Effect of annealing on phase transition in poly(vinylidene fluoride) films prepared using polar solvent

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Abstract. The γ-phase poly (vinylidene fluoride) (PVDF) films are usually prepared using dimethyl sulfoxide (DMSO) solvent, regardless of preparation temperature. Here we report the crystallization of both α and γ-phase PVDF films by varying preparation temperature using DMSO solvent. The γ-phase PVDF films were annealed at 70, 90, 110, 130 and 160°C for five hours. The changes in the phase contents in the PVDF at different annealing conditions have been described. When thin films were annealed at 90°C for 5 h, maximum percentage of β-phase appears in PVDF thin films. The γ-phase PVDF films completely converted to α-phase when they were annealed at 160°C for 5 h. From X-ray diffraction (XRD), Fourier transform infrared spectrum (FTIR), differential scanning calorimetry (DSC) and Raman studies, it is confirmed that the PVDF thin films, cast from solution and annealed at 90°C for 5 h, have maximum percentage of β-phase. The β-phase PVDF shows a remnant polarization of 4·9 μC/cm^2 at 1400 kV/cm at 1 Hz.

Keywords. PVDF; phase transition; XRD; FTIR; Raman-spectra; DSC; hysteresis.

1. Introduction

PVDF, a semi-crystalline polymer exists in four different forms. The β-phase is the desirable phase due to its ferroelectric characteristic. Phase I (β-phase) has a planer TTTT (all trans) zigzag chain conformation which has space group $Cm2m$ (orthorhombic, $a = 8\cdot58$ Å, $b = 4\cdot91$ Å, $c = 2\cdot56$ Å) (Lando $et\ al$ 1966; Hasegawa $et\ al$ 1972a). The α-form, phase II (monoclinic, $P2_1/c$; $a = 4\cdot96$ Å, $b = 9\cdot64$ Å, $c = 4\cdot62$ Å, $\beta = 90°$) has a chain conformation which is approximately TGTG (trans- gauche-trans-gauche) (Lando $et\ al$ 1966; Hasegawa $et\ al$ 1972b). Phase III (γ-phase) has a chain conformation which is approximately TTTGTTTG′, with the space group being $C2cm$ (Weinhold $et\ al$ 1980). Application of high electric field to phase II (α-form), may cause 180° rotation of alternate chains leading to a polar, monoclinic form IV crystal (δ-phase) (Davis $et\ al$ 1978; Dasgupta and Doughty 1978; Newman $et\ al$ 1979). In β-phase the dipole moments of the two F–C and two C–H bonds add up in such a way that the monomer gets an effective dipole moment in the direction perpendicular to the carbon backbone. So the β-phase has the largest spontaneous polarization per unit cell and thus exhibits the most superior ferroelectric and piezoelectric properties (Chen $et\ al$ 2007). It is important to maximize β-phase in PVDF film. Different phases exist in PVDF depending on synthesis conditions like solvent, melt temperature, method of casting, stretching of thin films and annealing conditions. Buonomenna $et\ al$ (2007) show the effect of casting, solvent and coagulation conditions on the crystalline structure of PVDF.

PVDF films derived from DMF (dimethylformamide) polar solvent have been reported in literature to have a polar β-phase. But the β-phase is only stable at low temperatures (less than 50°C), at which the films are too porous for electrical applications (He and Yao 2006; Chen $et\ al$ 2007). Dense β-phase is dominant in PVDF thin films which have been obtained by spin coating PVDF/DMF solution with addition of Mg(NO$_3$)$_2$·6H$_2$O and dried at 100°C (He and Yao 2006; Chen $et\ al$ 2007). Only below a certain temperature the deformation of the α-phase results in transformation to the β-phase (polar) form.

