Dielectric behavior and AC electrical conductivity analysis of PMMA films

Bushra A.Hasan[1], Ikhlas H.Shalal [2]

[1]Department of Physics, College of Science, University of Baghdad

[2]Department of Physics, College of Education Ibn-Al-Haitham for Pure Sciences, University of Baghdad

E-mail:bushra_abhasan@yahoo.com

Abstract

PMMA films of different thickness (0.006, 0.0105, 0.0206, 0.0385 and 0.056cm) were synthesized by casting process. The temperature and frequency dependence of dielectric constant and AC electrical conductivity measurements at various frequencies (10kHz-10MHz) and temperatures (293-373K) were carried out. Few anomalies in dielectric studies were observed near 313 and 373 K respectively. These points were related to glass transitions temperature. The variation of activation energy and conduction behavior was studied .From the AC conduction studies, it is confirmed that the mechanism responsible for the conduction process is hopping of carriers. The variations of the dielectric constant and loss as function of frequency at different temperature was observed and the results were discussed. The calculated activation energy varied with the thickness, temperature, and applied frequency. Conductivity plots against frequency suggested that the response obeying the universal power law concerning the AC conductivity and dielectric behavior of polymer. The polarizability α increases with temperature but decreases with thickness indicating weekends and rising of intermolecular forces respectively.

Key words
Polymer Dielectric properties, Universal power law, Dielectric loss spectra.

Article info
Received: Sep. 2012
Accepted: Feb. 2013
Published: Apr. 2013

التوصيلية الكهربائية المتناوبة لأغشيةPMMA

بشرى عباس حسن[1]، اخلاص هميم شلال[2]

[1]قسم الفيزياء، كلية العلوم، جامعة بغداد

[2]قسم الفيزياء، كلية التربية ابن الهيثم للعلوم الصرفة، جامعة بغداد

الخلاصة

حضرت أغشية من بولي مثيل اكرليت وبأسماك مختلفة بواسطة طريقة الصب.أجريت قياسات التوصيلية الكهربائية المتناوبة $\sigma a.c(w)$ في مدى درجات الحرارة (293-373)K وفي مدى التردد (10^4-10^7Hz). لوحظ سلوك غير اعتيادي في دراسة معامل العزل والذي اعزي إلى درجة حرارة التحول الزجاجي .تم دراسة تغير سلوك التوصيل الكهربائي وتأثيره على طاقة التنشيط. أظهرت النتائج إن ميكانيكية التوصيل المسوؤلة عن التوصيل هي التنطط.القيم المحسوبة لطاقات التنشيط تغيرت مع السمك، التردد ودرجة الحرارة. علاقة التوصيل الكهربائي مع التردد آسية تؤكد التوصيل المتناوب والسلوك العزلي للبوليمروالاستقطابية ازدادت مع درجة الحرارة بينما تناقصت مع زيادة السمك والذي يشير إلى ضعف وزيادة قوى الترابط الجزيئي وعلى التوالي.

Introduction

Electrical properties constitute one of the most convenient and sensitive methods for studying the polymer structure Ferraro and Walkar 1965[1]; Kimura and Kajiwara 1998[2].The interest in organic and polymeric semiconductors has arisen, particularly because of their electro photo graphic and solar cell applications. The electrical conduction in iodine doped polystyrene (PS) and poly(methyl methacrylate) (PMMA) has already been reported (Chakraborty et al 1991[3]; Sangawar 1995[4].Keller et al (1991) [5]reported the thermally stimulated discharge current (TSDC) study of poly blends of PS and PMMA. Belsare and Deogaonkar (1998) [6] measured the electrical conductivity of iodine doped poly blend films of polystyrene (PS) and poly (methyl methacrylate) (PMMA). Deshmukh *et al* (2005) [7] reported electrical conduction in semiconducting PVC–PMMA thin film. The electrical conductivity of polyaniline doped polyvinylchloride (PVC) and poly (methyl metha-crylate (PMMA) thin films has been measured by studying the I–V characteristics at various temperatures in the range 323–363 K by DESHMUKH et al 2007 [8]. Hasan et al (2011) [9] made comparison study about the effect of beta and gamma irradiation on the optical properties of PMMA films with different thickness.

For the understanding of basic features of PMMA films and their potentiality in application, the knowledge of the electron states and their behavior with different frequencies and at high fields becomes important. The present paper reports the AC Conduction and Dielectric studies made on PMMA thin films.In the present investigation, the synthesis of PMMA is achieved. The temperature dependence of dielectric constant, loss and ac conductivity were (range 293-373K) carried out in wide range of frequency (100 Hz - 2MHz). The results are analyzed and discussed in detail.

