹ is 156 ± 28 Jkg⁻¹K⁻¹ (or a Q = 56.6 Jg⁻¹) while in the cooling half cycle ΔS_c = 48.9 ± 0.4 Jkg⁻¹K⁻¹, which is still quite large albeit much smaller than ΔS_h. It is noted that ΔS_h exhibits a large variation between samples and hence exhibits a large data scattering, indicating the result is history dependence. On the other hand, ΔS_c does not show much change between samples. Figure 3.12(a) also reveals that a large difference between ΔS_h and ΔS_c exists for the whole temperature range measured (35 °C to 100 °C) where the data is acquired in the first field cycle after the sample is stabilized at a fixed temperature T. The ΔS difference between the two half cycles under 50 MVm⁻¹ (Figure 3.12(b)) becomes much smaller, especially at high temperatures. For example, at 116 °C, ΔS_h is nearly the same as ΔS_c.

The large different between ΔS_h and ΔS_c can be from hysteresis loss and from the difference between the entropies of the initial S_i(0, T) and final S_f(0, T) states since the data in Figure 3-12 are acquired at the first cycle of the electric field after the film temperature is stabilized (It takes about 30 minutes to take one temperature data point). That is,

\[ \Delta S_h = S_i(0, T) - S(E, T) + \Delta S_{hys(h)}, \]
\[ \Delta S_c = S_f(0, T) - S(E, T) - \Delta S_{hys(c)}, \]

where \( \Delta S_{hys(h)} \) and \( \Delta S_{hys(c)} \) are hysteresis losses at the two half cycles, respectively, and the total polarization hysteresis loss is \( \Delta S_{hys} = \Delta S_{hys(h)} + \Delta S_{hys(c)} \). \( \Delta S_{hys} \) under 100 MVm⁻¹ and 85 °C is 107 Jkg⁻¹K⁻¹ (6.7 Jmol⁻¹K⁻¹) which corresponds to \( \Delta Q = 38.3 \text{ Jg}^{-1} \) (or 70 Jcm⁻³). The polarization hysteresis loss can be determined from the polarization (P) – electric field (E) hysteresis loops.
The maximum polarization hysteresis loss under 100 MVm\(^{-1}\) at 85 °C is less than 1 Jg\(^{-1}\) (< 2.8 Jkg\(^{-1}\)K\(^{-1}\)) which is much smaller than \(\Delta S_h - \Delta S_c\). The result points to a large change in the entropy between the initial and final states \(S_i(0, T) - S_f(0, T)\). Even at 35 °C, which is far below the FE-PE transition, \(S_i(0, T) - S_f(0, T) > 62\) Jkg\(^{-1}\)K\(^{-1}\). Here \(S_i(0,T)\) is the entropy of the polymer films right after electric field poling and \(S_f(0,T)\) is the entropy after the film is aged for about 30 minutes. The fact that a large \(S_i(0, T) - S_f(0, T)\) exists below the FE-PE transition indicates a high degree of disorder in the ferroelectric phase, which is consistent with earlier observations and suggests possible intermediate phases with different degree of polar-ordering in the P(VDF-TrFE) 65/35 copolymer.\(^{[110]}\) The phase (or state) of the copolymer right after the application of high electric fields (right after the poling) possesses low dipolar entropy (as reflected by small \(\Delta S_c\) and \(S_f(0,T)\)). As the film is aged (without external fields), the copolymer relaxes to a phase with high dipolar entropy. This is also consistent with the observation that \(S_i(0,T)\) exhibits large data scatter since its value depends on the film aging time. In some films, a \(\Delta S_h - \Delta S_c\) value as large as 150 Jkg\(^{-1}\)K\(^{-1}\) has been observed at 85 °C, pointing to a significant change in the molecular structures between the poled state and aged state.

This scenario suggests that when the copolymer is subject to continuous field pulses with short time interval between the pulses, \(\Delta S_h\) and \(\Delta S_c\) should approach each other since the polymer does not have time to relax back to a highly disordered state. The ECE of P(VDF-TrFE) 65/35 mol% copolymer is measured at 85 °C beyond the first cycle under 100 MVm\(^{-1}\) unipolar square wave at 0.05 Hz. Indeed, the results in Figure 3-12(c) show that \(\Delta S_h - \Delta S_c\) decreases substantially even at the second cycle. At the twentieth cycle, \(\Delta S_h\) and \(\Delta S_c\) becomes nearly the same, implying that the \(\Delta S\) measured approach the intrinsic isothermal entropy change and \(\Delta S_{int} \geq 67\) Jkg\(^{-1}\)K\(^{-1}\) under 100 MVm\(^{-1}\). Now the difference \(\Delta S_h - \Delta S_c\) can be accounted for by the polarization
hysteresis loss. The difference $\Delta S_h - \Delta S_c$ returns to large values when increasing the time interval between the applied electric fields to several minutes.

Figure 3-12 $\Delta S_h$ and $\Delta S_c$ (the isothermal entropy change during applying field and removing the electric field to the polymer film) of 65/35 ml% copolymer films (a) under 100 MVm$^{-1}$ uni-polar field (from the first field cycle at each temperature) as a function of temperature; (b) under 50 MVm$^{-1}$ uni-polar field (from the first field cycle at each temperature) as a function of temperature; and (c) under 100 MVm$^{-1}$ uni-polar square wave of 0.05 Hz and at 85 °C as a function of field cycle number. Dada points are shown and solid curves are drawn to guide eyes.
Interestingly, by irradiating the copolymer with 20 Mrad (200 kGy) dose of high energy electron (1.2 MeV energy), the dielectric hysteresis is significantly reduced, as shown in Figure 3-1, along with a marked reduction in the dielectric peak temperature. $T_m$ at the heating run is reduced to 49 °C. $\Delta S_h$ and $\Delta S_c$ acquired in the first cycle of 100 MVm$^{-1}$ square wave at different temperatures near $T_m$ are presented in Figure 3-13(a), showing significant reduction in $\Delta S_h - \Delta S_c$ compared with the normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer. In the whole temperature range measured (from 25 °C to 60 °C), $\Delta S_c$ for the modified copolymer is higher than that of the normal ferroelectric 65/35 mol% copolymer. At 50 °C, $\Delta S_h$ and $\Delta S_c$ are 87.1 Jkg$^{-1}$K$^{-1}$ and 59.2 Jkg$^{-1}$K$^{-1}$, respectively. The difference between the two becomes small with the field cycle as presented in Figure 3.12(b) which is acquired under a 100 MVm$^{-1}$unipolar square wave of 0.05 Hz at 50 °C. At the twentieth cycle, $\Delta S_h$ and $\Delta S_c$ become 72.6 Jkg$^{-1}$K$^{-1}$ and 71.6 Jkg$^{-1}$K$^{-1}$, respectively, implying $\Delta S_{int} \sim 72$ Jkg$^{-1}$K$^{-1}$ which is larger than the peak value of $\Delta S_{int}$ of the normal ferroelectric P(VDF-TrFE) 65/35 mol% copolymer. $\Delta S_{int} \sim 72$ Jkg$^{-1}$K$^{-1}$ is also very close to the average of $\Delta S_h$ and $\Delta S_c$ for the first cycle is 73.1 Jkg$^{-1}$K$^{-1}$), meaning that one may use $\Delta S_{ave} = (\Delta S_h + \Delta S_c)/2$ to estimate $\Delta S_{int}$.

The large $\Delta S_{int}$ and much smaller hysteresis loss in the modified copolymer are highly desirable for practical cooling device applications. The directly recorded first cycle ECE data at $T=50$ °C under 180 MVm$^{-1}$ for the copolymer irradiated with 20 Mrads is presented in the inset of Figure 3-13(c), which has a $\Delta S_h = 190$ Jkg$^{-1}$K$^{-1}$, $\Delta S_c = 130$ Jkg$^{-1}$K$^{-1}$, $\Delta S_{int} \sim 160$ Jkg$^{-1}$K$^{-1}$. The inset in Figure 3-13(c) also shows that the irradiated copolymer with 20 Mrads dose does not show much conduction loss at 50 °C where the data after 5 seconds under the field is nearly the same as that without electric field (~ 0). Combining $\Delta S_{int}$ with the DSC data yields a $\Delta T_{int} = 35$ °C and
ΔTc = 28 °C under 180 MVm⁻¹. Irradiating the copolymer with higher than 20 Mrad dose causes a reduction of ΔSh and ΔSint. Hence, the results are not further discussed here.

Figure 3-13 ΔSh and ΔS of 20 Mrads irradiated 65/35 mol% copolymer films (a) under 100 MVm⁻¹ uni-polar field (from the first field cycle at each temperature) as a function of temperature; (b) under 100 MVm⁻¹ uni-polar square wave of 0.05 Hz at 50 °C as a function of field cycle number, and (c) at 50 °C under different electric field amplitude. ΔSavg (~ ΔSins) as a function of...
temperature is also presented in (c). Data points are shown and solid curves are drawn to guide eyes. At 180 MVm$^{-1}$, $\Delta S_h$ is 190 Jkg$^{-1}$K$^{-1}$ and $\Delta S_{int} \approx 160$ Jkg$^{-1}$K$^{-1}$.

Through literature search, it can be noted that Furukawa and Takahashi have evaluated the dipolar entropy in the disordered phase of P(VDF-TrFE) copolymer (crystalline phase) by linking them to the molecular conformations of the polymer chains.[111] By assuming the molecular conformation of the dipolar-disordered copolymer adapts a mixture of trans-trans (TT), trans-gauches (TG), and TG’ with some degree of correlations, the dipolar entropy $S(0,T)$ is derived to be 4 Jmol$^{-1}$K$^{-1}$ (or 62.7 Jkg$^{-1}$K$^{-1}$), which is apparently much smaller than $\Delta S_h$ of 190 Jkg$^{-1}$K$^{-1}$ in the normal ferroelectric material near the FE-PE transition under 100 MVm$^{-1}$ field. This value is also smaller than $\Delta S_h$ in the 65/35 mol% copolymer at 35 °C, which is far below FE-PE transition. If the molecular conformation of dipolar disordered phase is a random mixture of TT, TG, and TG’, the dipolar entropy $S(0,T)$ is increased to 9 Jmol$^{-1}$K$^{-1}$ (or 141 Jkg$^{-1}$K$^{-1}$), which is still smaller but closer to the 190 Jkg$^{-1}$K$^{-1}$ observed here. For the case of the conformation of all carbon-carbon bonds consisting of random T and G sequences, a $S(0,T)$ of 18 Jmol$^{-1}$K$^{-1}$ is derived. The high crystallinity (>80 %) of the copolymer studied here will not change the comparison very much. The results indicate that there might exist multiple intermediate phases with different degrees of dipolar disorder in the normal ferroelectric copolymer, resulting in a large entropy $S(0,T)$ near the first order FE-PE transition due to mixing of these states.

To summarize, directly measured ECE is presented from the P(VDF-TrFE) 65/35 mol% copolymer which displays a first order FE-PE transition. The data reveal that there is a large difference in the ECE between that measured in applying field and in removing the electric field. Near the FE-PE transition, a $\Delta S_h \geq 190$ Jkg$^{-1}$K$^{-1}$ is observed under 100 MVm$^{-1}$. After a few field cycles, $\Delta S_h$ and $\Delta S_c$ becomes nearly the same, implying that a $\Delta S_{int} \approx 67$ Jkg$^{-1}$K$^{-1}$ under 100 MVm$^{-1}$ can be induced at the FE-PE transition and the largest ECE occurs at the first order FE-PE transition temperature.
By modifying the copolymer with 20 Mrads of high energy electron irradiation, the hysteresis is substantially reduced. At the dielectric peak of 50 °C, $\Delta S_{\text{int}}$ becomes $72 \text{ Jkg}^{-1}\text{K}^{-1}$ under 100 MVm$^{-1}$. Under a 180 MVm$^{-1}$, $\Delta S_h = 190 \text{ Jkg}^{-1}\text{K}^{-1}$, $\Delta S_{\text{int}} \sim 160 \text{ Jkg}^{-1}\text{K}^{-1}$ and $\Delta T_{\text{int}} = 35 ^\circ \text{C}$ can be induced. Even including the loss, the directly measured data show that the irradiated copolymer still exhibits $\Delta S_c = 130 \text{ Jkg}^{-1}\text{K}^{-1}$ and $\Delta T_c = 28 ^\circ \text{C}$ under 180 MVm$^{-1}$. $\Delta S$ obtained here is much higher than that achievable in P(VDF-TrFE) with a continuous phase transition ($\Delta S = 34 \text{ Jkg}^{-1}\text{K}^{-1}$ under 100 MVm$^{-1}$ at the transition temperature for 55/45 mol% copolymer) and in the P(VDF-TrFE) based relaxor ferroelectric polymers ($\Delta S \sim 40 \text{ Jkg}^{-1}\text{K}^{-1}$ under the 100 MVm$^{-1}$).

The large difference between $\Delta S_h$ and $\Delta S_c$ also suggests that there are intermediate states with a large difference in dipolar ordering but a small free energy difference, which is consistent with earlier experimental observations. The mixing of large number of coexisting phases near the first order FE-PE transition leads to the high ECE observed. These results demonstrate the promise of achieving a significant ECE in ferroelectric polymers or ferroelectrics in general by operating near first order FE-PE transition in which multiple intermediate phases can exist. By properly modifying (or tailoring) these materials, the hysteresis losses can be significantly reduced while a significant ECE can be maintained.

In contrast to Figure 3-8(a), the electrocaloric effect as a function of temperature in irradiated P(VDF-TrFE) 65/35 mol% copolymers with 0 Mrad, 20 Mrads, 40 Mrads, 60 Mrads and 75 Mrads during cooling process, i.e., as sample temperature decreases, is presented in Figure 3-14. The peak temperatures of ECE in P(VDF-TrFE) 65/35 mol% copolymer and irradiated P(VDF-TrFE) 65/35 mol% copolymer with 20 Mrads measured during cooling process shift to lower end compared with those measured during heating process, respectively, which indicates the existence of hysteresis in these two series of samples. On the other hand, the ECE response in irradiated P(VDF-TrFE) 65/35 mol% copolymer with 40 Mrads exhibits little difference in
heating and cooling processes, thus further proving that the hysteresis in the P(VDF-TrFE) 65/35 mol% copolymer has been mostly eliminated when irradiation dose reaches 40 Mrads, and the material becomes relaxor ferroelectric.

Figure 3-14 Entropy change as a function of temperature in irradiated P(VDF-TrFE) 65/35 mol% copolymers with different doses during cooling process, measured at a constant electric field of 100 MVm$^{-1}$.

The ECE data acquired upon applying and removing electric field during cooling process are summarized in Figure 3-15. Again, the entropy change difference between two cycles gradually decreases as irradiation dose increases. By comparing entropy change results in 0 Mrad, 20 Mrads and 40 Mrads samples, it can be seen that irradiation lowers peak temperature yet only moderate dose increases the absolute value of ECE response. Therefore, it is critical to control dose when modifying P(VDF-TrFE) copolymer using high-energy electron irradiation.
Figure 3-15 Comparison of entropy change between applying and removing electric field in copolymer P(VDF-TrFE) 65/35 mol% with 0 Mrads, 20 Mrads and 40 Mrads, measured during cooling process.

3.3 Other irradiated copolymers

3.3.1 Irradiated P(VDF-TrFE) 75/25 mol% Copolymer

In P(VDF-TrFE) copolymer, generally the lower the TrFE content is, the more ferroelectric the copolymer is. In other words, P(VDF-TrFE) with lower TrFE content is more difficult to be converted from normal ferroelectric into relaxor ferroelectric through defect modification such as high energy electron irradiation. Thus it can be predicted that for P(VDF-TrFE) 75/25 mol%, which has a lower TrFE content compared with P(VDF-TrFE) 65/35 mol%, its properties will be more close to normal ferroelectric.

