CHAPTER III

STUDY OF THIN FILMS OF POLY(VINYLLIDENE FLUORIDES)

3.1 INTRODUCTION

Poly(vinylidene fluoride), PVF₂, is the first semicrystalline polymer reported to be ferroelectric (1-5). PVF₂ has attracted much scientific and technological interest in recent years as a result of unique combination of properties it possesses. Important amongst these are non-linear optical effect (6), piezoelectric effect (1, 7-11), pyroelectric effect (1, 3, 6, 12-15) and high dielectric constant (16-19). Experiments on PVF₂ have shown its application potentiality as versatile acoustic transducers (20, 21), infra-red detectors (6, 22, 23) and thermal imaging devices (24). Its use as transducers has several technological advantages. In the experimental stage it has also several other device potentials viz. biomedical devices (24-27), pressure gauge (28), monitor for laser (29) etc.

Polymer PVF₂ is a kind of fluorocarbon resin, and has the following chemical constitution:
The dipoles of CF$_2$ and CH$_2$ are placed perpendicular to the chain axis of the polymer.

3.1.1 MORPHOLOGY:

Being in semicrystalline state, its microcrystals are dispersed in the polymer matrix. The crystalline structure exists in three different conformations which are Forms I, II and III or $\beta$, $\alpha$ and $\gamma$ phases respectively (30-43). The Form I, in which it has a polar structure, belongs to orthorhombic system. In this form the molecules have a planar zigzag conformation (Fig. 3.1A) with two polymer chains per unit cell (34, 41). The dipole moments of the monomer units (-CH$_2$-CF$_2$-) are all aligned parallel to each other. This crystalline structure suggests the presence of spontaneous polarisation in the Form I. Since the dipole moment of the monomer is $7 \times 10^{-30}$ Cm (1), the spontaneous polarisation of the Form I single crystal is estimated to be 130 mC/m$^2$ (44). In Form II, which belongs
FIG. 31. CRYSTAL STRUCTURE OF PVF$_2$

(A) FORM I ($\beta$)

$\alpha = 8.58 \, \text{Å}$

$\beta = 4.91 \, \text{Å}$

(B) FORM II ($\alpha$)

$\alpha = 9.64 \, \text{Å}$

- $\bigcirc$ = F
- $\bullet$ = C
- $\bigcirc$ = H
to primitive monoclinic system, the molecules take trans-
gauchoe-trans-gauchoe ' (TGTG') or a planar Cis (21 helix)
conformation (Fig. 3.1B) (31). The orientation of dipoles
in adjacent molecules is opposite in Form II. Thus no net
spontaneous polarization can exist in this form. Form III
is monoclinic and structural features are similar to that
of Form I, i.e. planar zigzag conformation (41). The
crystallographic data of these three forms are summarized
in Table -3.

Recently, a highly polar Form IIp (Kp) of PF2
has also been reported which is formed by subjecting the
Form II to a high electric field (45-47).

High pressure crystallization has been studied
by different workers (48-50). So far only one paper (51)
has appeared on the preparation of single crystals of PVF2
from solution in a form other than Form II.

3.1.2 CHARACTERIZATION

Individually, the Form I and Form II of PVF2 are
characterised by well defined X-ray diffraction patterns
(31, 34). However, in mixed systems relatively weak
reflections of the Form II are so dominated by those of
the Form I that the detection of small amounts of Form II
crystals becomes exceedingly difficult. Hasegawa et al. (41)
<table>
<thead>
<tr>
<th>Crystallographic data of the three forms of Poly-(Vinylidene Fluoride)</th>
<th>Form I</th>
<th>Form II</th>
<th>Form III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cm2m (C\textsuperscript{14}2\textsubscript{1}2\textsubscript{1}2\textsuperscript{1})</td>
<td>P2\textsubscript{1} (C\textsubscript{2}2\textsubscript{1})/P1(C\textsubscript{1}1)</td>
<td>C\textsubscript{12}1 (C\textsubscript{2}3)</td>
</tr>
<tr>
<td>Lattice constants</td>
<td>\begin{align*} a &amp;= 8.58 \text{ Å} \ b &amp;= 4.91 \text{ Å} \ c (f.a.) &amp;= 2.56 \text{ Å} \end{align*}</td>
<td>\begin{align*} a &amp;= 4.96 \text{ Å} \ b &amp;= 9.64 \text{ Å} \ c = (f.a.) &amp;= 4.62 \text{ Å} \end{align*}</td>
<td>\begin{align*} a &amp;= 8.04 \text{ Å} \ b &amp;= 4.96 \text{ Å} \ c (f.a.) &amp;= 2.58 \text{ Å} \end{align*}</td>
</tr>
<tr>
<td>( \beta )</td>
<td>90°</td>
<td>97°</td>
<td></td>
</tr>
<tr>
<td>Number of chains in lattice</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Molecular information</td>
<td>T\textsubscript{2}</td>
<td>TGTG'</td>
<td>T\textsubscript{2}</td>
</tr>
<tr>
<td>Density, \textsuperscript{1}</td>
<td>Obsd. at 30°C</td>
<td>1.80 g/c.c.</td>
<td>1.76 g/c.c.</td>
</tr>
<tr>
<td>Calc'd. (X-ray)</td>
<td>1.97 g/c.c.</td>
<td>1.93 g/c.c.</td>
<td>1.94 g/c.c.</td>
</tr>
<tr>
<td>Melting point</td>
<td>168-173°C</td>
<td>175-178°C</td>
<td>171-179°C</td>
</tr>
</tbody>
</table>

\( \text{f.a.} = \text{fibre axis.} \)
have shown that there are only very small differences between the diffraction patterns of the phase I and phase III. On the other hand, the characteristic IR absorption spectra (4, 32, 40, 41, 52-57) clearly identify the presence of each polymorph. The absorption peaks or shoulders appear in the IR spectra at 490, 530 and 610 cm\(^{-1}\) for phase II; at 445, 475, 510 and 598 cm\(^{-1}\) for phase I and at 435, 445, 485, 510 and 598 cm\(^{-1}\) for phase III.

