Effect of molecular weight on electrical properties of PMMA – $TiCl_3$ composite

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Abstract

Poly(methyl methacrylate) was prepared with different molecular weight by bulk polymerization (M = 0.578 x 10^5 , 1.28x10^5 & 1.64 x 10^5 g/mole). Film of PMMA with $TiCl_3$ salt additive ranged from (1-5%) cast from chloroform solutions onto glass plates (the films thickness was ~ 100μm) . The experimental results show the relationship between electrical properties & Viscosity average molecular weight. σ_{DC} (DC conductivity) increased three order of magnitud with increasing molecular weight, the E_{ac} (activation energy) values accordingly decrease as the average molecular weight increase. On the other hand , σ_{DC} increased by several orders of magnitude with increasing $TiCl_3$ content and applied temperature ranged from $(40-100)^0C$. The activation energy is also determined and found to decrease with increasing salt content.

Keywords: Polymer composites, Electrical properties, Molecular weight.

الخلاصة

بولي مثيل ميثاكريلايت حضر بطريقة البلمرة وبأوزان جزيئية مختلفة (M= 0.578 x 10^5 , 1.28x10^5 1.64 x 10^5 g/mole). وتم تحضير اغشية من PMMA و$TiCl_3$ وبنسب مختلفة من المضاف تتراوح(1-5%) بطريقة الصب من المحاليل وبسمك 100μm. النتائج التجريبية بينت العلاقة بين الخصائص الكهربائية ومعدل الوزن الجزيئي اللزوجي. حيث وجد ان التوصيلية الكهربائية المستمرة ازدادت ثلاث مراتب بزيادة الوزن الجزيئي، وطاقة التنشيط تقل مع زيادة معدل الوزن الجزيئي. من جهة اخرى التوصيلية الكهربائية المستمرة ازدادت عدة مراتب مع زيادة نسبة$TiCl_3$ ومدى درجات الحرارة $(40-100)^0C$. كذلك طاقة التنشيط وجدت مع زيادة نسب الملح المضاف.

Introduction

It is well known that physical properties such as electrical, mechanical and thermal characteristic of polymer are highly dependent on its molecular weight distribution [Tagger, Trs and Mohammad, 1984, Marquez *et al*, 1990] . This feature encourages interest for finding suitable conditions that allow us to control the molecular weight of the polymer films by controlling the experimental polymerization parameters (e.g. initiator, monomer concentrations and polymerization temperature .

Polymer molecular weight is important because it determines many physical properties . unlike small molecules , however , the molecular weight of a polymer is not an unique value . Rather , a given polymer will have a distribution of molecular weights, this distribution will depend on the way the polymer is produced . Polymer physical properties will be functions of the molecular weight distribution [Flayih, 2000]. Most chains reaction and step reaction polymerizations produce chains with many different length , so polymers also differ from small molecules in that the polymer molecular weights are average values [Flayih, 2000] .

In recent years, conducting polymers have been the main focus of research throughout the world, nowadays, conducting polymers also know as conductive plastics are being developed for many uses such as corrosion inhibitors, compact capacitors, antistatic coating, electromagnetic shielding and smart windows; which are capable to vary the amount of light to pass [Hamzah *et al*, 2009], self regulating heaters, over current and over temperature protection devices [Bhattacharya, Sachdev, 2008]. Conducting polymer composite materials consist of random distribution of conducting filler throughout an insulating polymer [Gubbels, *et al,* 1995] . The purpose of use of fillers can be divided into two basic categories , first , to improve the properties of the material and second , to reduce the cost of component . The electrical properties of Conducting polymer composite materials depend on several factors: including the kind of conducting filler , the spatial distribution of filler particles , the interaction between polymer and filler , and the contact interaction between particles [Zhou *et al,* 2006] .

The aim of this work is to study the effect of molecular weight on the electrical properties of PMMA-$TiCl_3$ composite.