Experimental details

Polymethylmethacrylate PMMA supplied by Intermediate Petrochemicals Industries Co. was used in this study.(0.6)gm of PMMA were dissolved in 10 ml of Chloroform to given solution of 6%wtvol. After allowing to dissolve completely. 3 ml of this solution was transferred into clean Petri dish of 20 cm in diameter and put in an oven at temperature 50°C for 2 hours and left to cool slowly to room temperature. Different concentrations of PMMA were used to obtain different thickness. The average measured thickness of the prepared films was found to be 0.006, 0.02, 0.038 and 0.056 cm using digital micrometer. The prepared films were kept in desiccators in order to be moisture free.

Aluminum electrodes with thickness 2000°A were deposited on each adjacent surfaces of specimen by thermal evaporation technique under pressure of (10^{-5} mbar) using coating unit type Edward model E306A. The specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). High and low holder terminals are connected to dielectric analyzer type Hewlett Packard model (HP4274A & HP4275A), the third holder terminal was connected to the earth. Three dielectric parameters were measured directly from above setup total resistance (R), total capacitance (C) and dissipation factor tanδ with an accuracy of 0.1%. All measurements were performed in the frequency range 10^{3} - 10^{7} Hz and temperature range (293- 373) K, the temperature was changed by constant rate of 2K/min, A constant voltage of (1V) was applied in all frequency range and temperature. AC. conductivity has been evaluated from dielectric data in accordance with the relation: The

dielectric constants (ε_1,ε_2) can be calculated using the following relations:

$\varepsilon_1 = C.t / \varepsilon_0 .A$ (1)

where C is Capacitance, ε_0 is the Permittivit of free space =$8.854x10^{-14}$ (F/cm).

$\varepsilon_2 = \sigma_{AC} / \omega\varepsilon_o$ (2)

Where t is thickness of film, ω is the angula frequency, A is Effective area for capacitance σ_{AC} is the AC conductivity given by th relation:

$$\sigma_{AC} = \omega\varepsilon_0\varepsilon_1 \tan\delta \quad (3)$$

where tanδ is the dielectric tangent loss.

The structures of the prepared thin film alloy are demonstrated by the x-ray diffractio technique using (Siemens D500 diffract mete CuKα1 radiation and λ =1.5405 A◦).The XRI pattern of PMMA shows that it has a sem crystalline nature, which is in good agreemen with the results reported earlier [10]. The XRD patterns of PMMA show that as the thickness increases, crystallinity increases and reaches a maximum at t=0.0206 cm.

Results and discussion

1. The Dielectric Constants

Fig.1 and 2 show that the variations of ε_1, with frequency for the PMMA films having different thickness and at different temperatures respectively. In all the cases, a strong frequency dispersion of permittivity is observed at low frequency region followed by a nearly frequency independent behavior above10 kHz. The decrease of (ε_1) with increase in frequency may be attributed to the electrical relaxation processes, but at the same time the material electrode polarization cannot be ignored. The material electrode interface polarization superimposed with other relaxation processes at low frequencies. It is seen that with increase of thickness, (ε_1) value increases in the lower frequency and nearly same in the higher frequency region. The thickness increment may result in more localization of charge carriers along with mobile ions causing higher conductivity. This may be the reason for higher (ε_1) and strong low frequency dispersion.

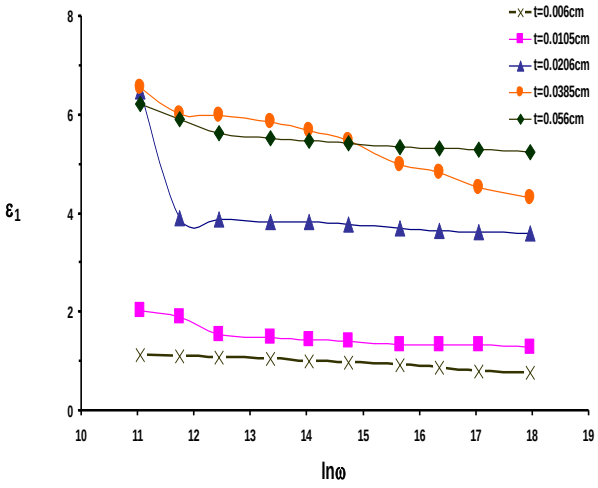

Fig.1: Variation of real part of permittivity (ε_1) with frequency of PMMA films for different thickness at room temperature.

