



Electrical and Dielectric Properties of Copolymer Poly[trans-Dichlorobis(carboxyl penta methylene amine)bisphenoly- A Platinum(II) terephthalate] (PDPT)

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Abstract

Electrical and dielectric properties of Poly[trans dichlorobis (carboxylpentamethylene amine bisphenoly A)platinum(II) terephthalate](PDPT) have been investigated as a function of temperature, to study the mechanism of electrical conduction, the current was measured by applying d.c voltage in the range(1-120V)at various thermostatically controlled temperature(308-383K).The results obtained predict the variable hopping range(VRH)conduction mechanism .Futher,the conductivity of sample increase with increased temperature and applied voltage indicated that the sample has semiconducting behaviour and the value of conductivity is order of magnitude 3.72×10^{-13} (S/cm) at R.T with activation energy 0.82eV to transport the electrons from valance band to conduction band .The dielectric constants of the sample at various temperatures have been calculated which increased with increasing in temperature above 340K due to increase in density of the dipole orientation .

Keyword: Electrical conduction, dielectric constant, bisphenol-A,platinum (II).

1. Introduction

Electrical conduction and dielectric constant in polymers have been extensively studies in recent years to understand the nature of charge transport in these materials [1].Various conduction mechanism such as Scottky and Pool-Frenkle effect , Space charge limited coduction and

hopping conduction [2] have been suggested for the charge transport .Bisphenol A is a good insulating materials with low conductivity and hence is of importance to industrial applications [3] .There are several methods have been used to improve the processibility of conductivity polymers ,one of this turn of copolymerization by introduce metal complex with backbone of

polymer matrix ,So, in this work represent electrical and dielectric properties of PDPT.

2. Chemical Section

Bis phenol-A, terphthaloyl chloride and 6-amino hexanoic acid were purchased from Aldrich Chemical Company. K_2PtCl_4 was purchased from Johnson Matthey (Seabrook, N.H). All chemicals obtained from commercial supplier were used as received. Infrared spectra were measured as KBr disk on FT-IR spectrophotometer Shimadzu model 8400S in the range of $4000-200\text{ cm}^{-1}$.

2.1 Synthesis of trans-dichlorobis(carboxyl penta methylene amine)platinum(II) complex

This complex was prepared as the following :

6-amino hexanoic acid (1.31g ,10 mmol) in 15 ml of water was add to K_2PtCl_4 solution(2.05g , 5mmol) in 25 ml of water and the reaction mixture was stirred for 2 hrs.The mixture condensed to 5ml by rotary evaporator and then excess acetone was added to form a solid product . The crude product was washed by a mixture of water and acetone (1:1) to obtain yellow crystals yield 80% .

2.2 Synthesis of Poly[trans-dichlorobis(carboxyl penta methylene amine bisphenolyl-A)platinum(II) terephthalate (PDPT)]

This polymer was prepared as follows :

In a three- necked flash 250ml equipped with a reflux condenser, trans–dichlorobis(carboxyl methylene amine) platinum(II) complex (5.2g ,10 mmo)l was mixed with toluene 100ml and bisphenol-A (4.56g , 20 mmol) in 100 ml of toluene was added drop wise. Then, 2 ml of 6 N of HCl was added and the reaction mixture was

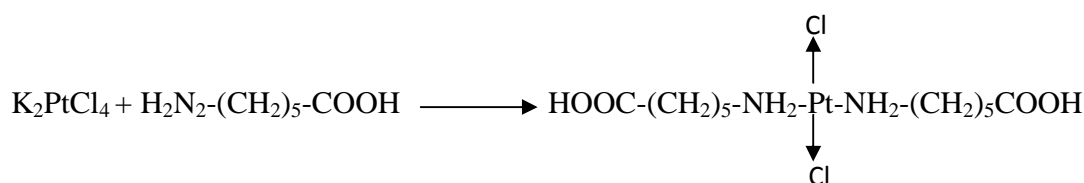
refluxed for 5 hrs. The crude product was reacted with (2.03 g , 10 mmol) terephthaloyl chloride . The prepared copolymer was then precipitated from solution by pouring the solution into distilled water 500 ml .The precipitated copolymer crude was collected by filtration , washed thoroughly three times with hot distilled water then was dried under vacuum at $40\text{ }^\circ\text{C}$ for 2hrs yield 65% .

