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Investigation of the dielectric Properties of (PPAB) terminated by phenylenediamine doped by $Na_2[Fe(CN)_5.NO].2H_2O$ using Lumped equivalent circuit

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Abstract

The aim of this paper is to demonstrate the effect of $Na_2[Fe(CN)_5.NO].2H_2O$ impurity (0.1 M) concentration on the dielectrical properties of poly (P-Aminobenzaldehyde) terminated by pheneylenediamine in the frequency and temperature ranges (1-100)KHz and (283-348) K respectively.

These properties include dissipation factor, series and parallel resistance, series and parallel capacitance, real and imaginary part of the dielectric constant, a.c conductivity and impedance (real and imaginary) part, that have been deduced from equivalent circuit.

The investigation shows that adding $Na_2[Fe(CN)_5.NO].2H_2O$ as additive to the polymer lead to increase of the dielectric constant with increasing temperature and it is decreasing with increasing the frequency .The dissipation factor is increasing with as the frequency increased.

Key words: resistance, capacitance, dielectric properties, a.c conductivity, dissipation factor.

Introduction:

Organic molecular systems have been rapidly developed due to the newly developed technologies of synthesing a new molecular materials with compatible desirable properties. [1]
Studying the dielectric properties of polymers are of increasing importance because it provided an understanding to the molecular chains which reflect the wide polymer applications and usage in Engineering [2]. Most of polymer materials are used as insulators in wires, cables, printed circuit boards and in many other electronic devices such that poly alpha naphthyle acrylate. [3].

Insulators with low dielectric constant are preferred to be use in the industry of communication coaxial cables to minimize as much as possible the electron density on the conductor surface, whereas the high dielectric constant materials are preferred to be used in the industry of capacitors[4].
The evaluation of dielectric properties of the insulator film is carried out by measuring simultaneously the capacitance and the dielectric losses of the film over a wide range of frequencies and temperatures. Although the dielectric properties of a number of polymers have been

investigated the molecular orientation behavior and the associated relaxation mechanisms of the polymers are not fully understood. [5] . The study of dielectric loss as a function of temperature and frequency, is one of the most convenient and sensitive methods of investigating polymer structure of a polymeric film[6] .
Polymer characterization can be achieved by studying the complex impedance spectroscopy. From Cole-Cole plots the bulk resistance R_b of the polymer can be determined and consequently frequency dependent conductivity can be evaluated[7]. The molecular motion and dielectric relaxation behavior of the polymer can also be analysed via studying the dielectric loss as a function of temperature and frequency [8].
In general, polymers posses many dielectric relaxation α, β ,γ,etc.starting usually from the highest observed transition temperature. It is well known for amorphous polymer α- peak is absent , β and γ peaks occur at temperature less than Glass transition temperature (T_g) in that order [9]. Cole-Cole plots of ε'' vs. ε' reveals a non –Debye type dielectric relaxation and relaxation loss type β was observed from frequency dependence of imaginary part of dielectric constant and dissipation factor for (PPAB) terminated by phenylenediamine doped with LiCl [10] .
In the present study relaxation specrrooscopy of poly (P-Aminobenzaldehyde) terminated by phenylenediamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$ have been investigated in different frequencies and temperatures.
Dielectric parameters such as permittivity, dielectric loss, dissipation factor and impedance have been analysed depending on Lumped equivalent circuit.

Experimental Procedure

Poly (P-Aminobenzaldehyde) terminated by phenylenediamine was synthesised used condensation polymerization adopting to method previously reported [11].
Figure (1) shows the expected structure of the polymer under the present study.

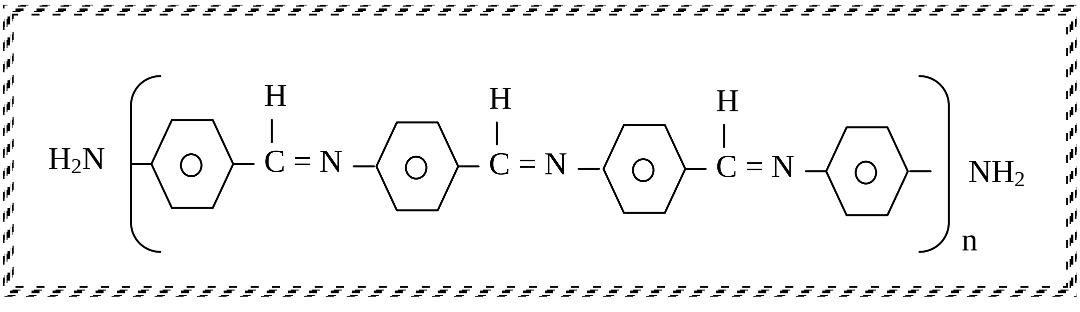

Fig. (1) Expected structure of the polymer used .