However, Tamura et al. (4) in their work have referred the two bands found at 446 and 510 cm\(^{-1}\) to characterise the Form I crystals. The absorbance at 530 cm\(^{-1}\) which is assigned to Form II crystal disappears while that at 510 cm\(^{-1}\) assigned to Form I crystal increases as an effect of heat treatment and stretching.

Raman studies on the three forms have been made by many workers (43, 53-60). Kobayashi et al. (43) have measured IR and Raman spectra in these three crystal forms in the region from 4000 to 30 cm\(^{-1}\).

3.1.3 MUTUAL TRANSFORMATIONS:

The three Forms I, II and III can be mutually transformed (32, 36, 39, 52, 54, 61-66) by chemical, thermal and mechanical treatments. The conditions of formation and mutual transitions of Forms I, II and III are shown in Fig. 3.2.
FIG. 3.2. TRANSFORMATIONS AMONG THREE FORMS OF PVF₂
In addition to what has been shown in Fig. 3.2, Form II was also found by precipitating it from a solution in monochlorobenzene-dimethyl formamide mixture or from acetone solution (61). Form III has also been obtained either by casting from dimethyl sulfoxide (DMS) or dimethyl formamide (DMF) solutions (40, 41, 52, 54, 61, 62).

3.1.4 DIELECTRIC PROPERTIES AND MOLECULAR RELAXATIONS

The high permittivity of PVF$_2$ arises from a large dipole moment of the CF$_2$ group and its freedom of orientation along the electric field on account of the small atomic volume of fluoride. An extensive investigation of dielectric behaviour of PVF$_2$ as a function of frequency, temperature, and degree of crystallization has been made by many workers (16-19, 67-78). The dielectric constant and loss change abruptly at the melting temperature (77). Buchman (3) has measured dielectric constant of PVF$_2$ at 25°C to be ~1000 by switching current technique at very low frequency which is two order of magnitude larger than the value measured at 50 Hz. For different preparations of PVF$_2$ the dielectric constant varies between 8 to 12 in AF range at room temperature.

From the dielectric (16-19, 67-78) thermocurrent (79, 80) and NMR (81) studies in PVF$_2$ it has been shown that it exhibits three principal molecular
relaxations $\alpha$, $\beta$ and $\gamma$ (or $\alpha_0$, $\alpha$ and $\beta$) respectively in the descending order of temperature. The fourth relaxation $\beta'$ was observed between $\alpha$- and $\beta$- relaxations by Akutani (73) and McBrierty et al. (81).

The $\alpha$-relaxation in PVF$_2$, which is reported to occur in the temperature range 50 to 100°C depending upon film preparation and thermal history, is related to the molecular motion in crystalline region (18, 19, 76, 81). This can be either the rotational oscillation about the main chain axis or complete rotation of a percentage of crystalline chains in the region of defects (81). It also depends on lamellar thickness and crystal defects. Uniaxial drawing and rolling reduces the magnitude of $\alpha$-relaxation.

$\beta$-relaxation is associated with the glass transition temperature $T_g$ (-35°C to -51°C) (75, 82) in PVF$_2$, while $\gamma$-relaxation occurs below $T_g$. The $\beta$-relaxation is a manifestation of micro-Brownian motion of amorphous chain segments (18, 19, 68, 72). Local restricted motion of chains in the amorphous region are deemed responsible for the $\gamma$-relaxation (19). Rotation of amorphous chains is a possible mechanism for the $\gamma$-relaxation process while motions of a general nature are responsible for the $\beta$-relaxation. Motion of folds on the surface of crystal
lamellae is deemed to be the responsible mechanism for the \( \beta' \)-relaxation which occurs between \( \alpha' \) and \( \beta \)-relaxations (81).

3.1.5 EFFECT OF POLING AND STRETCHING

Either of these treatments improves the electrical properties of PVF₂. On a molecular level the poling of PVF₂ in a static electric field increases the polar properties through following mechanisms:

(a) Alignment of C-F dipoles in a crystalline phase and/or amorphous regions (1, 3, 6, 83, 84).

(b) Injection of homocharges or space charges into the film from the electrodes (9, 13, 85-88).

The actual mechanism of polarisation occurring in PVF₂ is probably a combination of the two (55, 89, 90), the contribution of each depending on the poling conditions. Treatment of PVF₂ film by poling in a high dc electric field at elevated temperature may also convert phase II to phase I (6, 12, 13, 91-93). The process of poling orients the axis of crystalline regions in the thin films of PVF₂ and has been evidenced by X-ray studies (5). Blavin (94) reported that the choice of poling temperature within the range 20 - 100°C is immaterial provided that the poling is continued long enough. It may be inferred that the poling mechanism is the same at any temperature in this range.
Orientation of the polymer chains along with a conversion to crystalline phase I conformation can also be achieved by uniaxial or biaxial stretching at low temperatures (34, 40-43, 52). Increasing the draw temperature increases the phase II content (34). The piezoelectric activity is enhanced by stretching or rolling the film prior to poling (55). Recently, a technique of corona poling has also been developed for this purpose (11, 15, 95-97).

Typical poling and stretching conditions (55) are

\[ E_p = 600 \text{ kV/cm}; \quad T_p = 105^\circ C; \quad t_p = 45 \text{ min} \]

and draw ratio = 6/1; feed rate = 15 ft/min;

drawing drum = 90 ft/min; Film exit temperature = 80°C.

3.1.6 ELECTRICAL CONDUCTION:

PVF$_2$ exhibits ionic conduction (19, 74). At lower frequencies two types of ionic conduction were observed. One appears below melting temperature $T_m$ and is attributed to interfacial polarisation and the other above $T_m$ related to the electrode polarisation. These results suggest that a crystalline polymer is a heterogeneous medium for ionic transport while the melt is a homogeneous medium (47). Electrical conduction of PVF$_2$ has been investigated extensively. These investigations
include conduction current dependence on crystal structure (99, 100), depolarisation characteristics related to trap behaviours (98), surface charge behaviours (9) and conduction characteristics in relation to crystal structure and molecular motion (100).