P(VDF-TrFE) 75/25 mol% copolymer was prepared using solution casting method followed by annealing process, both of which have been described earlier in the previous section of P(VDF-TrFE) 65/35 mol%. Again the irradiation was carried out using the facility at NIST, in
a N₂ atmosphere to avoid oxidation of the polymers in the irradiation. The specially designed setup allowed heating which provided high temperature above the phase transition of P(VDF-TrFE) 75/25 mol%. The electron energy about 1.2 MeV was used for the irradiation. To avoid possible overheating of the polymer films in the irradiation process, the irradiation rate is maintained at 1 Mrad per minute. For P(VDF-TrFE) 75/25 mol%, the irradiation dose was fixed at 60 Mrads. The characterization conditions for dielectric constant, hysteresis loop, DSC, and electrocaloric effect were the same as those shown in the previous section of P(VDF-TrFE) 65/35 mol%, therefore would not be repeated hereby for the sake of space saving.

The dielectric constant of irradiated copolymer 75/25 mol% is presented in Figure 3-16. The dielectric peaks in both P(VDF-TrFE) 75/25 mol% copolymer and irradiated P(VDF-TrFE) 75/25 mol% copolymer show weak dependence on measuring frequency, representing the sample still remains in the normal ferroelectric phase, even with an irradiation dose of 60 Mrads. Intriguingly, high energy electron irradiation shifts dielectric constant peak temperature as well as lowers dielectric constant peak value, yet it fails to convert the copolymer into relaxor ferroelectric phase, which should exhibit strong frequency dependence for both dielectric constant peak and loss peak. The comparison between the two in Figure 3-16 also illustrates the fact that high energy electron irradiation does reduce the dipole correlation and crystallinity in the P(VDF-TrFE) 75/25 mol% copolymer, yet again, the material still remains rather normal ferroelectric since it is more resistant to irradiation. It should be also noted that a peak around 20 °C corresponding to the glass transition of nonpolar phase gradually disappeared as measuring frequency increases. That is because those nonpolar regions could not follow the switching speed of the AC field thus do not contribute to the dielectric constant as frequency increased to MHz level. Also conduction loss due to defects and impurities followed the same rule, i.e., at high measuring frequency they do not respond to the AC field therefore do not contribute to dielectric constant.
The hysteresis loop data are presented in Figure 3-17 (a) and (b). Figure 3-17 (a) shows the unipolar P-E loops measurement at 100 MVm\(^{-1}\) and 10 Hz during heating process. It can be observed that the hysteresis is still relatively large compared with the slim loops in irradiated P(VDF-TrFE) 65/35 with 60 Mrads, which further confirms that irradiation dose of 60 Mrads is not able to convert 75/27 into relaxor ferroelectric. As measuring temperature increases, the polarization value also increases, which can be attributed to more conduction loss in the sample. Similarly in the bipolar P-E loop, the hysteresis loss is large and as temperature rises, the polarization value increases as well.

Figure 3-17 (a) unipolar and (b) bipolar hysteresis loop data measured in irradiated P(VDF-TrFE) 75/25 mol% as a function of temperature from 0 °C to 60 °C.
The ECE data in Figure 3-18 illustrates a clear characteristic behavior for normal ferroelectric, which shows a large response only around F-P transition. Such an observation can be attributed to the fact that at temperature below F-P transition, it is very difficult to rotate and realign the dipoles by external electric field since the correlation length (or domain size) is too large. Also the difference of entropy change acquired between applying and removing the electric field is large, possibly because of large hysteresis which causes excessive heat and prevents the dipoles to rotate freely. These results once again confirms that irradiation has little impact on the structure of P(VDF-TrFE) 75/25 mol% copolymer.

![Figure 3-18 ECE as a function of temperature in irradiated P(VDF-TrFE) 75/25 mol% with 60 Mrads measured under constant electric field of 60 MVm⁻¹.]

### 3.3.2 Irradiated P(VDF-CTFE) Copolymer

The dielectric constant of P(VDF-CTFE) and irradiated P(VDF-CTFE) is shown in Figure 3-19. It can be observed that dielectric constants under various frequencies decrease upon irradiation, which may be attributed to the reduction of correlation length in the irradiated samples. On the other hand, the dielectric loss at 1 KHz is suppressed while loss above 10 KHz increases after the irradiation process.
Figure 3-19 Dielectric constant as a function of temperature and frequency in P(VDF-CTFE) copolymer and irradiated P(VDF-CTFE) copolymer.

DSC data also reveal the reduction of correlation length, i.e., crystallite size or ferroelectric domain size in irradiated copolymer, as evidenced in Figure 3-20. Before irradiation the melting temperature of P(VDF-CTFE) copolymer is 150.60 °C, compared with the lower melting temperature at 108.59 °C in irradiated P(VDF-CTFE) copolymer. It should be noted that during first heating process, the heat of fusion shows little difference, indicating the crystallinity does not change much upon irradiation.

Figure 3-20 DSC data as a function of temperature during first heating and cooling cycle in P(VDF-CTFE) copolymer and irradiated P(VDF-CTFE) copolymer.

The ECE entropy change as a function of temperature under constant electric field of 150 MVm⁻¹ measured in irradiated P(VDF-CTFE) with 60 Mards is presented in Figure 3-21. As
temperature rises, the difference between entropy change acquired on application of electric field and that on removal of electric field becomes larger, suggesting that higher temperature favors mechanisms that increase hysteresis and other types of loss, which hinders ECE during the cooling half-cycle.

![Figure 3-21](image)

Figure 3-21 ECE as a function of temperature in irradiated P(VDF-CTFE) copolymer under constant electric field of 150 MVm$^{-1}$ during heating process. Data acquired on both applying and removing electric field are compared.

### 3.3.3 Irradiated P(VDF-HFP) Copolymer

Similar to the experimental data observed in irradiated P(VDF-CTFE) copolymer, the dielectric constant, DSC and ECE results in irradiated P(VDF-HFP) copolymer also indicate that while irradiation breaks long correlation, or reduce correlation length and ferroelectric domain size, it has little impact on improving ECE. Since the gap between heating half-cycle and cooling half-cycle is large and even further broadens as temperature increases. Such observation is in clear contrast with the impact of high-energy electron irradiation on P(VDF-TrFE) 65/35 mol%.
Figure 3-22 Dielectric constant as a function of temperature and frequency in P(VDF-HFP) copolymer and irradiated P(VDF-HFP) copolymer.

Figure 3-23 Dielectric constant as a function of temperature and frequency in P(VDF-HFP) copolymer and irradiated P(VDF-HFP) copolymer.

Figure 3-24 ECE as a function of temperature in irradiated P(VDF-HFP) copolymer under constant electric field of 150 MVm$^{-1}$ during heating process. Data acquired on both applying and removing electric field are compared.
Based on the discussion above, it is concluded that high energy electron irradiation is able to affect the structures and properties of \( \text{P(VDF-TrFE)} \ 65/35 \), while for \( \text{P(VDF-TrFE)} \ 75/25 \) and \( \text{P(VDF-CTFE)} \) and \( \text{P(VDF-HFP)} \) the irradiation has little impact on the materials’ behaviors. It is believed that in order for irradiation to play a role in the copolymers, an aforehand interchain distance expansion is needed, by using the TrFE which is larger than VDF yet compatible with PVDF crystal. In \( \text{P(VDF-TrFE)} \) with high VDF content (>75%), the microstructure is close to that of PVDF thus irradiation is not able to effectively introduce defects into the system by crosslinking and expanding the interchain distance. For \( \text{P(VDF-CTFE)} \) and \( \text{P(VDF-HFP)} \), since the sizes of CTFE and HFP units are too large to be included into the PVDF crystal, the irradiation is not effective in these two copolymers due to the small inter-chain distance.

### 3.4 Summary

Chapter 3 aims at providing an insight of how high-energy electron irradiation impacts different PVDF-based copolymer, and thus modifies their properties, especially electrocaloric effect. The high-energy-electron irradiation, by introducing defects into the \( \text{P(VDF-TrFE)} \) copolymer, modifies dielectric properties and thus ECE response of the films. As irradiation dose increases, the \( \text{P(VDF-TrFE)} \ 65/35 \) mol% copolymer gradually transforms from normal ferroelectric into relaxor ferroelectric material, with dielectric constant peak and ECE response peak shift from high temperature to room temperature. In irradiated \( \text{P(VDF-TrFE)} \ 65/35 \) mol% copolymer with 20 Mrads, an entropy change as high as 130 J Kg\(^{-1}\)K\(^{-1}\) and large temperature change of 28 °C. Thus, moderate irradiation dose is preferred since large ECE can be generated around temperature range that is of significance to practical applications such as on-chip cooling and refrigeration. It should be noted that the mechanical stretching process does not change the
dielectric properties and ECE response in the irradiated copolymer films, possibly due to the fact that the impact of uniaxial stretching on copolymer microstructure is eliminated by the following high energy electron irradiation. Cycle impact is also observed, where as ECE measurement repeats, the entropy change from the heating half-cycle decreases while that from the cooling half-cycle increases and eventually those two entropy changes merge into one, which is the intrinsic entropy change in irradiated P(VDF-TrFE) 65/35 mol% copolymer.

In P(VDF-TrFE) with high VDF content (> 75 mol%), the microstructure is close to that of PVDF with closely packed crystallites and strong ferroelectricity thus irradiation is not able to effectively introduce defects into the system by crosslinking and expanding the interchain distance. Similarly, for P(VDF-CTFE) and P(VDF-HFP), since the sizes of CTFE and HFP units are too large to be included into the PVDF crystal, thus in these two copolymers the irradiation is not effective possibly due to the small inter-chain distance.
Chapter 4
ECE in P(VDF-TrFE-CFE) terpolymer

4.1 Motivation

There are many similarities between relaxor ferroelectric irradiated P(VDF-TrFE) copolymer and relaxor ferroelectric P(VDF-TrFE-CFE) terpolymers. Both exhibit slim hysteresis loop with low dielectric loss as well as a broad FE-PE transition, which are desirable for electrocaloric applications. Since ECE shows a weak temperature dependence in irradiated P(VDF-TrFE) 65/35 mol% copolymer with 40 Mrads, as the material system is in relaxor ferroelectric phase, a large response should also be achieved over a broad temperature range in the relaxor P(VDF-TrFE-CFE) terpolymer. Besides, as discussed in Chapter 1, large entropy change over a wide temperature range is crucial for development ECE cooling device with high efficiency and large temperature span, thus making relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer an excellent candidate for realizing practical cooling device.

Electrocaloric and dielectric response in P(VDF-TrFE-CFE) relaxor terpolymers are investigated as a start of this chapter. Specially, the impact of uniaxial stretching on the ECE behavior in P(VDF-TrFE-CFE) terpolymer is elaborated. It is known that stretching of polymer films strongly affects their microstructure, i.e., the conformation of polymer chains. For example, a well known ferroelectric polymer PVDF spontaneously crystallizes into a nonpolar trans-gauche chain conformation or α phase, which is transformed into a ferroelectric all-trans conformation or β phase only after uniaxial stretching at least 3 times the original length.[112] It has been found that the uniaxial stretching changes the dipole alignment, thus the entropy of disorder states, and affect the dielectric and electrocaloric effect, despite the fact that the low-field
complex dielectric constant is almost identical in the non-stretched and stretched samples. Interestingly, different from the fact that the uniaxial stretching has little impact on electrocaloric properties of irradiated copolymers, it is shown that relaxor P(VDF-TrFE-CFE) terpolymer exhibits a large ECE response ($\Delta T >15^\circ\text{C}$) which is also nearly temperature independent from 5 $^\circ\text{C}$ to 45 $^\circ\text{C}$ for non-stretched films. On the other hand, the uniaxially stretched terpolymer films exhibit a much pronounced temperature variation of ECE over the same temperature range. The results here reveal the possibility of tuning the temperature dependence of ECE by tailoring the material processing conditions, which can influence the number of possible polar-states and polar-correlations in relaxor ferroelectrics.

It is also important to understand the fundamental physics behind these novel ferroelectric behaviors for terpolymers and how the defects impact the material structures and thus ECE properties. Fundamentally, the crystalline structure is a major factor that affects the ferroelectric behavior of polymers, and specially electrocaloric effect. For P(VDF-TrFE) random copolymers, repeating unit isomorphism takes place,[113] because TrFE is similar in both chemical structure and size as VDF. When CFE monomer is introduced into P(VDF-TrFE) lattice, it randomizes the system and reduces the polar correlation in the polymer. In other word, the normal ferroelectric copolymer is converted into relaxor ferroelectric terpolymer. For a microscale level, the size of CFE is larger than that of TrFE or VDF as shown in Figure 4-1, CFE units also increase the distance between polymer chains thus reduce hysteresis loss as a result. It can be concluded that CFE units plays the same role as high-energy electron irradiation does.
Figure 4-1 Schematic illustration of VDF (VF$_2$), TrFE(VF$_3$) and CFE monomers.

Finally, the comparison of ECE data measured in P(VDF-TrFE-CFE) terpolymer by both indirect and direct methods is presented, in order to explain the special case of the relaxor ferroelectric terpolymer and further complete the previous discussion in Chapter 2 on the limitation of indirect method using Maxwell relations. The results show that the directly measured $\Delta T$ in the relaxor terpolymer is much larger than that indirectly deduced from Maxwell relation. The large difference between the directly measured $\Delta T$ and that deduced indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers, which are nonergodic (polar-glass) material systems.

4.2 Experimental

P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer was synthesized using a suspension polymerization process by Piezotech (France). The films were fabricated using a solution-cast method by dissolving P(VDF-TrFE-CFE) powders in N,N-dimethyl formamide (DMF) solvent. Then, the polymer solution was cast onto clean glass plates. The terpolymer solution coated glass plates were dried at 70 °C for 22 hrs in an oven and then the terpolymer films were peeled off from the plates and annealed at 105 °C for over 10 hours to increase crystallinity and further remove the residual solvent. Some of the films were uniaxially stretched 4 times of the original length while others remained non-stretched in order to study how the unaxial stretching of the films affects various terpolymer properties. The thickness of non-stretched film was 30 µm and the thickness of stretched film was 7 µm. Gold electrodes were sputtered on both sides of the films for electric characterization. The ECE, dielectric properties, DSC and polarization responses are measured in the same manner as irradiated copolymers described in Chapter 3.
4.3 ECE in Stretched and Nonstretched P(VDF-TrFE-CFE) Terpolymer

ECE as a function of temperature under different applied electric fields for non-stretched films is presented in Figure 4-2(a). The inset shows the adiabatic temperature change $\Delta T$ as a function of applied field acquired at 30 °C, where $\Delta T > 15$ K is induced under 150 MVm$^{-1}$. Besides a very large ECE, the data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what observed in the normal ferroelectric P(VDF-TrFE) copolymer in Chapter 3, where ECE shows a sharp peak at FE-PE temperature. Compared with the ECE performance of irradiated P(VDF-TrFE) 65/35 mol% copolymer with 40 Mrads, the property of P(VDF-TrFE-CFE) terpolymer is improved in terms of temperature change, as at 100 MVm$^{-1}$ $\Delta T$ measured in terpolymer from 5 °C and 50 °C would exceed 6 °C while $\Delta T$ in irradiated copolymer 65/35 mol% with 40 Mrads is less than 6 °C. Such a difference indicates that both being relaxor ferroelectric materials, P(VDF-TrFE-CFE) terpolymer is an even more promising system compared with irradiated P(VDF-TrFE) 65/35 mol% copolymer.

Figure 4-2(b) presents $\Delta T$ for stretched terpolymer films as a function of temperature under 100 MVm$^{-1}$ field and inset shows the field dependence of $\Delta T$ measured at 30 °C. At 30 °C, both non-stretched and 4 times uniaxially stretched films display nearly the same ECE, e.g., $\Delta T$ measured at 150 MVm$^{-1}$ is above 15 °C, as observed in the non-stretched P(VDF-TrFE-CFE) terpolymer samples. What is interesting is that within the same temperature range (from 0 °C to 55 °C), the uniaxially stretched films display much pronounced temperature variation and at 5 °C and 55 °C, $\Delta T$ of the ordered uniaxially stretched films is more than 15% smaller, compared with that of the non-stretched films. It can be tentatively concluded that uniaxially stretching process, while may induce more polar phase and increase the crystallinity in the terpolymer, is an unfavorable factor for ECE properties by rendering a strong temperature dependence which is undesirable for ECE cooling device perspective.
Figure 4-2 (a) Adiabatic temperature change of ECE as a function of sample temperature, (b) and as a function of electric field at 30 °C in non-stretched P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer under different constant electric field of 50 MVm⁻¹ – 100 MVm⁻¹, while inset shows the adiabatic temperature change of ECE as a function of applied electric field. (c) Adiabatic temperature change of ECE as a function of sample temperature, (d) and as a function of electric field at 30 °C in stretched P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer under constant electric field of 100 MVm⁻¹, while inset shows the adiabatic temperature change of ECE as a function of applied electric field.