Mohammadi $et\ al$ (2007) have shown the effect of stretch rate on conversion of α-phase to β-phase (Sajkiewicz $et\ al$ 1999). Maximum β-phase content was obtained at 90°C during stretching (Salimi and Yousefi 2003). The abrupt increase in orientation of β crystallites and maximum content of the β-form occur closely above the temperature of α_c relaxation temperature (between 70–87°C) (Salimi and Yousefi 2003).

The γ-phase has been produced by either casting from DMSO or dimethylformamide solution regardless of preparation temperature (Cortili and Zerbi 1967; Okuda $et\ al$

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1967; Gal'Perin *et al* 1970; Hasegawa *et al* 1972a; Park *et al* 2005). The γ-phase can be produced by crystallizing from melt under high pressures (Welch and Miller 1976) and can also be produced as a result of an atmospheric pressure annealing induced transformation from the α-phase (Prest Jr and Luca 1975). The percentage of γ-phase increases when α-phase thin film annealed at 158°C for 95 h (Prest Jr and Luca 1978). When β-phase thin film is annealed at 181°C at heating rate 0·31 K/min, then large percentage of β-crystallite is transformed to γ-phase (Prest Jr and Luca 1978). There is no clear report on the transformation of γ-phase to β-phase in PVDF.

In this paper we report the crystallization of α and γ-phase PVDF using DMSO solvent at preparation temperatures 50°C and 90°C respectively contradicting earlier reports. We choose preparation temperatures above α-phase relaxation temperature (90°C) and below α-phase relaxation temperature (50°C) because above and below α-phase relaxation temperature different phases exist in the PVDF films.

The conversion of γ-phase to β-phase (which is still unclear from studies) and γ-phase to α-phase at different annealing conditions has also been reported. We show that the α, β and γ-phase PVDF films can be produced using same polar solvent. Strong correlations have been observed among the characterization results.

2. Experimental

PVDF thin films were prepared from DMSO solvent at two different temperatures (90°C and 50°C). The granular PVDF (Sigma Aldrich) was dissolved in the solvent DMSO (15 wt% concentration). In the first case the temperature of the solution was increased to 90°C for complete dissolution of the polymer. The solution was cast uniformly on the glass substrate at room temperature. The films were kept at room temperature for one hour and then dried at 60°C. Free standing thin films were obtained after immersing in water. The thickness of PVDF films is 30 μm.

In the second case, the PVDF (15 wt%) dissolved completely at 50°C and was cast at room temperature on glass plates. The thin films were kept at room temperature for one hour and then dried at 60°C.

The films (which were cast at room temperature from solution at 90°C) were annealed at 70, 90, 110, 130 and 160°C for 5 h. In each annealing condition PVDF films were heated at a heating rate 2°C/min to reach annealing temperature and these films were cooled to room temperature at the same rate. To study the presence of different phases these PVDF films were characterized at room temperature. Phases of thin films were analyzed by XRD, using CuKα radiation, with the generator working at 40 kV and 40 mA. FTIR spectra of the films were recorded by a Perkin Elmer Spectrometer over a range of

400–2000 cm^{-1}. The Raman measurements on PVDF films were carried out using 632·8 nm excitation source using LABRAM-HR spectrometer equipped with a peltier cooled CCD detector. The melting behaviour of PVDF films (annealed at different temperatures) were investigated by DSC at a heating rate of 5°C/min. The melting point, crystallization and phase transition of α-, β- and γ-phases of PVDF were observed from DSC curves during heating cycle of DSC. Polarization (hysteresis loop measurement) measurements of PVDF thin films were performed using RT66A radiant ferroelectric loop tracer.

3. Results and discussion

3.1 *Crystallization of α and γ-phase PVDF films using DMSO solvent*

Figure 1 shows the X-ray diffraction pattern of PVDF thin films, prepared at 90°C and 50°C using DMSO solvent. The peak at $2\theta = 20·3(101)$ in XRD pattern (figure 1a) confirms the presence of γ-phase (Takahashi and Tadokoro 1980) in PVDF films cast at room temperature from solution at 90°C. But small α-phase peaks at 17·6 (100), 18·4 (020), 19·9 (110) and 26·6 (021) (Newman *et al* 1979) peaks are also present in XRD pattern which indicate the existence of small percentage of α-phase along with γ-phase in PVDF film cast at room temperature from solution at 90°C.