3. Preparation of Samples

PDPT was dissolved in a solvent dimethyl sulphoxide(BDH Ltd.Co.).For complete dissolution,the solvent was cast on plane aluminum plate (cast methods from solution) [4] at normal equilibrium condition for 24h allowed to evaporate solvent in air at room temperature ,Thereafter, sample dried in evacuated oven at temperature raised gradually up to $120\text{ }^\circ\text{C}$ by a rate $10\text{ }^\circ\text{C/h}$ for 24h . to remove any traces of solvent . The upper electrode was platinum metal .The area of electrode is 0.1 cm^2 . Current-voltage characteristics measured with Ammeter model MEGOHHMETER(IM6) at the range (10^{-12} - 10^{-4} A) were carried out in dark and electrically shielded box. The films thickness were measured by micrometer model köller with the range (1-1000 μm) Voltmeter model SC-Multi LOGGER IWATSU Electrical Co.LTD., Regulator DC Power supply voltage range from (1-120V) were supplied by power supply model hp 6443B.

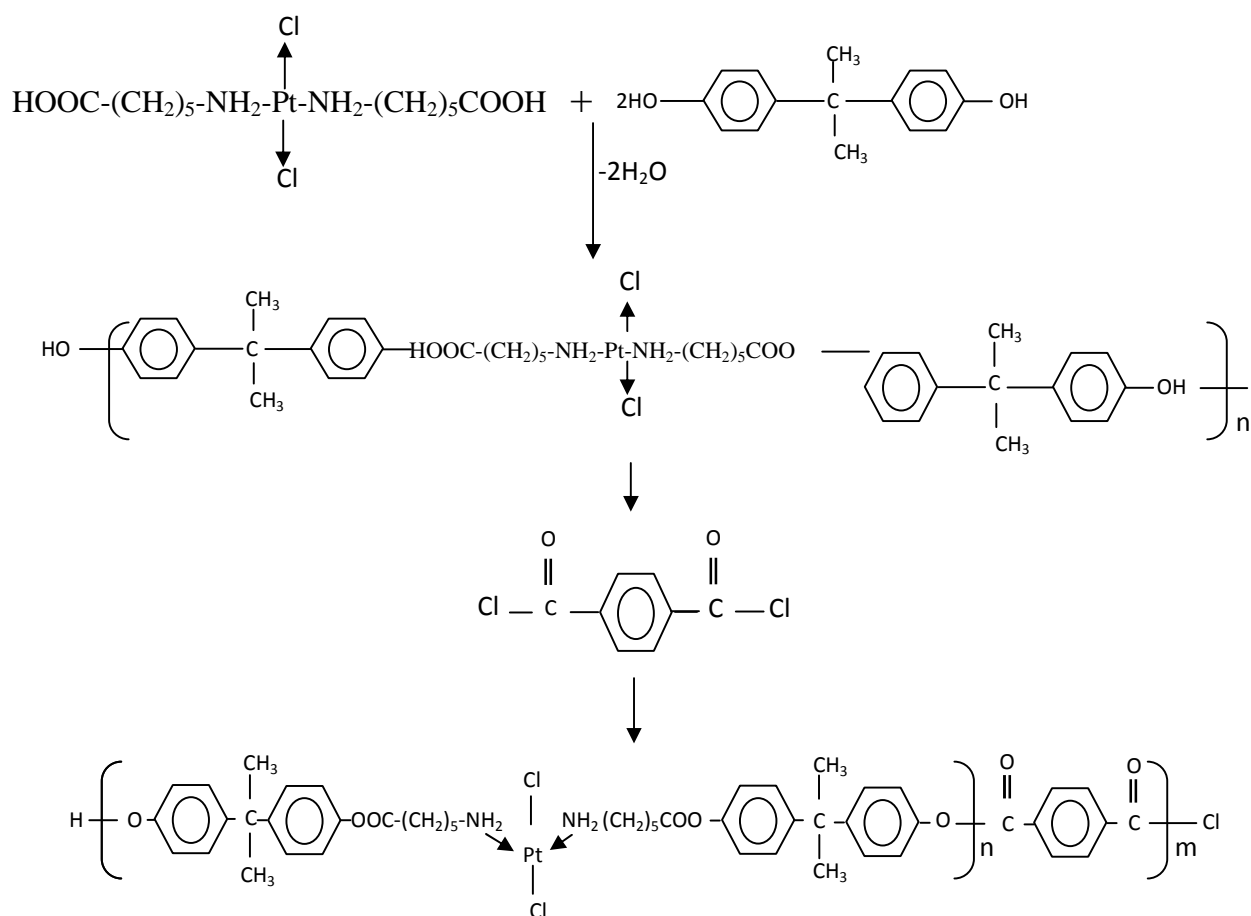
4. Results and discussion

A new alternative copolymer was synthesized by two steps, the first was synthesis platinum(II) complex which contains two terminal carboxylic groups by reaction K_2PtCl_4 with 6-amino h exanoic acid.



The second step reacting of platinum(II) complex with bisphenol-A with ratio 1:2 then the product

with reacted terephthaloyl chloride with ratio 1:1 as shown in scheme 1:



Scheme 1: Preparative method of Poly(trans-dichlorobis(carboxyl penta methylene amine bisphenolyl - A)platinum(II) terephthalate) (PDPT)

Generally, the prepared copolymer is insoluble in water, ethanol and methylene chloride but can be dissolved partially in DMSO solvent. The colour of the prepared alternative copolymer is brown and decomposed in 335 °C . The IR spectrum of this copolymer displays characteristic bands in certain frequencies, Figure (1) shows the IR spectrum of the prepared copolymer and Table (1) summarized the important vibration bands for the prepared copolymer (PDPT) . The vibration bands which are observed in the IR are spectrum agreement with the literatures [5,6].

