

# Development of Flexible Low Dielectric Constant Polyimide Films Based on Iso-Propylidene, Aryl-Ether Linked Dianhydride/Diamine

M. Dhakshnamoorthy\*, S. Vikram and R. Vasanthakumari

**Abstract-** The effect of iso-propylidene and aryl ether linked dianhydride and diamine monomers such as 4,4'-(4,4'-isopropylidene diphenoxy) bis (phthalic anhydride) (IDPA), 4,4'-oxydianiline (ODA) and 4,4'-(4,4'-isopropylidene diphenyl-1,1'-diyl dioxy) dianiline (IDDA) on dielectric properties of two polyimides (PI) namely PI-1 (IDPA-ODA) and PI-2 (IDPA-IDDA) synthesized by a conventional two-stage method was studied. The poly amic acids (PAA) obtained in the first stage were thermally treated at 100 - 300 °C in the second stage to obtain the polyimide films by solution casting. The inherent viscosity of PAAs was around 1.0 dL/g and the PIs obtained, exhibited good solubility in polar aprotic solvents such as N-methyl pyrrolidone, N, N-Dimethyl acetamide, N, N-Dimethyl formamide, etc. due to flexible backbones. The PIs showed 10 % degradation temperature of 530 and 541°C in TGA analysis and wide angle X-ray diffraction profiles confirm that the PI films were amorphous in nature. The viscoelastic behavior and glass transition temperature (T<sub>g</sub>) of PI films were determined by dynamic mechanical analyser and the values were 216.7 and 238.8 °C. The films showed high tensile strength, modulus and optical transparency upto 88 % and the dielectric constants were measured at various frequencies and temperature levels and the polyimide film derived from IDPA and IDDA monomers showed dielectric constant value as low as 2.25 at 5 MHz, 100 °C.

**Index Terms-** Aryl ether linkage, dielectric constant, Polyimide film, Thermal property.

## 1 INTRODUCTION

In recent years, polyimides have become most demanding for high performance polymers because of their outstanding properties such as thermal stability, mechanical and electrical. Among these polyimides, aromatic polyimides are well known for their excellent mechanical and chemical properties, like resistance to acids as well as their solubility in polar aprotic solvents [1-5]. The modifications in this type of polyimides have been made and used in aerospace, optoelectronics, liquid crystal display (LED) and other needful industries [6-10]. In-addition with these Polyimides have also been used as sensors, membranes in fuel cell, gas separation, ultrafiltration and nanofiltration applications due to their flexibility, toughness and thermo-oxidative resistance [11-14, 24-26]. Most of the aromatic polyimides have high melting temperature and poor solubility in most of the aromatic solvents due to the rigid backbone and strong interaction between the polymer chains. Many modifications have been made to improve the flexibility and solubility with reservation of other advantageous properties by introducing flexible linkages, non-coplanar units or bulky substituents [15-23].

Most of the polyimides are light brown in colour which is due to inter and intramolecular charge transfer (CT) interaction between alternating electron-donating diamine and electron accepting dianhydride components. It has been shown that the polyimides with unsymmetric structure of

dianhydride or diamine components prevent the close packing of chains and also the CT interactions. It is also found that the introduction of bulky groups with unsymmetric structure into the polyimides rendered the polymer to have better solution processability, improved flexibility, less colour and lower dielectric constant [29 - 30].

In this study, we report the synthesis and characterization of two polyimides from symmetrical monomers with high thermal stability, good solubility, high transparency with lowest dielectric constant attainable so far. The effect of phthalic *iso*-propylidene group and ether linkage on thermal stability, dielectric property and optical property will be discussed. In addition to the bulky, packing-disruptive -CH<sub>3</sub> groups, the unsymmetrical structure of the bis(ether anhydride) or bis(ether amine) component will prevent the extended close packing of chains and also the CT interactions. Thus, the polymer would be expected to exhibit high transparency, flexibility, good solubility and low dielectric constant. By comparative studies of these polymers with their non *tert* butyl bulky group analogs, we confirmed in this paper that the introduction of both bulky group and the ether linkage into the polyimide structures rendered the polymer better solution processability, improved flexibility, transparency and lower dielectric constant values.