3.1.7 THERMOCURRENT:

Thermally stimulated current (TSC) from polarised \( \text{PWF}_2 \) was studied below room temperature by Pfister and Abkowitz (79). The maximum of TSC observed at \(-50^\circ C\) is due to reorientation of dipoles in a process associated with the glass transition. Abkowitz and Pfister (80) have taken combined measurements of ac and dc thermocurrents as a continuous function of temperature on \( \text{PWF}_2 \) film and characterised both the \( \beta \) - and \( \alpha \) - molecular relaxation processes by their studies.

3.1.8 PYROELECTRIC AND PIEZOELECTRIC EFFECTS:

Interest in pyroelectric and piezoelectric properties of polymeric materials has increased rapidly in the past several years because the polymeric films can be used more conveniently in place of crystalline or ceramic materials for pyroelectric and piezoelectric devices. Also the piezo- and pyroconstants have become valuable tools in the study of the mechanism of polarisation of the polymers.
Major interest has centered on PVF$_2$ because of its comparatively large pyroelectric response. PVF$_2$ is truly pyroelectric and the effect is not just depolarisation as observed in several electrets.

The pyroelectric study on PVF$_2$ has been done by many workers (1-3, 6, 12-15, 44, 56, 86, 88, 90, 94, 101-107) with different treatments of poling and stretching. Lang (103) observed that the static pyroelectric coefficient was small and constant below T$_g$ but increased rapidly above T$_g$. A pyroelectric coefficient $2.4 \pm 0.7 \text{nC/cm}^2$ $\text{°C}$ comparable to that of single crystal of lithium niobate was observed by Bergman et al. (6). For different types of samples the values of pyrocoefficient differed. Wada and Hayakawa (44) pointed out that, with PVF$_2$ as a typical example, the piezo- and pyroelectricity of polymer electrets originate from either of the following two mechanisms:

(A) Intrinsic piezoelectricity and pyroelectricity due to strain and temperature dependences of the spontaneous polarisation.

(B) Piezo- and pyroelectricity due to heterogeneity of the film and embedded charges.

Several workers (6, 9, 12-14, 85, 86, 104, 107) have proposed different models and explained the origin of pyroelectricity in PVF$_2$. The observed pyroelectricity is
not entirely from the contribution of primary pyroelectric effect. Kepler and Anderson's work (14) suggests that the secondary pyroelectricity (contribution coming from thermal expansion) can account for about half of the observed pyroelectricity. This finding has been supported by Glua and Negran (104).

Its application as a versatile transducer has initiated active interest on piezoelectric investigations of this material (1, 4, 7-11, 21, 44, 55, 85, 86, 89, 90, 93, 95-97, 105-120). The piezoelectricity in this material originates from the mechanisms similar to that of pyroelectricity.

3.1.9 FERROELECTRICITY

Stretched and poled PVF$_2$ films exhibit hysteresis characteristics similar to those of ferroelectric crystals under high alternating field (2-5, 21, 121). Pyroelectric study (101) indicates that Curie point of PVF$_2$ may be near the melting point. Nakamura and Wada (1) interpreted the electrical behaviour of PVF$_2$ in terms of ferroelectric nature of Form I crystal. From pyroelectric and polarisation reversal measurements, Glass et al. (2) concluded that PVF$_2$ is certainly a ferroelectric by usual definition, i.e. a pyroelectric with a reversible spontaneous polarisation (122).
Fuchman (3) obtained spontaneous polarization $p_s$ to be 8 $\mu$C/cm$^2$ at 140°C and switching time of the order of several minutes at 150°C for biaxially stretched films. These results suggested that polarization reversal is associated with the rotation of long chain molecules by the applied field. Tamura et al. (4) obtained $p_s = 2.2$ $\mu$C/cm$^2$, and $E_c = 250$ KV/cm for a uniaxially stretched film from hysteresis loop while Kepler (121) reported $p_s = 5.83$ $\mu$C/cm$^2$ and 6.33 $\mu$C/cm$^2$ at room temperature for uniaxially and biaxially stretched films, respectively.

PVF$_2$ is birefringent. For biaxially and uniaxially stretched films the values of $\Delta n_{yz}$ and $\Delta n_{xz}$ are 0.018, 0.011 and 0.000, 0.013 respectively (12).

Kepler and Anderson (5) proved that PVF$_2$ is indeed a ferroelectric and that it behaves like a ferroelectric ceramic. The model they used also relies on the fact that the orthorhombic symmetry of the unit cell results from a small distortion of a hexagonal primitive lattice, the distortion being 1% decrease in the separation between molecules in the direction of the dipole moments. This model is consistent with the assumption that PVF$_2$ is a ferroelectric.
3.1.10 **PURPOSE OF STUDY:**

PVF$_2$ being the only polymer to be ferroelectric, the objective of the present study was to understand the dependence of its electrical properties on conditions of preparation, poling, temperature and pressure. A comparative study was planned for the solution-casted films prepared in the laboratory with those industrially supplied films (sheets) from Pennwalt (UK) and Kureha (Japan).

The $\alpha$-relaxation in PVF$_2$ which is associated with the crystallinity of the sample was investigated via conductivity study (ac and dc both). Studies of thermocurrent and thermally stimulated current, which also shed light on this relaxation, are relevant to assess poling effect and pyroelectric characteristic of this material. It was followed by dielectric and loss study. Effect of pressure has been observed on $\varepsilon$ and tan $\varepsilon$. Pyroelectric measurement has also been done to characterise the sample from different origins. Lastly, ferroelectric hysteresis, the main criterion of ferroelectricity, was investigated in the solution-casted films (thin) along with those in the various industrially available films (thick).
3.2 STUDY OF SOLUTION CASTED THIN FILMS OF PVF$_2$

In the available literature, the study on thin films of PVF$_2$ less than 5 µ thick is scarce since most of the reported works are on industrially supplied film sheets. It has been tried to make PVF$_2$ thin films by (a) vacuum evaporation which has not been very successful due to degradation; (b) the method of solution casting, as described in the experimental portion, successfully yielded clear and transparent PVF$_2$ thin films of thickness less than 1 µ. Since no measurements were available in such thin films, it was worthwhile to take up investigations on such samples.