The copolymer (PDPT) showed one weak band in 550 cm^{-1} . It can be attributed to (Pt-N), this indicates that platinum(II) bind with 6-amino hexanoic acid through nitrogen atom [6]. The spectrum of (PDPT) copolymer showed broad absorption centered at 3200 cm^{-1} due to N-H stretching of the NH_2 groups while the bending band of N-H appeared in 1600 cm^{-1} . The carbonyl of ester group (COO) shows strong vibration absorption bands in the region at 1740 cm^{-1} while carbonyl group absorption of terephthalate group (C=O) was observed at 1682 cm^{-1} [5,6].

Table 1: The important IR bands for functional groups in copolymer

Functional groups	ν cm ⁻¹
Pt – Cl	450
Pt – N	550
C=C	1590
N – H (bend)	1600
Y (C=O)	1682
ν (COO)ester	1740
C – H (aliphatic)	2900
C – H (aromatic)	3050
H-bonding	3200

4.1 Electrical properties

The electrical measurements of the copolymer were measured at steady state conditions. Figure (2) shows the relationship between current and applied voltage at different temperature range (308-383K). The temperature dependence of the dc electrical conductivity for the investigated samples was measured. Figure (3) shows the dependence of dc conductivity as a function of temperature. The plots suggest that there are two types of conduction mechanism contributing to the conductivity and the linearity in the two high-temperature regions (308 - 333 K and 343 – 383 K) which indicate that dc conductivity in the regions exhibits activated behavior according to the relation [7] :

$$\sigma(T) = \sigma_o \exp\left(\frac{-\Delta E}{kT}\right) \quad (2)$$

Where σ_o is the pre-exponential factor including the charge carrier mobility and density of localized states, k is the Boltzmann's constant, T

is the absolute temperature and ΔE is the corresponding activation energy.