The resulted resin then doped with $Na_2[Fe(CN_5).NO].2H_2O$.
The polymer was first dissolved in Dimethyl Formamide (DMF) with stirred at room temperature for(4 – 6) hrs. Samples of polymer films with thickness
~ 25µm were deposited on aluminum substrates using solution cast technique .Heat treatment was performed by inserting the sample into a vacuum oven with gradual temperature increase in the rate 5 C̊ /hr up to 90C̊ .It held at this temperature about 4 hrs and then cooled gradually up to

room temperature and finally being kept at room temperature for 10 hrs.

The top electrode was evaporated on the polymer surface using aluminum by evaporation method under vacuum 10^{-4}Torr .Evaporation method was used in order to avoid any air gap existing between the polymer and the metallic contact , other techniques may create series capacitance that affects both the capacitance and the dissipation factor measurements [12].The specimen is staked between a sandwich configuration fixed by platinum electrodes cited above with pressure contact .The specimen was connected to the electrical circuit by fine copper lead wire.

Dielectric measurements were measured using RLC Bridge model PM 6303 in the frequency and temperature range (1-100)KHz and (283-343)K respectively.

All measurements were carried out under vacuum environment and thermocouple of type cupper Constantan were positioned near the temperature of the samples.

Results and Discussion:

Fig (2): Shows the frequency dependency of the impedance for a samples of $Na_2[Fe(CN)_5.NO].2H_2O$ doped film. The impedance decreases monotonically from $5.9x10^5$ Ω to 3.5 $x10^5$ Ω with increasing frequency from 5KHz to 55 KHz .It can be seen from the figure that the low frequency range (5-13)KHz , the impedance was nearly independent on frequency and d.c conductance can be estimated in this region which equal to $1.69x10^{-6}$ Ω^{-1}. The value of d.c conductance in this investigation was less than the value of same polymer doped by other impurities such that (LiCl ,NaF) ,where these values were 5.2 $x10^{-6}$ Ω^{-1}, 6.9 $x10^{-6}$ Ω^{-1} respectively [13].

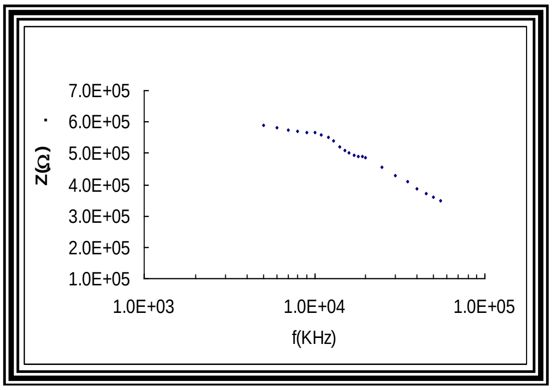

Fig (2): The frequency dependence of impedance at T=293K

Fig(3): shows the dependency temperature of impedance for a sample of $Na_2[Fe(CN)_5.NO].2H_2O$ measured at two different frequency ,1KHz and 5KHz .It can be intereplotinterms of the increasing of the charge carriers as the temperature increased.

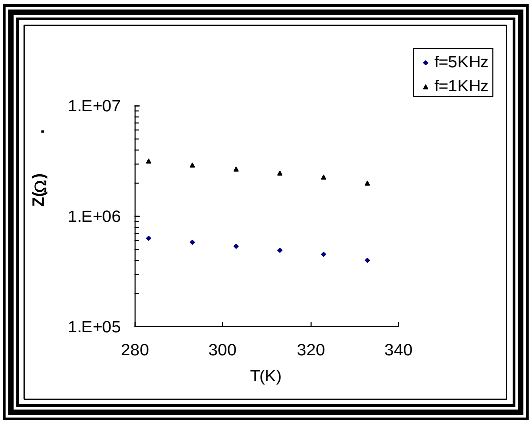

Fig (3): The temperaturedependence of impedance at f=1KHz and f=5KHz.

