Grazing incidence reflection absorption Fourier transform infrared (GIRA-FTIR) spectroscopic studies on the ferroelectric behavior of poly(vinylidene fluoride–trifluoroethylene) ultrathin films

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Abstract

Grazing incidence reflection absorption Fourier transform infrared (GIRA-FTIR) spectroscopy was used to characterize the ferroelectric behavior of a thin poly(vinylidene fluoride–trifluoroethylene) P(VDF–TrFE) copolymer. The lab-built GIRA-FTIR apparatus allowed the heating and corona poling process to be carried out whilst collecting the GIRA spectra of the thin polymer film. The Curie transition from the ferroelectric to paraelectric phase was confirmed from the abrupt change in intensity of the 849 cm^{-1} band in the RA-FTIR spectrum. It was found that the Curie temperature dropped dramatically when the film thickness was lowered to below a certain critical value of approximately 100 nm. The switching of the CF_2 dipoles in the ferroelectric crystals after applying the external electric field could be determined by monitoring the change in the 849 cm^{-1} band intensity. For the 600 nm thick P(VDF–TrFE) film, the switching of the dipoles appears to occur almost instantaneously, while the kinetics of dipole switching of the 75 nm thick film were significantly retarded. The repeated switchability of the CF_2 dipoles upon the application of a bipolar cyclic electric field was also confirmed. The bistability of the film due to remnant polarization was also confirmed from the absorbance of the 849 cm^{-1} band after removing the applied voltage during corona poling.

Keywords: GIRA-FTIR; Curie transition; Corona poling

1. Introduction

Poly(vinylidene fluoride–trifluoroethylene), P(VDF/TrFE), is a semicrystalline statistical copolymer. The copolymer with a VDF content ranging from 50 to 85 mol% exhibits a stable ferroelectric phase at room temperature [1–4]. Its ferroelectric properties are attributed to the electrical dipoles that are formed by the difference in electronegativity between the hydrogen and fluorine atoms, which are perpendicular to the main chain [5]. This ferroelectric phase transition is unique in that the chain conformation changes between the *trans* and the *gauche* conformers at the so-called Curie transition temperature (T_c) [6–8].

Many studies have been carried out on the ferroelectric behavior of P(VDF/TrFE) as a bulk material. Since the

ferroelectric properties are closely related to the crystal structures such as the overall crystallinity and crystal size, the effect of thermal annealing and external stretching on the crystal structure has been mainly examined using X-ray diffraction [9–12]. The detailed chain conformation changes in the various ferroelectric crystal phases upon thermal treatment has been also analyzed using vibrational spectroscopy and thermal analysis methods, and the changes in the structural and electrical properties upon the application of an external electric field during poling have been studied [13–15]. However, the ferroelectric behavior of the P(VDF/TrFE) as an ultrathin polymer film for potential use as a ferroelectric material for the memory devices has not been reported. The microstructure and electric properties can be significantly affected by the film thickness particularly when it is reduced below a certain critical value [2,9,12,16].

Recently, the ferroelectric properties of ultrathin P(VDF/TrFE) films, <1 μm in thickness, has attracted a great deal of attention. Thin films with a thickness <100 nm enables the use of an applied voltage as low as 10 V to achieve 1 MV/cm for the switching of electrical dipoles [9]. This

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development suggests many new applications such as organic ferroelectric memory devices for computers and related devices [9,16–19]. Nevertheless, the limited thermal stability of P(VDF/TrFE) copolymers prevent them from being integrated into the usual manufacturing process for Si-based data storage devices (DRAM and S-RAM), which is a major hindrance in achieving the desired objective of producing nonvolatile random access memory (NV-RAM) [17].

For ultrathin polymer films, the increased specific surface and interface area was found to play an important role in determining the microstructure such as the chain orientation, the degree of crystallinity, and the chain mobility [12,15,19]. For example, the crystallization process in films with thickness <100 nm was reported to be severely affected [9,12]. Even though the chains at the air surface show increased mobility, which facilitates the crystallization process, the final degree of crystallinity of the thin film was generally observed to be lower than the corresponding values of the thick films. Such a low crystallinity in films below a critical thickness leads to a large and discontinuous change in the dielectric constant and ferroelectric polarization [15,20,21].