In figure 1(b), the maximum intensity peak is observed at 19·9 (2θ values) along with peaks at 17·7 and 18·4 (2θ values), which belong to α-phase. Therefore only α-phase exists in PVDF films, cast at room temperature from solution at 50°C.
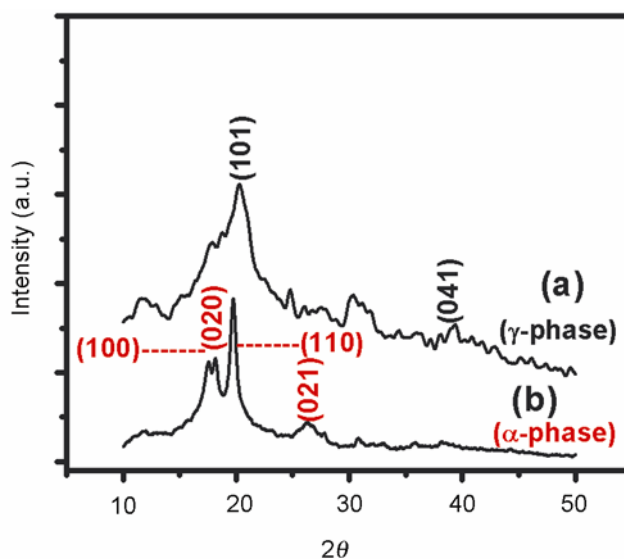

Figure 1. X-ray diffraction pattern of PVDF films. Thin film cast at room temperature from 15 wt% DMSO solution at (a) 90°C and (b) 50°C.

When the PVDF crystallizes from a high polar solvent, the polar groups of the solvent tend to rotate the strong dipoles of the C–F bond in the PVDF molecular chain and reduce the energy barrier for forming the more expanded all trans conformation while solvents with a lower dipole moment always favors alternate *trans* and *gauch* conformation (Salimi and Yousefi 2004; Chen *et al* 2007). But same polar solvent can produce different phases depending on the preparation temperature. The existence of α, β and γ phases in the PVDF for a particular polar solvent depends on the mobility of conformers which are mainly affected by the thermal energy (Gregorio and Cestari 1994). At 50°C, where the viscosity of the PVDF solution is high, the thermal energy is not sufficient to rotate the CF$_2$ group. So there is no *trans–gauch* conformational change. In solution the *trans* and *gauch* conformers remain as it is which results in α-phase after cast of the PVDF films.

When the solution is prepared at 90°C using DMSO solvent then viscocity of the solution decreases and the thermal energy is enough to rotate CF$_2$ dipoles resulting a cooperative motion of the neighboring CF$_2$ groups through the large scale *trans–gauch* conformational change. So conformers aligned either in TTTGTTTG′ or TTTT form. In our case the conformers are aligned in TTTGTTTG′ sequences (γ-phase). Therefore the solutions prepared using DMSO solvents at 90°C and immediately cast at room temperature produce polar PVDF films have large percentage of γ phase. Hence solvent does not matter to produce different phases of PVDF. Same solvent can yield α, β and γ phase.

3.2 *Effect of annealing on transformation of γ-phase PVDF to β and α-phase PVDF*

The PVDF films with maximum percentage of γ-phase were annealed at 70, 90, 110, 130 and 160°C for 5 h to observe the changes in crystalline phases in PVDF films.