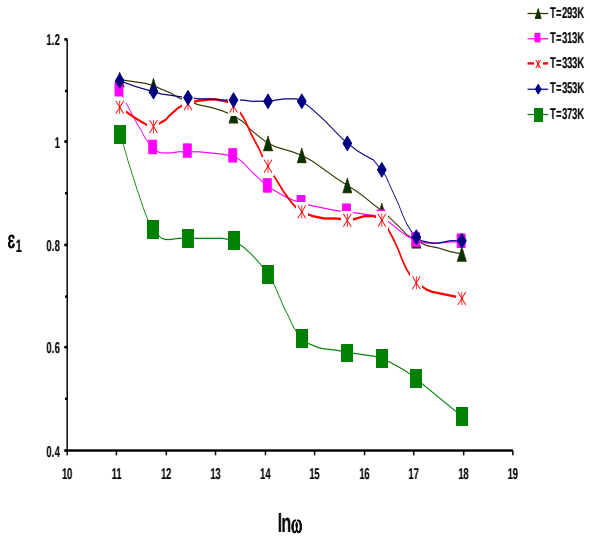

Fig.2: Variation of real part of permittivity (ε_1) with frequency of PMMA films for different temperatures.

On the other hand the dielectric constant increases with temperature at low temperature range but then decreases with further increase of temperature. Indeed ε_1 increases from 1.1219 to

6.229when thickness increases from 0.006 to 0.056cm.

The temperature dependence of dielectric constant at different fixed frequencies over the temperature range of 293-373 K of PMMA films is shown in Fig. 3. A broad dielectric peak near 313 and 333K for thickness (0.0385 and 0.056 cm) is attributed to the glass transition temperature[11] .

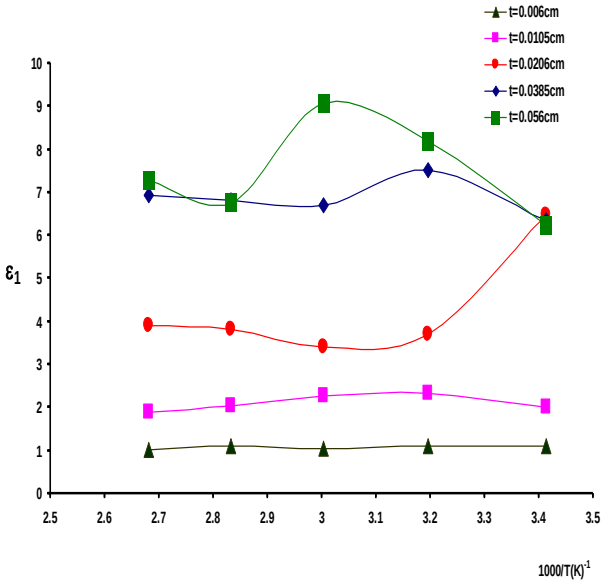

Fig.3: Temperature dependence real part of permittivity (ε 1) for PMMA film of different thickness at 10 kHz.

Fig.4 and 5 show the ε_2 spectra with frequency for PMMA samples for different thicknesses and temperature respectively. The spectra characterized by a peak appearing at a characteristic frequency suggest the presence of relaxing dipoles in all the samples. The strength and frequency of relaxation depend on characteristic property of dipolar relaxation. The relaxation peaks shift towards higher frequency side with the increase of thickness for low thickness values 0.006, 0.0105, 0.0206 cm but then shifts to lower frequency side. With the increase of thickness it is believed that there is an increase in the crystalline content in the materials.

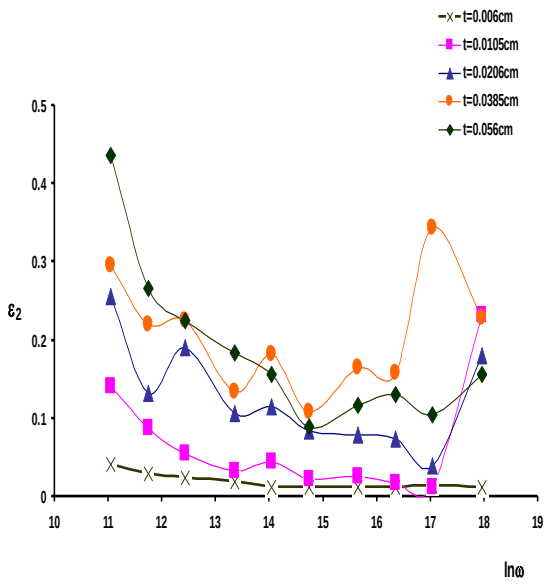

Fig.4: Variation of imaginary part of permittivity (ε 2) with frequency of PMMA films for different thickness at room temperature.

