Study on the Curie transition of P(VDF-TrFE) copolymer

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Abstract. A systematic study was carried out to decipher the mechanism of Curie transition of piezoelectric crystals of poly(vinylidene fluoride trifluoroethylene) P(VDF-TrFE). The unique polarity of P(VDF-TrFE) crystalline phase below Curie transition temperature is attributed to the lattice packing of all-trans molecular chains, which allocates all the substituted fluorine atoms on one side of molecular chains and hydrogen atoms on the other side. Therefore, a net dipole moment is created across the lateral packing of molecular chains. Nevertheless, due to the mutual repulsion among fluorene atoms, this all-trans conformation is not stable, and ready to change above Curie temperature, where thermal kinetic energy is sufficient to cause segmental rotation. As being illustrated by in-situ recorded X-ray diffraction and thermal analysis, the concerned Curie transition is deciphered as a one-step process which is involved two process and this is different from conventional one-step solid-solid transitions. Accompanied with this one-step process during heating, the occurrence of lamellar bending is inferred for elucidating the decline of stacking regularity of crystalline lamellae, which reversibly recover during subsequent cooling. However, as the crystalline lamellae of P(VDF-TrFE) are confined in between the stacking of crystalline lamellae of PVDF, lamellar bending is restricted accordingly. As a result, a certain fraction of the piezoelectric crystalline lamellae was found to survive through the Curie transition. Thus, in addition to the suggestion of a one-step process as a new concept for understanding the Curie transition, the relationship between the lamellar stacking and transition of molecular packing is unveiled as well in this research.

Keywords: Curie transition, lamellar bending, confinement effect

1. Introduction

Ferroelectric polymers have attracted lots of attention for decades due to the characteristics of their phase transitions. Among these polymers, poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) are of particular interest. The unique ferroelectric feature of the PVDF and P(VDF-TrFE) crystalline phase is derived from the packing of molecular chains in an all-trans conformation, which arranges all the substituted fluorine atoms on one side of the molecular chain and the hydrogen atoms on the other side, thus producing a net dipole moment. The trans and gauche conformations are feasible to switch over within the ferroelectric phase transition, which is known as the Curie transition. Due to mutual repulsion among fluorine atoms, this all-trans molecular conformation is not stable. In order to lessen encountered steric hindrance, the gauche conformation is ready to develop above the Curie temperature, where thermal energy is sufficient to cause segmental rotation.

The ferroelectric polymer P(VDF-TrFE) has two crystalline forms, the low-temperature (LT) and the cooled (CL) ones. The LT form consist of an all-trans conformation with parallel arrangement of CF₂,
as in the case of PVDF form I. In the CL form, the long trans segments consist of irregular trans-gauche conformation. This form can transform into the high-temperature (HT) form above the Curie temperature. The HT-form consists of TT, TG, and TG conformation, where the molecular chains are able to rotate through this trans-gauche conformation, as noted above.

As an attempt to widely enhance the use and stability of low-temperature piezoelectric crystalline form of P(VDF-TrFE) copolymer, this study focuses on further deciphering the mechanism of Curie transition of P(VDF-TrFE) copolymer. This research approach aims to establish the fundamental background of curie transition in order to learn essential knowledge needed for optimizing the use of precious piezoelectric feature of polymeric crystals.

2. Methodology

Blended samples of P(VDF-TrFE)/HMB and PVDF/ P(VDF-TrFE) were dissolved in N,N-dimethylformamide (DMF) (bp = 153 °C) for 1 day. The resulting, solution was then cast on a glass at 70 °C and the solvent evaporated immediately. The obtained film (1wt% P(VDF-TrFE), P(VDF-TrFE)/HMB 30/70 and PVDF/ P(VDF-TrFE) 30/70) was annealed at 80 °C (below Tc) for 1 hour and 120 °C (above Tc) for 45 minutes, then observed with DSC, 2D XRD, and SAXS. For the TEM sample, 2wt% P(VDF-TrFE)/HMB with a blend ratio of 2/98 was casted on glass at 70 °C and melted together. The HMB substrate was able to dissolved P(VDF-TrFE) at 180 °C. After melting, the sample was quenched by liquid nitrogen in order to grow P(VDF-TrFE) crystal first and then HMB crystal, and then annealed at 80 °C (below Tc) for 1 hour and annealed at 120 °C (above Tc) for 45 minutes.