As a comparison, the induced polarization under a unipolar field of the two types of films was measured at frequency of 10 Hz, over the same temperature range from 5 °C and 55 °C. The data presented in Figure 4-3 reveal that the induced polarizations of two types of films show similar temperature variation. In fact, the polarization level of the uniaxially stretched films is slightly higher than that of non-stretched films. Yet again, polarization value in stretched samples show strong temperature dependence, i.e., as temperature increases, the polarization value of
stretched terpolymer quickly reduces to the same level of non-stretched terpolymer. Such phenomenon can be interpreted in the following way: uniaxial stretching induces ferroelectric phase and may increase crystallinity, both of which increase the polarization level, while as temperature increases, the weak ferroelectric phase induced by stretching disappears or transfers into paraelectric phase which makes little contribution to polarization.

![Figure 4-3](image)

**Figure 4-3** (a) Polarization data in non-stretched P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer. (b) Polarization data in stretched P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer.

These results indicate that even though the two types of films exhibit similar level of macroscopic polarization responses, there exist differences in the microscopic and molecular origins of these polarization responses.

ECE in a dielectric is determined by the dipolar entropy change $\Delta S_p$ between the polar- and non-polar states, i.e., $\Delta S_p = S_p(0,T) - S_p(E,T)$, where $S_p(0,T)$ is the dipolar entropy when $E=0$ and $S_p(E,T)$ corresponds to the dipole aligned state when external electric field $E$ is applied. As shown by Pirc et al., for a dipolar disordered state at $E=0$ such as the relaxor at temperatures above the broad dielectric constant peak here, $S_p(0,T)$ is proportional to $P^2 \ln(\Omega)$, where $\Omega$ is the number of possible polar states in the dielectrics, while $S_p(E,T)$ can be approximated as zero (much smaller than $S_p(0,T)$) when $E$ is high.[100] Therefore, in general, $\Delta S_p$ or $\Delta T$ under a given
field E will increase as temperature is reduced towards the broad dielectric constant peak (P increases with reduced temperature). As the temperature is further lowered towards the freezing temperature of the relaxor, remanent polarization will be developed after application of high electric fields, which will result in a decrease of $\Delta S_p$ with reduced temperature.[31, 100, 101, 105, 114] Uniaxial stretching of terpolymer films causes preferred polymer chain orientation and hence reduces the number of possible polar states in the dipolar-disordered states and hence $\Omega$. Consequently, $\Delta S_p$ is reduced due to a reduced $\Omega$ at temperatures above the broad dielectric peak.

In addition, uniaxial stretching in general will favor all-trans molecular conformation and hence increase the polar-correlation which might be the reason for the faster reduction of ECE with reduced temperature below the broad dielectric maximum in the uniaxially stretched films.[112] Increasing polar-correction length in the relaxor polymer at E=0 state will cause a reduction of $S_p(0,T)$. These results indicate that ECE temperature behavior of relaxor polymer or even normal ferroelectric polymer can be tailored by controlling the polymer film processing conditions. Moreover, large ECE with weak temperature dependence in non-stretched terpolymer is attractive for various cooling applications over a broad temperature range, especially for ECE cooling device with high efficiency and large temperature span.

4.4 Structural and Dielectric analysis

In order to obtain a deep understanding on the ECE behaviors in P(VDF-TrFE-CFE) terpolymer, structural and dielectric analysis are conducted. From the discussion in Chapter 3, it has been pointed out that expanded interchain distance and nanodomains with reduced spontaneous polarization are critical to reduce intermolecular friction in ferroelectric crystals. This knowledge is helpful for the design and development of novel ferroelectric polymers with large electrocaloric response. To further expand the interchain distance, an even larger monomer
than TrFE needs to be incorporated into the P(VDF-TrFE) random copolymers. Possible candidates are 1,1-chlorofluoroethylene (CFE), chlorotrifluoroethylene (CTFE), and hexafluoropropylene (HFP).[115] Intriguingly, direct copolymerization of VDF with these monomers most likely will not result in the formation of repeating unit isomorphism because of their large sizes. For example, CTFE repeating units are mostly excluded from the PVDF crystals in P(VDF-CTFE) and no expansion of the interchain distance is observed experimentally. On the other hand, TrFE repeating units can be integrated into the PVDF crystals and thus expand the interchain distance in the material structure.[111, 116] Therefore, presence of TrFE in PVDF is important for the third comonomer to be incorporated in the crystal and further expand the interchain distance.

In this study, P(VDF-TrFE-CFE) 59.2/33.6/7.2 terpolymer is used as an example to probe the ferroelectric behavior after further enlarging the interchain distance. With 7.2 mol% of CFE content, the ferroelectric (FE) P(VDF-TrFE) has been successfully converted into a relaxor ferroelectric (RFE) terpolymer.[117] DSC results are presented in Figure 4-4 to explore the thermal properties and crystal structures of both non-stretched and stretched terpolymers. Stretching terpolymer thin film increases its crystallinity, as can be seen in Figure 4-4(a), the melting enthalpy of stretched terpolymer is 26.12 J g\(^{-1}\) compared with that of non-stretched terpolymer at 23.55 J g\(^{-1}\). The stretching process does not affect the melting point, though. Meanwhile, upon mechanical stretching, a certain amount of ferroelectric phase is developed, which is reflected in the first heating curve in DSC (Figure 4-4 (b)). From DSC, two \(T_c\)s are observed with a weak peak at 27 °C corresponding to the relaxation process of amorphous phase, and another peak at 49 °C corresponding to the ferroelectric-paraelectric phase transition. After melt-recrystallization, only one broad \(T_c\) is seen at 22 °C for the second heating in Figure 4-2(b), meaning the induced ferroelectric phase has disappeared after the first heating process. Note that
mechanical stretching results in a larger ferroelectric domain size and thus a slightly higher $T_C$ at 27 °C for the terpolymer.

Crystal orientations in the uniaxially stretched P(VDF-TrFE-CFE) terpolymer film during the first and second heating cycles are shown in Figure 4-5. The one-dimensional (1D) WAXD
profiles on both equator and meridian during the first heating cycle are shown in Figure 4-5 (a). At -38 °C, the \((110/200)_{\text{RFE}}\) reflection is seen at 4.81 Å, which is similar to the \((110/200)_{\text{PE}}\) reflection (4.86 Å) of the P(VDF-TrFE) 50/50.[118] The \((110/200)_{\text{FE}}\) reflection appears as a shoulder at 4.57 Å. As the temperature increases to 47 °C, both \((110/200)_{\text{FE}}\) and \((001)_{\text{FE}}\) reflections disappear, indicating ferroelectric phase transfers into paraelectric phase, which corresponds to the DSC results in Figure 4-4. The \((110/200)_{\text{RFE}}\) reflection continuously shifts to lower \(q\) values and finally the \((110/200)_{\text{PE}}\) \(d\)-spacing increases to 4.98 Å at 90 °C, again, suggesting the ordered ferroelectric phase to the disordered paraelectric phase. After the first heating cycle, the stretch-induced FE phase disappears and 1D WAXD profiles during the second heating cycle are shown in Figure 4-3(b). Upon increasing the temperature, the \((110/200)\) reflection continuously shifts to lower \(q\) values, and correspondingly the \(d\)-spacing increases from 4.84 Å at -38 °C to 4.98 Å at 90 °C. Regardless of the \((110/200)\) \(d\)-spacing changes, the \((002)\) reflection remains constant at 27.4 nm\(^{-1}\), with \(d\)-spacing of 2.29 Å.
Figure 4-5 1D WAXD profiles of stretching terpolymers for the equator and meridian reflections during (a) the first and (b) the second heating cycles.

In addition to DSC and WAXD, FTIR is another useful technique to detect chain conformations and local bonds for polymers. The FTIR results for the uniaxially stretched P(VDF-TrFE-CFE) terpolymer film during the first and second heating cycles are shown in Figure 4-6. From the first heating cycle (Figure 4-6(a)), the long T sequence for the stretch-induced FE phase is evidenced by absorption bands at 507, 848, and 1287 cm\(^{-1}\).
Note that all trans conformation can be obtained for the P(VDF-TrFE-CFE) terpolymers due to the presence of VDF to relieve the steric hindrance caused by the large Cl atoms in the main chain. Upon increasing the temperature to 45 °C, the band at 507 cm\(^{-1}\) (the second dashed line from the right) gradually disappears and a new doublet band at 514/527 cm\(^{-1}\) appears, indicating the FE\(\rightarrow\)PE transition. The band at 848 cm\(^{-1}\) decreases its intensity and the band at 1287 cm\(^{-1}\) disappears. Meanwhile, another doublet band at 605/614 cm\(^{-1}\) becomes more pronounced. Note that the absorption bands at 514/527 and 605/614 cm\(^{-1}\) can be assigned to mixed TG and TTTG conformations. After cooling from 90 °C to -40 °C in Figure 4-6(b), the stretch-induced FE phase disappears, because the bands at 507, 848, and 1287 cm\(^{-1}\) become weaker and the bands at 514/527 and 605/614 cm\(^{-1}\) become stronger. Intriguingly, two bands at 772 and 800 cm\(^{-1}\) become much more pronounced, and they are assigned to the T\(_3\)G sequence for the \(\gamma\) PVDF crystal. Therefore, a short T sequence (i.e., nanodomains) results for the RFE P(VDF-TrFE-CFE). This is possibly attributed to the random sequence of CFE along the chain [i.e., 14 repeating units of VDF/TrFE per CFE unit]. During the second heating cycle in Figure 4-6(b), the bands at 772 and 800 cm\(^{-1}\) clearly decrease their intensities. This indicates the disappearance of nanodomains with a short T\(_3\)G sequence above the \(T_C\) at 22 °C.
The micro scale modification of CFE in P(VDF-TrFE-CFE) terpolymers is once again explained in the following section. In the first step, pre-expansion of the interchain distance in PVDF crystals by TrFE via repeating unit isomorphism is important, namely, $l_2 > l_1$ where $l_1$ and $l_2$ are interchain distances in PVDF and P(VDF-TrFE) crystals, respectively. This first step expansion of interchain distance makes it possible to further incorporate the even larger third comonomer, such as CFE and CTFE, into the isomorphic crystalline structure. A good example for this effect is to compare P(VDF-CTFE) with P(VDF-TrFE-CTFE). For P(VDF-CTFE), the CTFE repeating units are too large to be effectively incorporated in a PVDF crystal. As a result, most CTFE units are repelled from the PVDF crystal and no RFE behavior can be observed in P(VDF-CTFE).[17, 116] However, CTFE can be effectively incorporated into a P(VDF-TrFE) crystal, leading to an RFE behavior.[119, 120] The incorporation of the even larger third comonomer further expands the interchain distance, namely, $l_3 > l_2$, where $l_3$ is the interchain distance of the terpolymer crystal. Note that HFP cannot be effectively incorporated into P(VDF-TrFE) to form the RFE phase because the HFP unit is too large. Meanwhile, these larger comonomers can effectively pin the P(VDF-TrFE) chains, if they are randomly distributed along the chain. For example, in the P(VDF-TrFE-CFE) 59.2/33.6/7.2 terpolymer, on average two neighboring CFE units can pin about 14 VDF/TrFE repeating units. This pinning will allow the in-between P(VDF-TrFE) chains to rotate more freely because of the increased interchain distance. However, these CFE units can only provide temporary physical pinning. When the poling electrical field becomes high enough, dipoles start to switch because the CFE unit also has a dipole moment. Consequently, the high electric field will generate FE domains within the RFE matrix. However, these FE domains should be weaker than those formed by mechanical stretching because they can transform back to the RFE phase after a decrease in the poling field.
4.5 Dielectric Properties in Stretched and Nonstretched P(VDF-TrFE-CFE) Terpolymer

In this section dielectric properties in non-stretched and stretched terpolymers are investigated and compared. Figure 4-7 shows the temperature dependences of the real, $\varepsilon'$, and imaginary, $\varepsilon''$, parts of the complex dielectric constant, detected at various frequencies in the non-stretched P(VDF-TrFE-CFE) terpolymer in different dc bias electric fields. It can be clearly observed that the dielectric constant as well as the dielectric loss shift to higher temperature as frequency increases, which is a characteristic feature for relaxor ferroelectrics. Without bias field, an additional increase at high temperatures in both low-frequency $\varepsilon'(T)$ and $\varepsilon''(T)$ has been detected, representing the conduction loss of the system possibly due to the existence of ionic impurities. Another detected feature is barely noticeable dielectric relaxation in the temperature region of 250 K to 275 K, which is associated with the dynamic manifestation of the glass-to-rubbery state transition in the amorphous phase of the terpolymer. With dc bias electric fields, for the relaxor contribution, both $\varepsilon'$ and $\varepsilon''$ decrease, indicating the reduction of correlation length in the crystalline phase; and the dielectric peaks occur at lower temperatures, while there is almost no influence of the bias field on the glassy processes in the matrix. The conduction loss astonishingly decreases in low frequency range, i.e., below 0.3 KHz, as a strong increase of $\varepsilon''(T)$ curves in zero bias field at the highest measured temperatures is almost completely suppressed by the field. Obviously, the charge carriers or ionic impurities which are responsible for the conduction loss migrate in a dc bias electric field and become pinned, mainly at the interface of sample and electrode.
The comparison of the influence of the dc bias electric field on the dielectric response of the stretched and non-stretched samples measured at the frequency of 10 kHz is shown in Figure 4-8. As dc bias field increases, the dielectric constant decreases. Especially, when temperature rises above phase transition, the stretched terpolymer shows more pronounced reduction compared to its own peak value. On the other hand, the decrease of dielectric constant caused by the bias electric field is higher in the non-stretched samples; in the stretched terpolymer, the first two curves almost coincide, what is emphasized in the inset which shows normalized $\varepsilon'$ peak values as a function of the dc bias electric field in both samples. It is understandable since the uniaxially stretching process pre-aligns dipoles, rendering more ordered states in the sample, thus following dc bias electric field show less impact. While for non-stretched terpolymer, the dipoles stay in relatively random states, and will rotate and realign when external bias electric field is applied on the samples.
Figure 4-8 Dielectric constant as a function of temperature, detected at the frequency of 10 kHz in the stretched and non-stretched P(VDF-TrFE-CFE) samples in different dc bias electric fields (0, 11.8, 23.6, and 47.2 MVm\(^{-1}\)). The inset compares normalized $\varepsilon'$ peak values as a function of the dc bias electric field in both samples.

Indeed, Figure 4-9 shows that the nonlinear dielectric constant $\varepsilon_3$, which is a coefficient corresponding to $E^3$ in nonlinear dielectric constant expansion, is in the less-oriented non-stretched samples at all temperatures and both measured frequencies approximately twice higher than in the stretched terpolymer. The results exhibit more nonlinear behavior in non-stretched samples, indicating that more disorder states exist in the non-stretched samples. It should be noted that $\varepsilon_3$ for both non-stretched and stretched terpolymers stay positive, indicating the material system remains in relaxor phase even after the uniaxially stretching process.
Figure 4-9 Temperature dependence of the third order nonlinear dielectric constant $\varepsilon_3$, detected at two frequencies in the stretched and non-stretched P(VDF-TrFE-CFE) terpolymer.