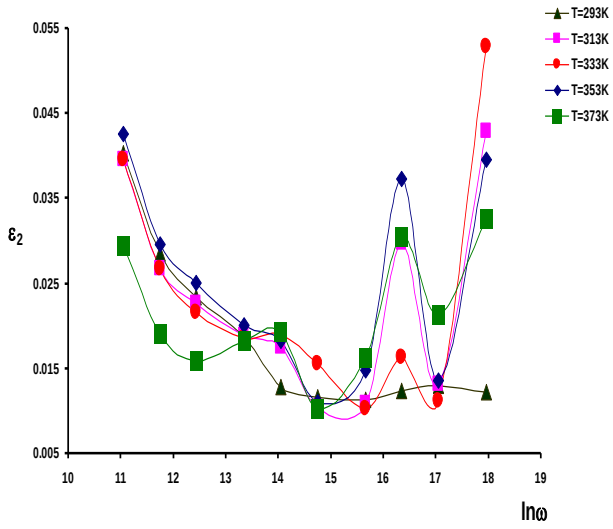

Fig.5: Variation of imaginary part of permittivity (ε 2) with frequency of PMMA films for different temperatures.

The increase of thickness speed up the segmental motion by reducing the available free volume. It is evidenced by the peak shifting toward higher frequency side, thereby reducing the relaxation time, but with further increase of thickness the relaxation peak shifts to

lower frequency side thereby increasing the relaxation time.

It is generally believed that dielectric data is characterized by superposition of two processes: a conductivity contribution that produces an increase of both real part ε_1 and the imaginary part ε_2 of the dielectric function on decreasing frequency and a relaxation process exhibiting a maximum in ε_2 that shifts lower frequency side with increase in temperature. The measured dielectric loss ε_2 spectrum contains contribution from two sources: dipolar orientation and diffusion of charge carrier.

The relaxation time were calculated from frequencies corresponding to the loss maxima using equation $w_D=1/\tau$ and the values of τ were listed in Table 1. The w_{max} which is corresponding the peak is approximately equal the reciprocal macroscopic relaxation time ,moreover it is clear that the increase of temperature of the ε_2 spectrums of PMMA films result in appearing of more than relaxation peak which get to disappear with further increase of temperature.

The reason of declaring more than one peak in the spectrum of ε_2 versus frequency is the foundation of multiphase in our blends samples (i.e. amorphous and crystalline phase of PMMA, the disappearing of relaxation peak in the low frequency range confirms the dominating of one phase.

Increase of thickness resulted in overall increase of ε_1 and ε_2 due to both dipolar and free charge contributions. So the increase of the molecular mobility is reflected both by increase of free charge mobility and the shift of the peak towards the higher frequency side with simultaneous increase of its magnitude (Fig. 4 and 5). The over all result is enhancement of conductivity with increase of thickness up to 0.0206 cm, but then the opposite case take place, i.e the molecular mobility decreases which in turn decreases ε_1 and ε_2.

2. A.C Conductivity

The AC conductivity σ is directly related to the imaginary part of dielectric constant ε_2 as $\sigma_{A.C} = \varepsilon_0\omega\ \varepsilon_2$ where ε_0 and ω is the permittivity of the free space and angular frequency respectively. Fig. 6 and 7 show the variation of σ_{AC} with frequency for different thickness and temperatures of PMMA films. The AC conductivity patterns show a frequency independent plateau at low frequency region and exhibits dispersion at higher frequencies. This behavior obeys the universal power law, $\sigma(\omega) = \sigma_0 + A\omega^s$, where $\sigma_0$is the dc conductivity (frequency independent plateau in the low frequency region). The deviation from σ_{dc} (plateau region) value in the conductivity spectrum (at low frequency region) is due to the electrode polarization effect. The observed frequency depends upon AC conduction which can be considered to be the sum of two conduction mechanisms, i.e., single polaron and bipolaron hopping. This can be explained on the basis of CBH (Correlated Barrier Hopping) model. According to this model, the conduction occurs via a bipolaron hopping process wherein two electrons simultaneously hop over the potential barrier between two charged defect states (D^+ andD^-) and the barrier height is correlated with the intersite separation, via a columbic interaction[12].