Figure 2 shows the XRD pattern of PVDF thin films, annealed at 70, 90, 110, 130 and 160°C for 5 h. For comparison, the XRD pattern of PVDF film (as cast) is also shown in figure 2a. The XRD peak position at $2\theta = 20\cdot3$ confirms the presence of maximum percentage of γ-phase in PVDF films without annealing. At 160°C for 5 h annealed condition, only α-phase is present in the film (figure 2f) which is confirmed from the presence of XRD peaks at 17·6 (100), 18·4 (020) and 19·9 (110). For other annealing conditions, β- or γ-phases are present along with α-phase. Presence of peaks at 20·7 (200) and 20·8 (110) in XRD pattern (Chen *et al* 2007) confirm the existence of maximum β-phase in PVDF films (figure 2c) for annealing condition 90°C for five hours. For further confirmation of phases in PVDF films they are subjected to DSC, FTIR, and Raman characterizations.

Figure 3 shows the DSC curves (heating rate 5°C/min) of PVDF films annealed at different temperatures. Figure

3a shows endothermic peaks at 170°C for PVDF film prepared from DMSO solvent without any annealing. This endothermic peak shows the presence of γ-phase (confirmed from XRD) in the as cast PVDF films. For PVDF films annealed at 70°C for 5 h, two overlapping endothermic peaks at 157 and 161°C appear in the DSC curve (figure 3b). According to Prest and Luca (1975) both solvent cast and the oriented β-phase can be made to melt near the α-phase that thermal measurement alone cannot distinguish the presence of either structure (Prest and Luca 1975). The melting point of β-phase is less than the melting point of α-phase (Gregorio Jr and Nociti 1995; Constantino *et al* 2005). To assign these peaks to proper phases of PVDF, first we consider the DSC curve (figure 3f) of PVDF film annealed at 160°C for 5 h. At this annealed temperature only α-phase is present in the film (confirmed from XRD and FTIR). So the endothermic peak at 161°C corresponds to α-phase of PVDF. Similarly for the PVDF films annealed at 90°C for 5 h, one endothermic peak is observed at 157°C in DSC curve (figure 3c). According to XRD curve, maximum percentage of β-phase is present in the PVDF film at this annealing condition. Hence the endothermic peak at 157°C corresponds to β-phase present in the PVDF films. From above results it is clear that the two peaks at 157°C and 161°C present in the PVDF film at annealing condition 70°C for 5 h correspond to β and α-phases respectively. Therefore at this annealing condition both β and α-phases are present in the PVDF films. The presence of both β and α-phases in PVDF films (when it is annealed at 110°C for 5 h) is also confirmed from two endothermic peaks at 157°C and 161°C. When PVDF films annealed at 130°C for 5 h, three broad endothermic peaks are present in the DSC thermographs (figure 3e). Peak at 157°C gets broader and the peak at 161°C becomes sharper which shows the decrease in β-phase content and increase in α-phase content. The endothermic peak at 144°C corresponds to relaxation of conformer. Also some kind of bond deformation may occur at this annealing condition.