3.2.1 EXPERIMENTAL:

Preparation of the film:

Selected Blue Star super deluxe glass slides of size 75 mm x 25 mm were taken as substrates. These were cleaned in a way described in Chapter II. Aluminium thin film electrode was first vacuum deposited on 3/4 portion of the substrate (Fig. 3.3A). A saturated solution of Kynar PVF$_2$ powder was prepared in analar grade dimethyl formamide (DMF) solvent. The solution was filtered by centrifuge method. This solution was constantly heated to about 50°C. The Al coated glass slide and an uncoated glass slide were also maintained at this temperature.
FIG. 3.3A. SOLUTION CASTED PVF₂ FILM ELECTRODE ARRANGEMENT.

FIG. 3.3B. SAMPLE HOLDER FOR SOLUTION CASTED PVF₂ FILMS.
A coated glass slide was dipped in the solution for one minute and then slid over the portion of Al coated glass slide leaving a small portion of Al coated portion untouched. This is to ensure uniformity of film thickness. Then it was dried. The casted films of PVF$_2$ were heated to about 100°C in an oven over night to remove retained solvent in the film. Al film was again vacuum deposited for the top electrode with the help of a mask in such a way that the circular portion of 1 cm diameter overlaps the lower Al electrode. Thus the sandwich circular cell was obtained for electrical measurements. The specimen was again annealed for about two hours at around 130°C.

Sample holder:

The sample holder used for measurement of solution-casted thin films is as shown in the Fig. 3.3B. It consists of a rectangular brass block whose upper portion was engraved equal to the slide size. The fibre plate used to support the measuring electrode contacts was fixed parallel to brass plate. The electrodes were in the form of two brass screws. These screws were contacted with the films through polished brass blocks to avoid scratching on the electrode - Al films. The whole arrangement was shielded by Al enclosure and was earthed to avoid influence of external field/charges. Shielded wires were used for
connections. The specimen was cycled and recycled twice before final measurements were taken.

**Measurements:**

The diameter of the top electrode was precisely measured by a vernier microscope. The thickness of PTF$_2$ film was measured by observing Fizeau's fringes as described in Chapter II. The thickness of the film was also evaluated by measurement of capacitance of the sandwich capacitor. For this the dielectric constant of PTF$_2$ solution-casted film was taken to be 8.8 as reported in earlier literature. The thickness measured by both the processes agreed fairly well.

The dielectric constant ($\varepsilon$), dielectric loss (tan $\delta$) and a.c. conductivity were measured by Wayne Kerr Bridge as a function of temperature from room temperature to 130°C. The dc electrical conductivity and thermo-current were measured by ECIL electrometer amplifier in the same temperature range. The heating rate was maintained as ~ 1°C/minute. The temperature was measured by pre-calibrated chromel-alumel thermocouple, Toshniwal portable potentiometer and polyflex galvanometer having a resolution of 10 µV.

The solution-casted films were poled at different fields from 200 KV/cm to 900 KV/cm at 100°C for one hour.
The above measurements were repeated for these poled films.

The hysteresis loops were observed on CRO by Sawyer-Tower circuit (Fig. 2.7A) for unpoled and poled films. Experimental details have been discussed in Chapter II.

Characterisation:

To characterise the PVF$_2$ thin film prepared by solution cast method the IR spectra of the film deposited on KCl plate were taken by Perkin-Elmer Spectrophotometer which is shown in Fig. 3.4. The absorption peaks or shoulders appear in the IR spectra at 478, 515 and 598 cm$^{-1}$ which are characterised to be due to Form III crystallites and those appearing at 610, 760, 780, 870, 970, 1060, 1145, 1180, 1210 and 1420 cm$^{-1}$ are due to Form II crystallites. Thus solution-casted PVF$_2$ thin sample has Form II and Form III crystallites. These forms of PVF$_2$ are not supposed to exhibit ferroelectric property unless transformed to Form I.

3.2.2 RESULTS AND DISCUSSION:

3.2.2.1 Dielectric Study:

Measurement of the dielectric constant is a useful technique in the study of the physical properties of the polymer having a finite dipole moment. The electronic
displacement and the dipole orientation polarizability are affected by crystalline and amorphous component conditions. Such effects can be more conspicuous in the temperature dependent dipole contribution, being a function of chain mobility and orientation. The complex dielectric constant, therefore, depends on dipole orientation in the amorphous regions of the sample and on crystal defects caused by free chain and chain folds.

The variation of dielectric constant with temperature of solution-casted film of PVF$_2$ of thickness 0.3 $\mu$ has been shown in graph (Fig. 3.5a). The effect of poling field has also been shown in the graph. In the measurement of dielectric constant the value of $\varepsilon$ steadily increases from about 8.5 to a maximum value of about 12.5 to 13 around 110$^\circ$C. A tendency of very slight decrease in the temperature scale where the peak is observed, is also noticeable. In addition to the peak, the change in slope is observed around 60$^\circ$C. The peak at 110$^\circ$C and the slope change at 60$^\circ$C in the dielectric variation with temperature can be related with the conduction process in the solution-casted film.

The dielectric loss is measured in terms of $\tan\delta$ which varies from $2.2 \times 10^{-2}$ at room temperature to a maximum value of about $17.5 \times 10^{-2}$ around 80$^\circ$C and then
FIG. 3 TEMPERATURE DEPENDENCE OF (A) DIELECTRIC CONSTANT AND (B) LOSS OF SOLUTION CASTED PVF₂ FILM (0.3 μ)
lowering to a dip value of about \(7.6 \times 10^{-2}\) around \(120^\circ C\) (Fig. 3.5). The peak value and the dip minima are also shifted towards lower temperature side with increasing poling field. The peak in loss around \(80^\circ C\) characterises the \(\alpha\) -relaxation in the material of solution-casted film of PVF₂. The peak in loss has been reported earlier by one of the workers (18) at this temperature. The sharpness of the peak suggests further (i) that the Form II crystallinity is much more dominant than any of the other forms and (ii) as suggested by earlier workers (18,19,76), the loss peak around \(80^\circ C\) signifies the molecular motion in crystalline region.