Fourier transform infrared (FTIR) spectroscopy is an important technique for characterizing the conformation changes in many polymers. However, it is difficult to observe the structural changes in thin polymer films using conventional FTIR in transmission mode due to the very low signal-to-noise ratio. Reflection absorption FTIR (RA-FTIR) spectroscopy with an incidence angle ranging from 75 to 88° can be a good alternative for characterizing the physical structure of ultrathin films because the incident infrared radiation used for grazing incidence angle RA-FTIR spectroscopy spans a wider surface area. For the incidence angle given above, the illuminated surface area from RA-FTIR can be 3 to 30 times greater than the corresponding area analyzed in transmission FTIR with a normal incidence.

This study investigated whether or not the ferroelectric behavior of P(VDF/TrFE) ultrathin films could be conveniently characterized using RA-FTIR spectroscopy using a grazing incidence angle. In particular, the dipole orientation, which is necessary process to be used as a nonvolatile ferroelectric memory device material, was examined using the corona poling process in an attempt to simulate the industrial process as much as possible. The effect of the film thickness on the transition from the ferroelectric to paraelectric phase was examined. The switching of the electrical dipoles of P(VDF/TrFE) after applying an external electric field and the effect of film thickness on the switching dynamics was also characterized.

2. Experimental section

2.1. Sample preparation

The P(VDF/TrFE) (72/28, molar ratio) copolymer was spin-coated from methyl ethyl ketone (MEK) solution on a silver deposited glass substrate. The film thickness was controlled by changing the P(VDF/TrFE) concentration in the solution and
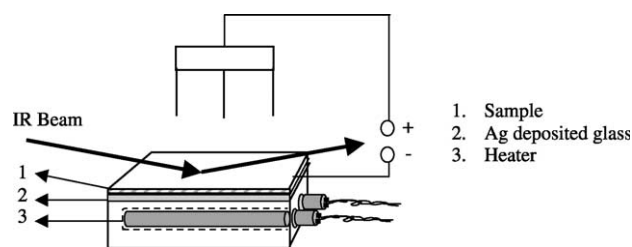

Fig. 1. Schematic drawing of the grazing incidence RA-FTIR accessory for the heating and corona poling process.

the spin speed. The film thickness was measured using an alpha step (DEKTAK3, Veeco Instruments Inc.). All the samples were annealed at 120 °C, which is above the Curie transition temperature, for 3 h to ensure the maximum crystallinity in the ferroelectric phase after cooling to room temperature.

2.2. Reflection–absorption FTIR measurement

The reflection–absorption FTIR spectra were collected using a Bruker IFS 66v/S spectrometer equipped with a variable angle reflection accessory. An incidence angle of 80° (angle from the plane normal) was found to be suitable for obtaining FTIR spectra with a good signal-to-noise ratio. A special sample holder was made to carry out the in situ heating and corona poling process whilst collecting the RA-FTIR spectra. Fig. 1 shows a schematic drawing of the sample holder.

2.3. Corona poling

A high voltage power supply (Nano NC, Korea) was used to supply the electric power during the poling process. Sample-to-tip distance of approximately 3 cm was used. As shown in Fig. 1, there were three tips on one electrode, which appear to be useful for ensuring a uniform field strength over the sampling area. The tip-to-tip distance was 1 cm.

3. Results and discussion

DSC thermograms of the bulk sample were obtained during the heating and cooling process in order to observe the thermal behavior of the P(VDF/TrFE) sample, and the results are shown in Fig. 2. Two endothermic peaks are observed during the heating process. The peak at approximately 104 °C was attributed to the Curie transition during which the ferroelectric crystal phase transforms to the paraelectric phase, and the peak at 153 °C corresponds to the melting transition. During the cooling process, melt-crystallization to form paraelectric α-phase crystals was observed at 140 °C. Upon further cooling, the α-phase crystals transformed to the ferroelectric β-phase crystals, which was confirmed from the two small exothermic peaks at approximately 60 °C and wide angle X-ray diffraction (WAXD) (data not shown).