In accordance with this fact, Figure 4-10 reveals that dc bias field has higher impact on the characteristic relaxation frequency of the non-stretched sample. The temperature evolution of the characteristic relaxation frequency is interesting by itself. While it follows the Vogel-Fulcher law, the temperature dependence is a combination of the ferroelectric and relaxor behaviors. This is associated with the evolution of the polymer system from the normal ferroelectric with a long-range polar order to relaxor with a short-range order system. Again, this is similar to the inorganic lanthanum-modified lead zirconate titanate ceramics (PLZT), where increasing of the La content transforms a ferroelectric PZT into a relaxor system via intermediate ferroelectric-relaxor compounds, where relaxor glasslike and ferroelectric order dominated regions coexist[108], here the introduction of CFE monomer, which breaks the polar all-trans configurations, also transforms a ferroelectric P(VDF-TrFE) into a complete relaxor system, such as P(VDF-TrFE-CFE) 68/32/9[105] via intermediate systems, as is the one being reported here. Therefore the impact of CFE monomer on P(VDF-TrFE) copolymers are analogous to that of high energy electron irradiation, as presented in Chapter 3.
Figure 4-10 Temperature evolution of the characteristic relaxation frequencies, determined from peaks in $\varepsilon''$, for both, the stretched and non-stretched P(VDF-TrFE-CFE) samples in different dc bias electric fields.

Although the temperature dependence of the low-field complex dielectric constant is almost identical in the non-stretched and stretched samples, the dc bias electric field obviously, via higher nonlinear contribution, more heavily alters the dielectric response of the less-oriented non-stretched terpolymer. Uniaxially stretching namely orders polymer chains in the amorphous matrix and changes the non-polar trans-gauche conformation into polar all-trans conformation in the crystallites. It is thus not surprising that the induced polarization is higher in the stretched sample. These results suggest that electrically induced properties of relaxor polymer films can be tailored by controlling the preparation conditions.

4.6 Comparison between Indirect and Direct Measurements of ECE in Terpolymer

In this section, the ECE in relaxor ferroelectric P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol% terpolymer is investigated by directly measuring the adiabatic temperature change $\Delta T$ in the polymer films upon variation in applied electric field and then compared with that obtained using Maxwell relations, i.e., the indirect measurement. The experimental results show that the directly measured $\Delta T$ near room temperature in these relaxor ferroelectric polymers is much larger than that deduced from the Maxwell relation. The results indicate that the Maxwell relation cannot be used to deduce ECE in the relaxor ferroelectric polymers.

The directly measured $\Delta T$ for the P(VDF-TrFE-CFE) terpolymer versus temperature under different applied electric fields is shown in Figure 4-11. Electric field up to 70 MVm$^{-1}$ was applied in the measurement and the terpolymer films still exhibit a $\Delta T = 3.6$ °C at room temperature. Besides, above 40 °C ECE under a fixed electric field decreases with increasing temperature. All these results are in sharp contrast to those deduced from the Maxwell relation.[8]
For example, the deduced ECE shows an increase with temperature in the same temperature range and is much smaller than that directly measured.\cite{8} The deduced ECE at 70 and 100 $\text{MVm}^{-1}$ presented in Figure 4-11 was obtained by using the $(\text{d}D/\text{d}T)_E$ data in Ref. \cite{8} and Maxwell relations (Equations 2.6 and 2.7). At 70 $\text{MVm}^{-1}$ deduced ECE from the pure terpolymer has a $\Delta T = 0.87 \, ^\circ\text{C}$, much smaller than that directly measured. As the temperature increases, the difference between the ECEs directly measured and deduced becomes smaller.

![Figure 4-11](image)

Figure 4-11 Temperature dependences of the directly measured $\Delta T$ (solid symbols) of the terpolymer under different measuring electric fields. The $\Delta T$ deduced from the Maxwell relation at 70 and 100 $\text{MVm}^{-1}$ (open circles and crosses) is also shown for comparison. The $\Delta T$ deduced from the Maxwell relation is much smaller than that directly measured. Data points are shown and solid curves are drawn to guide eyes.

Although the Maxwell relation has been widely used in deducing ECE from ferroelectric materials, there is a concern on its validity when applying it to relaxor ferroelectrics since these are nonergodic material systems, i.e., polar-glasses.\cite{101, 121} The Maxwell relation is derived based on the assumption that the thermodynamic system is ergodic.\cite{13, 28} The large difference between the directly measured $\Delta T$ and that deduced indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers, which are nonergodic (polar-glass) material systems.
It is noted that the directly measured results are from free-standing films while that deduced from the Maxwell relation was obtained from films fixed on substrates, which may cause some difference. The electric displacement $D$ of the free-standing films and films on substrates is measured and no difference in $D$ is found between the two. Since $\Delta T \sim D^2$, the results suggest that observed large difference in $\Delta T$ is not caused by different film conditions in the experiment. It should be pointed out that in the indirect ECE measurements, thin films (1 $\mu$m thick) with much smaller electrode ($1 \text{ mm}^2$ electrode area) on glass substrate was used,[8] which leaded to much higher breakdown field and measuring fields compared with large area electroded free-standing films used here. The results indicate that even at temperatures far above the relaxor freezing temperature and the broad dielectric constant peak temperature, the Maxwell relation cannot be used to deduce the ECE reliably in the relaxor ferroelectric polymers. On the other hand, it should be noted that under high electric fields, some relaxors can be converted to normal ferroelectric. In the field range, the Maxwell relation may be used to deduce the ECE for the relaxors.

4.7 Summary

The influence of uniaxial stretching on the electrocaloric, structural, and dielectric properties of P(VDF-TrFE-CFE) relaxor terpolymer has been investigated. Although the temperature dependence of the low-field complex dielectric constant is almost identical in the non-stretched and stretched samples, the dc bias electric field via higher nonlinear contribution more heavily alters the dielectric response of the non-stretched terpolymer. As stretching favors polar all-trans chain conformation, it creates more ordered states and thus increases the electric polarization. On the other hand, stretching decreases the number of possible polar states $\Omega$, and consequently, the electrocaloric response of the terpolymer is smaller, except near the temperature of the dielectric maximum where this effect is compensated by higher induced
polarization in the stretched sample. We can thus conclude that electrically induced properties of relaxor polymer films can be tailored by controlling the preparation conditions, which influence the trans-gauche and trans-trans polymer chain conformations.

ECE as a function of temperature under different applied electric fields for non-stretched films shows the adiabatic temperature change $\Delta T$ as a function of applied field acquired at 30 °C, where $\Delta T > 15 °C$ is induced under 150 MVm$^{-1}$. Besides a very large ECE, the data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what observed in the normal ferroelectric polymer where ECE shows a sharp peak at FE-PE temperature. Both non-stretched and uniaxially stretched films display nearly the same ECE. What interesting is that in the same temperature range from 0 °C to 55 °C, the uniaxially stretched films display much pronounced temperature variation and at 5 °C and 55 °C, $\Delta T$ of the uniaxially stretched films is more than 15% smaller, compared with that of the non-stretched films.

Besides, the directly measured electrocaloric effect and the indirectly measured results of P(VDF-TrFE-CFE) terpolymer are compared. The results show that the directly measured $\Delta T$ in the relaxor terpolymer is much larger than that indirectly deduced from Maxwell relation. The directly measured electrocaloric effect, i.e., the adiabatic temperature change $\Delta T$ of relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer is much larger than that deduced from Maxwell relation and that the relaxor terpolymer possesses a giant ECE at room temperature. The large difference between the directly measured $\Delta T$ and that deduced indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers, which are nonergodic material systems.
Chapter 5

ECE in P(VDF-TrFE-CFE)-based Composites

5.1 Introduction

It is well known that for polymeric materials, nanocomposites such as polymer blends are able to enhance various properties.[112, 122, 123] As for electrocaloric effect, the enhancement in polarization as well as crystallinity due to the interface effect between different components is especially favorable for large ECE. Besides, composite approach such as polymer/nano-particle blends, is another facile method of tuning polymer performances, and has demonstrated great success in enhancing dielectric, thermal, mechanical properties of ferroelectric polymers.[122-128] Moreover, the blends of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) also provide a model system to study how the random defects in the terpolymer further increase the polarization response and consequently ECE in the blends, by generating internal bias electric field upon poling.

In this chapter, several P(VDF-TrFE-CFE)-based composites, including P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends and P(VDF-TrFE-CFE) terpolymer/Zirconium dioxide (ZrO$_2$) nano-particle blends, are elaborated in terms of structural analysis, dielectric responses and most importantly, electrocaloric behaviors. A variety of electroactive properties of PVDF-based ferroelectric polymers can be tailored by polymer blending. In terpolymer/copolymer blends, when copolymer content is relatively low (<15 wt%), the coupling between the relaxor ferroelectric terpolymer and the nano-phase copolymer converts the normal ferroelectric copolymer into relaxor ferroelectric phase and also causes an increase in the crystallinity in the terpolymer structure, compared with that in the neat terpolymer. As a result,
the terpolymer/copolymer blends exhibit an enhanced relaxor polarization response and a significant increase in the electrocaloric effect. While copolymer content is high, the blends exhibit mixed structures of the two components, i.e., the terpolymer and copolymer fail to co-crystallize when copolymer content is higher than 20 wt%. By varying composition, the dielectric and ferroelectric properties of blends can be adjusted in the range between the copolymer and terpolymer. Moreover, blending a small amount of P(VDF-TrFE) of 10 wt% can cause a more than 10% increase in the crystallinity in the blends and a 30% increase in the adiabatic temperature change originated from electrocaloric effect over the entire experimental temperature range (20 °C – 60 °C).

An enhancement of ECE is also observed in relaxor ferroelectric terpolymer (P(VDF-TrFE-CFE))/ZrO₂ nanocomposites. The interface effect between the polymer matrix and nano-fillers enhances the polarization response and provides additional electrocaloric entropy changes. As a consequence, the nanocomposites exhibit a larger ECE than that of the neat terpolymer, i.e., the adiabatic temperature change of the nanocomposite with 3 vol% of nano-fillers is 120% of that of the neat terpolymer. The results, for the first time, demonstrate that ECE can be controlled and enhanced through nanocomposite approach in the ferroelectric polymers.

5.2 P(VDF-TrFE-CFE) Terpolymer/P(VDF-TrFE) Copolymer Blends

5.2.1 Experimental

P(VDF-TrFE-CFE) terpolymer and P(VDF-TrFE) copolymer powders were dissolved in N,N-dimethylformamide at room temperature, respectively. Then the two solutions were mixed by proper ratios for different blend compositions. The final solution was filtered using 0.2 µm sized polytetrafluoroethylene filters and then cast on cleaned glass plates and dried at 70 °C for
24 hrs. Afterwards, the films were peeled off from the glass plates and further annealed at 110 °C for 24 hrs. The thickness of final films is 8 ~ 10 µm.

The melting points and melting heat of the pure terpolymer and blends were measured by differential scanning calorimetry (DSC) (TA Q100). The heating rate is 10°C/min. The x-ray diffraction (XRD) was performed using a PANalytical X'Pert Pro MPD diffractometer equipped a copper target with an average wavelength of 1.542 Å. FTIR spectra were obtained using a Bruker V70 infrared spectrometer equipped with a diamond ATR accessory.

FTIR spectra were obtained using a Bruker V70 infrared spectrometer equipped with a diamond ATR accessory. To calculate the variation of infrared absorption intensities for polymer chains of all trans (T₃GT₃G’, absorbance peak at 1285 cm⁻¹), T₃GT₃G’ (504 cm⁻¹), and TGTG’ (613 cm⁻¹) conformation with respect to copolymer content, first, the fraction $F_i$ of each chain conformation in every sample was calculated:

$$F_i = A_i / (A_I + A_{II} + A_{III}),$$

where $i = I, II, III$, and $A_I, A_{II}, A_{III}$ are the absorption area of the chain conformations with all trans ($T_3GT_3G'$), $T_3GT_3G'$, and $TGTG'$, respectively. After this procedure, the total fraction of all the chain conformations in each sample is normalized to 1, thus the difference brought by the experiments can be eliminated.

Gold electrodes were sputtered on both surfaces of the polymer films for electric characterization. The dielectric properties as a function of temperature were characterized using a precision LCR meter (HP4284A) equipped with a temperature chamber (Delta9023). The data were recorded every 3°C. The dielectric properties as a function of frequency were recorded by a HP4294A Precision Impedance Analyzer from 40Hz to 10MHz. Polarization-electric field (P-E) loops were measured using a modified Sawyer–Tower circuit at a frequency of 10Hz at room temperature.
For ECE measurement, Al electrodes were thermally evaporated on both surfaces of the polymer films. The ECE temperature change was measured using a high sensitivity heat flux sensor in a precise temperature controlled chamber, as described earlier in Chapter 4.

5.2.2 Electrocaloric Properties and Polarization Responses

Figure 5-1(a) summarized the maximum polarization of each sample measured at 10Hz. All the samples’ maximum polarizations increase with elevation of electric field. The growth of polarization at low electric field (<100 MVm\(^{-1}\)) is faster than that at high electric field (>150MVm\(^{-1}\)), suggesting there is a gradual saturation in polarization. The blends with 5 wt% and 10 wt% copolymer exhibit higher polarization level than that of pure terpolymer at all electric field measured. For example, the polarization of the blends with 10 wt% of the copolymer is 0.095 Cm\(^{-2}\) at 300 MVm\(^{-1}\), higher than 0.088 Cm\(^{-2}\) of pure terpolymer. Although for the blends with 15 wt% of the copolymer, the enhancement in polarization becomes smaller, the polarization at fields below 150 MVm\(^{-1}\) is still higher than that of terpolymer. Changing frequency does not change the trend, indicating the enhancement of polarization is intrinsic and is not caused by conduction loss (data is not shown here). With further addition of the copolymer, the maximum polarization drops monotonously at all electric field. Figure 5-3(b) shows the variation of maximum polarization measured at 200 MVm\(^{-1}\) regarding to the composition of the blends, and the insets show the typical P-E loops of these samples. It can be clearly seen that small amount of the copolymer can enhance the polarization, while further increase in copolymer content will reduce the polarization.

As we discussed earlier, small amount of the copolymer added into the blends can be transformed into relaxor through interfacial couplings with the terpolymer. The crystallinity can also be increased as determined by DSC. Both the factors contribute to the enhancement of
relaxor behavior and polarization. The polar nanoscale regions in the terpolymer and blends with low copolymer content (<10 wt%) are randomly distributed and weakly coupled among each other. Therefore they can be easily aligned with electric field, and tend to go back to the random state upon the removal of external electric field. With increased copolymer content (15 wt% ~ 20 wt%), the interface effect becomes less effective, as evidenced by an increase in the broad dielectric constant peak towards higher temperature shown in following section. The addition of the copolymer will gradually increase the couplings between polar entities in the blends, which are not likely to depolarize upon removal of electric field. Since the unipolar electric field cannot reverse the polarization state in the blends, the difference between the polarization at zero electric field and maximum electric field becomes smaller and smaller with increasing content of the copolymer, just as the increased activation energy reflected by $T_f$ in Vogel-Fulcher equation and increased relaxation time (decreased $\alpha$) indicate.

An outcome of the tunable polarizations is the change in electrocaloric effect (ECE) in these polymer blends. The ECE is a result of direct coupling between the thermal properties such as entropy and electric properties such as electric field induced polarization in a dielectric material. Figure 5-1(c) presents the adiabatic temperature change ($\Delta T$) of the terpolymer as a function of electric field measured at room temperature. And $\Delta T$ also shows a composition-dependent behavior. A $\Delta T$ of 5.1 °C is observed for pure terpolymer under 100MVm$^{-1}$. The blends with 5 wt%, 10 wt%, and 15 wt% copolymer have $\Delta T$ of 6.5 °C, 7 °C, and 5.7 °C, corresponding to ~25%, ~35%, ~10% enhancement respectively. While for blends with 20 ~ 50wt% copolymer, the $\Delta T$ is 4.4 °C, 3.9 °C, 3 °C, and 2 °C, respectively. It should be noted that the P(VDF-TrFE-CFE) terpolymer with a composition of 62.5/29/8.5 mol% yield a lower ECE response compared with P(VDF-TrFE-CFE) 59.2/33.6/7.2 mol terpolymer demonstrated in Chapter 3, due to a higher VDF/TrFE ratio. Nevertheless, the trend of ECE increase is valid in the polymer blends when compared with pure terpolymer from the same composition.
Figure 5-1 (a) Maximum polarizations of the terpolymer and its blends measured at 10 Hz from 50MV/m$^{-1}$ to 300MV/m$^{-1}$. (b) Variation of maximum polarizations with respect to the composition of the blends measured at 10 Hz and 200MV/m$^{-1}$. The inset shows typical unipolar P-E loops of blends measured at 200MV/m$^{-1}$. (c) shows adiabatic temperature change as a function of electric field at room temperature.
The $\Delta T$ as a function of sample temperature under 100 MVm$^{-1}$ is shown in Figure 5-2. The $\Delta T$ displays a weak temperature variation, whose trend is similar to the temperature variation of the dielectric response observed in terpolymer and its blends. That is, the $\Delta T$ peak shifts towards higher temperatures with increased copolymer content, in analogous to the dielectric behavior. These results indicate that the dielectric responses observed in the blends affect directly the electrocaloric properties.