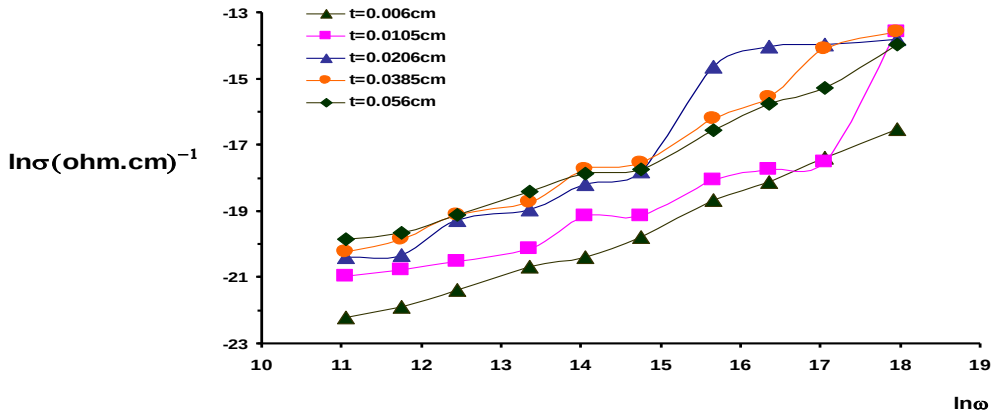

Fig.6: Frequency dependence of AC conductivity for PMMA film of different thickness at room temperature.

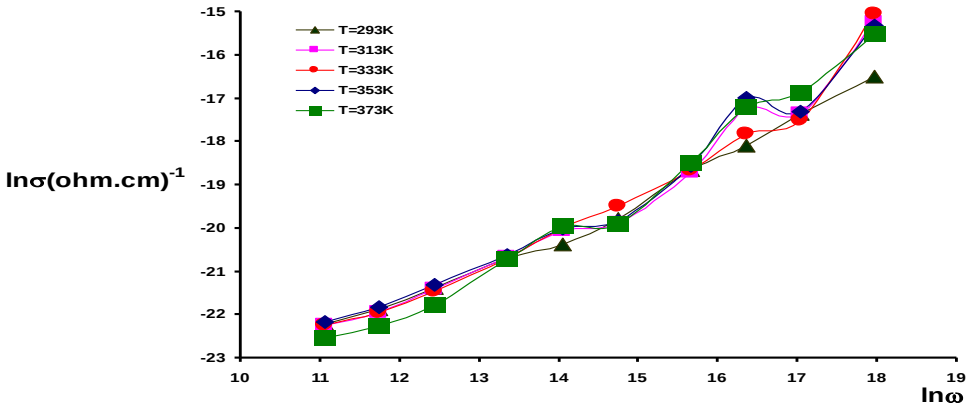

Fig.7: Frequency dependence of A.C conductivity for PMMA film of different temperatures.

The value of the exponent s of different temperatures and thicknesses are calculated by fitting the curves of between lnσ and lnω for all thicknesses and listed Table1. It found that s changes in different manner with temperature and thickness, i.e. s increases and decrease with thickness, indeed s increases from 0.83 to 1.03 and from 0.84 to 0.90 when temperature increases from 293 to 373K for thickness 0.006 and 0.056 cm while s decreases with temperature for residual thicknesses 0.0105, 0.0206 and 0.0385cm. To explain these results we suggest Correlated Barrier Hopping (CBH) model for thickness 0.006 and 0.056 cm, while small polaron (SP) model is convenient for residual thicknesses (0.0105, 0.0206C and 0.0385cm). Small Polaron Tunneling is the most suitable when the exponent s get to rise with increasing of temperature, this occurs when addition of charge carrier to the covalent solid causes a large degree of local lattice distortion, which form small polaron.