Fig. 3 shows the CF_2 stretching band region of some selected RA-FTIR spectra of a 75 nm thick copolymer film obtained during the heating and cooling processes. The 849 cm^{-1} band is associated with the symmetric CF_2
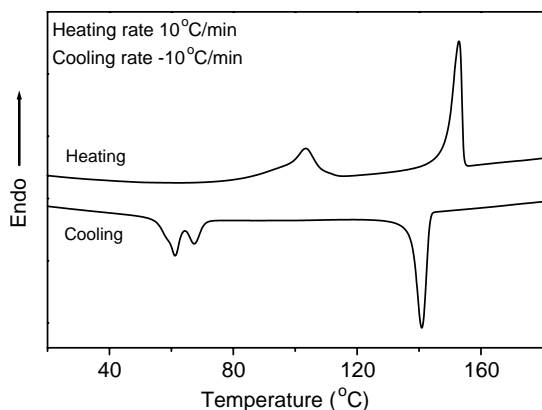
Fig. 2. DSC thermograms of the P(VDF/TrFE) (72/28) random copolymer obtained during heating and cooling.

stretching vibration coupled with the symmetric CC stretching vibration ($\nu_s CF_{2+}$, $\nu_s CC$) of *trans* sequences longer than three or more units. The 883 cm^{-1} band is related to the CF_2 asymmetric stretching coupled with the CH_2 rocking modes [13,14]. The 849 cm^{-1} band intensity was gradually decreased with increasing temperature. The peak almost disappeared at above the Curie transition temperature, as shown in Fig. 3. From this result, it can be concluded that the 849 cm^{-1} band is indicative of the presence of the ferroelectric phase [2]. As expected, the long *trans* sequence conformers are not obvious in the molten state. As the temperature decreases from the molten state, the 849 cm^{-1} band begins to appear at approximately 70 °C and its intensity increases continuously upon further cooling. This phenomenon indicates that the long *trans* sequence conformers have formed again during the cooling process, as the paraelectric phase has transformed into the ferroelectric phase.

Fig. 4 shows the intensity of 849 cm^{-1} band as a function of temperature during the heating and cooling periods for two thin films with different thickness. A sudden change in intensity, which is a direct indication of the Curie transition, began at approximately 88 °C for the thicker film. However, a sudden change in intensity during the cooling period was observed well below the corresponding temperature during the heating
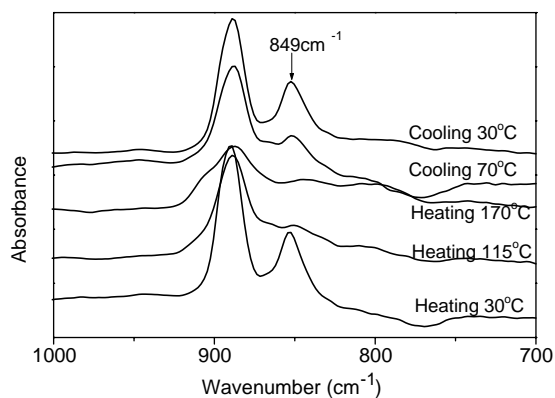

Fig. 3. CF_2 stretching band of the infrared spectra of a 75 nm thick P(VDF/TrFE) (72/28) thin film obtained at various temperature during the heating and cooling periods.
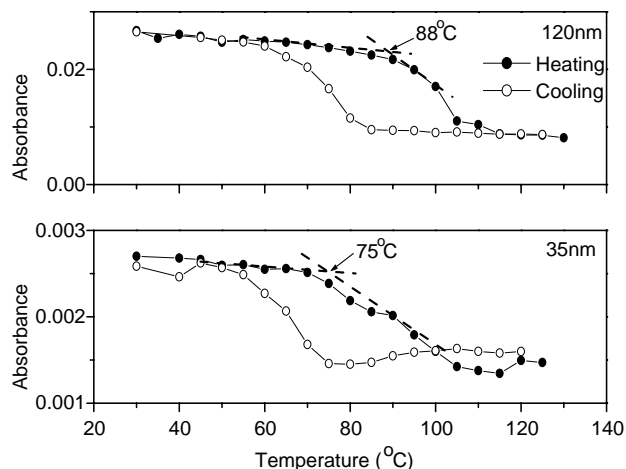