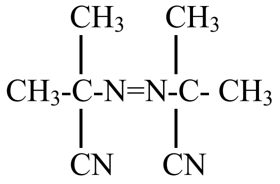
Experimental details

Preparation of PMMA with different molecular weight

To control the molecular weight of (PMMA) material, samples were prepared by bulk polymerization using the following procedure. MMA monomer was purified from inhibitor (0.1% hydroquinone) by washing in aqueous sodium hydroxide (10% w/v) by using separating funnel, then washing three time with distilled water. The monomer was stored in a dark place and dried by using anhydrous calcium chloride ($CaCl_2$) as drying reagent . Then MMA monomer was distilled under reduced pressure at (43 ^oC) under argon atmosphere before the polymerization process.

PMMA polymerization

Three samples of (PMMA) were prepared by using different concentrations of azobis isobutyro nitrile AIBN



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3- & C & -N=N- & C & -CH_3 \\ & | & & | & \\ & CN & & CN & \end{array}$$

as initiator : (25ml) of (MMA) monomer was prepared in bulk. Table (1) shows the initiator concentration and viscosity average molecular weight of PMMA.

It is known that, in free radical polymerization, the number average molecular weight is inversely proportional to the initiator concentration (rate of initiation) according to the following kinetic equation [Camphell, 2000].

$$\overline{M}n = \frac{K_p}{\sqrt{K_t}} * [M] * \frac{1}{I^{\frac{1}{2}}} \text{ ……………………………..(1)}$$

K_p = rate constant of polymerization
K_t = rate constant of termination
[M] = monomer (MMA) concentration
I = rate of initiation

The polymerization processes is carried out at (70 ^oC) for (2) hours by using water bath model (HAAKE K15). The polymer samples were purified twice by precipitation from benzene solution in ethanol and dried under reduced pressure for (24) hours before being blended with $TiCl_3$ salt.

Techniques

viscosity average molecular weight determination by viscometric techniques .

The viscosity technique was used to determine the viscosity average molecular weight M_v of PMMA in chloroform solution. The relationship between the intrinsic viscosity & molecular weight M_v is given by Mark. – Houwink equation [Houwink, 1940].

$$[\eta] = K \bar{M}_v^{a} \quad \text{..(2)}$$

$[\eta]$ = intrinsic viscosity

a and k are constants for a given polymer – solvent system at particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U – tube Viscometer. Solution were made by dissolving the polymer in a solvent (chloroform) (in gm/100ml) and the flow times of polymer solution and pure solvent at t and t_o respectively .

The specific viscosity (η_{sp}) was calculated using equation :

$$\eta_{sp} = \frac{t - t_o}{t_o} = \eta_{rel} - 1 \qquad \text{..................................(3)}$$

η_{rel} = relative viscosity = t/t_o

Molecular weight of PMMA without additives, was calculated from intrinsic viscosities measured in chloroform solution at (25 ^oC), the temperature was controlled by a cooler type (HAAKE k45), the following relation was used [Adam, Mohammad, 1980].

$$\text{PMMA} = [\eta] = 4.8 \times 10^{-3} \bar{M}_v^{0.8} \ .$$

see figure (1).

Polymer – salt films preparation

The purified (PMMA) was dissolved in chloroform. The desired salt % wt additive $TiCl_3$ was added & the mixture was cast onto a glass – sheet of dimensions (5 x 5) cm^2 and kept in a dry atmosphere at (40 ^oC) for (24) hours. Thickness of samples was about (100) μm measured by digital micrometer type Mitutoyo with measuring range of (0 – 25 mm) .

Measurement of electrical properties

The resistivity data were obtained with specimens shaped according to ASTM. D257 -66 standard by means of there electrodes arrangement [Buch, 1983]. This technique has been used to decrease the effect of the fringing of the electric field at edges, and to distinguish between the surface and the volume resistivity of the sample. Therefore, it permits measuring the bulk resistivity of the material. The specimens were molded in disc-shape.