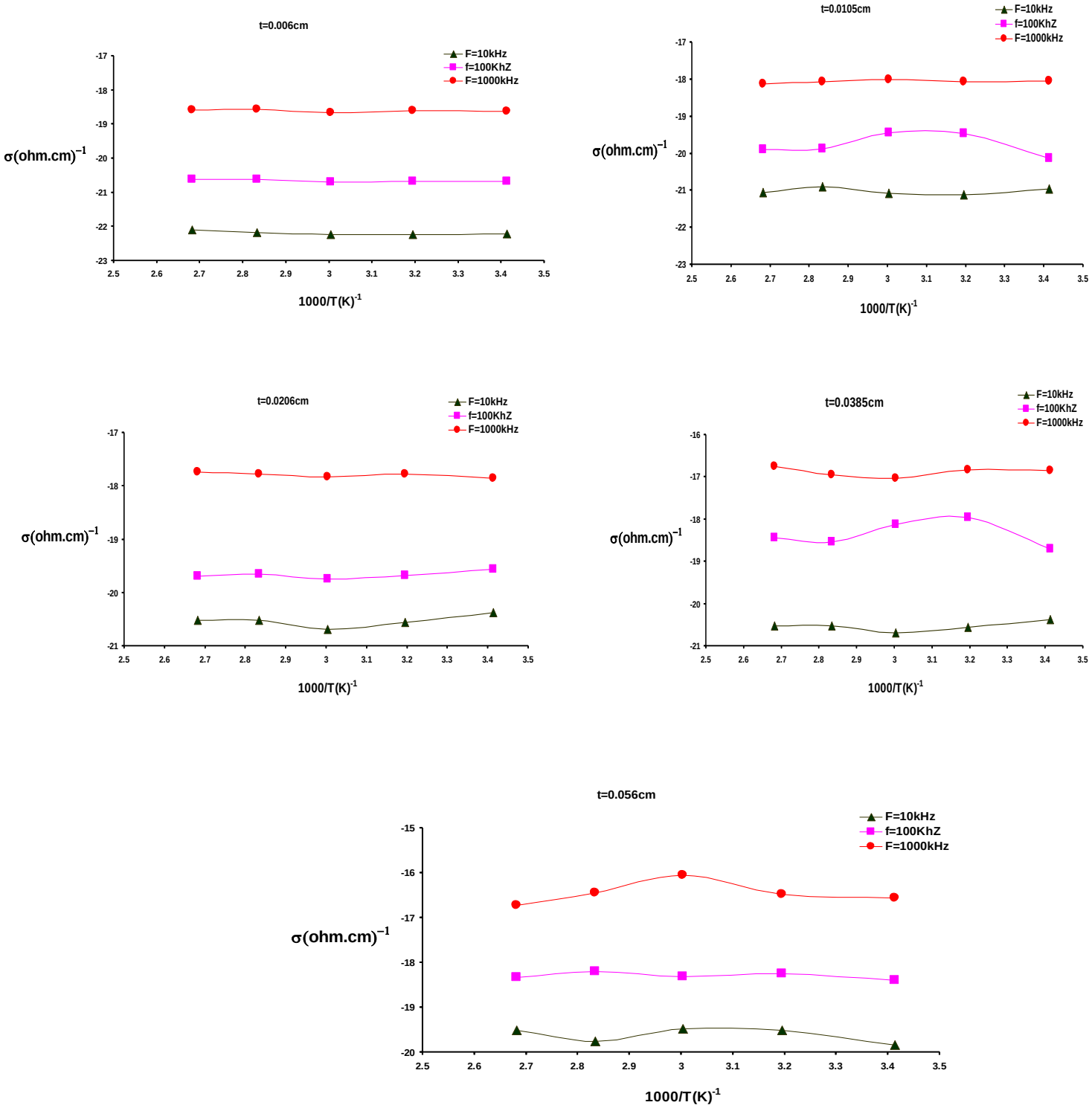

Fig.8: Temperature dependence of AC conductivity for PMMA film of different thickness at different frequencies.

Table1: The values of s, α and τ of PMMA films.

Thickness(cm)	Oven Temperature (K)	s	τx10^{-7}(sec)	α
0.006	293	0.8396	----	0.168
	313	0.9678	8.315 0.796	0.392
	333	0.9562	8.315 1.593 0.796	0.5264
	353	0.9603	0.796	0.0336
	373	1.0346	0.796	0.392
0.0105	293	0.8721	1.593	0.2016
	313	0.7848	39.809 0.796	0.168
	333	0.8376	------	0.0896
	353	0.7854	------	0.168
	373	0.8258	0.796	0.3584
0.0206	293	1.1352	39.809 0.796 1.593	0.112
	313	0.6692	8.315	0.0784
	333	0.8257	8.315 0.796	0.0784
	353	0.7157	8.315	0.0336
	373	0.7968	39.809 0.413	0.504
0.0385	293	0.9927	39.809 8.315 1.593 0.398	0.112
	313	0.8054	39.809 3.983	0.168
	333	0.9642	8.315	0.0336
	353	0.7919	8.315	0.168
	373	0.9253	0.796	0.1904
0.056	293	0.8406	-------	0.112
	313	0.8746	39.809 0.796	0.0896
	333	0.9103	-------	0.0896
	353	0.8345	-------	0.0336
	373	0.9085	0.796	0.448

The activation energy for conduction E_{ac} in the entire region estimated from the plot of σ_{AC} with reciprocal temperature for various frequencies are calculated by fitting different regions with the equation $\sigma = \sigma_0 e^{-E_a/k_B T}$. The activation energy is found to decrease with increasing frequency which is given in Table 1. This can be possible due to the increase of applied field frequency and enhances the electronic jumps between the localized states, while E_{ac} decreases when thickness increases from 0.006to 0.0206 cm and decreases with further increase of thickness.