From figure (3) the straight line of slope can be estimated ΔE about 0.82eV, these value larger than the compounds including the vinyl groups in bake bone structure and. The dc conductivity at R.T ($\sigma_{R.T}$) will also estimated to be about 3.72×10^{-13} S/cm .The increase dc conductivity with increasing temperature due to increases in the homogeneity of the copolymer chains and this lead to decreases the degree of disorder and density of defect states .

The exponential band tail in the compound as observed us from UV - Visible absorption spectra of the compound indicated that there are localized states [8],which lead to variable hopping conduction region ,can be expressed according to the relation[9]:

$$\sigma(T) = \frac{\sigma_o}{T^2} \exp\left(\frac{-T_o}{kT}\right)^{\frac{1}{4}} \quad (3)$$

where T_o represents the degree of disorder. The $\ln(\sigma T^{1/2})$ can be plotted linearly against $T^{-1/4}$ as shown in Figure(4),indicating that in this region, the transport is due to variable-range hopping (VRH) of the charge carriers in the localized states near the Fermi level .

The thermal conductivity Ψ for PCPT copolymer was measured as a function of temperature. The values of the room temperature electronic and bipolar thermal conduction Ψ_e and Ψ_{bp} respectively, using the DC conductivity (σ_{RT}) and ΔE obtained from Figure(3) were calculating according to the following equations[9]:

$$\Psi_e = L \sigma T \quad (4)$$

$$\Psi_{bp} = \frac{3}{4\pi^2} \Psi_e \left[\frac{\Delta E}{KT} + 4 \right]^2 \quad (5)$$

Where L is the Lorentz number= $(\pi^2/3)(K/e)^2$.

The value of Ψ_e and Ψ_{bp} were found to be at R.T (2.80×10^{-18} and 2.58×10^{-16}) Watt.cm⁻¹. K⁻¹, respectively. As clear from these results, although the contribution of Ψ_{bp} is greater than that of Ψ_e by about two orders of magnitude. Thus, the main contribution of the thermal conductivity is due to the lattice (phonon) thermal conductivity [10].