In our case the melting point of different phases are low compared to reported values (Prest Jr and Luca 1978; Salimi and Yousefi 2003; Judovits 2006; Campos *et al* 2007). The endothermic peak positions of α, β and γ-phases depends on heating rate and also on polymerization condition of PVDF (Prest Jr and Luca 1975). The complexity of this polymeric behaviour is also reflected by its melting behavior. The melting point of the different phases in PVDF is a function of polymerization condition. The higher molecular weight polymer produced by emulsion polymerization at 350–400 K typically melts lower than the product of a room temperature suspension polymerization (Prest Jr and Luca 1975). In our case the molecular weight of PVDF films ($M_w \approx 5, 30,000$), is high compared to reported values (Prest Jr and Luca 1975). Therefore the observed melting points of different phases are lower than some reported values.
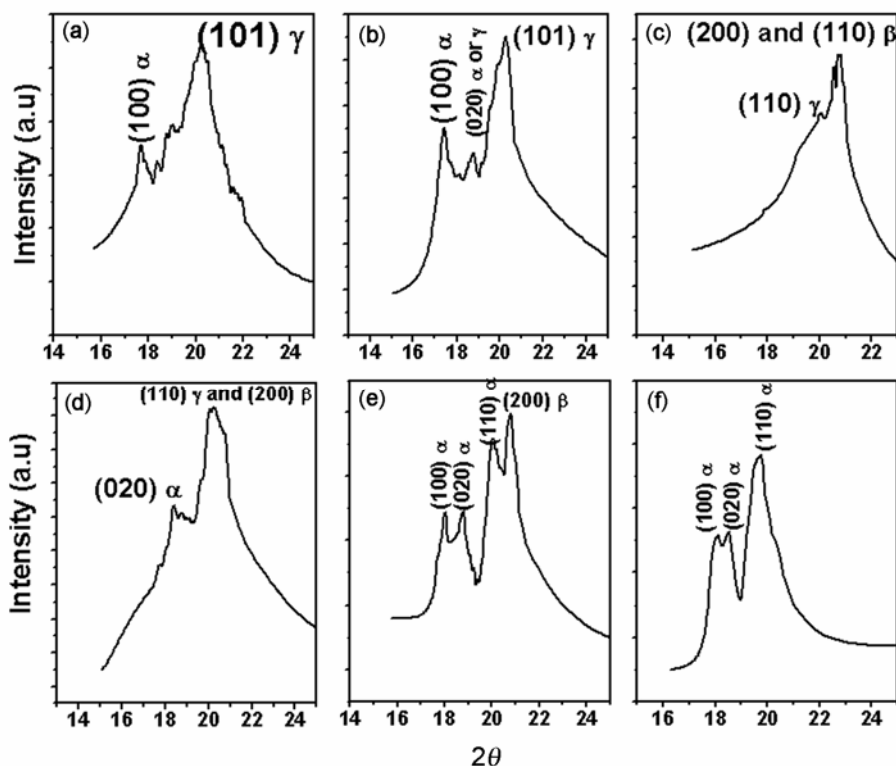
Figure 2. X-ray diffraction pattern of PVDF films (**a**) without annealing, (**b**) annealed at 70°C for 5 h, (**c**) annealed at 90°C for 5 h, (**d**) annealed at 110°C for 5 h, (**e**) annealed at 130°C for 5 h, (**f**) annealed at 160°C for 5 h.
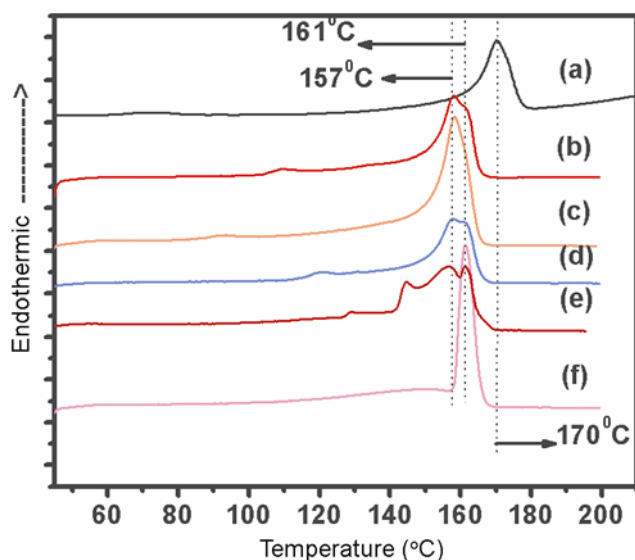

Figure 3. DSC curves of PVDF films with heating rate of 5°C/min: (a) without annealing (b) annealed at 70°C for 5 h, (c) annealed at 90°C for 5 h, (d) annealed at 110°C for 5 h, (e) annealed at 130°C for 5 h, (f) annealed at 160°C for 5 h.