Fig. 4. 849 cm^{-1} band intensities as a function of temperature for the 35 and 120 nm thick films.

period. This type of hysteresis behavior, which has been observed with the bulk, also appears to be a typical phenomenon in the thin P(VDF/TrFE) films. For the thin sample with a 35 nm thickness, the overall behavior of the intensity change with the temperature was similar with that of the thick sample. However, there was a noticeable difference in the precise transition temperature. The Curie transition during heating period of the thin film began at approximately 75 °C, which is well below the corresponding temperature of the thick sample. This result indicates that the Curie transition temperature is definitely affected by the film thickness. The large interfacial area of the thin film appears to destabilize the ferroelectric crystalline phase, which induces the Curie transition at a lower temperature.

Several films with different thicknesses were also tested in order to evaluate the thickness effect on the Curie transition temperature quantitatively. The results are shown in Fig. 5 as a function of the P(VDF/TrFE) film thickness. As shown in Fig. 5, the Curie transition temperature appears to remain almost constant as long as the film thickness is above a critical thickness of approximately 100 nm. There is a significant decrease in the Curie temperature as the film thickness is reduced to <100 nm. For the film with a 35 nm thickness, its value was reduced to 75 °C, which is approximately 15° lower
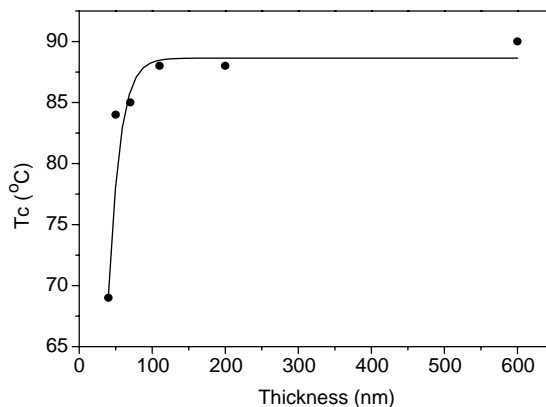

Fig. 5. Curie transition temperature (T_c) as function of film thickness.

than the corresponding temperature of the thicker film. Similar observations have been reported for the P(VDF–TrFE) copolymers at compositions ranging from 50/50 to 83/17 mol% using XRD and electrical property measurements [9,12,16]. In those studies, the crystallinity and size of the crystal were decreased drastically as the film thickness was lowered to below a critical value of 100–150 nm. The dielectric constant and remnant polarization also changed significantly at the critical film thickness region. Fig. 5 indicates that the GIRA-FTIR spectroscopy is a useful method for characterizing the ferroelectric behavior of ultrathin P(VDF–TrFE) copolymer films.

The critical thickness phenomenon, which shows a depression in the Curie transition temperature and degree of crystallinity of the thin film whose thickness is <100 nm, might be ascribed to the restriction of crystal growth in the confined space of the ultrathin film. The crystal formed within the confined space should have a limited size. The higher specific surface area and probably the larger number of defects in the crystals of the ferroelectric phase could reduce the thermodynamic stability of the ferroelectric crystal phase and lower the Curie transition temperature.

When an electric field is applied to the film, the CF_2 dipoles can be aligned along the electric field direction. Fig. 6 shows the RA-FTIR spectra showing the effect of the CF_2 dipole orientation before/after applying of the electric field. The two spectra in the figure show a very different intensity. The intensities of the 883, 1200, 3010 cm^{-1} bands observed before poling were much higher than those of the corresponding bands observed after poling. The relative intensities of the other bands at 849, 1300, and 2975 cm^{-1} bands were totally reversed. The peaks at 2975 and 3010 cm^{-1} are associated with the symmetric and asymmetric stretching mode of the CH_2 groups, respectively. The transition dipole moment angles of the two bands are perpendicular to each other, and both are perpendicular to the main chain direction.