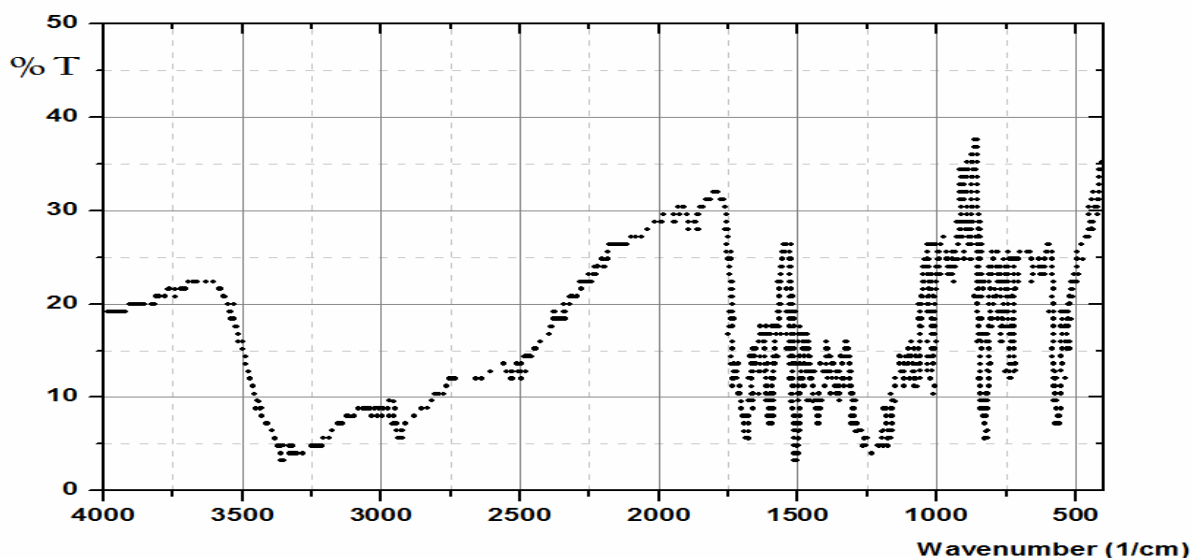


Figure 1: FTIR chart of PDPT

In this study another possible conduction mechanisms such as ionic, space charge limited current, Schottky and Poole-Frenkel effect and tunneling were also studied to identify the proper investigation. Figure(5) shows the relationship between $-\ln(\sigma T)$ and $10^3/T$, where the linear relation can exclude the ionic mechanism from our speculated [11]. The possible existing of Schottky or Poole-Frenkel effect can be investigated from the relationship between current and square root of electric field ($E^{1/2}$). A nonlinear behavior was obtained at high electric field, also (current-voltage) characteristics does not obey the general space charge limited current [12].

4.2 Dielectric properties

In order to study the dielectric properties of the polymer one can be represent the polymer by equivalent electric circuit consist of pure capacitor and resistor connected either in series or parallel in condition that both circuits has equivalent impedance, AC resistance and power factor [13]. Figures (6, 7 and 8) show the relationship between the C_p , R_p and Z (parallel capacitor, parallel resistance and impedance) respectively versus temperature. On the other hand the real and imaginary part of dielectric constant ϵ_1 and ϵ_2

respectively can be calculated from the relation [14]:

$$\epsilon_1 = \frac{C_p}{C_o} \quad (6)$$

and

$$\epsilon_2 = \frac{1}{R_p C_o \omega} \quad (7)$$

where is C_o the capacitance of two metallic electrode in free space separated by a distance equal to the polymer thickness, ω is the angular frequency. For most practical purpose, the series and parallel capacitance are nearly equal. Figures(9 and 10) show the relationship between ϵ_1 and ϵ_2 versus temperature. A useful information can be obtained from the relaxation process in polymer matrix. Starting from the highest temperature ($T > T_g = 333$ K) the maximum referred to α process which is ascribe by micro-Brownian molecular motion of the main chains. At ($T < T_g$) another maximum (with low intensity) was observed which may be related to the β - process which is due to the local molecular motion of the ester and hydroxyl groups. Other important results can be also be concluded from the dielectric constant that the possibility of utilizing the polymer in the insulation purpose in working temperature below T_g , as shown in figure

(9) because ϵ_1 reflected the amount of stored electrostatic charges within the polymer. The dissipation factor ($\tan\delta$) was also studied according to the relation [14] :

$$\tan \delta = \frac{\epsilon_1}{\epsilon_2} \quad (8)$$

Figure (11) show the relationship between $\tan\delta$ and temperature ,it has similar behavior as ϵ_2 .At

glass transition temperature ,loss tangent has a value (0.136) .At temperature equal to 340 K $\tan\delta$ increase with increasing temperature this increase can explained due to increasing in density of the dipole orientation because the increase of kinetic motion of the molecules. In general ,the measuring circuit component are so arranged to give the appropriate capacitance and power factor in terms of the parallel equivalent circuit