FTIR spectra of PVDF thin films in the range 400–2000 cm^{-1} are shown in figure 4. According to earlier reports, the peaks at 490, 530, 615, 766, 795, 974, 1149, 1210, 1383, 1402, 1432 and 1455 cm^{-1} are used for α-phase identification. The peaks at 511, 840 and 1275–1279 cm^{-1} are fingerprints of β-phase (Kobayashi et al 1975; Boccaccio et al 2002; Bormashenko et al 2004). The molecular vibration peaks of γ-phase are very close to β-phase. Therefore it is very difficult to separate γ and β using FTIR spectroscopy. Only two peaks 1279 and 1234 cm^{-1} can be unambiguously used to distinguish forms β and γ respectively (Boccaccio et al 2002).

Figure 4(a–f) shows the FTIR spectra of PVDF at different annealing conditions. When γ-phase PVDF films are annealed at 160°C for 5 h, then absorption peaks appear at 490, 532, 615, 764, 796 and 975 cm^{-1} (figure 4f), indicating the complete conversion of thin film into α- phase. The FTIR spectrum of PVDF without annealing is shown in figure 4a. Figure 4(b–e) show the FTIR spectra of PVDF films, at annealing condition 70, 90, 110 and 130°C for 5 h respectively. There is not much difference in FTIR spectra of without annealing condition and annealing at 70°C for 5 h. From FTIR spectra it is very difficult to distinguish the presence of γ and β in PVDF. Only one distinguishable small peak at 1235 cm^{-1} is present in FTIR spectrum of without annealed PVDF (figure 4a). But from other characterizations it is clear that the maximum percentage of γ-phase is present in without annealed PVDF film. The maximum increase of β-phase is observed when thin film of PVDF is annealed at 90°C

for 5 h (figure 3c). The increase in intensities of the peaks at 511, 840 and 1276 cm^{-1} indicates the increase of β-phase in PVDF thin films compared to other annealing conditions.

Figure 5 shows the Raman spectra of PVDF films at different annealing temperatures for 5 h. In figure 5f the Raman spectrum is dominated by characteristic bands at 613 and 796 cm^{-1} which confirm the complete conversion of PVDF into α-phase at annealing condition 160°C for 5 h (Boccaccio *et al* 2002). At all other annealing temperatures including without annealing condition, the Raman spectra are dominated by a band at 839 cm^{-1}
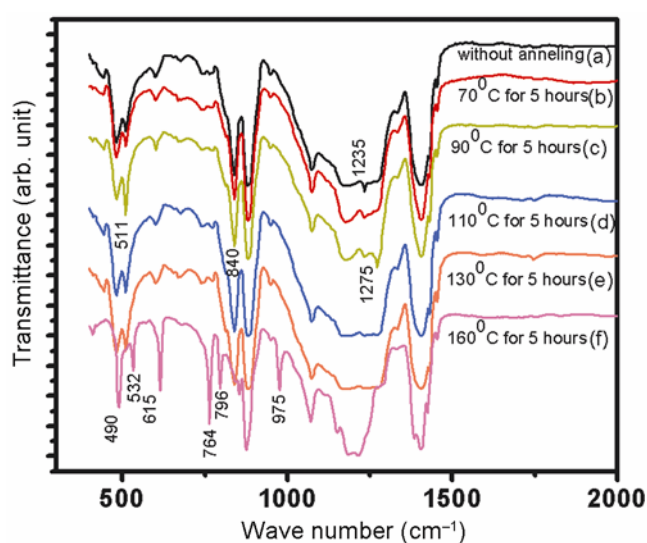