It should be noted that the spectra was obtained using grazing angle RA-FTIR. Since the incident infrared radiation used was not polarized, there are two polarization directions that are either para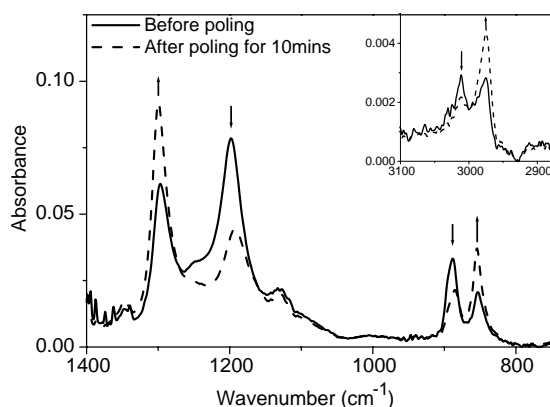llel or perpendicular to the plane of incidence. When the perpendicular component of the incident infrared radiation is reflected at a metal surface, the phase of the reflected light is shifted by 180°. Since the electric field vector of the incident radiation is combined with the one of the reflected radiation, the electric field intensity of the resulting infrared radiation of perpendicular polarization becomes almost negligible near the metal surface [22]. Therefore, the electric field vector at the metal surface, which is solely due to the incident radiation of parallel polarization, becomes parallel to the plane of incidence and almost perpendicular to the metal/film surface.

When an external electric field is applied, the CF_2 dipoles in the ferroelectric crystal phase can be aligned along the field direction. Therefore, the transition dipole moment direction of the CH_2 symmetric stretching mode at 2975 cm^{-1} becomes perpendicular to the film plane, while that of the CH_2 asymmetric stretching mode at 3025 cm^{-1} becomes parallel to the film plane. Therefore, the change in the absorbance of the two CH_2 stretching modes shown in the small inset in Fig. 6 is a direct indication of the CH_2 dipole (and CF_2 dipoles also) orientation along the external electric field direction. Since the absorbance of the 849 cm^{-1} band behaves in a similar manner to that of the 2975 cm^{-1} band, it is clear that the transition moment angle of the 849 cm^{-1} band is parallel to that of the 2975 cm^{-1} band. Hence, the change in absorbance of the 849 cm^{-1} band can be used to monitor the CF_2 dipole orientation.

Fig. 7 shows the intensity of the 849 cm^{-1} band of a 75 and 600 nm thick P(VDF–TrFE) film as function of the poling time. The ordinate values are the absorbance of the 849 cm^{-1} band at a specific poling time normalized to the corresponding value of the maximum poled state. It is clear that the polarization switching time increases significantly with decreasing film thickness. For the 75 nm thick film, which is thinner than the critical thickness (obtained from Fig. 5), it takes about 5 min to reach to 90% of the saturation poling state, while the 90% poled state can be obtained almost instantaneously for the 600 nm thick film. Although additional studies will be needed to determine the precise origin of the thickness effect on
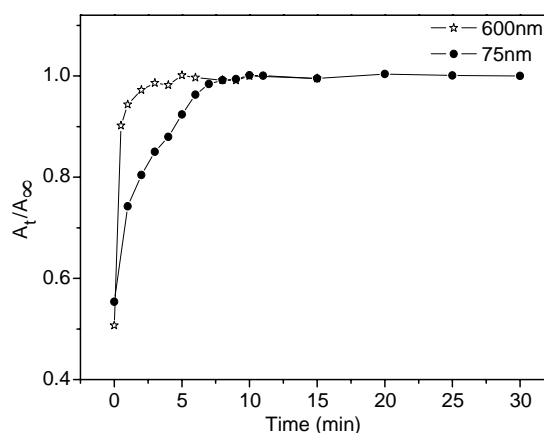

Fig. 6. Infrared spectra of P(VDF/TrFE) before and after poling for 10 min. The CH_2 stretching region is shown in the inset (applied voltage was 15 kV).