3. Cole-Cole diagrams

The polymer material exhibits three dispersion peaks which are (α, β , and γ) each of which represents an individual relaxation process, (1) weak α-peak observed at temperature range 30 and 80^{0}C, (2) a well pronounced. a β-peak at approximately 0^{0}C, γ-peak in the temperature range -50 and -100^{0}C. The γ-dispersion is probably due to torsional motion of the chain units, the origin of α-dispersion is the relaxation process in the crystalline phase, the β-dispersion produced by far the largest peak and is due to the motion of comparatively long chain segments in the amorphous phase, the intensity of β-peak depends on the relative concentration of non crystalline phase, thus the measurements of dielectric loss of polymer lead to analogous results regarding the molecular motion responsible for the relaxation processes.

A direct evidence of the existence of multi-relaxation time in PMMA films is obtaining by plotting Cole-Cole diagrams as shown in Fig.9 for different thickness. It has been observed that for all films reported here ε_1 versus ε_2 curves represent the arc of circles having their centers lying below the absicca axis. This confirms the existence of distribution of τ in all films. By measuring the angles $\alpha\pi/2$ the values of the polarizability (α) had been determined and are listed in Table.2.We can notice that the values of α shows systematic decrease with the increase of thickness, the decrease of α with the increase in thickness results from rise of the forces of the intermolecular [11,12], while α exhibit to increase with the increase of temperature, the increase of α value came from the weaken the forces.

Conclusions

From this work, the following prints may be concluded:

1. Slope values (s) of PMMA films show progressive increase with thickness up to 0.0206cmbut then decreases.
2. The increase of PMMA thickness causes the proceeding increment of s, i.e. the conductivity is pure ac.
3. The increase of thickness leads to reduces the values of polarisability α of PMMA films consequently increases the intermolecular force while the increase of temperature reduces the force of the intermolecular through out formation a barrier.

5-The steady value of α in spite of thickness increase indicate that PMMA films reach Steady structure.

Acknowledgments

The Authors wish to thank the Department of Physics /College of Science/University of Baghdad for supporting this work.

References

[1]A.Walkar, J. Chem. Phys., 4, 2 (1965) 1273.
[2] T.Kimura and M. Kajiwara J. Mater. Sci., 33 (1998) 2955.
[3] S.Chakraborty, N. Patil, S Das and S. Basu, Indian J.Pure & Appl. Phys., 29 (1991) 478.
[4] V.Sangawar, Study of dielectric and other properties of doped thin film polystyrene (PS) and poly (methyl methacrylate) (PMMA) thermo electrets, Ph.D Thesis, Amravati University, Amravati ,1995 .
[5] J.Keller, S. Dubey and S. Datt, Indian J. Pure & Appl. Phys., 29 (1991)150.
[6] N.Belsare and Deogaonkar Indian J. Pure & Appl.Phys., 36 (1998) 280.
[7] S. Deshmukh, D. Burghate, V. Deogaonkar and P .Deshmukh , Indian J. Phys. 79 (2005)1263.
[8] S. Deshmukh, D. Burghate, V. Akhare, V .Deogaonkr, Bull. Mater. Sci., 30, 1, February (2007) 51–56. © Indian Academy of Sciences.
[9] B. Hasan, M. Saeed, A.Abbas, ATTI DELLA "FONDAZIONE GIORGIO RONCHI" ANNO LXVI, - N. 4 (2011) 505.
[10]R.Baskaran, S.Selvasekarapadian, N. Kuwata, J.Kawamura,T. Hattori Solid State Ionics, 177, 26-32 (2006) 2679-82.
[11] Y. J,ing, X. Meng, W. Yiu, J. Liu, J. Ding, C. Lee, S. Lee, J. Phys. Chem. B Y. Jing, X. M. Meng, W. C. Yiu, J. Liu, J. X. Ding, C. S. Lee, S. T. Lee, J. Phys. Chem., B 108 (2004) 2784.
[12] D. Bower, Introduction to Polymer Physics, (Cambridge Univ. Press, 2002), Chs. 4, 6, 9.