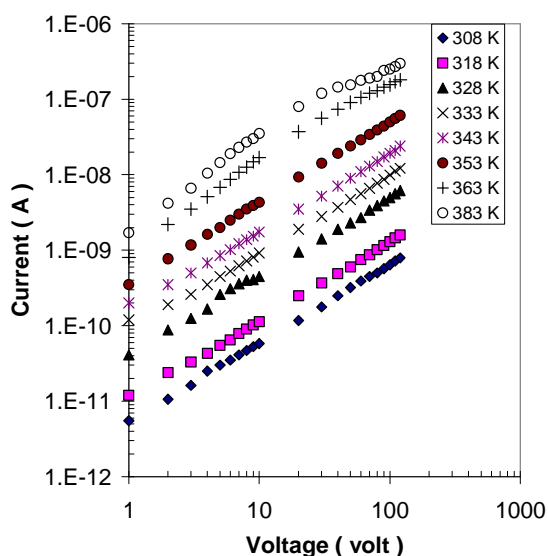


Figure 2: The current – voltage characterization of PDPT at different temperature range (308-383K).

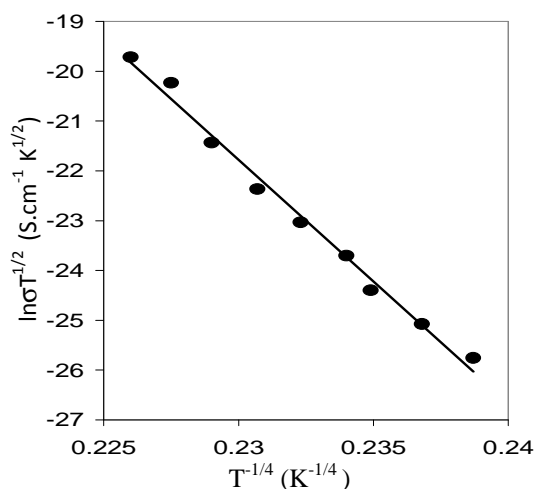


Figure 4: The relationship between $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ of PDPT