3. Results and Discussion

3.1 Mechanism of curie transition of P(VDF-TrFE)

The DSC thermograms of VDF 70% - TrFE sample shows that two endothermic peaks are involved during Curie transition, including an endotherm shoulder and a sharp peak. Conventionally the curie transition is recognized as a kind of one-step transition of crystalline packing without involving the melting of original crystals. Thus the involvement of two endothermic processes during curie transition is curious, and further examinations were carried out via in-situ X-ray experiments, which will be discussed later. As the heating rate is increased, the occurrence of Curie transition shifted to higher temperatures. At the end of heating process, there is a very sharp endothermic melting peak. As the heating rate is increased, this melting peak shifts to higher temperatures. As the heating rate at 30 °C/min, two endothermic melting peaks were found. It appears that there is no sufficient time for the reorganization process, and thus crystalline domains of disparate stability are present.

![Figure 1. Thermal diagram of different heating rates for pure P(VDF-TrFE). The melting point and the Curie transition temperature of P(VDF-TrFE) occurs at higher temperature when increasing the heating rate.](image1.png)

![Figure 2. Thermal diagram of different cooling rates for pure P(VDF-TrFE). The crystallization point occurs at a higher temperature during the cooling process, and there are two exothermic peaks for the Curie](image2.png)
a sharp exothermic peak. As the cooling rate is decreased, the Curie transition and crystallization temperature shifts to higher temperatures. The crystallization peak gradually become thinner as the cooling rate decreases. The sample has more time for crystallization at a lower cooling rate. During faster cooling processes, a wider temperature range is needed for the crystallization to finish, which is found as a common crystallization feature of polymeric materials.

The phase identification of P(VDF-TrFE) can be further studied by in-situ X-ray diffraction experiments. Figure 3 shows the in-situ X-ray diffraction profiles of pure P(VDF-TrFE) sample obtained during heating at 10 °C/min. This sample was prepared by solution casting and annealed at 80 °C for 1 hour afterwards. According to this result and based on the peak area, the curie transition can be classified as a one-step process during heating and cooling. The cooling process of pure P(VDF-TrFE)-showed similar phenomena. The (110)/(200) diffraction of the LT-form appears at 70 °C and the Curie transition during cooling begins with the gradual disappearance of the (001) diffraction of the HT-form, which finishes until reaching 50 °C.

This one-step process involved two process, the first process is the appearance of (001) diffraction of HT form and followed by the increase of lattice dimension along the c-axis. The second process is the rotational motion of molecular chains increases with the increase of temperature, which cause the disappearance of (110)/(200) diffraction of LT-form.

![Figure 3. In-situ X-ray diffraction of the pure P(VDF-TrFE) profiles during heating at 10 °C/min. The arrow indicates the shift of the (001) diffraction peak of HT form during heating.](image1)

![Figure 4. In-situ X-ray diffraction profiles of pure P(VDF-TrFE) sample during cooling at 10 °C/min.](image2)

3.1.1 The influence of curie transition on the evolution of lamellar stacking
For the VDF 70%-TrFE-sample without annealed, annealed at 80 °C and 120 °C for 1 hour and 45 minutes, the small angle x-ray scattering (SAXS) experiment was conducted to examine the influence of the Curie transition on the evolution of lamellar stacking. For the P(VDF-TrFE) sample without annealing process, as shown in Figure 5, a sharp peak was observed, indicating the established regularity of lamellae stacking upon annealing. As the temperature increased and approached around 115 °C, which is about the Curie transition temperature, the scattering peak shift to lower angle accompanied with the decrease of scattering intensity. The decrease of scattering intensity reflects the decline of stacking regularity. Hence the lamellar stacking was recognized to become less regular upon the occurrence of Curie transition.