The electrodes were made of copper metal and a uniform pressure on the specimen was applied by four adjustable screws. The electrical input was provided by means of stabilized DC power supply (Philip Harris Limited) which provide an output voltage from (0- 3000) volt.

The output current was measured by Keithley 616 c/ digital solid state electrometer which provides direct current reading ranges to 10^{-12} ampere full scale.

The test sample is placed between two electrodes and left at a desired temperature for half hour, then the desired test voltage is selected from the voltage supply and the current passing through the bulk of the test sample at this selected temperature, is measured by the electrometer. The volume resistivity measurements were performed over the temperature range (40-100 ^oC) by using a temperature controlled oven which has been shielded against external electromagnetic filed.

DC. Electrical characteristics

The volume resistivety was determined from the equation [Scaife, 1989].

$$\rho_V = R_V \frac{A}{L} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where R_v is the volume resistance between the guarded and the bottom electrodes in ohm, measured as the ratio between desired applied test voltage and the current passing through the test sample, L is the average thickness of the sample, A is the guarded electrode effective area. The volume conductivity:

$$\sigma_V = \frac{1}{\rho_V} = \frac{L}{RA} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The activation energy Ea was calculated from the slopes of the fitted straight lines using the Arrhenius equation

$$\sigma_V = \sigma_O \exp\left(\frac{-Ea}{KT}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

K is the Boltzman constant, and T is the absolute temperature .

Results and discussion

Volume conductivity σ_v, was determined adopting equation (6). It is generally accepted that both concentration of additives and temperature greatly affect the DC conductivity characteristics of polymers and polymeric additives [Lai, 1989].

Figure (2) shows the variation of σ_v with weight % of salt additive and temperatures (40 $^oC \rightarrow 100$ ^oC) at fixed molecular weight (1.28×10^5 g/mole). σ_v increases with salt additive weight. This is expected result (at fixed temperature) and this might be due to the increase in ionic charge carriers created from the salt similar to what have been found by other workers [Tunstall *et.al*, 1989, Zhao and Buck, 1998] .

Figure (3) shows the dependence of σ_v on temperature at different molecular weight. It was seen that δ_{DC} increased exponentially with increasing temperature. This behavior can be explained by increasing ionic charge carriers as well as increasing of polymer segmental motion as a result of temperature increase [Wood, 1976] . Similar behavior was reported by Frand , 1992and Anber , 2000 .

In order to calculate the values of the activation energies of the DC conduction process, Eq. (6) is adopted. The relation of In δ_v against the reciprocal temperatures is shown in Figure (4) .

The high activation energy value for PMMA sample without additive (control) can be attributed to the thermal movement of the macromolecules, whereas the low activation energies value for PMMA composite can be attributed to the electronic conduction mechanism which is related to the decreasing distance between salt particles. It has been reported that, for these kinds of composites; ionic, electronic or even mixed conducting processes are possible [Murray, 1984, Blonsky, 1985] .

Figure (5) shows the E_{ac} versus $TiCl_3$ concentration at different molecular weights. It was seen from figure (5) that E_{ac} is decreases with increasing molecular weight. These changes may be understood as follows : the intermolecular interactions increase with increasing molecular weight and relaxations have to overcome an increasing energy barrier with increasing molecular weight hence, the movement of polymer chains turns into segmental motions, which means increased kinetic energy of the chain segments, which in turn translated into a smaller cooperative segment movement region and decreasing activation energy [Obida, 2005].

Results show that σ_v increase with $TiCl_3$ % salt increase and this is expected because the charge carrier increases as the salt content in polymer material increases[Obida, 2005] and it is observed that σ_{dc} increases with increasing molecular weight, the effect of molecular weight is pronounced.

Conclusions

1. The viscosity increases with increase of the molecular weight.
2. The electrical conductivity increases with increase of the $TiCl_3$ concentration and the temperature.
3. The activation energy decreases with increase of $TiCl_3$ concentrations at different molecular weights .