Fig(4 a): indicates the variation of series capacitance (C_s) with temperature .Nearly similar behavior obtained from parallel capacitance (C_p) as shown in Fig(4 b). Since the D is small and $C_p=C_s/(1+D^2)$.

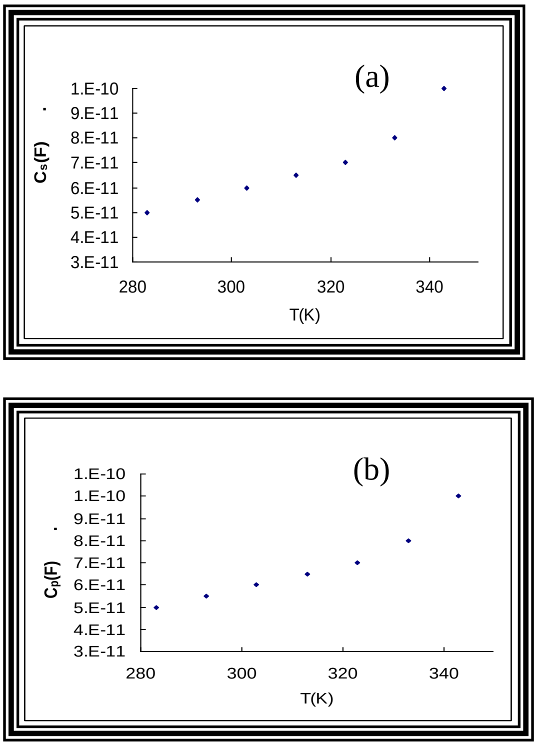

Fig (4): The The temperature dependence of
a: series capacitance
b: parallel capacitance

Figs (5): show the temperature dependency of series and parallel resistance in the temperature range (283-343) K .Both of them show similar behavior. The value of R_s was decreased from 3.18 x10^4 Ω to 1.59 x10^4 Ω while $R_p$was decreased from 3.18 x10^8 Ω to 1.59 x10^8 Ω in the same temperature range.

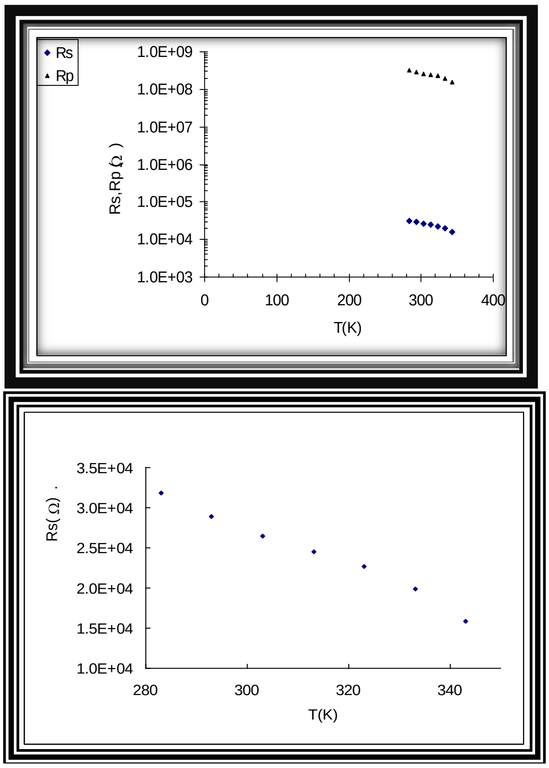

Fig (5): The temperature dependence of series and parallel resistance.

Fig (6): shows the variation of dissipation factor with temperature at 1 KHz .It is clear from the figure that the dissipation factor was independent on temperature.