Figure 5-2 Adiabatic temperature changes measured in various blends as a function of temperature at 100 MVm$^{-1}$. Data points are shown and curves are drawn to guide eyes.

To make quantitative comparison, $\Delta S$ in a dielectrics is related to the electric displacement $D$ through

$$\Delta S = -\beta D^2/2,$$  \hspace{1cm} (5.1)

where $\beta$ is a coefficient. Applying $c_E \Delta T = T \Delta S$ yields the adiabatic temperature change

$$\Delta T = -\beta D^2/(2c_E),$$  \hspace{1cm} (5.2)

where $c_E$ is the specific heat capacity. Using the data in Figure 5-1(c) for $\Delta T$ at room temperature (25 $^\circ$C) and Figure 5-1(a) for $P$, $\beta$ in Equation 5.2 can be deduced for the blends. Within the experimental error, $\beta$ does not show marked change for those with low copolymer content (inset of Figure 5-3), indicating that the enhancement in ECE in blends is a direct consequence of the
enhanced polarization response. However, decrease in $\beta$ is found when copolymer content further increases, indicating the structure changes and formation of ferroelectric phase may be the reason of lowered electrocaloric effect.

Figure 5-3 $\Delta S$ vs $P^2$ for the terpolymer and its blends with the copolymer. The fitted straight lines are drawn to guide eyes. The inset shows changes in $\beta$ with respect to the copolymer content.

The ferroelectric properties are also investigated for the blends with high content of the copolymer. The coercive field for P(VDF-TrFE) copolymer are larger than 50 MVm$^{-1}$, which is an order of magnitude higher than that of traditional ferroelectric ceramics. To facilitate application of ferroelectric copolymer in organic electronics, it is essential to lower its coercive field ($E_c$) while maintaining a large polarization. It has been tried to fabricate blends with polar polymers like PMMA, but the amorphous nature of PMMA will interrupt the crystallization and reduce the crystallinity significantly, which fails to reduce the coercive field but lower the polarization. While in the terpolymer/copolymer blends, both the polarization and coercive field can be tuned by the varying the blend composition. Figure 5-4(a) shows the bipolar polarization loops of the blends measured under an electric field of 200 MVm$^{-1}$ at room temperature. Since the maximum polarization of the terpolymer and copolymer differs little from each other, there is not only minor difference between maximum polarizations of the blends. However, significant variations are found in the coercive field and remnant polarization as shown in Figure 5-4(b).
Figure 5-4 (a) Bipolar polarization hysteresis loops and (b) The variation of maximum polarization ($P_{\text{max}}$), remnant polarization ($P_r$), coercive field ($E_c$) of the terpolymer, copolymer, and their blends measured at a maximum electric field of 200MVm$^{-1}$.

The copolymer film exhibits a well defined near square polarization hysteresis loop with a large remnant polarization ($P_r \approx 6 \mu$Ccm$^{-2}$). While a very slim hysteresis loop with very low remnant polarization and coercive field, which is typical for ferroelectric relaxor, is observed for the terpolymer. With the addition of the copolymer, both the coercive field and remnant polarization increases. The maximum polarization hysteresis ($E_c$-$E_l$)/2 at $P_{\text{max}}/2$ are also calculated and presented in Figure 5-4(b). Monotonously increase of ($E_c$-$E_l$)/2, i.e. hysteresis, are also observed. Since the coercive field and remnant polarization reflects the size and perfectness of ferroelectric domains, all of these data indicate the coupling among dipoles in the polymer ferroelectric domains become stronger and stronger with the increase of the copolymer content.
5.2.4 Structural Analysis

FTIR is usually employed to detect local conformational structure changes of PVDF-based copolymers because three kinds of conformations (TGTG’, T\textsubscript{3}GT\textsubscript{3}G’ and T\textsubscript{m>3}) adopted by PVDF chains have their characteristic absorption bands in FTIR spectra respectively. The normalized FTIR absorption spectra of the terpolymer, copolymer and their blends are shown in Figure 5-5(a). The terpolymer shows mixed chain conformations consisting of trans and gauche bonds, i.e. TGTG’ (613 cm\textsuperscript{-1}), T\textsubscript{3}GT\textsubscript{3}G’ (504 cm\textsuperscript{-1}) and T\textsubscript{m>3} (1285 cm\textsuperscript{-1}) conformations.\cite{129} With addition of copolymer, crystal bands at 1285 cm\textsuperscript{-1} and 848 cm\textsuperscript{-1} corresponding to all trans (T\textsubscript{m>3}) conformation gradually grow up, while those bands representing TGTG’ conformation slowly diminish, representing the fact that as copolymer content increases, more ordered states on a local scale exist in the blends structure. The ratio of representative absorption bands’ intensities of blends to those of terpolymer are presented in Figure 5-5(b) to show the changes in portions of chain conformation with respect to the copolymer content. It can be seen that at low copolymer content (< 20%), the increase of T\textsubscript{m>3} conformation and decrease of TGTG’ conformation is not obvious, which means the copolymer embedded in the blends adopts a mixed structure consisting of three conformations just as terpolymer does. In other words, the copolymer and terpolymer co-crystallize based on the existing structure of the terpolymer lattice. As copolymer content becomes higher than 20%, a quick increase or decrease is observed, which indicates the influence of copolymer becomes larger that the two types of polymers can no longer form a uniform structure. The T\textsubscript{3}GT\textsubscript{3}G’ conformation only increases a little in the whole copolymer content range.
To further understand the structure from a crystallographic view, XRD is performed and the data are shown in Figure 5-6. Copolymer exhibits two partially superimposed peaks located at 18.8° and 19.3°, reflecting interchain lattice spacing, denoted by d, of 4.71 Å and 4.60 Å, in accord with (110) and (200) reflection respectively. [112] The terpolymer exhibits only one peak at 18.4° with their interchain lattice space of 4.86 Å (calculated by Bragg’s equation $2dsin\theta = n\lambda$). Blends with low copolymer content (<15 wt%) also exhibit only one narrow peak at the same position as terpolymer does. The nearly identical interchain crystal spaces of these samples indicate that the copolymer chains do not interpenetrate with the terpolymer chains and form co-crystals to change...
the basic crystallographic structure, and no large coherent polar crystals of P(VDF-TrFE) exists in the blends, which are consistent with the previous analysis of the FTIR results.

![X-ray diffraction patterns](image)

**Figure 5-6** X-ray diffraction patterns of the terpolymer/copolymer blends with different compositions.

The crystallite sizes or coherence lengths (L) perpendicular to (110, 200) crystallographic plane of terpolymer, corresponding to the sizes of polar or nonpolar domains, are estimated using the Scherrer equation: 

\[ L = \frac{0.9\lambda}{B \cos \theta} \]

where \( \lambda \) is X-ray wavelength, \( B \) is full width at half-maximum (FWHM, in 2\( \theta \)), and \( \theta \) is angular position of the diffraction peaks, respectively. The coherence lengths are listed in Table 5-1. It should be noted that for P(VDF-TrFE-CFE) terpolymer, (110) and (200) planes provide same signals in XRD pattern, therefore these two planes are listed as one and will be discussed together.
Table 5-1 Lattice constant and coherence length for the (110,200) reflection of the terpolymer, copolymer, and their blends

<table>
<thead>
<tr>
<th>Blends Ter/Co</th>
<th>(110,200)\textsubscript{ter}</th>
<th>(110)\textsubscript{co}</th>
<th>(200)\textsubscript{co}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d,Å</td>
<td>L,nm</td>
<td>d,Å</td>
</tr>
<tr>
<td>100/0</td>
<td>4.86</td>
<td>40.5</td>
<td>95/5</td>
</tr>
<tr>
<td>90/10</td>
<td>4.86</td>
<td>31.8</td>
<td>85/15</td>
</tr>
<tr>
<td>80/20</td>
<td>4.87</td>
<td>31.2</td>
<td>70/30</td>
</tr>
<tr>
<td>60/40</td>
<td>4.87</td>
<td>25.0</td>
<td>4.72</td>
</tr>
<tr>
<td>50/50</td>
<td>4.87</td>
<td>26.4</td>
<td>4.72</td>
</tr>
<tr>
<td>Copolymer</td>
<td>4.71</td>
<td>12.0</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Decreased coherence lengths are observed with the increasing amount of copolymer, indicating the addition of copolymer can reduce the crystallite size. Then the coherence length reaches a limit when copolymer content approaches 20 wt%, and further addition will not increase the FWHM, suggesting there’s certain saturation in the interaction between the two components. It seems that the copolymer defects interact with the terpolymer crystalline phases most probably through interfacial couplings since no large normal ferroelectric copolymer crystals are observed, thus polymer chains of the moderately blended copolymer are forced to twist to adopt a mixed structure with all three conformations as the relaxor ferroelectric terpolymer, and subsequently only one characteristic reflection peak in XRD can be observed. As the copolymer content increases, a bump gradually grows up at around 19°, gradually evolves into two peaks with slightly shifting toward high angular position, and finally become two observable at 18.7° and 19.2°, corresponding to the reflection of (110) and (200) crystal planes of ferroelectric phases in P(VDF-TrFE) copolymers, respectively. The peak fitting results show decreased d spaces and increased coherent lengths, indicating more and more perfect ferroelectric copolymer crystallites are formed with the increase of copolymer content. The co-existence of reflection peaks of the two components suggests that the copolymer and terpolymer are immiscible when copolymer is at a large content, instead both of them tend to maintain their own
crystal structures at high load of copolymer. This is understandable due to the large d space difference between P(VDF-TrFE-CFE) terpolymer and P(VDF-TrFE) copolymer.

The immiscibility can also be proved by DSC data. Figure 5-7 shows the DSC traces of blends with different compositions acquired during the first heating run, when temperature ramps up from -50 °C to 200 °C. The relaxor ferroelectric terpolymer shows no FE-PE transition and only exhibits a melting peak at 128.3 °C. The ferroelectric copolymer exhibits two peaks, one melting peak at 156.6 °C and the other at 64 °C representing FE-PE transition. Two melting peaks in all blends samples suggest that the two components are not completely miscible on molecular level. Nevertheless, melting point depressions and broadening of the melting peaks in the terpolymer components indicate that the copolymer indeed influences the crystalline phases of the terpolymer. Thinner lamellae or smaller crystallites with low melting points are formed in the blends, which corroborates the decreased coherence lengths derived from XRD results. The higher melting peak shifts gradually from 150.5 °C to 154.4 °C as the amount of the copolymer increases to 50 wt%, indicating the copolymer will develop more perfect crystallites when they are rich in the blends.
The total melting heat can be calculated through integrating the DSC peak area. It has been found that the total melting heat increases after addition of copolymer compared with that of pure terpolymer. One possible explanation is that compared with terpolymer, it is easier for copolymer to crystallize. Therefore, the copolymer will first crystallize and then serve as nuclear center so as to favor the crystallizing process and increase the crystallinity of terpolymer, as a result the normalized melting heat of terpolymer is increased. Another possible explanation is that the thin copolymer lamellae are confined between terpolymer chains and the interfacial couplings between terpolymer and copolymer crystallites make them only can grow into very thin lamellae, and therefore, they melt at low temperature as the tiny terpolymer crystallites do. From the data obtained by peak fitting, it is believed that it should be mostly the latter case in two reasons: first, the normalized $\Delta H_{m(\text{ter})}$ increases while the normalized $\Delta H_{m(\text{co})}$ decreases, and second, there is no
large copolymer crystals with characteristic reflection peak of ferroelectric phase found in the blends with low copolymer content from the XRD profiles. Another evidence of this supposed case is that the ferroelectric-paraelectric phase transition of P(VDF-TrFE) 55/45, which is supposed at around 65 °C, is not detected at low content copolymer blends. Only when the copolymer weights over 20%, does the FE-PE transition gradually increase since the interface effect saturates and crystallites of copolymer itself grow up. Meantime, the FE-PE transition peak slightly shifts towards high temperature, indicating increasing perfectness of ferroelectric domains with increase of the copolymer, which coincides with the XRD and dielectric data shown below.

From the structural data, e.g. the absence of reflection peak of ferroelectric phase in XRD and phase transition peak in DSC, it is reasonable to infer that in the blends with low copolymer content there is no normal ferroelectric copolymer phase. Furthermore, the copolymer is likely to be converted to relaxor with a mixed structure composed of TGTG’, T3GT3G’ and Tm>3 conformations. Besides, the incorporation of copolymer increases the blends crystallinity. These facts result in enhanced relaxor ferroelectric behavior and thus electrocaloric behavior, as can be seen in the following sections. In the blends with high copolymer content, the normal ferroelectric copolymer phase arises and becomes more distinguished with increase of copolymer, as can be seen in XRD. However, the defects in terpolymer still affect the copolymer, mainly in the perfectness of ferroelectric domains in crystalline regions, which can be employed to tailor ferroelectric properties of the blends system.

In summary, blends of ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer and normal ferroelectric P(VDF-TrFE) are prepared. Although the terpolymer and copolymer are not miscible completely, there is still some certain interaction between these two components. At low copolymer content, the random defects in the terpolymer influence the ferroelectric response in the copolymer through interfaces between the two polymers, convert the copolymer into relaxor.
Consequently, the whole blends exhibit relaxor ferroelectric response. Besides, the crystallinity also increases. The combination of increased crystallinity and interfacial coupling leads to an enhanced polarization and a larger (> 30%) increase in ECE in the blends compared with that in the neat terpolymer. At high copolymer content, the two immiscible phases become more distinguished, and each component tends to keep their own structures, leading to intermediate electric properties. This blend provides a model system to study how random defects influence the polarization response in the copolymer, and also provide evidence for us to understand the relationship between the polarization response and ECE in the blends. The results demonstrate the promise of composite approaches in tailoring and enhancing ECE and ferroelectric properties in PVDF-based ferroelectric polymers.

5.2.2 Weak Field Dielectric Properties

Figure 5-8(a) shows weak field dielectric constant of the blends with various compositions. It can be observed that all dielectric constants decrease with increasing frequency due to dielectric relaxation. The dielectric constant for the terpolymer at 1 kHz is about 48. It is believed at lower frequency, high dielectric constant of the terpolymer is caused by the response of dipoles in the randomly distributed polar nano region. As frequency goes up, the dielectric relaxation, which originates from responses of defects such as amorphous-crystalline interfaces and grain boundaries, occurs. For the blends, the dielectric constant first increases by ~10% when the copolymer content is 5 wt%, which may be attributed to the increase of crystallinity in the blends, and then gradually decreases but still is higher than that of pure terpolymer as the copolymer content increases to 15 wt%. The enhancement of dielectric constant can be observed through all frequencies where the data are measured. It is interesting that an increase in dielectric constant is obtained by adding a low dielectric constant component (~17 at 1 kHz at room
temperature for the copolymer). When the copolymer weighs over 20%, the dielectric constant of the blends becomes lower than that of pure terpolymer, which is believed to be a compensation of the low dielectric constant from the P(VDF-TrFE) copolymer. However, it is noted that for the blend with 20wt% copolymer, its dielectric constant (~45) is 10% higher than the weighted average of the two components (~41), indicating the interface effect still play its role in the blends. With further increase of the copolymer content, the dielectric constants decrease monotonously in the whole frequency range. Finally, $\varepsilon'$ of all the samples tends to converge at one point when frequency approaches $10^7$Hz.