The crystal structure of solution-casted undrawn films will be mainly Form II and Form III type as obvious from IR characterisation. The stretching or drawing in this case was not possible because its adherence with glass substrate does not allow it. The dielectric constant of solution-casted film is less than the stretched sample because the stretched samples are rich in Form I (polar) crystallinity. However, it has been tried by application of field alone to see whether the crystalline phase of the solution-casted film can be changed into Form I or not. The \(\alpha\) -relaxation mainly appearing around \(80^\circ C\) can be inferred to be due to crystalline dispersion of Form II. Poling does not significantly affect the loss peak at \(80^\circ C\)
and hence one can infer that by poling alone upto 900 kV/cm Form II crystallinity is not transformed to Form I.

Pronounced peak in the loss plot suggests that solution-casted film is more lossy in comparison to the loss in industrially supplied stretched and poled films. (cf Fig. 3.5B and Fig. 3.9).

The peak around 115°C in the dielectric constant and dip in the loss around the same temperature are further suggestive of certain dispersion behaviour at this temperature range. It has also been reported by Sasabe et al. (18) from their NMR line width measurement on Form II PVF₂ as a function of temperature that a narrowing of broad line component occurs at about 90°C and at 100°C instead of two line components only one narrow line component has been observed. It has been inferred that in PVF₂, in this temperature region at least two kinds of molecular motion must be active.

3.2.2.2 Thermocurrent

The variation of thermocurrent (TC) as a function of temperature of solution-casted PVF₂ film of less than 0.5 μ thickness is shown in the Fig. 3.6. The effect of poling has also been shown therein (TSC). The maximum value of TC has been observed for unpoled samples at around 90°C when compared with the poled samples at this
FIG. 3-6. THERMO-CURRENT VS. TEMPERATURE OF SOLUTION CASTED PVF$_2$ FILM (0.3 µm)
79

temperature. This is of the order of $10^{-8}$ Ampere.

Between $70$ and $80^\circ$C anomalous behaviour is seen in the plot of TC vs temperature for all the poled and unpoled samples. Necessarily, it is not an effect of the poling temperature since the samples were poled at $100^\circ$C. These anomalies again characterise $\alpha$-relaxation in the present sample of PVF$_2$. About $75^\circ$C in the region of high temperatures, the precipitous increase in current characterised in TC measurement is suggestive of dispersive dielectric activity in that temperature range. The amplitude of the TC measured peaks associated with $\alpha$-process can be shown to be sensitive to particular film origin and poling history.

3.2.2.3 **Negative Result of Pyroelectric Investigation**

After keeping the sample slightly below the poling temperature and then repeating the measurement in the cooling cycle, the solution-casted film of PVF$_2$ does not show a current in the reverse direction which is the criterion of pyroelectric behaviour. However, in the cooling cycle the thermocurrent is of reduced order of magnitude which may be due to depolarisation current. Cooling the film in the presence of dc bias field can freeze-in the charge carriers which are released in the heating cycle and, as a result, the cooling current is lesser in comparison to the current in the heating cycle.
It can be said that inspite of high order of poling field, i.e. 900 kV/cm, the crystallites in the polymer matrix of the solution-casted film have not been transformed significantly to Form I which is the essential ingredient for $P_{VF_2}$ for its pyroelectric, ferroelectric and piezoelectric behaviours. The reason for this may also be seen in the size effect that adversely affects the polar behaviour in thin films of thickness less than 1 micron.

3.2.2.4 Electrical Conductivity:

The dc electrical conductivity of solution-casted $P_{VF_2}$ film has been studied as a function of temperature and poling field in the temperature range RT to 130°C (Fig. 3.7A). The field applied on the sample during measurement was about 3 kV/cm. Around RT, the value of conductivity for unpoled sample is nearly $3 \times 10^{-14}$ ohm$^{-1}$cm$^{-1}$. The conductivity gradually increases with the increase of temperature and change of slope around 112°C has been observed. In the temperature range above 100°C the corresponding increase in film conductivity can be considered to be due to progressively increasing ionic mobility. In the poled samples the anomaly in the graph around 70°C again suggests the occurrence of $\alpha$-relaxation around this temperature. The inference of this observation is again the same that the temperature region ($\sim 70°C$)
FIG. 3.7. VARIATION OF (A) D.C. AND (B) A.C. ELECTRICAL CONDUCTIVITY WITH TEMPERATURE OF SOLUTION CASTED PVF_{2} FILM (0.3 μm).
corresponds to crystalline dispersion. The complicated behaviour of conductivity between 60 to 70°C in poled films has been related with the molecular motion in the crystalline region or in the region of chain folding (81). One of the features of this graph is that the conductivity value is lesser for the poled samples. Further higher the value of the poling field, lesser is the conductivity value particularly at temperatures above 80°C. It can be suggested that some sort of ordering takes place in the poled samples and may be that the free charge carriers incorporated at the time of film preparation from organic solvent are considerably swept off. Another finding of this study is on the nature of the slope change in the $\log \sigma_{dc} vs. 10^3/T$ plot around 100°C. At the two sides of this temperature region the electrical conduction seems to be affected by certain physical change in the polymer matrix. Above 110°C the electrical conduction in PTF$_2$ has been suggested (100) as due to ions and hence decreasing trend of electrical conductivity due to capture of carriers on crystal interiors or boundaries. The bend in the plot has been ascribed to the carriers being trapped at deeper energy levels. The increased slope below the bent portion in the unpoled sample is because of the capture of carriers at the fold portion. The change in slope at 100°C has opposite nature for unpoled
and insufficiently poled films (200 kV/cm field) as compared to that of poled films for poling fields equal to or higher than 300 kV/cm. This observation does indicate that sufficient poling (field $\geq 300$ kV/cm) affects the conduction mechanism particularly in the region 70 to 130°C where the molecular motion at the folded portion of polymer might be drastically changing around 100°C. On either side of this the different slopes are due to different capture mechanisms for the carriers.