Upon subsequent cooling process, the intensity of scattering peak increases again as the temperature approached the Curie transition temperature around 70 °C. Thus a reversible restoration of regular lamellar stacking is recognized. According to this result, irregular lamellar bending is proposed to occur during the Curie transition, which account for the decline of stacking regularity of crystalline lamellae, and thus the decrease of scattering intensity. The transformation of lattice packing is thus now unveiled capable of influencing the stacking of crystalline lamellae.
After reaching 110 °C during heating, the SAXS intensity decreases with the restoration of scattering shoulder. This result means the stacking of crystalline lamellae become less regular due to the occurrence of curie transition. As the temperature was decreased upon cooling process, the intensity increased again due to the restoration of regular lamellar stacking. The cooling process appears to recover the stacking of thinner crystalline lamellae also, as being indicated by the reversible presence of scattering shoulder.

Figures 7 and 8 show the in-situ SAXS experiments of the P(VDF-TrFE) annealed at 80 °C, which is below the Tc. A sharp peak was observed below curie transition and a new peak, shoulder peak, was observed above curie transition. This results is similar with without annealing process, but the shoulder peak was more higher when the sample annealed at 80 °C.

Figures 9 and 10 show the in-situ SAXS experiments of the P(VDF-TrFE) annealed at 120 °C, which is above the Tc. A sharp scattering peak is observed to slightly overlap with another scattering shoulder at higher angle. During the heating process at 10 °C/min, the intensity of scattering peak was found to increase first with the progressive intensity decay of scattering shoulder. The increase of SAXS intensity indicates the lamellar stacking becomes more regular, which appears accompanied with the melting of thinner lamellae based on the disappearance of scattering shoulder.
As shown in figure 11, the confinement effect yielded by surrounding PVDF crystals is proposed. In order to explore the impact of the mixing ratio on the phase stability, both PVDF and P(VDF-TrFE) molecules were mixed together in different ratios. As shown in figure 11, multiple endothermic peaks were found. For the mixture containing 70 wt% of P(VDF-TrFE) component, the Curie transition of P(VDF-TrFE) results in one endothermic peak and one shoulder around 90 and 104 °C upon heating. The endothermic shoulder begins at 70 °C and overlaps with the second peak of the Curie transition. The PVDF component does not have a Curie temperature. The melting temperature of P(VDF-TrFE) crystals shifts to higher temperatures upon the increase of PVDF content, but the melting point of PVDF remains at 168 °C. Regarding the increase of melting temperature of P(VDF-TrFE) crystals upon the increase of PVDF content, the confinement effect yielded by surrounding PVDF crystals is proposed. As P(VDF-TrFE) crystalline lamellae are sandwiched in between PVDF crystals, the melting of P(VDF-TrFE) crystals is likely to be delayed and occur at higher temperatures.

3.2 Confinement effect on the melting of P(VDF-TrFE) crystals in binary mixtures

In order to explore the impact of the mixing ratio on the phase stability, both PVDF and P(VDF-TrFE) molecules were mixed together in different ratios. As shown in figure 11, multiple endothermic peaks were found. For the mixture containing 70 wt% of P(VDF-TrFE) component, the Curie transition of P(VDF-TrFE) results in one endothermic peak and one shoulder around 90 and 104 °C upon heating. The endothermic shoulder begins at 70 °C and overlaps with the second peak of the Curie transition. The PVDF component does not have a Curie temperature. The melting temperature of P(VDF-TrFE) crystals shifts to higher temperatures upon the increase of PVDF content, but the melting point of PVDF remains at 168 °C. Regarding the increase of melting temperature of P(VDF-TrFE) crystals upon the increase of PVDF content, the confinement effect yielded by surrounding PVDF crystals is proposed. As P(VDF-TrFE) crystalline lamellae are sandwiched in between PVDF crystals, the melting of P(VDF-TrFE) crystals is likely to be delayed and occur at higher temperatures.