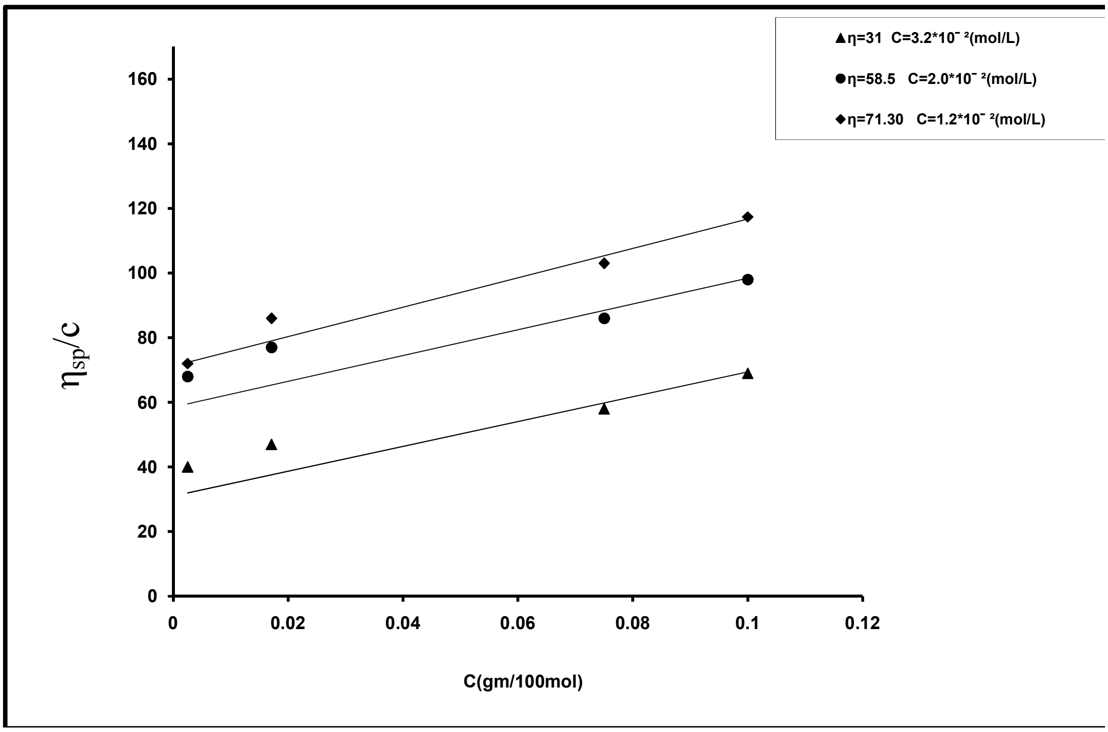


Fig. (1)