## 2 EXPERIMENTAL

### 2.1 Materials and measurements

4,4'-(4,4'-isopropylidene diphenoxy)bis (phthalic anhydride) (IDPA) (Sigma Aldrich m.p.184-187°C), 4,4'-Oxy dianiline (ODA) (Lotto chemicals), 4,4'-(4,4'-isopropylidene diphenyl-1,1'-diyl dioxy) dianiline (IDDA) (Sigma Aldrich m.p.127-130 °C) were used as received after drying them. The chemical structures of the monomers used are shown in Figure 1. N, N-Dimethyl acetamide (DMAc) solvent obtained

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- **M. Dhakshnamoorthy** is currently pursuing PhD degree program in Polymer Technology in B S Abdur Rahman University, Chennai, India, PH-+919962633181. E-mail:m.dhakshnamoorthy@gmail.com
  - **S.Vikram** is currently pursuing PhD degree program in Physics in B S Abdur Rahman University, Chennai, India, E-mail:vikram625001@gmail.com
  - **R. Vasanthakumari** is currently working as Professor&Head, Polymer Nanotechnology Centre, B S Abdur Rahman University, Chennai, India.

from Merck chemicals was vacuum distilled and dried using molecular sieves.

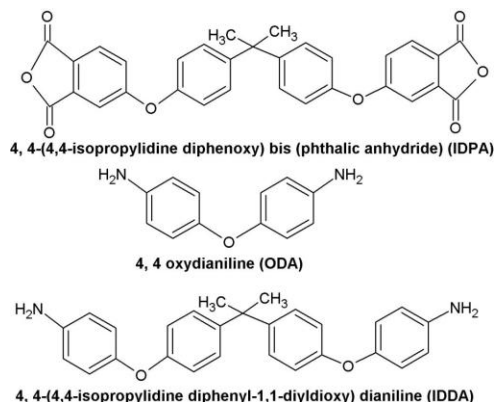


Fig 1. Chemical Structure of the monomers

The fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Fourier transform infrared spectrophotometer. The inherent viscosities of the poly (amic acid)s were measured with an Ubbelohde viscometer at 25°C at a concentration of 0.5 g/dl in DMAc at 25°C.

The crystallite particles size measurements were performed Wide-angle X-ray diffraction (WAXD) at room temperature (RT) (25 °C) on a Bruker D8 Focus X-ray diffractometer, using nickel filtered Cu K $\alpha$  ( $\lambda=0.1541$  nm, scintillator detector, operating at 40 kV and 30 mA). The step time was 1 second at 0.02°/ step between the 2 $\theta$  angle of 5 to 50°.

The mechanical property using dynamic mechanical analyses (DMA) were conducted for polyimide films using Seiko Instrument DMS 6100. The frequency was set at 1 Hz and the heating rate was 2 °C/min in air atmosphere. The relaxation temperatures were determined from corresponding peak top temperatures on the damping (tan  $\delta$ ) curves.

Thermogravimetric analyses (TGA) were determined for polyimide films using Seiko Instrument TG/DTA6200, EXSTAR 6000. The experiments were carried out on 5 - 7 mg of samples in flowing of nitrogen gas (flow rate 140 ml/min) and also in air atmosphere at a heating rate of 20 °C/min.

The optical transparency study by Ultraviolet-visible (UV-Vis) spectra of the polymer films were recorded on a CARY 5E UV-VIS-NIR spectrophotometer. Lloyd's instrument with an LF plus model 1 KN load cell was used to study the tensile properties of the polyimide films. The specimens of 70 mm long, 5 mm wide, about 0.05 mm thick were cut and the tensile properties were determined following the general procedure in ASTM D882 using 4 - 5 specimens from each film. The test specimen gauge length was 5 cm and the crosshead speed for film testing was 0.5 cm/min.