3.2.1 The influence of curie transition on the evolution of lamellat stacking PVDF/P(VDF-TrFE)

For the binary mixture PVDF/P(VDF-TrFE) samples annealed at 80 °C for 1 hour. As shown in Figure 12, in addition to the sharp scattering peak located at a lower angle, one broader scatter peak at higher angle was observed also. Figure 12 shows the increase of SAXS intensity of the sharper peak first upon heating, indicating the enhancement of stacking regularity of crystalline lamellae. As the temperature approached to 115 °C, the sharper scattering peak shifts to lower angle with the decrease of intensity.
indicating the lamellar stacking become less regular upon Curie transition. Oppositely, the broader scattering peak becomes stronger above Curie transition. During the cooling process, the SAXS intensity of scattering peak at lower angle increased again after passing 70 °C, indicating the restoration of regular lamellar stacking. In contrast, the SAXS intensity of second scattering peak decreased as the sample is cooled below 70 °C.

The presence of the broader scattering peak is likely attributed to the less regular stacking of thinner crystalline lamellae of the minor PVDF component. Considering the crystallization history of mixture, thinner PVDF crystalline lamellae are derived to stack randomly in between thicker crystalline lamellae of copolymer. These thinner PVDF crystalline lamellae are all of nonpolar phase, which do not have curie transition. With the occurrence of curie transition during heating, the stacking of thicker copolymer crystalline lamellae becomes less regular and therefore occupies a larger amount of volume, which causes these thinner PVDF lamellae to stack in a closer manner. Thus the stacking of PVDF thinner lamellae becomes more regular above the Curie transition temperature, yielding a stronger scattering peak. As the sample is cooled below the Curie transition temperature, a certain fraction of free volume is restored via the regular stacking of copolymer lamellae. Thus the stacking of thinner PVDF crystalline lamellae become less regular again.

Thus these results shown on the Figure 12 and 13 are deciphered as a result of random stacking of thinner PVDF crystalline lamellae in between crystalline lamellae of copolymer, and also the impact of curie transition.

3.3 Curie transition of binary mixture P(VDF-TrFE)/HMB
The in-situ X-ray profile of the 30/70 mixture of P(VDF-TrFE) /HMB after annealing at 80 °C for 1 hour are shown in Figures 14 and 16 during heating and cooling. Consistent with in-situ x-ray of pure P(VDF-TrFE)-result, there are one-step process also for the mixture of P(VDF-TrFE)/HMB 30/70 which is involved two process. The first process is (001) diffraction of HT form appears at 90 °C, where this peak is 10 °C more earlier than pure P(VDF-TrFE). Nevertheless, the second process is the (110)/(200) diffraction of LT form is suddenly disappears at 100 °C, 15 °C different with (110)/(200) diffraction of LT form pure P(VDF-TrFE) and the (001) diffraction of HT have more sharp peak than pure P(VDF-TrFE). This result is consistent with DSC data.

During cooling process, Figure 15 shows the curie transition is happened from HT form to LT form. The (001) diffraction of HT form gradually disappear and the intensity decrease during cooling process. Indicate the disorder molecular structure of P(VDF-TrFE)-due to the HT form was randomly rotate along chain axis. The (110)/(200) diffraction of LT form gradually appears at 70 °C during cooling process. Indicate the order of all-trans conformation of LT form. In-situ X-ray experiment shows that reversible phase transition was happened in this process.
3.3.1 Epitaxial organization of P(VDF-TrFE) on HMB
A transmission electron microscope (TEM) was used to explore the epitaxial relationship between P(VDF-TrFE) and HMB. The HMB melt was able to dissolve semicrystalline P(VDF-TrFE). The P(VDF-TrFE) and HMB were dissolved in the dimethylformamide (DMF) and melted together when kept at 180 °C for 20 seconds and then directly quenched. The sample was annealed at different temperatures and then stored in a vacuum to evaporate the HMB crystals. While the HMB is included as the major component in the prepared eutectic mixture, the HMB crystalline platelets occurs first from molten state below 165 °C, which serve as the substrate for later epitaxial organization of P(VDF-TrFE). The quenching process at room temperature is able to preserve the epitaxial organization of P(VDF-TrFE). Epitaxy of P(VDF-TrFE) on HMB during quenching can be seen in Figure 17(a), P(VDF-TrFE) crystallized on HMB without annealing. Upon the development of P(VDF-TrFE) packing, arrays of oriented stripes were observed by TEM which is the crystals growing in two directions. The orientation of these stripes are marked by yellow arrow. The HMB crystalline platelets indicated by the white arrow, which is related to the fast growth direction. Figures 17 (b – d) show the epitaxy of PVDF-TrFE on HMB during annealing process. When the samples annealed at 60 °C, curving lamellae has been developed. Nevertheless, lamellae become more regular and very straight when the sample annealed at 80 °C. At 120 °C, lamellae continuously grow on HMB and thicker lamellae has been observed during this annealing process. These results are consistent with what have been observed from SAXS data, lamellar bending was observed above curie temperature, indicating a very wavy lamellae at 120 °C.