In case of poled thin films of the order of 0.3 μ thickness the surface phenomena are also of paramount importance. The surface charge density of such films due to filling of surface states by the free/trapped carriers will affect the overall conduction gradient and parameter. It will also disturb the distribution of space charge in the thickness of the insulated film. The bend in the dc conduction plot around 100°C also establishes earlier finding of dielectric constant peak and dielectric loss dip around 110°C. This anomaly, in addition to that observed around 60 to 70°C (the region of $\alpha$-relaxation), suggests a different sort of molecular motion or some drastic change in it. As shown earlier, around 110°C the NMR study and loss modulus show anomalous behaviour. Below 60°C the displacement current appears along with the measured current and hence the electrical conduction in the region will be affected by the measurement technique.
It can be summarized from this study that the electrical conduction of PVF$_2$ is closely related with the molecular motion and that it varies widely with temperature and the poling field. It also suggests the possibility that the electric field applied at the time of poling can alter the conduction mechanism of PVF$_2$. However, it is suggested that the dispersion around 110 to 120°C warrants a more careful investigation.

The variation of ac conductivity with temperature is as shown in Fig. 3.7B. The value of $\sigma_{ac}$ at RT is about $2 \times 10^{-10}$ ohm$^{-1}$ cm$^{-1}$ which is four order higher than its dc value. However, log $\sigma_{ac}$ vs 1/T characteristic is very similar to that of the loss characteristic. The explanation of observed peaks and dips is the same as for loss.

3.3 STUDY ON INDUSTRIALLY SUPPLIED FILMS OF PVF$_2$

3.3.1 EXPERIMENTAL:

PVF$_2$ sheet (A) and powder were supplied by Pennwalt Chemical Corporation (UK) under the commercial name Kynar. Pellets (B) were prepared from Kynar powder by hydraulic press at 3.6 x $10^3$ Kg/cm$^2$ pressure. The other batch of films were obtained from Kureha Chemical Co. Ltd (Japan) under commercial name KF. These samples were uniaxially stretched, biaxially stretched and poled
piezo films of different thickness. Uniaxially stretched KF films of thickness 9 μ (C₁) and 29 μ (C₂) were poled piezo films and coated both sides with aluminium film electrodes. Biaxially stretched KF films of thickness 16 μ (C₃) and 25 μ (C₄) were unpoled. Al was vacuum deposited on both sides of A, B, C₃ and C₄ samples. An electrode area of one cm diameter was taken for the measurements. 25 μ film was poled at 100°C with poling field 120 kV/cm for 60 minutes.

The dielectric constant (ε) and loss tangent (tan δ) were measured by Wayne Kerr Bridge as a function of temperature. Thermocurrent on unpoled and poled samples of biaxially stretched 25 μ film was measured by ECIL Electrometer Amplifier. The dc conductivity was measured by BPL Megohmmeter and Electrometer Amplifier. The heating rate was maintained as ~1°C/minute. Details of each experiment have been described in Chapter II.

The current was measured by ECIL Electrometer Amplifier in the cooling cycle also which is the pyro-current. The hysteresis loop was observed on CRO by slightly modified Sawyer-Tower Circuit (Fig. 2.7 A).
3.3.2 **HIGH PRESSURE CELL AND MEASUREMENT:**

The high pressure cell designed for the study of pressure effect on the dielectric property of PVF$_2$ on piezo film is shown in Fig. 3.8. It is a slight modification of the pelleting dye. The only change is at the bottom portion of the dye where a hard steel disc (D) is electrically insulated by teflon and supported on the lower base (LB) of the dye. Heater wire is wound round lower base to increase the temperature. Over the sample on the top of the D, the pressure is applied through the cylindrical ram (R) of hard steel. The ram is vertically supported for its pressure moment by another annular cylinder (AC) of steel. The ram and the disc are connected with terminals which can enable measurement along with the application of pressure. The pressure is applied through the ram by AIMIL hydraulic press.

This measurement was done on 29 µ piezo PVF$_2$ film (KF). The variation of dielectric constant and loss tangent with pressure was measured by Wayne Kerr Bridge. The variation of pressure was from zero to 25 tonnes per square cm. The pressure was applied in both short circuit and open circuit conditions and was retained on the sample for more than an hour. The measurement was done after taking out the sample from the dye. In situ measurement
FIG. 3-8. HIGH PRESSURE CELL.
was done with the help of dye electrode but because of piezo charges the measurement could not be taken as reliable. Hence the reported results are only for after pressure effect. The thickness of the sample was measured before and after the pressure treatment by precise micrometer. The difference was negligibly small.

3.3.3 RESULTS AND DISCUSSION:

3.3.3.1 Dielectric Study:

The variations of dielectric constant and loss of 29 μm piezo film and 25 μm biaxially stretched poled and unpoled films are reported in the graph (Fig. 3.9) along with their temperature dependence. The piezo film has high dielectric constant. It varies from a value of 12 at RT to 14.5 at 130°C. Its loss (tanδ) varies from 0.015 at RT to 0.05 at 120°C. From a careful look of these two graphs two dispersive regions can be deciphered around 60°C and 105°C respectively from the change in slope of dielectric constant and around 115°C in the dielectric loss variation of 29 μm piezo film. The dispersive region around 60°C is associated with earlier reported α'-relaxation in P(VDF-TrFE) in case of solution-casted film. As inferred, at this temperature the dispersion is associated with molecular motion in the crystalline region and hence depends on the
FIG. 3.9. TEMPERATURE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS OF PVC FILMS.
crystallinity of the sample. However, the change in slope in a dielectric variation of 29 μ piezo film at around 60 and 105°C is of much lesser magnitude than in the solution-casted films, suggesting the crystallinity in the solution-casted 0.3 μ film to be of lesser order than 29 μ piezo film. In both, 29 μ poled piezo film and 25 μ poled and unpoled biaxially stretched film the change in slope of the dielectric variation around 105°C again seems related with different sort of molecular motion other than the one responsible for α-relaxation. Alternatively, it denotes the temperature region where this molecular motion drastically changes.