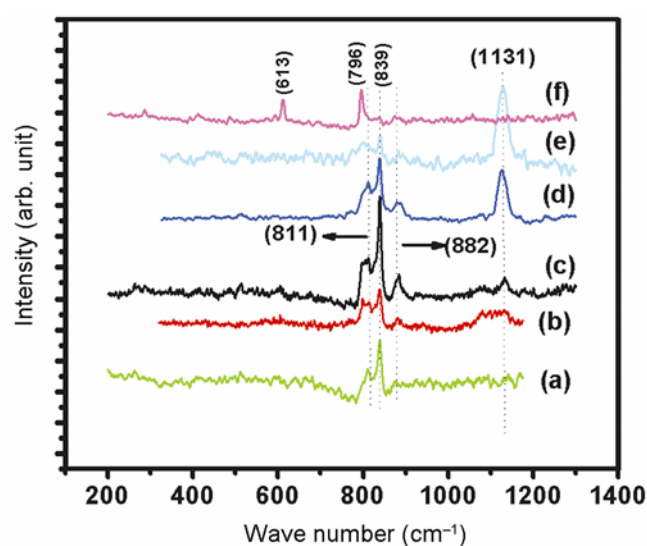**Figure 4.** FTIR spectra of PVDF films.

Figure 5. Raman spectra of PVDF films: (a) without annealing, (b) annealed at 70°C for 5 h, (c) annealed at 90°C for 5 h, (d) annealed at 110°C for 5 h, (e) annealed at 130°C for 5 h, (f) annealed at 160°C for 5 h.

(figure 5a–e). This band is common to both β and γ-phases of PVDF but very strong only in the first case. So the peak at 839 cm^{-1} confirms the presence of either γ, β or both phases (ferroelectric phase) in PVDF film. The high intensity peak at 839 cm^{-1} confirms the high percentage β-phase at annealing condition 90°C for 5 h (Boccaccio *et al* 2002). The Raman bands at 811 cm^{-1} in as cast PVDF films, correspond to γ phase. From Raman spectra it is clear that the PVDF film without annealing contains mainly γ-phase. The percentage of γ-phase decreases as annealing temperature increases to 90°C. At this annealing temperature the PVDF mainly consists of β-phase along with small percentage of α conformers. After 90°C the percentage of α-phase increases in PVDF film and the film is completely converted to α-phase at 160°C.

The broad Raman peak at 882 cm^{-1} represents the combination of all three phases (Bormashenko *et al* 2004). At annealing temperature 110 and 130°C, the extra peak appearing at 1131 cm^{-1} may be assigned to combination of α- and β-phases present in PVDF films (Constantino *et al* 2005).

The maximum percentage of β-phase PVDF is obtained by annealing the PVDF film (cast using DMSO solvent) at 90°C for 5 h. As per literature, for an applied field of 1200 kV/cm, the remnant polarization is 5 μC/cm^2 at 0·001 Hz. But at an applied field of 400 kV/cm the β-PVDF shows polarization of 0·2 μC/cm^2 at 0·001 Hz (Furukawa *et al* 1980). The figure 6a shows the hysteresis loops of unpoled β-phase PVDF for different frequencies at constant field 400 kV/cm. When frequency of applied field 400 kV/cm decreases from 50 Hz to 1 Hz the ferroelectric polarization increases from 0·045 μC/cm^2 to 0·186 μC/cm^2. Well saturated ferroelectric loop appears with remnant polarization 4·8 μC/cm^2 obtained at an applied field of 1400 kV/cm (figure 6b).