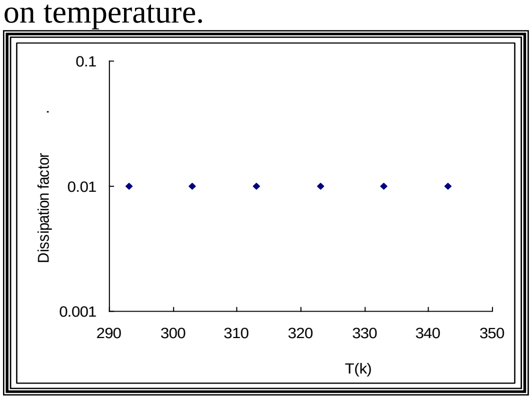

Fig (6): The temperature dependence of dissipation factor .

The variation of the dielectric constant (έ) as a function of temperature is shown in Fig(7) .The dielectric constant (έ) is increased from 17.82 to 35.67 with increasing temperature , this behavior indicates that the polymer under investigation was polar polymer (see ref.3 and 10).

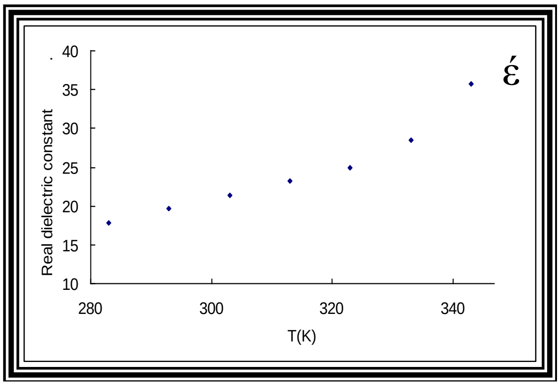

Fig (7): The temperature dependence of real dielectric constant.

Fig(8): indicates that the imaginary part of dielectric constant was increased from 0.17 to 0.35 with increasing temperature in the same range. Similar behavior was observed by other worker [14] see also ref.3.

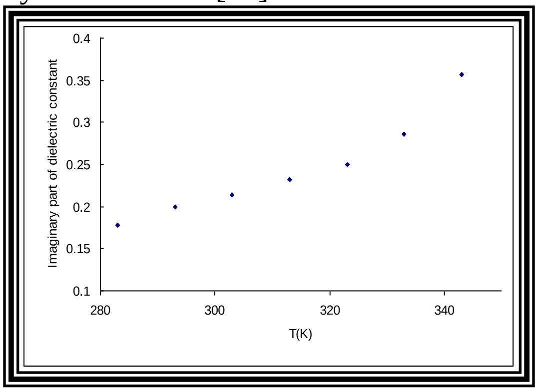

Fig (8): The temperature dependence of imaginary part of dielectric constant at a frequency of 10^3Hz.

Fig(9): shows the reduction of the series capacitance from $2.7x10^{-11}$ F to 5 $x10^{-12}$ F with increasing frequency from 1KHz to 100 KHz while for the same range of frequency ,the parallel capacitance was decreased from 2.69 $x10^{-11}$ F to 2.35 $x10^{-12}$ F .

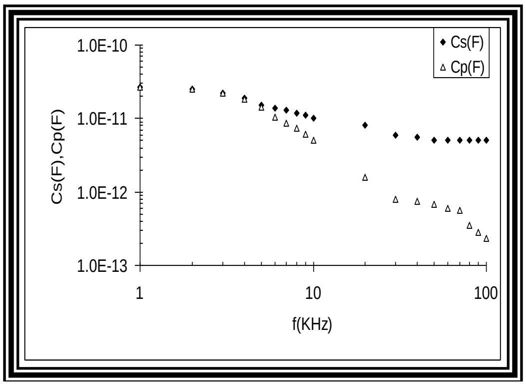

Fig (9): The frequency dependence of series and parallel capacitance at T= 313 K.

Fig(10): shows the variation of dissipation factor with frequency, it is clear from the figure that the dissipation factor was increased with increasing frequency.

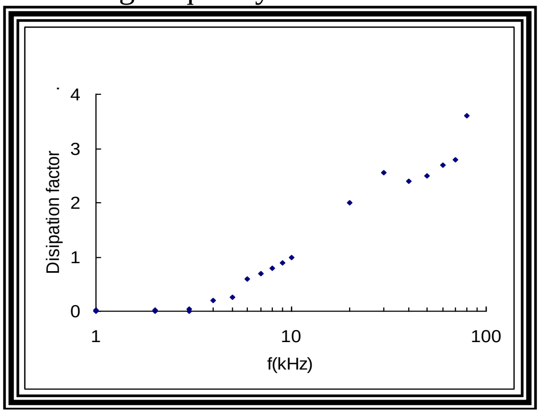

Fig (10): The frequency dependence of dissipation factor at temperature 313 K.