The measurement in 25 μ biaxially stretched film shows additional effect in the slope of poled and unpoled samples. In both, the dispersion in the region of relaxation are obvious from the change in the gradient around 55°C and 105°C. It is interesting to note here that the nature of the slope is opposite to each other in unpoled and poled sample plots at these temperatures. It is essentially an effect of ordering in the crystalline structure on poling. In the unpoled 25 μ sample an additional change in the slope observed around 68°C is completely absent in the poled sample plot. The plot of loss mainly indicates for the 25 μ sample that the unpoled
sample is more lossy than the poled one particularly in the region of high temperature. The poled sample is more dispersive than the unpoled around 115°C.

It can be summarised that there are two regions of dielectric dispersion in 29 μ piezo film and 25 μ biaxially stretched poled film which are mainly due to different nature or changes in the molecular motion at the folded portion of the polymer.

3.3.3.2 Effect of Pressure:

Since the mutual transformation of the three morphology of crystallites has been suggested also with an effect of pressure, it has been tried to investigate the effect of uniaxial pressure on the dielectric constant and loss on 29 μ piezo film. The result is shown in Fig. 3.10 as the variation in dielectric constant and loss tangent with pressure. The value of dielectric constant of about 12.3 at room temperature with zero pressure reaches a value of 12.94 after applying a 25 ton uniaxial pressure on this sample. The value of dielectric constant linearly increases with the increase of pressure up to a value of 15 tonnes. Thereafter the increase in ε is very slight. Similarly tan δ varies from 0.015 at zero pressure to 0.018 after an application of 25 tonnes pressure. In this plot also the initial increase in loss value with the increase of pressure
FIG. 3.10. VARIATION OF DIELECTRIC CONSTANT AND LOSS TANGENT WITH PRESSURE IN 29 µm PVF₂ FILM.
nearly subsides above the pressure of 15 tonnes. Two alternative interpretations of this observation can be suggested. The IR spectra of the sample before and after pressure treatment (Fig. 3.11) show a small change in the absorption peaks of 530 and 510 cm\(^{-1}\). The ratio of these absorption peaks \(\frac{D_{530}}{D_{510}}\) also slightly changes which qualitatively suggests a small transformation of Form II to Form I crystalline phase. Since the Form I crystalline phase is polar, the increase in dielectric constant is obvious. The nearly saturation region in the \(\varepsilon\) and \(\tan \delta\) value after 15 tonnes of pressure suggests that after this pressure the transformation to Form I crystallinity is very small or negligible and so also change in dielectric constant and loss become negligible. Alternatively, it may be also due to piezoelectric effect which will release piezo charges at stress condition in the polymer matrix reaching a saturation value at 15 tonnes of pressure. These additional frozen-in charges can account for the initial increase in dielectric constant and loss both. It cannot be ruled out that the behaviour shown in the graph depends on both the mechanisms playing their respective roles, howsoever small.
Fig. 3.11. IR spectra of 29μ PVF₂ film.
3.3.3.3 Thermocurrent:

The variation of thermocurrent of 25 μ biaxially stretched film with temperature is shown in Fig. 3.12. Due to ionic conduction the step increase starts at the dispersive region in the unpoled sample at 105°C and for poled samples at 90°C. In the poled samples the \( \alpha \)-relaxation region is shown around 53°C which is absent in the unpoled sample. Poling thus does affect the thermocurrent behaviour through depolarisation current which is of higher order of magnitude in the poled samples than in the unpoled ones.

3.3.3.4 Electrical Conductivity:

Figs. 3.13, 3.14 and 3.15 show the plots of log \( \sigma_{dc} \) vs \( 10^3/T \). From Fig. 3.13 it is seen that anomaly in electrical conductivity near melting temperature occurs at different temperatures for different samples as shown in Table 3.2. In pellet and Kynar sheet the crystallites are oriented at random. Crystallites are more closely packed in sheet than in pellet. Stretching and poling have been suggested for crystalline transformation and orientation in \( \text{PVF}_2 \). Due to distinct difference in crystallite conditions in different samples the anomaly occurs at different temperatures and so also their conductivity values show marked difference. Thus the \( \alpha \)-relaxation depends on the crystallinity of the sample. The anomaly
FIG. 3-12. THERMO-CURRENT VS. TEMPERATURE OF 25 μ PVF₂ FILM.
FIG. 3.13 VARIATION OF LOG $\sigma_{dc}$ VS $10^3/T$ ($P_{VF_2}$).
FIG 3.14 VARIATION OF LOG $\frac{1}{\sigma_{dc}}$ VS $10^3 / T$ OF PVP FILM (DIFFERENT THICKNESSES)

FIG. 3.15 VARIATION OF LOG $\frac{1}{\sigma_{dc}}$ VS $10^3 / T$ OF 25 µ FILM (PVP) (DIFFERENT FIELDS)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature of minimum conduction (°C)</th>
<th>Temperature at which anomaly takes place (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (150 μ)</td>
<td>~ 54</td>
<td>~ 142</td>
</tr>
<tr>
<td>B (790 μ)</td>
<td>~ 65</td>
<td>~ 168</td>
</tr>
<tr>
<td>C₁ - C₄</td>
<td>41.5 - 66</td>
<td>~ 120</td>
</tr>
</tbody>
</table>
at high temperature may be due to dielectric dispersion in the pre-melting region.