Figure 14 In-situ X-ray diffraction of the 30/70 mixture of P(VDF-TrFE)/HMB profiles during heating at 10 °C/min. The two different phases of P(VDF-TrFE) appear in different ways as the temperature increases.

Figure 15 In-situ X-ray diffraction of the 30/70 mixtures of P(VDF-TrFE)/HMB profiles during cooling at 10 °C/min. The two different phases of P(VDF-TrFE) appear in different ways as the temperature increases.

Figure 16 In-situ X-ray diffraction of the 30/70 mixtures of P(VDF-TrFE)/HMB profiles during cooling at 70 °C-30 °C.
4. Conclusion

The Curie transition of P(VDF-TrFE) copolymer has been investigated with a wide range of heating-cooling temperature. The Curie transition is deciphered as a one-step process which is involved two processes and this is different from conventional one-step solid-solid transition. The first-process of Curie transition: The increase of lattice dimension and intramolecular order and the second-process of Curie transition: The decrease of intermolecular order within larger unit cells. The transformation of lattice packing upon Curie transition is accompanied with the adjustment of lamellar stacking. The presence of PVDF crystalline lamellae is able to stabilize the LT-form of P(VDF-TrFE). The stacking of thinner PVDF crystalline lamellae is influenced by the curie transition of surrounding crystalline lamellae of copolymer. Finally, epitaxy effect causes the LT-form of P(VDF-TrFE) suddenly disappears at Curie transition temperature.

5. References

[1] G. Teyssedre, A. Bernes, and C. Lacabanne 1995 Cooperative movements associated with the Curie transition in P (VDF-TrFE) copolymers, Journal of Polymer Science Part B: Polymer Physics, vol. 33, pp. 879-890
[2] Mayergoyz and G. Bertott 2005 Hysteresis in Piezoelectric and Ferroelectric Materials, The Science of Hysteresis, vol. 3, pp. 338-465
[3] P. Dobis, J. Bruestlova, and M. Bartlova 2010 Curie Temperature in Ferromagnetic Materials and Visualized Magnetic Domains, 3rd International Symposium for Engineering Education, University College Cork, Ireland.
[4] R. Tanaka, K. Tashiro, and M. Kobayashi 1999 Annealing effect on the ferroelectric phase transition behavior and domain structure of vinylidene fluoride (VDF)–trifluoroethylene copolymers: a comparison between uniaxially oriented VDF 73 and 65% copolymers, polymer, vol. 40, pp. 3855–3865
[5] K. Tashiro and H. Hama 2004 Structural changes in isothermal crystallization processes of synthetic polymers studied by time-resolved measurements of synchrotron-sourced X-ray scatters and vibrational spectra, Macromolecular research, vol. 12, pp. 1-10
[6] R. Gregorio and M. M. Botta 1998 Effect of crystallization temperature on the phase transitions of P (VDF/TrFE) copolymers, Journal of Polymer Science B-Polymer Physics Edition, vol. 36, pp. 403-414
[7] A. Prabu, J. S. Lee, K. J. Kim, and H. S. Lee 2006 Infrared spectroscopic studies on crystallization and Curie transition behavior of ultrathin films of P(VDF/TrFE) (72/28) Vibrational Spectroscopy, vol. 41, pp. 1-13