The relation between a.c conductivity and frequency at 318 K is shown in Fig(11). It is clear that the a.c conductivity was increased with increasing frequency at the same range of frequency, similar behavior was observed by others.[15]

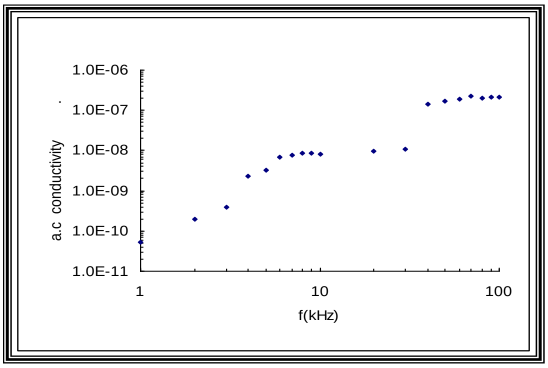

Fig (11): The relation between a.c conductivity and frequency at T=313K.

Fig (12): shows the relation between real and imaginary parts (Cole-Cole plots) of dielectric constant (ε',ε").It is clear from the figure that the ε" increases with increasing ε' until the value (ε'=3) and then ε" decreases with increasing ε'.

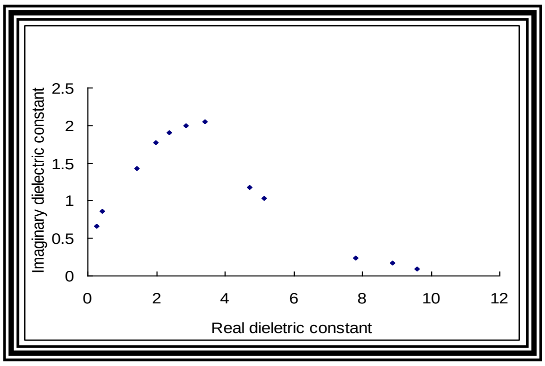

Fig (12): The relation between real and imaginary parts of dielectric constant.

Fig (13): shows the frequency dependence of real part of dielectric constant. The decreasing in the dielectric constant (έ) was observed with the increase in the frequency due to dielectric dispersion, similar behavior was observed by others [16],[17] and [18].

The frequency dependence of imaginary part of dielectric constant (ε") as shown in Fig(13)shows abroad peak was recorded at 6 KHz, this peak refers to a relaxation process type β which may be corresponded to the orientation of the polar groups present in the side groups of the polymer. The relaxation time (τ) can be calculated from the relation (ωτ =1) where ω is angular frequency which correspond to the maximum value of imaginary part of dielectric constant. Hence τ found to be ($2.65x10^{-5}$) sec.

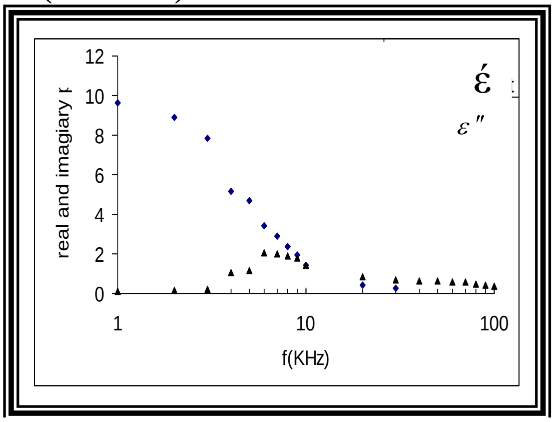

Fig (13): The frequency dependence of real and imaginary parts of dielectric constant.