The dielectric constants of the films were measured on a HIOKI 3532 - 50 LCR HITESTER in the frequency range from 50 Hz to 5 MHz. Using the gold electrodes were vacuum-

deposited on both surfaces of dried films. Experiments were performed at the temperature ranges from 40 °C upto 250 °C in a dry chamber.

## 2.2 Synthesis of PAA

The PAAs were prepared from dianhydride and diamine via a two-step method. In first step, PAA-1 was prepared by dissolving diamine ODA (0.155 g, 0.776 mmol) in 2 ml of CaH<sub>2</sub>-dried DMAc in a 50ml round bottom flask. After the diamine monomer dissolved completely, an equimolar amount (0.404 g - 0.776 mmol) of dianhydride IDPA was added. PAA-2 was prepared similarly by the same procedure, dissolving the diamine IDDA (0.317 g, 0.774 mmol) in 3 ml of CaH<sub>2</sub>-dried DMAc and dianhydride IDPA (0.403 g, 0.774 mmol) was added. The mixture of dianhydride and diamine were stirred at RT for 12 hrs under nitrogen atmosphere to afford a viscous PAA precursor. The polymer solution was poured into distilled water. The white precipitate of PAA was collected by filtration, washed thoroughly with distilled water, and dried at 60 °C for 6 hrs in vacuum oven to remove moisture and solvent.

## 2.3 Thermal cyclo-imidization

The dried PAA powder was redissolved in DMAc solvent at 30% solid content (w/v) to get homogenized PAA solution. The solution was poured on a glass surface and heated sequentially at 100 °C for 1 h, 200 °C for 1h and 300 °C for 1h. After cooling to RT the polyimide film was soaked in water, a flexible PI film was self-stripped from the glass surface.

## 3 RESULTS AND DISCUSSION

### 3.1 Organo solubility

The solubility of polyimides was tested in various solvents. The polyimides IDPA-ODA and IDPA-IDDA were soluble in polar aprotic solvents such as NMP, DMF, DMAc, etc. at RT (Table I). The inherent viscosities (Table I) were found at 0.872 and 1.091 for PAA1 and PAA2 respectively. Even though the PAAs showed low in solution viscosity values, they yielded quite flexible and strong PI film after imidization.

Table I. Inherent viscosities and solubility behaviours of PIs.

S. No	PI	N M P	DM -Ac	D M F	DM -SO	CH- Cl <sub>3</sub>	TH F	$\eta_{inh}$ (dL/g)
1.	IDPA ODA	++	++	++	±	±	±	0.872
2.	IDPA IDDA	++	++	++	±	±	±	1.091

++ = soluble; ± = partially soluble; - = insoluble at room temperature

### 3.2 FT-IR Analysis

The conversion of the PAA to the fully cyclized polyimide was determined by FT-IR. Figure 2 and 3 show the IR spectra of PAAs and polyimides respectively. The complete conversion of *o*-carboxylic amide to the imide ring was evidenced by the disappearance of the amic acid bands at 2500 - 3500  $\text{cm}^{-1}$  together with the appearance of characteristic molecular absorption vibrational bands at 1775 (asymmetrical C=O stretch), 1713 (symmetrical C=O stretch), 1382 (C-N stretch), 745 (C=O bending). (Figure 3)