Figure 5-8(b) shows the dielectric properties in the $\varepsilon''$ vs $\varepsilon'$ representation. One standard way to analyze these experimental data is fit to the Cole-Cole equation:

$$
\varepsilon''(\omega) = \varepsilon_i + \frac{\Delta\varepsilon}{1 + (i\omega\tau)^\alpha},
$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_i$ is the dielectric relaxation strength, with $\varepsilon_s$ the static dielectric constant and $\varepsilon_i$ the dielectric constant at “infinite” frequency; $\omega$ is the frequency, $\tau$ is characteristic relaxation time, and $\alpha$ is the parameter describing the distribution of the relaxation time. When $\alpha=1$, monodisperse relaxation following Debye model is presented. While in most cases, $\alpha$ varies between 0 and 1, indicating the broad distribution of the relaxation times in the system. The solid curves are the fitted results and the parameters are listed in Table 5-2. Both the static dielectric constant and the dielectric relaxation strength $\Delta\varepsilon$ first go up and then decline with the content of the copolymer. The increased $\Delta\varepsilon$ in the blends with low copolymer content (< 5wt %) indicates that the relaxor behavior is indeed enhanced. Besides, all the samples have nearly same $\varepsilon_i \approx 4$, suggesting the polar processes that govern the dielectric response tends to diminish at high frequency, as $\varepsilon_i$ only accounts for high frequency nonpolar processes.
Figure 5-8 (a) Dielectric constant under various frequencies of the terpolymer, copolymer, and terpolymer/copolymer blends at room temperature. (b) $\varepsilon''$ vs $\varepsilon'$ at room temperature. Solid lines are curve fitting obtained by the Cole-Cole expression.

Table 5-2 Summary of Cole-Cole parameters

<table>
<thead>
<tr>
<th>Blends</th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_i$</th>
<th>$\Delta\varepsilon$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ter/Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>48.0</td>
<td>4.7</td>
<td>43.3</td>
<td>0.575</td>
</tr>
<tr>
<td>95/5</td>
<td>55.5</td>
<td>4.9</td>
<td>50.6</td>
<td>0.575</td>
</tr>
<tr>
<td>90/10</td>
<td>53.4</td>
<td>4.8</td>
<td>48.7</td>
<td>0.568</td>
</tr>
<tr>
<td>85/15</td>
<td>49.1</td>
<td>4.2</td>
<td>44.9</td>
<td>0.558</td>
</tr>
<tr>
<td>80/20</td>
<td>46.2</td>
<td>3.8</td>
<td>42.5</td>
<td>0.580</td>
</tr>
<tr>
<td>70/30</td>
<td>42.0</td>
<td>3.8</td>
<td>38.2</td>
<td>0.558</td>
</tr>
<tr>
<td>60/40</td>
<td>33.5</td>
<td>3.6</td>
<td>29.9</td>
<td>0.542</td>
</tr>
<tr>
<td>50/50</td>
<td>26.8</td>
<td>3.4</td>
<td>23.4</td>
<td>0.533</td>
</tr>
<tr>
<td>0/100</td>
<td>17.3</td>
<td>3.2</td>
<td>14.1</td>
<td>0.456</td>
</tr>
</tbody>
</table>

The enhancement observed in the blends with low copolymer content is believed to be related with the interfacial couplings between the terpolymer and copolymer.[130] Just as shown
in XRD and DSC data, the defects in the terpolymer can hinder the formation of large ferroelectric domains in P(VDF-TrFE) copolymer, and convert the copolymer into relaxor. Meanwhile, the larger dipole density in copolymer increases the overall dipole density of the whole blend system. The dipoles in relaxor system can be easily affected by the electric field, which thus make the blends exhibit elevated dielectric constant and enhanced relaxor behavior. However, as copolymer content increases, not only the dipole density but also the interaction between dipoles increases, as evidenced by the emerging ferroelectric phase reflection peaks in XRD and phase transition peak in DSC. Therefore, the response of dipoles to electric field becomes more difficult, and consequently the $\epsilon'$ drops gradually. The observed decrease of $\alpha$ with increased copolymer content also implies the increased correlation between the local polar chain segment motions in the interface and crystalline region, which broadens the relaxation time distribution.

Figure 5-9(a) shows the temperature dependent dielectric properties of all the samples measured at 1 kHz. For the terpolymer there is one diffused peak observed near room temperature, and for the copolymer, a dielectric anomaly is observed at the ferroelectric-paraelectric phase transition temperature (~65 °C). With addition of small amount of the copolymer (5 wt%), the dielectric constants at room temperature increase. The enhancement saturates at 10 wt% copolymer, and then the dielectric constants gradually decrease with further addition of the copolymer. In the meantime, the maximum of dielectric constant gradually moves towards high temperature.
Figure 5-9 (a) Temperature dependent dielectric properties of blends measured at 1 kHz. Dielectric properties as a function of temperature and frequency in neat terpolymer (b) and blends with 10 wt% copolymer (c). Curves from left to right: $10^2$ to $10^6$ Hz at intervals of $10^1$ Hz. (d) Frequency dependence of dielectric constant peak in the terpolymer and its blends with copolymer content ≤ 15 wt%. The solid lines are fitting of the Vogel-Fulcher equation.
For the blends with small content of the copolymer (<15 wt%), no FE-PE transition is observed. Figure 5-9(b) and (c) give comparison of the terpolymer and blends with 10 wt% copolymer. For the terpolymer, the dielectric constant peaks are around room temperature, and move to higher temperature as the frequency increases. Along with the diffusive transition, the dielectric peaks clearly show typical relaxor characteristics. It should also be noted that there are two peaks observed in the low frequency dielectric loss data, one is near -20 °C whose peak temperature moves up with frequency and the other is much weaker and occurs at a temperature near 10 °C. This weak higher temperature peak merges with the shoulder of the low temperature loss peak at high frequencies. It is well-established that the lower peaks are related to glass-transition in the amorphous region of terpolymer, and the peaks at higher temperature are the characteristic of the relaxor nature.

While for the blends with 10 wt% copolymer, besides the enhanced dielectric constant at room temperature, another change caused by the addition of copolymer is that a new peak appears at the temperature higher than where the corresponding terpolymer peak lies, as indicated by the red arrow (→). The new peak is very clear at low frequencies, and gradually merges with the terpolymer relaxation peak at high frequencies. And also, the valley between two loss peaks is filled, suggesting a new peak grows up, as indicated by the black arrow (→).

The new peaks in both dielectric constant and dielectric loss spectroscopy should not be assigned to the molecular movement in amorphous regions, because movement in the amorphous regions like the glass transition does not affect the real part of the dielectric constant much.[131] One possible explanation is that a new phase may form in the blends with low copolymer content. The intermediate position of the peak indicates that the new phase is neither as disorder as the amorphous phase, nor as order as the crystalline phase. Thus, the most probable assignment of the new peak is the dielectric response of interface section. Since the P(VDF-TrFE) is not a strong ferroelectric, i.e., there are lots of defects in the ferroelectric domains and correlations in its
ferroelectric domains are not so strong, it is prone to be influenced by crystallizing conditions. Thus, the interfacial couplings with the terpolymer disturb the correlation in its ferroelectric domains, tear the correlated domains apart, and convert the nano-crystallites of the copolymer from a normal ferroelectric to a relaxor ferroelectric. This is the reason why no ferroelectric phase in XRD and no FE-PE phase transitions can be observed on DSC data for the low copolymer content blends.

Figure 5-9(d) shows the shift of dielectric peak temperatures with frequency follows the empirical Vogel-Fulcher equation:

$$\ln\left(\frac{f}{f_0}\right) = -\frac{E}{k_B(T - T_f)}$$

where $E$ is a parameter describing the distribution width of relaxation time (or energy), $k_B$ is Boltzmann constant, $f_0$ is the freezing frequency of the relaxation process, and $T_f$ is the reference temperature. It can be found that the $T_f$ is larger in the blends than in pure terpolymer. Since the peak position and $T_f$ are directly related to the activation energy, the results suggest that the addition of copolymer into terpolymer gradually increases the correlation between the local polar chain segments, which is consistent with the increased relaxation time obtained from frequency-dependent dielectric behavior at room temperature.

For the blends with high content of the copolymer (>30 wt%), they exhibit characteristics of both components: one relaxor peak locates around 20 °C whose maximum is independent of terpolymer/copolymer ratio, and an FE-PE transition peak is at around 60 °C. The latter moves slightly toward high temperature with increasing amount of P(VDF-TrFE), indicating the influence of defect introduced by the terpolymer to ferroelectric domains of the copolymer becomes smaller and smaller, i.e. the ferroelectric domains of the copolymer in blends become more and more perfect, as can be corroborated by growing ferroelectric phase peak in XRD and phase transition peak in DSC. It is worth noting that there is another peak observed at around
40 °C between the relaxor peak and the FE-PE transition peak, which can be interpreted as a less ordered ferroelectric phase. Such a peak may be caused by relatively high ordered phases in terpolymer which can be induced under certain circumstances (for here, it may be induced through interactions with P(VDF-TrFE), or less ordered ferroelectric states of the copolymer. It is reported that there is a “CL” phase exists in P(VDF-TrFE) 55/45 copolymer, which embraces more “tilt” defects and thus less ordered ferroelectric phases. However, the dielectric anomaly in the FE-PE transition (~65 °C) is so strong that the transition of less ordered phases (~40 °C) cannot be detectable clearly in the dielectric spectroscopy. Whilst the interaction with the terpolymer makes this phase more distinct so that it can be observed.

5.3 P(VDF-TrFE-CFE) Terpolymer/ZrO$_2$ Nanocomposites

Composite approach, such as polymer blends and polymer-inorganic nanocomposites, is one facile method of tuning polymer properties, and has demonstrated great success in enhancing the dielectric behavior of ferroelectric polymers.[122-128] Especially, for the polymer-inorganic nanoparticle composites, the interface effects may introduce additional polarization process that can result in an improved polarization response and elevated polarization level.[122-124] From the Landau-Devonshire (L-D) phenomenological theory, the isothermal entropy change $\Delta S$ from the ECE is directly proportional to the square of the electric displacement $\Delta D$

$$\Delta S = -1/2 \beta (\Delta D)^2,$$

where $\beta$ is a coefficient in the L-D theory.[13, 28] Therefore, it may be expected that the ECE can also be enhanced through nanocomposite approach.

This section presents the ECE results in nanocomposites comprising surface-modified ZrO$_2$ nanoparticles and a ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer, which show a large ECE near room temperature and the adiabatic temperature change of the nanocomposite with 3
vol% of nano-fillers is 120% of that of the neat terpolymer. Earlier studies revealed that the P(VDF-TrFE-CFE)/ZrO$_2$ nanoparticle composites can exhibit higher induced polarization than the neat terpolymer due to interface effects.[122] Here we show that the interface effects induced polarization increase can lead to enhance the EC. The results, for the first time, demonstrate that the ECE can be tailored and enhanced through polymer-inorganic nanocomposite approach in ferroelectric polymers.

Presented in Figure 5-10 is a SEM image of the nanocomposite with 3 vol% of ZrO$_2$ nanoparticles, which shows that ZrO$_2$ nanoparticles are evenly distributed in the polymer matrix without forming large agglomeration. This is distinctively different from the nanocomposites prepared using pristine ZrO$_2$ nanoparticles without surface modification.

![Figure 5-10](image-url) A SEM image of P(VDF-TrFE-CFE)/surface-modified ZrO$_2$ nanocomposites.

Figure 5-11(a) and (b) present the temperature dependence of the weak field dielectric properties of the terpolymer and its nanocomposite. The broad dielectric constant peaks shift progressively towards higher temperature with frequency, showing typical relaxor characteristics. It is noteworthy that a new dielectric anomaly appears in the dielectric constants of nanocomposite at around 20 °C, especially at low frequencies, which is believed to be caused by a low frequency relaxation process due to the heterogeneous nature of the composites. The
anomaly was not observed in the terpolymer-ZrO\textsubscript{2} nanocomposites studied earlier in which the nanoparticles were not modified\cite{122}, but observed in the other terpolymer nanocomposites with surface-modified nanoparticles.\cite{123} The surface modification allows polymer to wet surfaces of the nano fillers and improves the interaction between the nano-fillers and polymer matrix, which may enhance the interface effects.

Figure 5-11 Temperature dependent dielectric constant and dielectric loss of pure terpolymer (a) and nanocomposite with 2\% ZrO\textsubscript{2} nanoparticles (b) at different frequencies (from 100 Hz to 10 MHz) (c) Unipolar P-E Loops of terpolymer and nanocomposites measured at 10 Hz. (d) The induced polarization of terpolymer and nanocomposites as functions of applied electric field amplitude. The data was extracted from the P-E loops of (c). The inset shows variation of induced polarization under 150 MVm\textsuperscript{-1} vs. ZrO\textsubscript{2} content.

Figure 5-11(c) presents P-E loops of the terpolymer and its nanocomposites under a unipolar electric field of 150 MVm\textsuperscript{-1} at 10 Hz. The nanocomposites exhibit higher polarization than that of the terpolymer in the field range measured, similar to the previous results.\cite{122} It should also be noted that the polarization of the nanocomposite at E = 0 after one charge/discharge cycle is the same as terpolymer, indicating the enhancement of polarization is
intrinsic instead of caused by conduction. The nanocomposite with 1 vol% of ZrO$_2$ nanoparticles show the strongest polarization enhancement and enhancement gradually reaches saturation, as shown in Figure 5-11 (d). Earlier studies have shown that further increase of nanoparticle content will cause coalescence of interfaces and thus saturation of the interface effects. The nanocomposite with 3 vol% nanoparticles exhibits an induced polarization of 6.9 µCcm$^{-2}$ under 150 MVm$^{-1}$, which is 15% higher than that of neat terpolymer (6.0 µCcm$^{-2}$). That value is also higher than the results reported previously (~6.4 µCcm$^{-2}$), which was obtained in the nanocomposites with ZrO$_2$ nanoparticles of no-surface modification.[123] The difference may lie in the fact that the composition of terpolymers from different batches varies.

Figure 5-12(a) compares the isothermal entropy change ($\Delta S$) of the terpolymer and nanocomposites as functions of electric field at room temperature. As can be seen, nanocomposites show higher $\Delta S$ than that of the neat terpolymer at all electric fields measured, especially at higher electric field. For example, at 140 MVm$^{-1}$, a $\Delta S \approx 46$ J Kg$^{-1}$ K$^{-1}$, corresponding to a $\Delta T \approx 9.2$ °C, is induced in the nanocomposite with 3 vol% of nanoparticles, about 20% higher than that of the pure terpolymer ($\Delta S \approx 38$ J Kg$^{-1}$ K$^{-1}$, corresponding to a $\Delta T \approx 7.6$ °C).
Figure 5-12 (a) The isothermal entropy change ($\Delta S$) and adiabatic temperature change ($\Delta T$) of terpolymer and nanocomposites as functions of the applied field amplitude at room temperature. (b) The relationship of entropy change ($\Delta S$) and square of electrical displacement ($\Delta D^2$). The solid lines are fitted results to determine $\beta$ and drawn to guide eyes. (c) $\beta$ as a function of the ZrO$_2$ volume content.
Equation 5.5 is used to deduce the coefficient $\beta$ from the experimental data in Figures 5-11 (d) and 5-12 (a). As shown in Figure 5-12(b), the terpolymer and nanocomposites display nearly linear relationships between the entropy change and square of electrical displacement. $\beta$ obtained for the terpolymer and its nanocomposites with 1 vol%, 2 vol%, and 3 vol% ZrO$_2$, are $3.57 \times 10^7$, $3.44 \times 10^7$, $3.27 \times 10^7$, and $3.37 \times 10^7$ Jm$^{-1}$C$^{-2}$, respectively (Figure 5-12(c)). The slightly decrease of $\beta$ with the nanoparticle content indicates that the enhanced polarization due to the interface effects may not be as effective in generating ECE compared with that from the neat terpolymer. However, the large enhancement in polarization from the interface effects suppresses the decrease in $\beta$ and therefore the resulting ECE in the nanocomposites is still significantly enhanced.