Fig. 7. 849 cm^{-1} band intensities after applying an electric voltage of 15 kV to the (a) 75 nm (b) 600 nm thick films as a function of time.
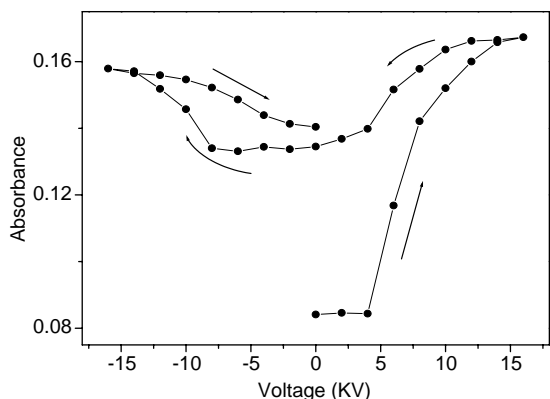
Fig. 8. 849 cm^{-1} band intensity of the 600 nm thick film as function of the applied bipolar cyclic electric voltage.

the poling kinetics, there appears to be a critical thickness that clearly differentiates the fast switching region from the slow one. The reason for the reduced switching kinetics appears to be related to the reduced crystallinity, smaller crystallite size, and possibly the large amount of crystal defects in the ferroelectric crystals. The increased specific crystal surface area appears to restrict the switching of the CF$_2$ dipoles in the ferroelectric crystal in the confined space. As expected, a similar behavior was also observed from the change in intensity of the CH$_2$ symmetric stretching bands at 2975 cm^{-1} (data not shown).

The poling and reverse poling needs to be carried out repeatedly in order for this material to be used as a polymeric material in a ferroelectric memory device. The aligned CF$_2$ dipoles as a result of external electric field could be reversed by applying a bipolar cyclic electric field. Fig. 8 shows the change in intensity of the 849 cm^{-1} band as a function of the cyclic electric field during corona poling. As mentioned above, the increased absorbance of the 849 cm^{-1} band can be a direct indication of the alignment of the CF$_2$ dipoles along the external electric field direction. After an initial increase in the applied voltage, the 849 cm^{-1} band intensity remained almost constant. A sudden increase in absorbance was observed once the applied voltage had increased above the coercive voltage of approximately 4 kV. When the applied voltage was further increased to 15 kV, the absorbance reached the asymptotic value of the saturated polarization value. 15 kV was almost the maximum voltage that could applied without electrical breakdown under the experimental conditions used. As the applied voltage was reduced to zero, the absorbance remained much higher than the initial value due to remnant polarization. As the reverse voltage was applied, the absorbance reached almost the maximum asymptotic value again. Remnant polarization could be also observed after removing the reversed applied voltage value.

4. Conclusions

The RA-FTIR technique was found to be very useful for characterizing the ferroelectric behavior of P(VDF–TrFE)

ultrathin films such as the Curie transition, the orientation of the CF$_2$ dipoles in the ferroelectric crystal phase under an electric field, and the switching kinetics during corona poling. The Curie transition temperature showed a precipitous reduction when the film thickness was decreased below a critical value of approximately 100 nm. This was attributed to the limited degree of crystallinity and crystallite size of the ferroelectric phase formed within the confined space of the ultrathin film. The higher specific surface area and defect content appears to decrease the thermodynamic stability of the ferroelectric crystals, resulting in a lower Curie transition temperature of an ultrathin film.

The orientation of the CF$_2$ dipoles after applying an external electric field during corona poling was successfully monitored using RA-FTIR even for films with a thickness lower than the critical value. Compared with the thicker film, the switching kinetics of the CF$_2$ dipoles in the ferroelectric crystal phase in the ultrathin film was significantly retarded. The small size and increased number of defects in the ferroelectric crystals appear to hinder the propagation of the dipole switching along the main chain direction. This suggests that the crystallite size in the ferroelectric phase needs to be maximized in order to facilitate the dipole switching motion.

The cyclic switchability of the CF$_2$ dipoles were also confirmed by observing the change in intensity of the 849 cm^{-1} band under an applied bipolar cyclic electric field, and a coercive field strength was observed at both positive and negative applied voltages. Overall, the P(VDF–TrFE) copolymer used in this study can be successfully used as a ferroelectric material in memory devices.

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