(η_{sp}/c) versus Solution Concentration

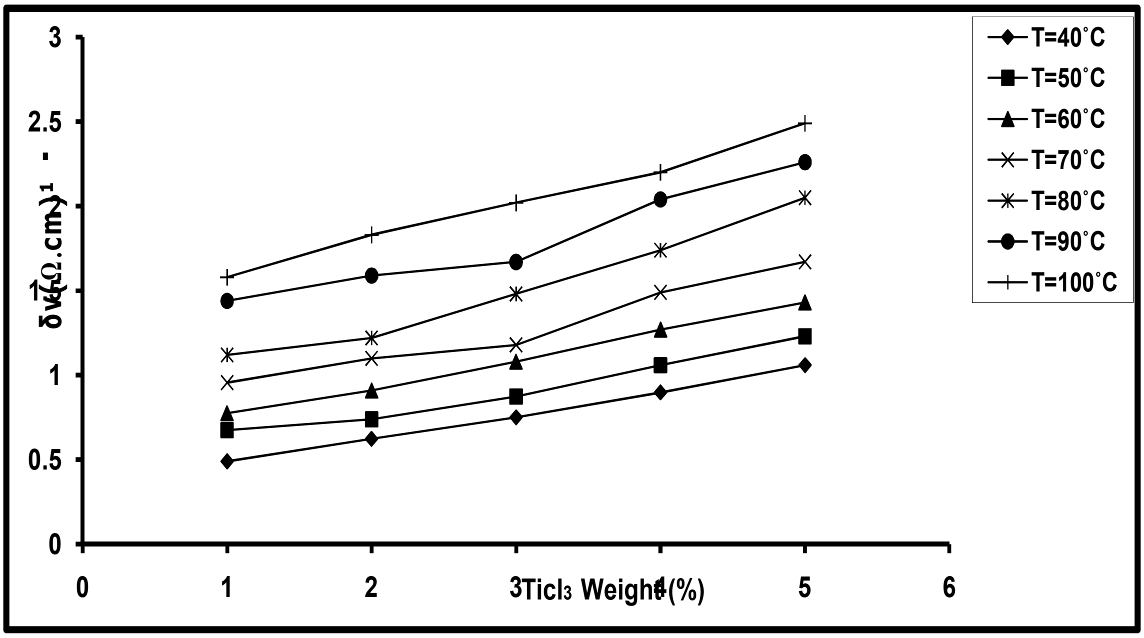


Fig. (2)
Variation of δ_v with Weight % of $TiCl_3$

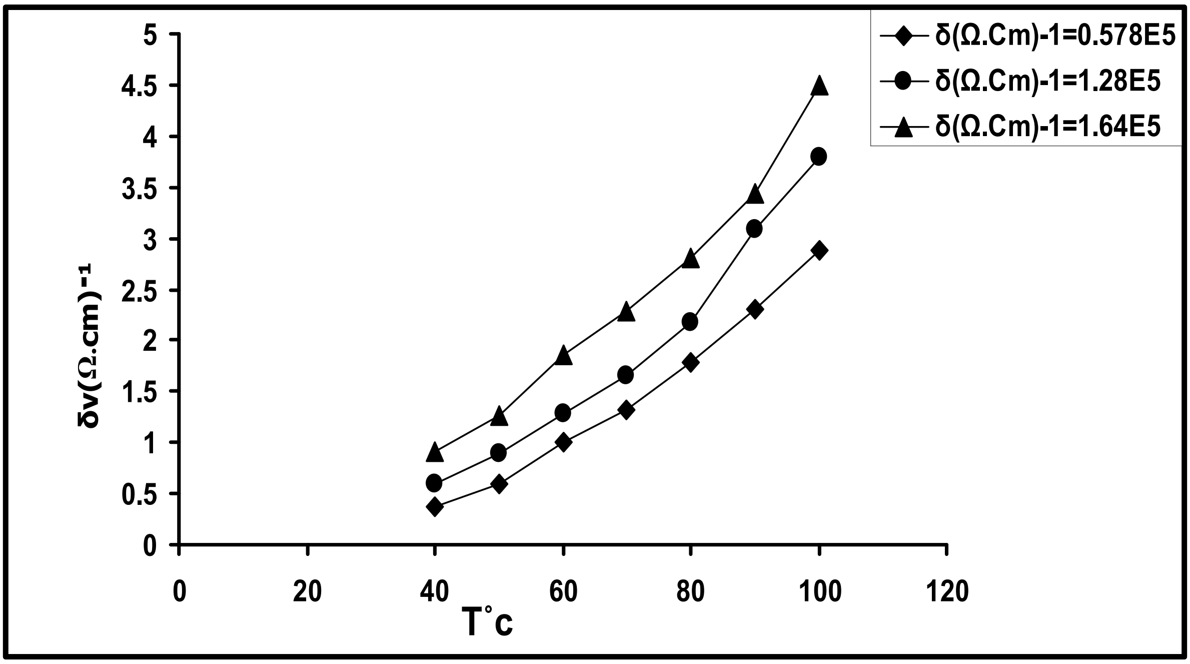


Fig. (3)
δ_v as a function of temperature for pure PMMA
(different molecular weight)