The real and imaginary parts of complex impedance Z^* can be calculated from the following equations [19].

$$Z' = D / \omega C \quad , Z'' = 1/ \omega C \text{ ……….. (1)}$$

Where D: dissipation factor, ω: angular frequency, C: capacitance of the film.
Fig (14): shows the typical real Z' and imaginary Z" parts of impedance data plotted in complex impedance plane. The figure clearly shows that there is an inclined straight line at lower frequency region followed by a semicircular arc at the higher frequency region, which indicates a non -Debye type dielectric relaxation while at higher frequency shows Debye behaviour. The intersection of the semicircular arc with the real X-axis given the bulk resistance (R_b) of the polymer.The frequency-dependence conductivity of the film was evaluated using the following equation:

$$\sigma(\omega) = \frac{d}{R_b . A} \text{ ....(2)}$$

Where A: effective area of the film,d: thickness of the film.

The value of bulk resistance is $5x10^8\Omega$ and a.c conductivity is nearly $1.59x10^{-10}$(S.cm $^{-1}$).

The activation energy $E_{a.c}$= 0.6eV for a.c conductivity was evaluated by using the Arrhenius equation [20].

$\sigma = \sigma_o e^{-Ea.c/KT}$ ……. (3)

Where; σ_o: constant, $E_{a.c}$: activation energy, T: absolute temperature and k:Boltzmanconstant.

It is clear that the activation energy was lower than the values obtained for other polymers [21],[22].

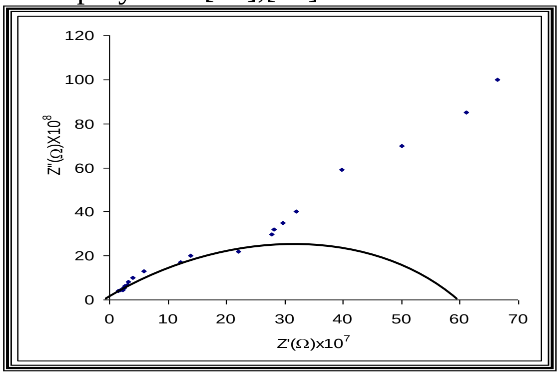

Fig (14): Cole-Cole plot for PPAB terminated by phenylenediamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$

Conclusion:

The dielectrical measurements of poly (P-Aminobenzaldehyde) terminated by phenylenediamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$ have been studied using Lumped equivalent circuit and from this study can be concluded the following:

1. The impedance was decreased with increasing of frequency and temperature.
2. Both of series and parallel capacitance were increased with increasing of temperature, while they decreased with increasing of frequency.
3. Both of series and parallel resistance were decreased with increasing of temperature.
4. The dissipation factor was independent of temperature but it increase with increasing of frequency.
5. The real and imaginary parts of dielectric constant were increased with increasing of temperature. While they decreased with increasing of frequency.
6. a.c conductivity was increased with increasing of frequency and the activation energy of the polymer used was 0.6 ev for a.c conductivity.

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دراسة الخواص العازلية للبوليمر (PPAB) ذي النهاية الطرفية ثنائي أمين فنيلين المشوب ب $Na_2[Fe(CN)_5.NO].2H_2O$ باستخدام الدائرة المكافئة التحملية

حسن كاظم ابراهيم **خالد ابراهيم عجيل**

قسم الفيزياء/كلية التربية/جامعة البصرة

الخلاصة:
الهدف من البحث هو دراسة تأثير الشائبة $Na[Fe(CN)_5].2H_2O$ بتركيز (0.1M) على الخواص العازلية للبوليمر بولي (بارا – أمينو بنزلديهايد) ذي النهاية الطرفية ثنائي أمين فنيلين كدالة لدرجات الحرارة في المدى (283-348)K ولمدى تردد (1-100)KHz .
تضمنت هذه الدراسة عامل التشتت،مقاومة التوالي والتوازي ،سعة التوالي والتوازي،ثابت العزل بجزئية الحقيقي والخيالي، التوصيلية المتناوبة والممانعة بجزئيها الحقيقي والخيالي باستخدام الدائرة المكافئة.
بينت الدراسة بان إضافة الشائبة الى البوليمر أدت الى زيادة ثابت العزل مع زيادة درجة الحرارة وقلته مع زيادة التردد.بينما ثابت التشتت ازداد بزيادة التردد.

الكلمات المفتاحية: المقاومة، المتسعة، الخواص العازلية، التوصيلية المتناوبة، عامل الفقد .