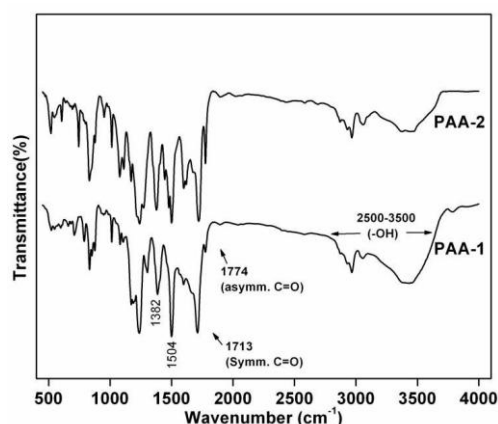


Fig 2. FT-IR spectra of poly(amic acid) powder

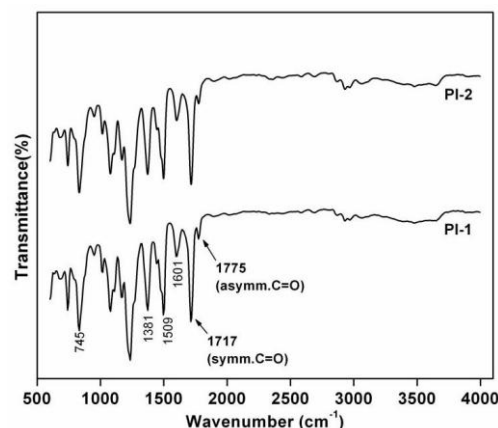
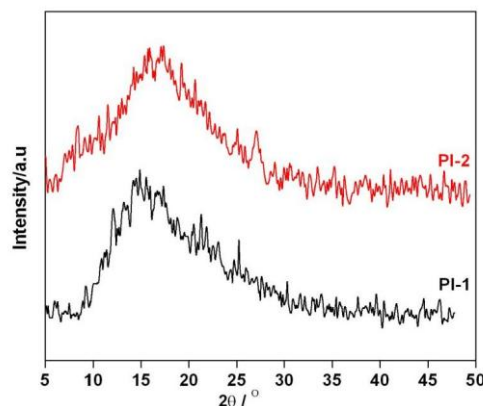


Fig 3. FT-IR spectra of polyimide films

### 3.3 X-ray Diffraction Data

Polyimide films were characterized by wide-angle XRD studies and the diffraction patterns are shown in Figure 4. A broad diffraction peak intensity was observed around  $2\theta = 10 - 25^\circ$  for PI films which showed amorphous nature with broad diffraction intensities peak due to flexible isopropylidene group present in the matrices.



Fig

4. XRD

pattern of PAA and PI

### 3.4 Dynamic Mechanical Analysis

The visco-elastic relaxation behavior of polyimide films were measured by DMA. The specimen dimensions for DMA measurements were about 40mm × 5mm × 0.03mm ( $l \times w \times t$ ). The storage modulus  $E'$ , loss modulus  $E''$  and a measure of dissipation or damping  $\tan \delta$  ( $\tan \delta = E''/E'$ ) at 1 Hz oscillatory deformation were recorded in the temperature range from 25  $^\circ\text{C}$  to 300  $^\circ\text{C}$ . The glass transition temperatures were determined as the temperatures of the maxima of  $\tan \delta$  (Figure 5 and 6) which showed 238.8  $^\circ\text{C}$  and 216.7  $^\circ\text{C}$  for PI films 1 and 2 respectively. The Arrhenius plot of  $\ln$  frequencies (Hz) corresponding to  $\tan \delta$  max against temperature for PI-1 & PI-2 is shown in Figure 7 & 8. The activation energies ( $\Delta E$ ) of polyimide films were found to be 781.43 and 981.01 kJ/mol for PI 1 and 2 respectively. The higher value of  $\Delta E$  for PI2 can be attributed to the presence of bulky symmetrical isopropylidene groups in both the monomers.