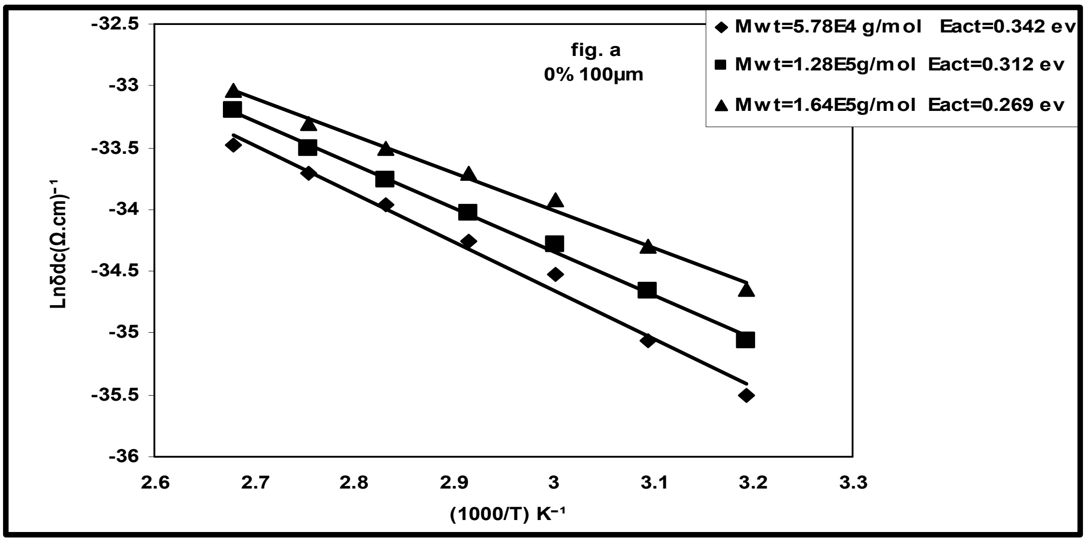


fig. a
0% 100μm
◆ Mwt=5.78E4 g/mol Eact=0.342 ev
■ Mwt=1.28E5g/mol Eact=0.312 ev
▲ Mwt=1.64E5g/mol Eact=0.269 ev
Lnδdc(Ω.cm)⁻¹
-32.5
-33
-33.5
-34
-34.5
-35
-35.5
-36
2.6
2.7
2.8
2.9
3
3.1
3.2
3.3
(1000/T) K⁻¹