The temperature and time of crystallization determine the presence of predominant phases in PVDF. Maximum percentage of γ-phase is present in initial PVDF film cast at 90°C. When thin films are annealed at 70°C, the thermal energy indeed changes the phases present in PVDF but the temperature is not sufficient enough to completely destroy the crystalline order present in PVDF film. There is rotation of dipole groups around chain axis to change the conformers. So the TTTGTTTG′ sequence present in PVDF chain try to acquire TTTT sequence. When PVDF films are annealed at 90°C for 5 h the viscocity of material decreases which in turn increases chain mobilty and thermal energy is enough to reorganize the structure of conformers. So the TTTGTTTG′ sequence in PVDF chain completely converts to TTTT sequence i.e. γ-phase to β-phase. At this temperature crystallization rate of β phase is also higher than among other phases. Therefore at annealing condition 90°C for 5 h, the characterizations show presence of maximum percentage of β-phase in PVDF film.
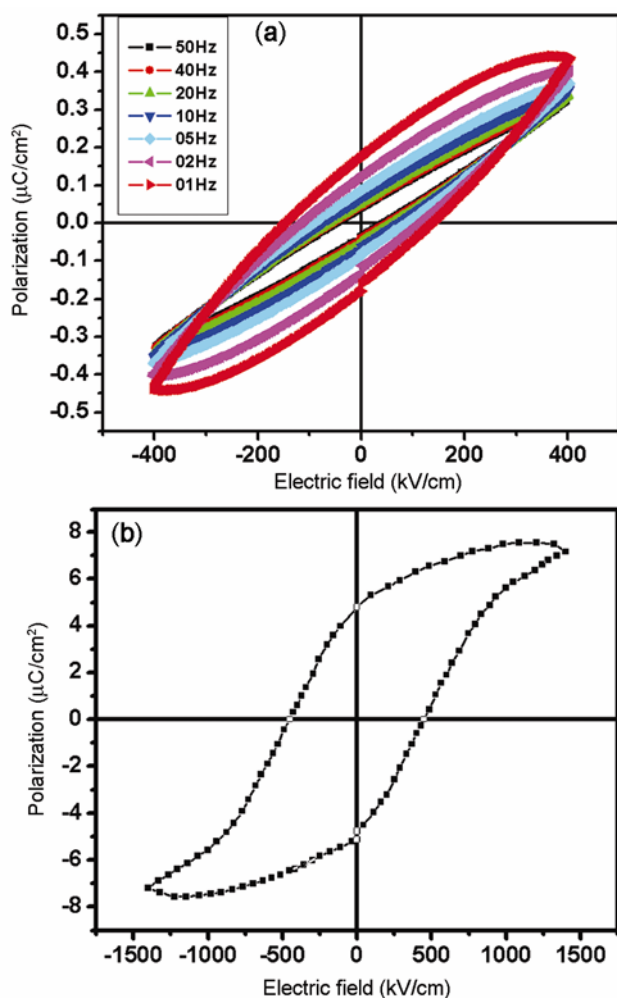
Figure 6. (**a**) Hysteresis loops of unpoled transparent PVDF films (cast using DMSO solution and annealed at 90°C for 5 h) at an applied field 400 kV/cm at different frequencies. (**b**) Hysteresis loop of β-phase PVDF film at an applied field 1400 kV/cm at 1 Hz.

As the annealing temperature increases above 110°C, the viscocity of PVDF decreases further to allow the active chain motion and chain reorientation in the crystalline region through the trans-gauche conformational exchange (Gregorio Jr and Cestari 1995). Therefore due to deformation in crystalline region and reorientation of chains, the more stable α phase reappears in the PVDF films at high temperature annealing conditions. Hence at 110 and 130°C there is increase in percentage of α-phase increase in PVDF film. Above 160°C PVDF completely gets converted to α-phase.

4. Conclusions

In this report it is observed that the same polar solvent can yield all the three phases of PVDF. By changing the solution temperature, different phases of PVDF can be obtained using polar DMSO solvent. The annealing conditions decide the presence of different phases and conversion of one phase to other phase of PVDF. The β-phase which is important for ferroelectric application is obtained using polar solvent and by suitable annealing. Maximum β-phase exist in the films when PVDF films are annealed at 90°C for 5 h. The γ-phase completely converts to α-phase at annealing temperature 160°C for 5 h. The phase conversion at different annealing condition has been confirmed from XRD, FTIR, DSC, and Raman studies. Polarization measurement of PVDF film, having high β-phase content shows a remnant polarization of 4·9 $\mu C/cm^2$ at 1400 kV/cm at 1 Hz.

Acknowledgement

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