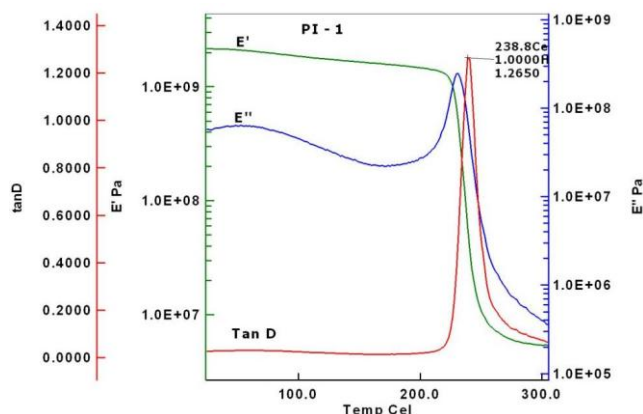


Fig 5. DMA curve of IDPA-ODA PI film 1

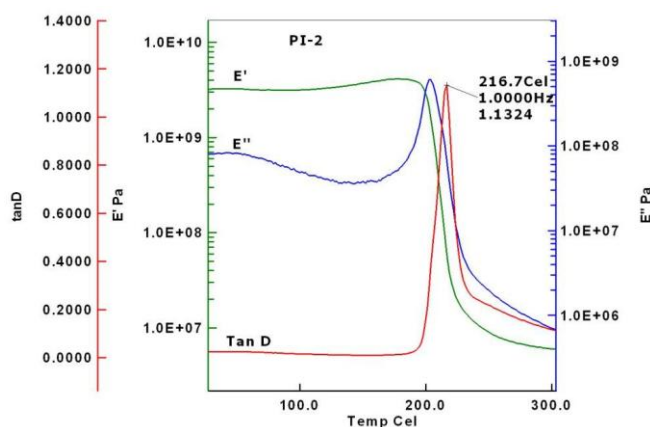


Fig 6. DMA curve of IDPA-IDDA PI film 2

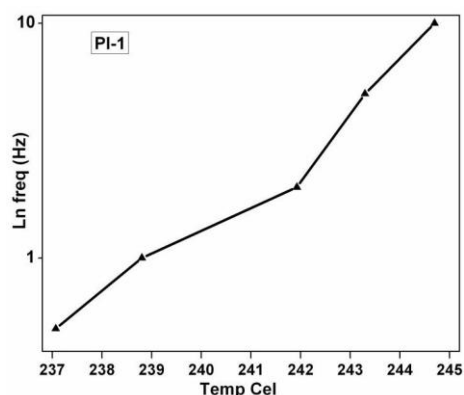


Fig 7. The curve of Temp. Vs ln freq. of PI-1

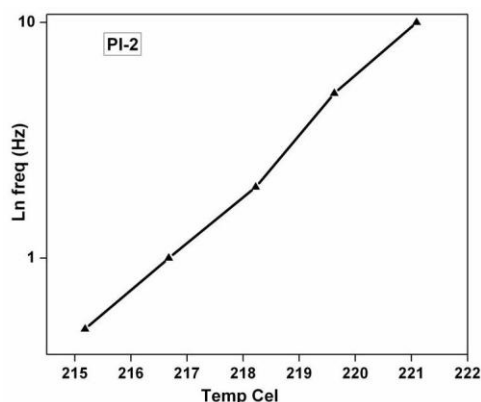


Fig 8. The curve of Temp. Vs ln freq. of PI-2

### 3.5 Thermogravimetric Analysis

Typical TGA curves for polyimides are shown in Figure 9 and 10 as determined at nitrogen ( $N_2$ ) gas and air atmosphere. The PI-1 is found to be more thermally stable compared to PI-2 and Thermal stability of polyimide (PI-1 & PI-2) films at 10 wt% decomposition temperature values ( $T_d$ ) was found to be 541.1 °C, 531.1 °C in  $N_2$  atm and 530.3 °C, 530.1 °C in air atm. Hence it is clearly evident for that in the polyimides, the nature of decomposition and the groups participating in it are same. Examination of the structures of the polyimides illustrates that the common decomposable group is the imide ring which is the target group for the decomposition stage. As the nature of cleavage in the imide ring is the same in all of them, the slight shift in their decomposition temperature for PI-1 & PI-2 is attributed to the influence of the electronic factors (electron releasing or electron withdrawing) associated with phenoxide oxygen and the iso-propylidene group of the dianhydride and diamine.