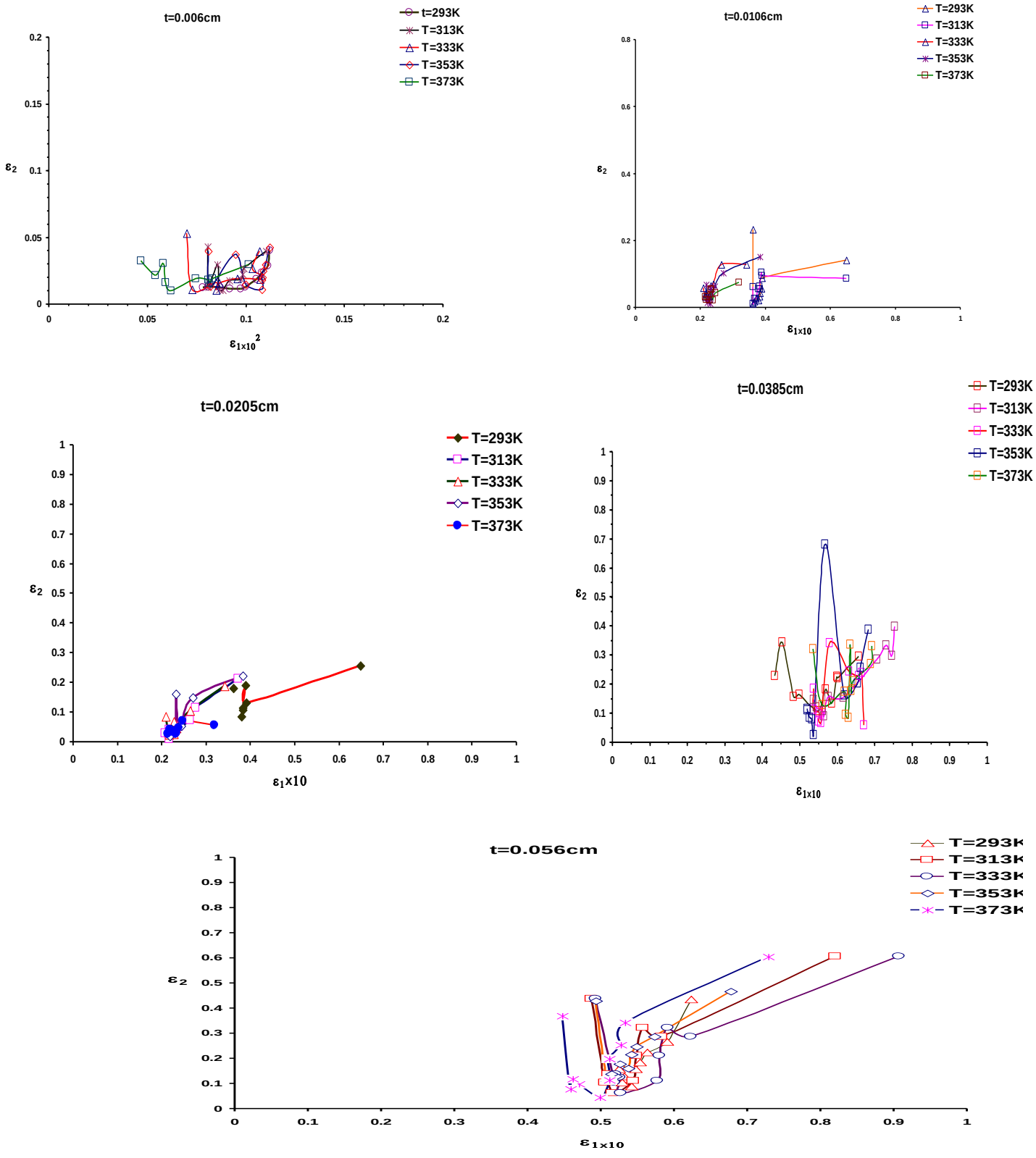

Fig.9: Cole – Cole diagrams of PMMA films for different thickness and temperatures.

Table 2: The $E_{A.C}$ values of PMMA films.

Thickness (cm)	$E_{A.C}$(eV)		
	F=10kHz	F=100kHz	F=1000kHz
0.006	0.01298	0.00915	0.00599
0.0105	0.00914	0.00821	0.00721
0.0206	0.01433	0.01172	0.01145
0.0385	0.01433	0.00365	0.00188
0.056	0.01956	0.00992	0.00984