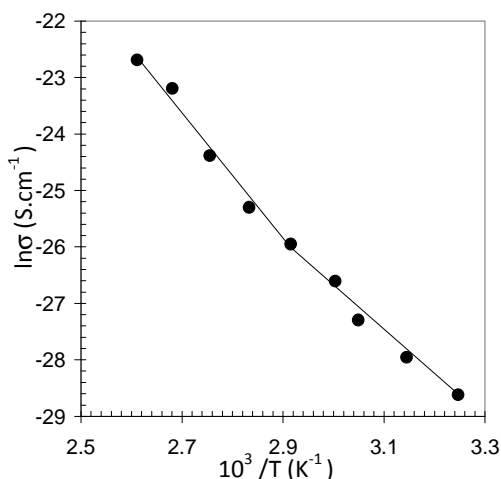


Figure 3 : The relationship between $\ln\sigma$ versus temperature of PDPT

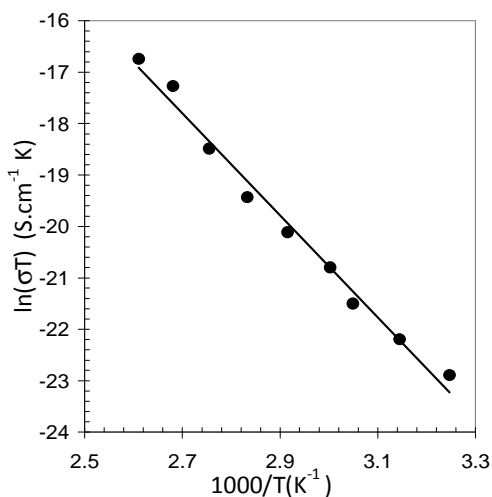


Figure 5 : The relationship between $\ln(\sigma T)$ versus $1000/T$ of PDPT

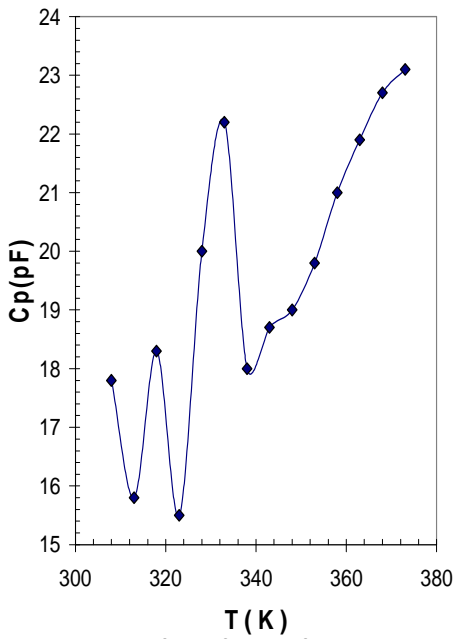


Figure 6 :The relationship between Cp versus Temperature

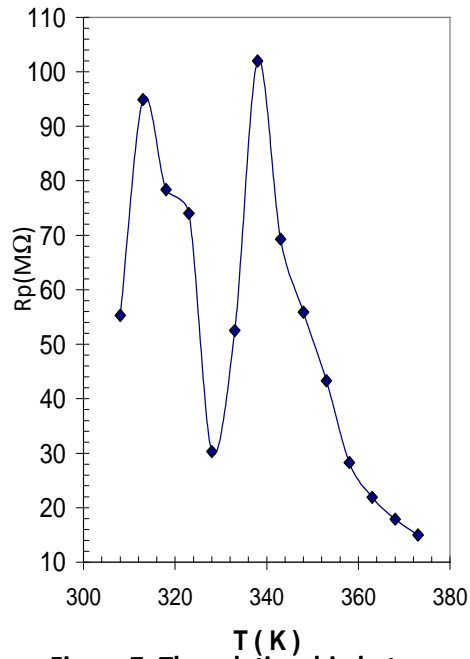


Figure 7 :The relationship between Rp versus Temperature of PDPT

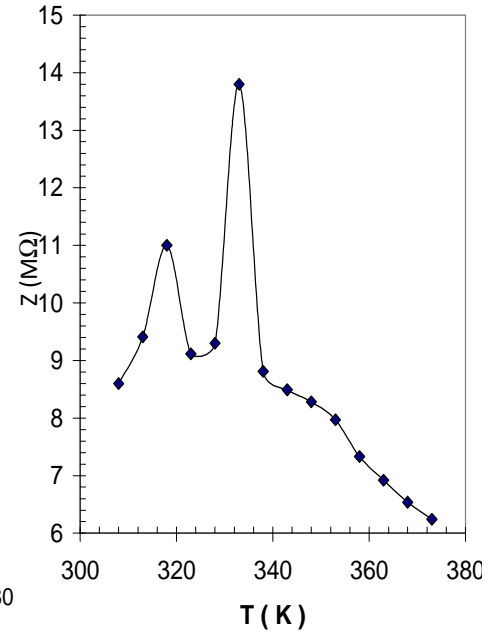


Figure 8: The relationship between Z versus Temperature of

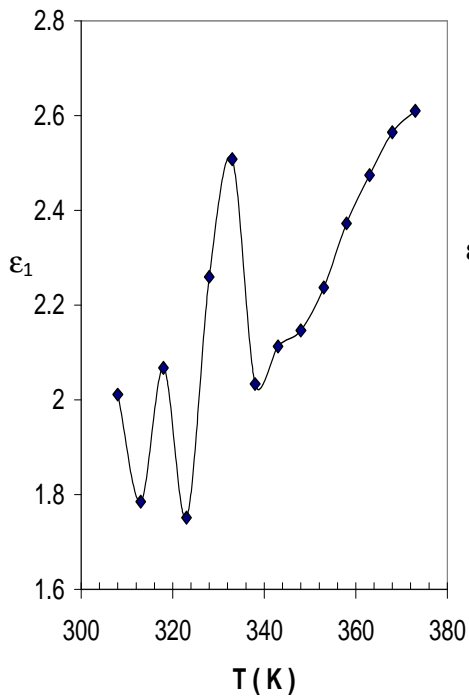


Figure 9: The relationship between ε1 versus Temperature of PDPT

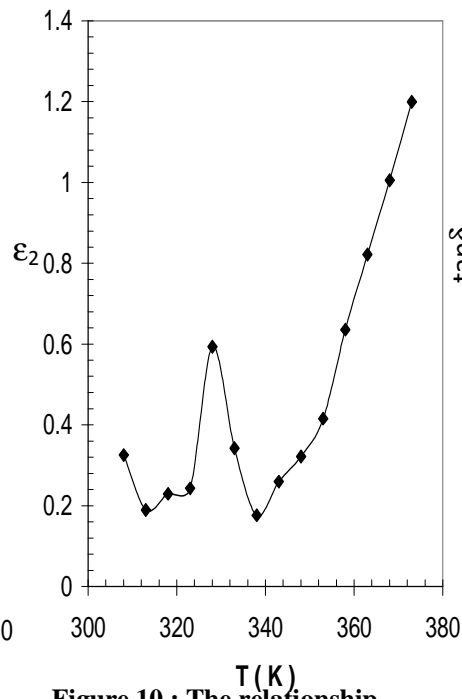


Figure 10 : The relationship between ε2 versus Temperature of PDPT

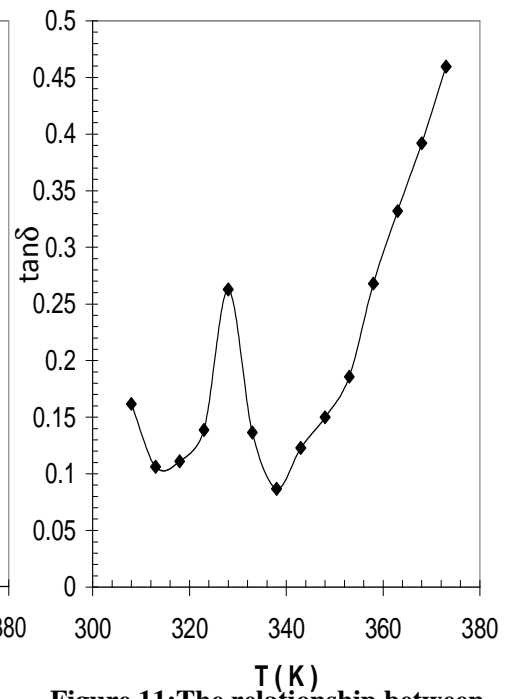


Figure 11: The relationship between tanδ versus Temperature of PDPT

Conclusion

Electrical and dielectric properties of new alternative copolymer Poly[trans-dichlorobis(carboxyl penta methylene amine bisphenoly-A)platinum(II) terephthalate](PDPT) have been investigated. From the FT-IR spectrum studies the important bands for the functional groups of PDPT. Sandwich structure of type Al/PDPT/Pt was formed to study the electrical properties. Electrical conduction mechanism studied by use tow point probe method. The temperature dependence of the conductivity of the samples indicating that the transport is due to variable-range hopping model (VRH) of the charge carriers in the localized states near the Fermi level. The dc conductivity at R.T ($\sigma_{R.T}$) estimated to be about 3.72×10^{-13} S/cm. The thermal conductivity Ψ of PDPT is studies at room temperature. As clear from results, the main contribution of the thermal conductivity is due to the lattice (phonon) thermal conductivity. Dielectric properties was characterized by using the lumped circuit. Two a distinct relaxation processes nominal α and β were identified from the temperature dependent of the imaginary part of the dielectric constant which was related to the Micro-Brownian molecular motion of the main chain at $T > T_g$ and to the different local molecular motion in the copolymer $T < T_g$ respectively. The kinetic motion of the molecules was noticed to appose the orientation effect due to the dielectric field at high temperature.

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