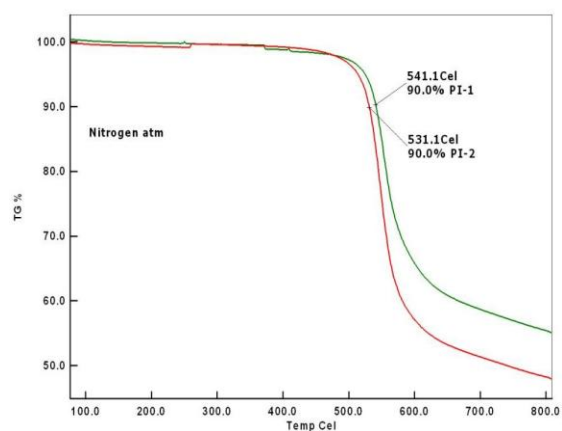


Fig 9. TGA curve of PIs in nitrogen atm

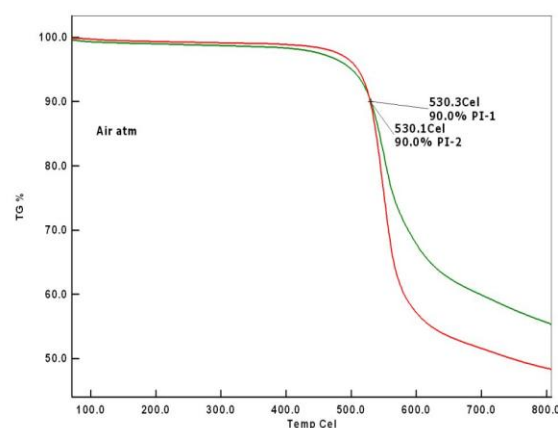


Fig 10. TGA curve of PIs in air atm



### 3.6 UV-Visible Spectroscopy

The UV-Visible spectra of the polyimides with film thickness of 70 - 90  $\mu\text{m}$  are shown in Figure 11. Both the polyimides show high transmission (85 - 88 %) in the wavelength range of 800 - 1600 nm.

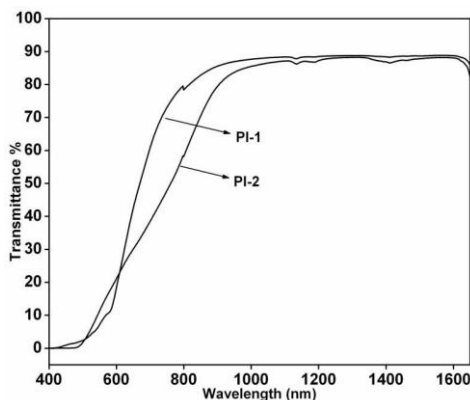


Fig 11. UV-Visible spectra of polyimide films

The *iso*-propylidene group and phthalic ether groups present in dianhydride and diamine moieties were effective in decreasing the charge transfer complex between polymer backbone chains through steric hindrance leads to increase in the intermolecular distance and thus decreased the interaction between the polyimide chains resulting in a good optical transparency.

### 3.7 Tensile Properties

The polyimide films were subjected to a tensile test, and their tensile properties are summarized in Table 2. The films had strength at break of 89.1 and 85.4 MPa for PI-1 & PI-2 respectively showing a decrease in tensile strength was observed, when ODA was replaced with IDDA. ODA containing polymer (PI-1) had more rigidity and low flexibility because there is only strengthened C-O-C bond and no flexible *iso* propylidene group. Similar to tensile strength which is suggested to be strongly dependent upon the bridging groups, the percentage of elongation of the polymer chain also depends on the properties of the bridge. As expected, in PI-2 there is an increase elongation of *iso* propylidene bridge than C-O-C bonding bridge.

Table II. Tensile strength of polyimide films

S. No.	PI film	Tensile Modulus (GPa)	Tensile strength (MPa)	Elonga-tion %
1.	PI-1	2.16	89.1	9.2
2.	PI-2	2.12	85.4	9.7

### 3.8 Dielectric Constant

The plot dielectric constant vs. frequency at different temperature ranging from 40 - 250  $^{\circ}\text{C}$  is shown in Figure 12 and 13 for PI-1 and PI-2 respectively. The dielectric constant values measured at 5 MHz at different temperature showed in Table III.