The superior dielectric and ferroelectric properties of the PVDF based electroactive polymers originate from their crystalline phases. To investigate the influence of the ZrO$_2$ nanoparticles on the crystallization behavior of the polymer matrix, DSC measurements were carried out. Figure 5-13 shows the DSC profiles of the polymer and nanocomposites during the cooling scan. The introduction of the nanoparticles into the polymer raised the crystallization temperature, from $\sim 99$ °C for terpolymer to $\sim 101$ °C for the nanocomposite containing 1 vol % ZrO$_2$, indicating the nanoparticles possibly serve as nucleating agent in the crystallization of the polymer matrix. It is noted that the crystallization temperatures of the nanocomposites do not show changes as the volume content of ZrO$_2$ nanoparticles increased further. The heat of melting $\Delta H$ increased from 23.2 Jg$^{-1}$ for the terpolymer to 24.1 Jg$^{-1}$, 24.8 Jg$^{-1}$ and 24.6 Jg$^{-1}$ for the composites with 1 vol%, 2 vol% and 3 vol% ZrO$_2$, respectively. The heat of metling, which is directly proportional to the crystallinity, varied slightly when the nanoparticle loading increased beyond 1 vol%, which suggests that the increased crystallinity is not the main reason for the enhanced EC effect observed. For example, assuming the isothermal entropy change $\Delta S$ is solely originated from the crystal phase, the neat terpolymer has a ratio of $\Delta S/\Delta H$ of 1.64. For the
composite with 3 vol\% ZrO$_2$, the increase in $\Delta S$ from the crystallinity is 40.3 Jkg$^{-1}$K$^{-1}$, which is much smaller than the observed $\Delta S = 46$ Jkg$^{-1}$K$^{-1}$, suggesting the interface effects cause additional polarization responses which are the major reason for the enhanced ECE observed.

![Figure 5-13 DSC traces of terpolymer and nanocomposites obtained during the cooling scan.](image)

In summary, for the first time, tailoring the electrocaloric effect in ferroelectric relaxor P(VDF-TrFE-CFE) terpolymer through inorganic nanoparticle-polymer nanocomposite approach was demonstrated. Compared with the terpolymer, the nanocomposite with 3 vol\% of ZrO$_2$ nanoparticles exhibits a $\Delta S$ and $\Delta T$ which are 120\% of those of the neat terpolymer. Since the interface effects are sensitive to the nanoparticle interface properties which may be tailored over a broad range, the results here suggest the potential of employing nanocomposite approach to generate significant polarization response and ECE compared with the neat ferroelectric polymers.

### 5.4 Poled Terpolymer/Copolymer Blends

Electrocaloric Effect (ECE) refers to the temperature change and/or entropy change induced by external electric field in certain dielectric materials.[8, 28] Materials with large ECE are very promising to realize efficient compact cooling devices for refrigeration, temperature
regulation and air-conditioning. Relaxor ferroelectric polymers such as high energy electron irradiated P(VDF-TrFE) copolymers and P(VDF-TrFE-CFE) terpolymer, and terpolymer/copolymer blends, which show large ECE over a broad temperature range, are believed to be among the best candidates.[104, 130] Recently a chip-scale prototypical cooling device using irradiated polymer multilayer structure has been fabricated and reported, advancing the field from material research to real device explorations.[85, 132] However, one practical issue is that in order to generate large response, a high electric field is generally required, e.g., for P(VDF-TrFE-CFE) terpolymer, the electric field applied across the polymer needs to be 150 MVm$^{-1}$ in order to get a temperature change of 15 $^\circ$C. Operating at such a high electric field will reduce device lifetime and also limit the integration of EC materials into low-voltage range, thus it is necessary to design a material system that can exhibit large response under a relatively low electric field, or in the figure of merit defined as electrocaloric coefficient, $\Delta T/E$.

P(VDF-TrFE-CFE) terpolymer and P(VDF-TrFE-CFE)/P(VDF-TrFE) polymer blends exhibit large ECE, i.e., large temperature change and entropy change, over a broad temperature range, thus these series of materials are very promising. Previous studies focused on tailoring the material properties by varying the copolymer ratio, which has more impact on the structure side.[130] Alternatively, poling ferroelectric materials to enhance their performance has been widely utilized in areas such as piezoelectrics[133] and magnetoelectrics[134], and recently in organic solar cells[135]. Generally, poling process could induce remanent polarization in normal ferroelectric materials, which produces internal bias field within the material system. The blends of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) provide a model system to study the internal bias field effect. Since P(VDF-TrFE) copolymer belongs to normal ferroelectrics, in which large remanent polarization will exist after poling, the copolymer may provide extra internal electric field in the blends, thus generating higher polarization and enhanced ECE.
In this section it is presented that by poling the terpolymer/copolymer blends, an internal electric field would be established which boosts the material performance so that large ECE can be obtained under relatively low electric field. An internal bias electric field is introduced through poling process in P(VDF-TrFE-CFE)/P(VDF-TrFE) blends by stabilizing the nano-polar structures in the samples. The internal bias electric field is about 10% when measured under 100 MVm\(^{-1}\), which generates an enhancement of ECE by 13.5%. Such poling process provides a simple but effective way to increase the material performance, i.e., \(\Delta T/E\), thus effectively reduces the level of external electric field if the same \(\Delta T\) is desired.

5.4.1 Experimental

Terpolymer P(VDF-TrFE-CFE) and copolymer P(VDF-TrFE) powders were dissolved in N,N-dimethylformamide at room temperature, respectively. For blends sample, the two solutions were mixed together by a weight ratio of 9:1. The final solution was filtered using 0.2 µm sized polytetrafluoroethylene filters and then cast on cleaned glass plates and dried at 70 °C for 24 hrs. Afterwards, the films were peeled off from the glass plates and further annealed at 105 °C for 24 hrs. The final films obtained have thickness of 8 ~ 10 µm. For the bilayer sample, the terpolymer and copolymer films were prepared separately using the solution casting method described above, and terpolymer film was transferred on top of copolymer film. The bilayer sample was put into vacuum oven of 140 °C for 24 hrs, followed by annealing process at 105 °C for 24 hrs. Both samples were poling at 90 °C for at least 10 mins, under an electric field of 60 MVm\(^{-1}\), which remained on as the samples cooled down to room temperature.

Scanning Electron Microscopy (SEM) was performed using NanoSEM 670. Melting points and melting heat of the pure terpolymer and blends were measured by differential scanning calorimetry (DSC) (TA Q100). The heating rate is 10°C per minute. FTIR spectra were obtained
using a Bruker V70 infrared spectrometer equipped with a diamond ATR accessory. Gold electrodes were sputtered on both surfaces of the polymer films for electric characterization. The dielectric properties as a function of temperature were characterized using a precision LCR meter (HP 4284A) equipped with a temperature chamber (Delta 9023). The data were recorded every 3 °C. Polarization-electric field (P-E) loops were measured using a modified Sawyer–Tower circuit at a frequency of 10 Hz at room temperature. ECE data were acquired using direct methods as described in Chapter 2.

5.4.2 Structural Analysis

Figure 5-14 presents the SEM images of the surface of blends samples. As can be seen, the terpolymer and copolymer are not completely miscible. The copolymer exists as nanoparticles whose size is in the order of tens of nanometers, in the terpolymer matrix. Upon poling, a net remanent polarization can be induced in the copolymer, thus forming an internal bias electric field in the blends sample.

Figure 5-14 SEM image of terpolymer/copolymer blends surface.

DSC profiles acquired during the first heating process are presented in Figure 5-15(a). Both unpoled and poled blends have two melting peaks, one at 129.7°C corresponding to the
melting peak of terpolymer and the other at 142.7 °C as a shoulder corresponding to that of copolymer. A ferroelectric-paraelectric phase transition of copolymer 65/35 generates a peak, at 85.5 °C for unpoled sample and at 86.2 °C for poled sample. The existence of F-P phase transition peak and extra shoulder melting peak means terpolymer and copolymer are not miscible, while the slight increase in F-P transition temperature can be attributed to larger ferroelectric domain size (polar structure) induced upon poling. The heat of fusion and phase transition are also calculated and listed in the figure. It can be seen that poling does not change the melting temperature and melting heat a lot. A smaller heat of fusion and phase transition in poled samples may be related to rapid cooling process (compared with annealing process), which reduces certain amount of crystallinity.

FT-IR spectrum shown in Fig 5-15(b) provides an insight on local chain segments change before and after poling process. After poling, two new peaks are observed at 1259 cm\(^{-1}\) and 802 cm\(^{-1}\), respectively, which represents of short-range ordered chain sequences (for example, T-G), indicating the copolymer in the blends can serve a role to stabilize the small polar structure after poling. Besides, compared with the unpoled sample, the poled sample shows strong absorption bands at 2917 and 2850 cm\(^{-1}\). These bands are assigned to the CH\(_2\) asymmetric and symmetric stretching with the dipole moments perpendicular to the polymer chain direction and parallel to the b axis (in our cases, the b axis is the direction of applied electric field). The strong absorption bands indicate preferred orientation of the dipoles after poling.
Figure 5-15 (a) DSC profile of terpolymer/copolymer blend before and after poling, (b) ATR-FTIR spectra of terpolymer/copolymer blend before and after poling.

5.4.3 Low-voltage Dielectric Analysis

Figure 5-16 shows the frequency dependent dielectric properties of the blends before and after poling. The difference can be observed at low frequency. After poling, both the dielectric constant and dielectric loss are decreased below 10 KHz, which means the contribution from conduction is suppressed, similar to what we observed in P(VDF-TrFE-CFE) terpolymer samples with dc bias field. The decrease of conduction can also be corroborated by the reduced dielectric constant observed at high temperature (>70 °C) as is shown in Figure 5-17. It is worth noting that a new dielectric anomaly can be observed around 40 °C, which can be ascribed to the polar structures induced by the internal bias field.
Figure 5-16 Frequency dependent dielectric properties measured at room temperature.

Figure 5-17 Temperature dependent dielectric constant measured at different frequencies.
5.4.4 Hysteresis Loops and Electrocaloric Effect

Figure 5-18(a) shows bipolar P-E loops of poled and unpoled samples measured at room temperature and 150MVm\(^{-1}\). It can be seen that the center of P-E loops shifts downward or upward with respect to the poling direction. To quantitatively compare the effect of poling to P-E response, the maximum polarizations at positive electric field (\(P^+\)) and negative electric field (\(P^-\)) are summarized at Table 5-3.

Table 5-3 Maximum polarization obtained from bipolar P-E loops measured at 150MVm\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>Not Poled ((\mu)Ccm(^{-2}))</th>
<th>Positively poled ((\mu)Ccm(^{-2}))</th>
<th>Negatively poled ((\mu)Ccm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P^+)</td>
<td>6.43</td>
<td>6.83</td>
<td>6.13</td>
</tr>
<tr>
<td>(P^-)</td>
<td>-6.43</td>
<td>-5.82</td>
<td>-6.85</td>
</tr>
<tr>
<td>(</td>
<td>P^+</td>
<td>-</td>
<td>P^-</td>
</tr>
</tbody>
</table>

The differences between the two maximum are also calculated. For the poled samples, the difference can be as high as 1 \(\mu\)Ccm\(^{-2}\). Figure 5-18(b) gives the typical unipolar P-E loops measured at 150 MVm\(^{-1}\) and Figure 5-18(c) summarized the maximum polarization obtained in each measure cycle. The results indicate the positively poled samples need smaller electric field to achieve the same polarization level compared with the unpoled samples. About 13 MVm\(^{-1}\) was built internally in the polymer films. The internally built electric field also has impact on the EC effect. Figure 5-18(d) shows the temperature change measured at room temperature. It can be seen the positively biased sample can achieve the same EC effect under lower electric field, and the bias effect become larger at electric field higher than 70 MVm\(^{-1}\).
Temperature change (ElectroCaloric Effect, or ECE) of poled blends measured at room temperature as a function of the electric field is presented in Figure 5-18(d). Since the temperature change is roughly proportional to the square of polarization change, it is as expected that ECE can be enhanced when measured with a positive field. For blends without poling, at electric field of 100 MVm$^{-1}$ and room temperature, the temperature change can reach about 7.01 °C, as a comparison, the temperature change in the poled sample measured under the same condition increases 13.5% to 7.95 °C. The average enhancement of ECE due to internal bias field over the measured electric field range is 11%, as shown in Table 5-4.
Table 5-4 ECE data comparison among unpoled sample, poled sample measured with an electric field in the same direction of poling field, and poled sample measured with an electric field in the opposite direction of poling field.

<table>
<thead>
<tr>
<th>E(MV)</th>
<th>$\Delta T$ (°C) Unpoled</th>
<th>$\Delta T$ Pole+</th>
<th>Ratio +/unpoled</th>
<th>$\Delta T$ Pole-</th>
<th>Ratio -/unpoled</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.76949</td>
<td>3.04367</td>
<td>1.099</td>
<td>2.43351</td>
<td>0.878685</td>
</tr>
<tr>
<td>60</td>
<td>3.96934</td>
<td>4.30568</td>
<td>1.084734</td>
<td>3.69553</td>
<td>0.931019</td>
</tr>
<tr>
<td>70</td>
<td>4.96931</td>
<td>5.53311</td>
<td>1.113456</td>
<td>4.61787</td>
<td>0.929278</td>
</tr>
<tr>
<td>80</td>
<td>5.53197</td>
<td>6.18497</td>
<td>1.118041</td>
<td>5.26973</td>
<td>0.952596</td>
</tr>
<tr>
<td>90</td>
<td>6.41587</td>
<td>7.13478</td>
<td>1.112052</td>
<td>6.11785</td>
<td>0.95355</td>
</tr>
<tr>
<td>100</td>
<td>7.01126</td>
<td>7.95951</td>
<td>1.135247</td>
<td>6.30468</td>
<td>0.899222</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>1.110422</td>
<td></td>
<td>0.924058</td>
</tr>
</tbody>
</table>

Using second order polynomial fitting, the relation between $\Delta T$ and $E$ can be modeled as,

$$\Delta T = 5.592 \times 10^{-2}E + 1.659 \times 10^{-4}E^2,$$

therefore, the effective electric field in poled samples can be deduced using such model. And the effective electric field data are listed in Table 5-5. At 100 MVm$^{-1}$, the effective electric field in poled+ sample reaches 110.79 MVm$^{-1}$, which is a 10% increase. It should be noted that the ratio of temperature changes between poled and unpoled samples, rather than the absolute temperature changes, were used to calculate effective electric field, since more accurate data can be acquired using the ratio in the model mentioned above.

Table 5-5 Effective Electric Field data for poled samples with measure electric field in the same direction of the poling electric field and opposite direction of the poling electric field.

<table>
<thead>
<tr>
<th>Electric Field (MVm$^{-1}$)</th>
<th>Ratio +/unpoled</th>
<th>Effective Electric Field (MVm$^{-1}$)</th>
<th>$\Delta E$ (MVm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 54.34</td>
<td>1.099</td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td>50 64.38</td>
<td>1.084734</td>
<td>4.38</td>
<td></td>
</tr>
<tr>
<td>50 76.68</td>
<td>1.113456</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>50 87.81</td>
<td>1.118041</td>
<td>7.81</td>
<td></td>
</tr>
<tr>
<td>50 98.19</td>
<td>1.112052</td>
<td>8.19</td>
<td></td>
</tr>
<tr>
<td>50 110.79</td>
<td>1.135247</td>
<td>10.79</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electric Field (MVm$^{-1}$)</th>
<th>Ratio -/unpoled</th>
<th>Effective Electric Field (MVm$^{-1}$)</th>
<th>$\Delta E$ (MVm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 44.56</td>
<td>0.878685</td>
<td>-5.44</td>
<td></td>
</tr>
<tr>
<td>50 56.38</td>
<td>0.931019</td>
<td>-3.62</td>
<td></td>
</tr>
</tbody>
</table>
In summary, an internal bias electric field is introduced through poling process in P(VDF-TrFE-CFE)/P(VDF-TrFE) blends by stabilizing the nano-polar structures in the samples. The internal bias electric field is about 10% when measured under 100 MVm$^{-1}$, which generates an enhancement of ECE by 13.5%. Such poling process provides a simple but effective way to increase the material performance, i.e., $\Delta T/E$, thus effectively reduces the level of external electric field if the same $\Delta T$ is desired.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rel. Permittivity</th>
<th>Dielectric Loss</th>
<th>Electric Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.929278</td>
<td>65.74</td>
<td>-4.26</td>
</tr>
<tr>
<td>80</td>
<td>0.952596</td>
<td>76.79</td>
<td>-3.21</td>
</tr>
<tr>
<td>90</td>
<td>0.95355</td>
<td>86.52</td>
<td>-3.48</td>
</tr>
<tr>
<td>100</td>
<td>0.899222</td>
<td>91.67</td>
<td>-8.33</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusion and Future Works

The work in this dissertation focuses on the electrocaloric effect (ECE), especially ECE in relaxor ferroelectric polymers. Through theoretical consideration, experimental demonstration and data analysis, various methods to enhance ECE in these polymeric materials have been elaborated.