The values of minimum conductivity and temperature of minimum conduction for different film samples are given in the Table 3.3 (Fig. 3.14). The minimum conduction occurs in the temperature region (40 - 65°C) where $\alpha$-relaxation is reported in the dielectric relaxation studies. In stretched samples, Form I relatively increases and the crystallinity of the sample differs. Again for samples of different percentage of crystallinity and crystalline form the temperature of minimum conduction appears at different temperatures. Thus due to difference in film preparation of different origin, $\alpha$-relaxation, being a function of crystalline condition, was obtained over a wide temperature region. The orientation of crystallites may also take place due to electric field of the order of $10^4$ V/cm. However, in all samples the minimum conduction dips shown in the figures are due to crystalline dispersion associated with $\alpha$-relaxation.

Fig. 3.15 shows the dependence of electrical conductivity on temperature of 25 $\mu$m biaxially stretched film at different biasing fields. The temperature of minimum conduction decreases with increasing field i.e. 4 kV/cm to 20 kV/cm. When the field is increased, the
TABLE 3.3

Temperature region of $\alpha$-relaxation in different $\mathrm{PVF}_2$ film samples and their minimum electrical conductivity values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature of $\alpha$-relaxation ($^\circ\mathrm{C}$)</th>
<th>Minimum value of electrical conductivity ($\text{ohm}^{-1} \text{ cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$\sim 48.6$</td>
<td>$\sim 1.2 \times 10^{-14}$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$\sim 66.0$</td>
<td>$\sim 2.6 \times 10^{-14}$</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$\sim 41.5$</td>
<td>$\sim 8.3 \times 10^{-15}$</td>
</tr>
<tr>
<td>$c_4$</td>
<td>$\sim 46.5$</td>
<td>$\sim 4.0 \times 10^{-15}$</td>
</tr>
</tbody>
</table>
molecular motion is set in at relatively lower temperature which, due to thermal agitation, would have occurred later. The change in slope observed in high biasing field 20 kV/cm at temperature 105°C suggests the orientation of crystal­lites at adequate fields.

3.3.3.5 Pyroelectric Measurement

The pyrocurrent (I) was measured in the cooling cycle at the rate of ~ 0.5°C/minute. The pyroelectric coefficient \( p \) was calculated using the formula

\[
p = \frac{I}{A} \frac{1}{\text{d} \theta / \text{d}t}
\]

where \( A \) is the area of the sample and \( \frac{d\theta}{dt} \) the rate of cooling.

The pyrocoefficient was plotted as a function of temperature as shown in Fig. 3.16. The pyrocoefficient for the poled uniaxially stretched 29 \( \mu \) piezo film is ~ 1.75 nC/cm\(^2\)/°K at RT and it increases to ~ 5 nC/cm\(^2\)/°K at 110°C. There is an exponential increase in the pyroelectric coefficient with temperature. The pyroelectricity arises due to either temperature dependence of spontaneous polarisation or due to heterogeneity of the film and the embedded charges. Since net dipole moment of Form II
crystallites is zero, the pyrocoefficient, which is due to change in dipole moment with respect to the change in temperature in PVF$_2$, is due to Form I crystalline phase. Stretching and poling transform Form II to Form I phase. This is also established from the IR spectra of the 29 µm piezo film which is characterised by a profound absorption peak at 510 cm$^{-1}$. The variation of pyrocoefficient with temperature rapidly increases after the second dispersive region i.e. about 105°C in the sample. The total pyrocurrent in PVF$_2$ is not entirely due to primary pyroelectricity. There is also contribution of secondary pyroelectric effect due to thermal expansion via piezoelectric effect. It is believed that the second mechanism will be contributing significantly to the total pyroelectric current at high temperature side. At still higher temperature, due to enhanced conductivity of the sample, the release of frozen charges injected from the poling electrode can be significant and the pyroelectric study at these regions may not be reliable. However, the change in slope in the pyrocoefficient vs temperature curve around 105°C again establishes the earlier inference that, at high temperature side, there is still another dispersive region of dielectric nature in the crystalline PVF$_2$. 
3.4 FERROELECTRIC STUDIES:

The modified Sawyer-Tower circuit (Fig. 2.7 A) was calibrated for barium titanate single crystal. And then the 29 μ uniaxially stretched piezo poled film and solution-casted poled (900 kV/cm) film (0.3 μ) were investigated with the same circuit at room temperature. The observed loops are shown in Fig. 3.17. Only piezo film exhibited the hysteresis loop. In solution-casted PVF₂ film an elliptical loop was observed at low fields. Some sort of nonlinearity was observable at high fields. These observations suggest that the ferroelectricity in PVF₂ is due to Form I crystallites which are present in the piezo film. The negative result in solution-casted film again confirms the previous conclusion that Form II and Form III crystallites do not exhibit ferroelectricity.

3.5 COMPARISON: The Solution-casted and Industrially Supplied films.

The dielectric constant, loss tangent, electrical conductivity, pyroelectric coefficient and ferroelectric measurements on solution-casted and industrially supplied PVF₂ films were done. Important points of difference in the two types of PVF₂ films are as follows:
FIG. 3.17 HYSTERESIS LOOPS

(A) BARIUM TITANATE SINGLE CRYSTAL
(B) 29 µ PIEZO FILM. (PVF$_2$)
(C) SOLUTION-CASTED FILM. (PVF$_2$)
(i) The solution-casted films are more lossy because they contain Form II and Form III crystallites.

(ii) \( \alpha \)-relaxation is more prominent in solution-casted films showing that \( \alpha \)-relaxation is more prominent in Form II.

(iii) Dielectric constant has a lower value in solution-casted films than in industrially supplied films. The value of \( \varepsilon \) is highest for piezo film due to richness in Form I crystallites.

(iv) Difference in electrical conductivity in the low temperature region is due to the difference in methods of measurement and hence dips were observed in sheets and anomalies in solution-casted poled films.

(v) The high temperature anomaly was not observed in solution-casted films as the electrical conductivity measurement was done only upto 130°C.

(vi) No pyroelectric current was observed in solution-casted film due to the absence of Form I crystallites but the pyroelectric coefficient in case of industrially supplied 29 \( \mu \) poled piezo film varied from 1.75 nC/cm\( ^2 \)/°C at RT to 5 nC/cm\( ^2 \)/°C at 110°C.


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