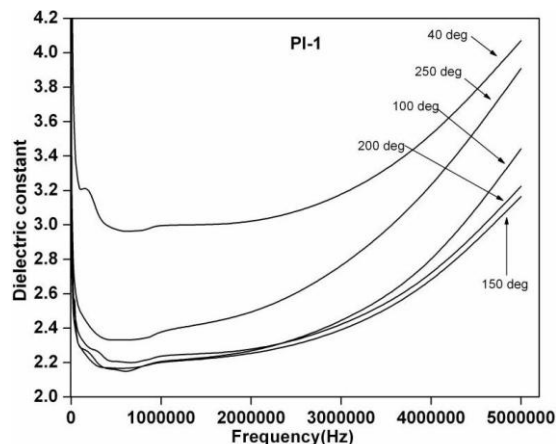


Fig 12. The curve of freq. Vs dielectric constant of PI film 1

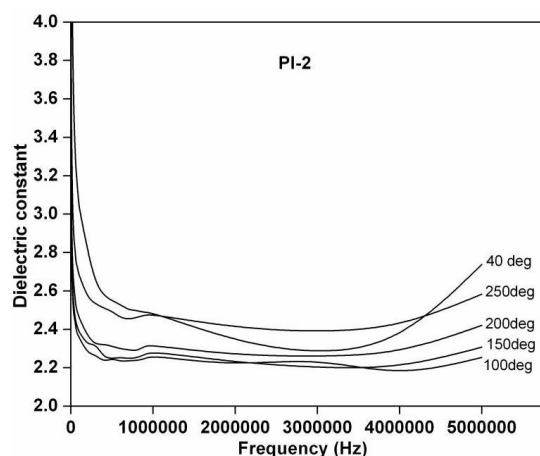


Fig 13. The curve of freq. Vs dielectric constant of PI film 2

It is observed that there is a decrease in dielectric constant with temperature from 40 to 200  $^{\circ}\text{C}$  at all the frequencies determined upto 5 MHz. Further it is interesting to find that PI-2 showed lower dielectric constant values ranging from 2.2 to 2.7 compared to PI-1 which showed in the range 3.1 to 4.0 at all the measured temperatures and frequencies. Chin-ping yang et al. prepared polyimides with keto groups in polymer chains which had dielectric constant of 3.47 at 1 MHz [14]. As shown in Table II, our polyimide film, PI 2 derived from IDPA and IDDA monomers shows dielectric constant as low as 2.25 at 5 MHz at 100 $^{\circ}\text{C}$ . The low dielectric constant here is attributed to the fact that the introduction of the *iso*-propyli-

-dene group and phthalic – ether group in both dianhydride and diamine leads to the formation of configuration of repeat units in the polymer backbone causing the decrease in the intermolecular force and packing ability of the resulting polymers. These results suggest that the PIs containing phthalic *iso*-propylidene groups loosen the polymer packing and increased the free volume, subsequently leading to reduced dielectric constant.

Table III. Dielectric constant of polyimide films

S. No.	PI film	Dielectric Constant (5 MHz)				
		40°C	100°C	150°C	200°C	250°C
1.	PI-1	4.0709	3.4427	3.1649	3.2244	3.9088
2.	PI-2	2.7384	2.2546	2.3077	2.4215	2.5841

#### 4 CONCLUSION

Two polyimides were prepared by the polycondensation reaction of IDPA with ODA and IDDA in DMAc solvent at RT and characterized for various properties. These aromatic polyimides showed good solubility in polar aprotic solvents, higher thermal stability, flexibility, toughness and optical properties. The XRD profiles of PI films showed that there was an absence of crystalline domains, revealing the amorphous nature of the films. PI-2 (IDPA-IDDA) showed lower dielectric constant values in the range of 2.2 – 2.7 compared to PI-1 (IDPA-ODA) at different frequencies up to 5 MHz. This low value is attributed to the presence of more free space between the polymer backbone chains created by the steric effect of bulky phthalic *iso*-propylidene groups in both alternate dianhydride and diamine components in PI-2. Because of low dielectric constant values of PI 2 even at high temperature, it can be the best candidate for use as insulator applications.

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