P(VDF-TrFE)-based relaxor ferroelectric polymers exhibit large ECE over a broad temperature range, therefore are considered as the most promising among all the electrocaloric materials for practical cooling applications with large temperature span, high cooling power and high efficiency. Through basic consideration on ECE, including Landau-Devonshire phenomenological theory, coexisting phases rule near invariant critical points, defect modification to increase random states, various ways can be found to predict ECE response in materials as well as design and tailor material systems exhibiting giant ECE. On the experimental side, defect modification shows a significant impact on tuning ECE properties in polymers, as seen in irradiated PVDF-based copolymers and P(VDF-TrFE-CFE) terpolymers.

High-energy electron irradiation partially melts the crystallites and creates crosslinking in PVDF-based copolymers, and thus modifies their properties, especially electrocaloric effect. The high-energy-electron irradiation, by introducing defects into the P(VDF-TrFE) copolymer, modifies dielectric properties and thus ECE response of the films. As irradiation dose increases, the P(VDF-TrFE) 65/35 mol% copolymer gradually transforms from normal ferroelectric into relaxor ferroelectric material, with dielectric constant peak and ECE response peak shift from high temperature to room temperature. It is also demonstrated that the reduction of hysteresis by high-energy-electron irradiation with a moderate dosage and such defect-modified copolymer
shows a large entropy change as high as 130 JKg\(^{-1}\)K\(^{-1}\) and large temperature change of 28 °C. Moderate irradiation dose is preferred since large ECE can be generated around temperature range that is of significance to practical applications such as on-chip cooling and refrigeration. It should be noted that the mechanical stretching process does not change the dielectric properties and ECE response in the irradiated copolymer films. Cycle impact has also been discussed, which could be important for real device operation. It is interesting that ECE is enhanced as measurement cycle increases. On the contrary, the impact of high energy electron irradiation on P(VDF-TrFE) 75/25 mol%, P(VDF-CTFE) and P(VDF-HFP) is feeble, especially in terms of ECE. The material properties among these irradiated copolymers are compared to that of P(VDF-TrFE) 65/35 mol% to understand the difference of high energy electron irradiation influence.

For relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer, ECE properties are also under influence of uniaxial stretching process. Although the temperature dependence of the low-field complex dielectric constant is almost identical in the non-stretched and stretched samples, the dc bias electric field via higher nonlinear contribution more heavily alters the dielectric response of the non-stretched terpolymer. As stretching favors polar all-trans chain conformation, it increases the electric polarization. On the other hand, stretching decreases the number of possible polar states and, consequently, the electrocaloric response of the stretched terpolymer is smaller compared with that of non-stretched terpolymer, except near the temperature of the dielectric maximum where this effect is compensated by higher induced polarization in the stretched sample. The adiabatic temperature change ΔT as a function of applied field acquired at 30 °C, where a ΔT > 15 °C is induced under 150 MVm\(^{-1}\). Besides a very large ECE, the data reveal that the relaxor terpolymer maintains a high ECE over a broad temperature range, which is in sharp contrast to what observed in the normal ferroelectric polymer where ECE shows a sharp peak at FE-PE temperature. Both non-stretched and uniaxially stretched films display nearly the same ECE. What interesting is that in the same temperature range from 0 °C to 55 °C, the uniaxially
stretched films display much pronounced temperature variation and at 5 °C and 55 °C, ΔT of the uniaxially stretched films is more than 15% smaller, compared with that of the non-stretched films.

Two different methods to characterize ECE, indirect measurement and direct measurement are compared. Special attentions need to be paid if the indirect method is utilized to calculate ECE in relaxor ferroelectrics which are non-ergodic material systems. Particularly, the directly measured electrocaloric effect and the indirectly measured results P(VDF-TrFE-CFE) terpolymer are compared. The results show that the directly measured ΔT in the relaxor terpolymer is much larger than that deduced from Maxwell relation and that the relaxor terpolymer possesses a giant ECE at room temperature. The large difference between the directly measured ΔT and that deduced indicates that the Maxwell relation, which is derived for ergodic systems, is not suitable for deducing ECE in the relaxor ferroelectric polymers, which are nonergodic (polar-glass) material systems. On the other hand, if the direct method is adopted to obtain ECE while the heat capacity is a function of sample temperature, one should take the variation of heat capacity into consideration should the sample temperature change is significant.

Beyond irradiated copolymers and terpolymers, several P(VDF-TrFE-CFE)-based composites, including P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends, P(VDF-TrFE-CFE) terpolymer/ZrO₂ nano-particle blends, are elaborated in terms of electrocaloric behaviors, structural analysis and dielectric responses. It is shown that the electroactive properties, especially ECE, of PVDF-based ferroelectric polymers can be tailored by blending. At low copolymer content (<15 wt%), the coupling between the relaxor terpolymer and the nano-phase copolymer converts the copolymer into relaxor and causes an increase in the crystallinity compared with neat terpolymer. As a result, the blends exhibit an enhanced relaxor polarization response and a significant increase in the electrocaloric effect compared with those in the neat terpolymer. At high copolymer content, the blends exhibit mixed structures of the two
components. By varying composition, the dielectric and ferroelectric properties of blends can be tuned in the range between the copolymer and terpolymer. Moreover, a small amount of P(VDF-TrFE) (10 wt%) can cause a more than 10% increase in the crystallinity in the blends. As a result, the blends with 10 wt% of P(VDF-TrFE) exhibit a 30% increase in the adiabatic temperature change over the entire experimental temperature range from 20 °C to 60 °C. The electrocaloric effect is also enhanced in ferroelectric relaxor terpolymer (P(VDF-TrFE-CFE)/ZrO$_2$ nanocomposites. The interface effect between the polymer matrix and nano-fillers enhances the polarization response and provides additional electrocaloric entropy changes. As a consequence, the nanocomposites exhibit a larger ECE than that of the neat terpolymer, i.e., the adiabatic temperature change of the nanocomposite with 3 vol% of nano-fillers is 120% of that of the neat terpolymer. The results, for the first time, demonstrate that ECE can be tailored and enhanced through nanocomposite approach in the ferroelectric polymers. Furthermore, the internal bias electric field generated in the poled blends of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) also improves material performance, i.e., yielding higher polarization and enhanced ECE. The blends of P(VDF-TrFE-CFE) with small amount of P(VDF-TrFE) also provide a model system to study how the random defects in the terpolymer influence the polarization response in the copolymer and consequently ECE in the blends. Since P(VDF-TrFE) copolymer belongs to normal ferroelectrics, in which large remanent polarization will exist after poling, the copolymer may provide extra internal electric field in the blends, thus generating higher polarization and enhanced ECE.

Relaxor ferroelectric polymers and polymer composites exhibit great potential for realizing ECE cooling device with large temperature span, high cooling power and high efficiency. Meanwhile, there are several technical barriers in the way for further advancing this field, beginning with the soft nature of polymeric materials. Low Young’s modulus in P(VDF-TrFE-CFE) terpolymer brings many difficulties to fabricate multilayer cooling unit, since any
damage to the samples or any defects introduced during the fabrication process would significantly reduce the breakdown field in multilayer structure, which hinders the ECE cooling device from achieving high performance. Moreover, low thermal conductivity in these series of polymer is also disadvantageous, which has been explained earlier in Chapter 1. Thermal conductivity plays a dominant role in the thermal transportation process of the ECE cooling device, and both cooling power and efficiency of cooling device would suffer if heat transportation process is inefficient. Another drawback for electrocaloric polymers is the requirement of high electric field, generally over 50 MVm\(^{-1}\). Compared with polymeric materials, it is plausible that ceramic materials with large ECE may need a lower driving electric field. One argument is that in order to compare the electric field and the degree of difficult to operate material under such a filed, reduce field, which is the ratio between applied field and the breakdown field, should be used, instead of the absolute value of the electric field. Since electrocaloric polymers generally have higher intrinsic breakdown field than electrocaloric ceramics, it is therefore not necessarily more difficult to apply a higher electric field on the polymers. Besides, the catastrophic breakdown mechanism in ceramics materials make severe damage and prevent them from being used once breakdown happens, while in polymers the “self-healing” process after breakdown would elongate the lifetime and increase the reliability of an ECE cooling device with electrocaloric polymers even after an initial breakdown takes place. [136, 137].

Based on the consideration in the previous section, suggested future works are presented below and can be categorized into three areas.

1. Adopting Novel Characterization Methods to Probe Polymer Structures

Due to the nature of their semicrystalline structures, it is difficult to characterize P(VDF-
TrFE) copolymers and P(VDF-TrFE-CFE) terpolymers on a micro scale using conventional facilities such as optical microscopy and scanning electron microscopy. Instead, detections such as X-ray diffraction, FT-IR and differential scanning calorimetry (SEM) are utilized to probe these polymer structures. While these indirect methods provide some general idea on P(VDF-TrFE) copolymers and P(VDF-TrFE-CFE) terpolymers, the lack of detailed information leaves a gap between the understanding of these materials on a micro scale and the macro scale response. Therefore it is essential to develop a facile way to directly visualize structures inside the polymers to further advance the understanding in this field.

Atomic Force Microscopy (AFM) is a versatile tool for acquiring topographic information for planar samples and has been widely used as a standard method to study material structures. Below are topography images of P(VDF-TrFE-CFE) terpolymer, P(VDF-TrFE-CFE)/P(VDF-TrFE) 65/35 polymer blends with a weight ratio of 9:1, and P(VDF-TrFE-CFE)/ZrO$_2$ nanoparticle blends with 3 vol% nanoparticles obtained by (AFM), with 1 $\mu$m by 1$\mu$m sample size. It can be seen that all samples showed rod-shaped structures, while the crystallite size decreases when terpolymer is blended with either copolymer or ZrO$_2$ nanoparticles. The size reduction of the crystallite is consistent with previous XRD study, where the size of the crystallite corresponds to the coherence length along the chain direction.
Figure 6-1 AFM image for P(VDF-TrFE-CFE) terpolymer sample.

Figure 6-2 AFM image for P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends sample.
Figure 6-3 AFM image for P(VDF-TrFE-CFE) terpolymer/ZrO$_2$ nano-particle blends sample.

Table 6-1 Diameter data for P(VDF-TrFE-CFE) terpolymer, P(VDF-TrFE-CFE) terpolymer/P(VDF-TrFE) copolymer blends, and P(VDF-TrFE-CFE) terpolymer/ZrO$_2$ nano-particle blends samples.

<table>
<thead>
<tr>
<th>Di for terpolymer (nm)</th>
<th>Di for polymer blends (nm)</th>
<th>Di for nano particle blends (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>42.1</td>
<td>37.7</td>
</tr>
<tr>
<td>73</td>
<td>50</td>
<td>39.5</td>
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<tr>
<td>76</td>
<td>42.1</td>
<td>36.5</td>
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<td>60</td>
<td>42.1</td>
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</tr>
<tr>
<td>63</td>
<td>42.1</td>
<td>44.7</td>
</tr>
<tr>
<td><strong>Average (nm)</strong></td>
<td><strong>Average (nm)</strong></td>
<td><strong>Average (nm)</strong></td>
</tr>
<tr>
<td>68</td>
<td>42.7</td>
<td>43.1</td>
</tr>
</tbody>
</table>

AFM images, as shown in Figure 6-1, 6-2 and 6-3, along with analysis such as XRD and DSC, are able to provide a comprehensive understanding of the material structures, especially on a macro scale. For probing micro scale visualization on the order of nanometer or sub-nanometer, transmission electron microscopy (TEM) can be of great importance.
2. Blending Nano-Fillers to Enhance Polymer Thermal Properties

From device point of view, besides large ECE response, the thermal conductivity of the electrocaloric materials is also crucial for development ECE cooling device with high cooling power. The performance of ECE cooling device based on P(VDF-TrFE) copolymers and P(VDF-TrFE-CFE) terpolymers would suffer from their thermal conductivities, which are intrinsically low at about 0.2 Wm$^{-1}$K$^{-1}$. Therefore it is essential to conduct research to increase thermal conductivity of EC polymers. Furthermore, through proper modification, it is possible to develop polymer composites with maximized EC effect and thermal conductivity.

Polymer/nano-particle composites may provide one viable method to address issue. With proper design, nano-particles may be distributed in the polymer matrix in a sense that a thermal link among these particles would be established while the composites as a whole remains in an insulator state with minimal leakage current. Besides nano-particles, other alternatives such as nanotubes or graphene may also be interesting for developing a polymer-based composite with not only high thermal conductivity, but at the same time, a high ECE response as well.

3. Designing Multilayer Configuration to Improve Electrocaloric Efficiency

The ratio of temperature change $\Delta T$ due to electrocaloric effect and the electric field $E$ applied to EC material in order to obtain $\Delta T$ is called electrocaloric coefficient. Electrocaloric coefficient is a figure of merit to characterize the efficiency of EC materials. The higher electrocaloric coefficient is, the lower electric field is required to generate same temperature response. One way to design material system with large EC coefficient is described earlier in Chapter 5, which is to induce internal bias field in polymer composites through poling process. Besides blending P(VDF-TrFE) copolymer and P(VDF-TrFE-CFE) terpolymer, a multilayer
design can also serve the purpose of providing the internal bias field to enhance the EC coefficient of the materials.

As shown in Figure 6-5, terpolymer/copolymer blends can be converted into terpolymer/copolymer bilayer tandem structure. Upon poling, the remanent polarization in the copolymer layer would act as the source of the internal bias field that increases the EC coefficient in the bilayer system.

![Figure 6-5](attachment:figure65.png)

**Figure 6-5** (a) terpolymer/copolymer blends, in which the blue matrix represents terpolymer, and the yellow dots represents copolymer dispersed in terpolymer, (b) terpolymer/copolymer tandem bilayer, where the blue represents the terpolymer layer and the yellow represents the copolymer layer.

Moreover, a multilayer structure can also be designed based on the cascade consideration. In the cascade case, each layer has its own optimal temperature range where material will exhibit large ECE, while these temperature ranges overlap among one another to some extent so that overall the material structure will provide a large ECE over a broad temperature range. For example, the optimal operating temperature for irradiated P(VDF-TrFE) 65/35 mol% copolymer with 20 Mrads is from 45 °C to 55 °C, if a P(VDF-TrFE-CFE) terpolymer layer, whose operating temperature can vary from 10 °C to 45 °C, is integrated with the irradiated copolymer layer, the whole structure will be able to provide large ECE over an extended temperature range from 10 °C to 55 °C. Likewise, the temperature range can be further broadened as more layers with different operating temperatures are stacked into one multilayer structure.
Reference

VITA

Xinyu Li

Xinyu Li was on July 7th, 1986 in Jilin Province, China. He attended Department of Materials Science and Engineering in Tsinghua University, Beijing, China in 2005 as a undergraduate student and obtained a B.E. degree in 2009. During his time in Tsinghua, Xinyu worked in the State Key Lab of New Ceramics and Fine Processing as a research intern. After graduation in 2009, he joined Professor Qiming Zhang’s group in Department of Electrical Engineering in the Pennsylvania State University as a Ph.D. student.

His research focuses on the development of organic materials exhibiting novel electrical properties, especially giant electrocaloric response, as well as the design of solid-state cooling devices based on electrocaloric effect. Throughout his Ph.D. study, Xinyu has authored or co-authored over 20 papers in peer-reviewed journals and conference proceedings, including 2 feature articles. He is also student member of IEEE, American Physical Society, Materials Research Society, and Royal Society of Chemistry.