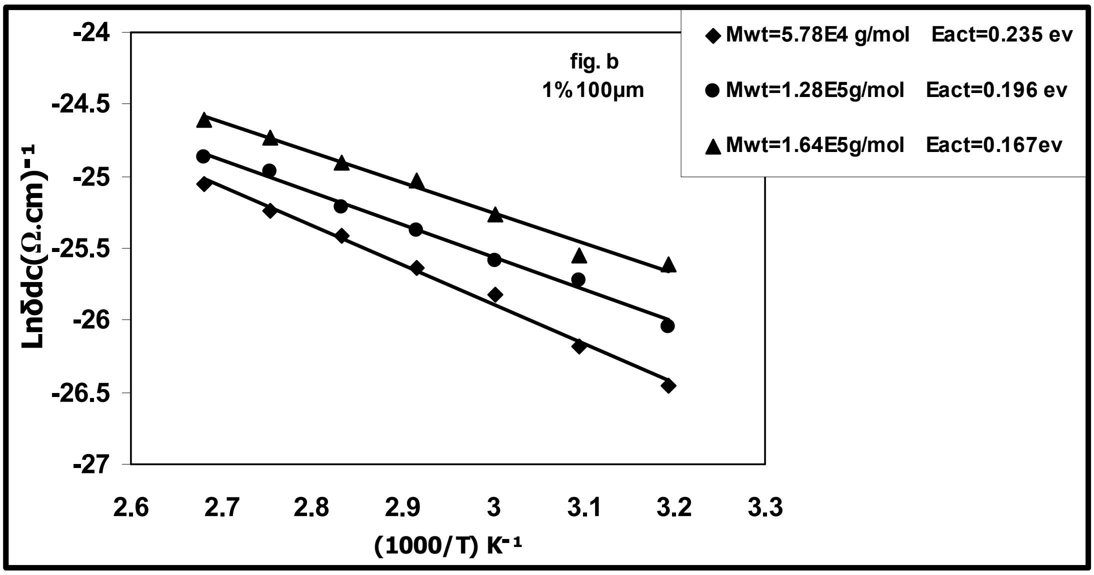


fig. b
1% 100μm
◆ Mwt=5.78E4 g/mol Eact=0.235 ev
● Mwt=1.28E5g/mol Eact=0.196 ev
▲ Mwt=1.64E5g/mol Eact=0.167ev
Lnδdc(Ω.cm)⁻¹
-24
-24.5
-25
-25.5
-26
-26.5
-27
2.6
2.7
2.8
2.9
3
3.1
3.2
3.3
(1000/T) K⁻¹

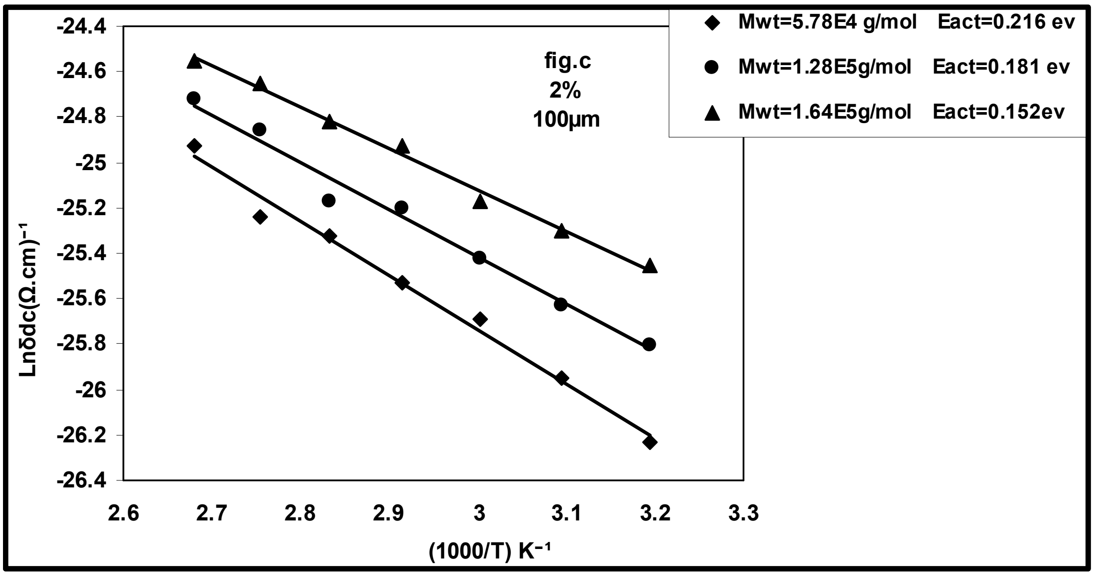


fig.c
2%
100μm
◆ Mwt=5.78E4 g/mol Eact=0.216 ev
● Mwt=1.28E5g/mol Eact=0.181 ev
▲ Mwt=1.64E5g/mol Eact=0.152ev
Lnδdc(Ω.cm)⁻¹
-24.4
-24.6
-24.8
-25
-25.2
-25.4
-25.6
-25.8
-26
-26.2
-26.4
2.6
2.7
2.8
2.9
3
3.1
3.2
3.3
(1000/T) K⁻¹

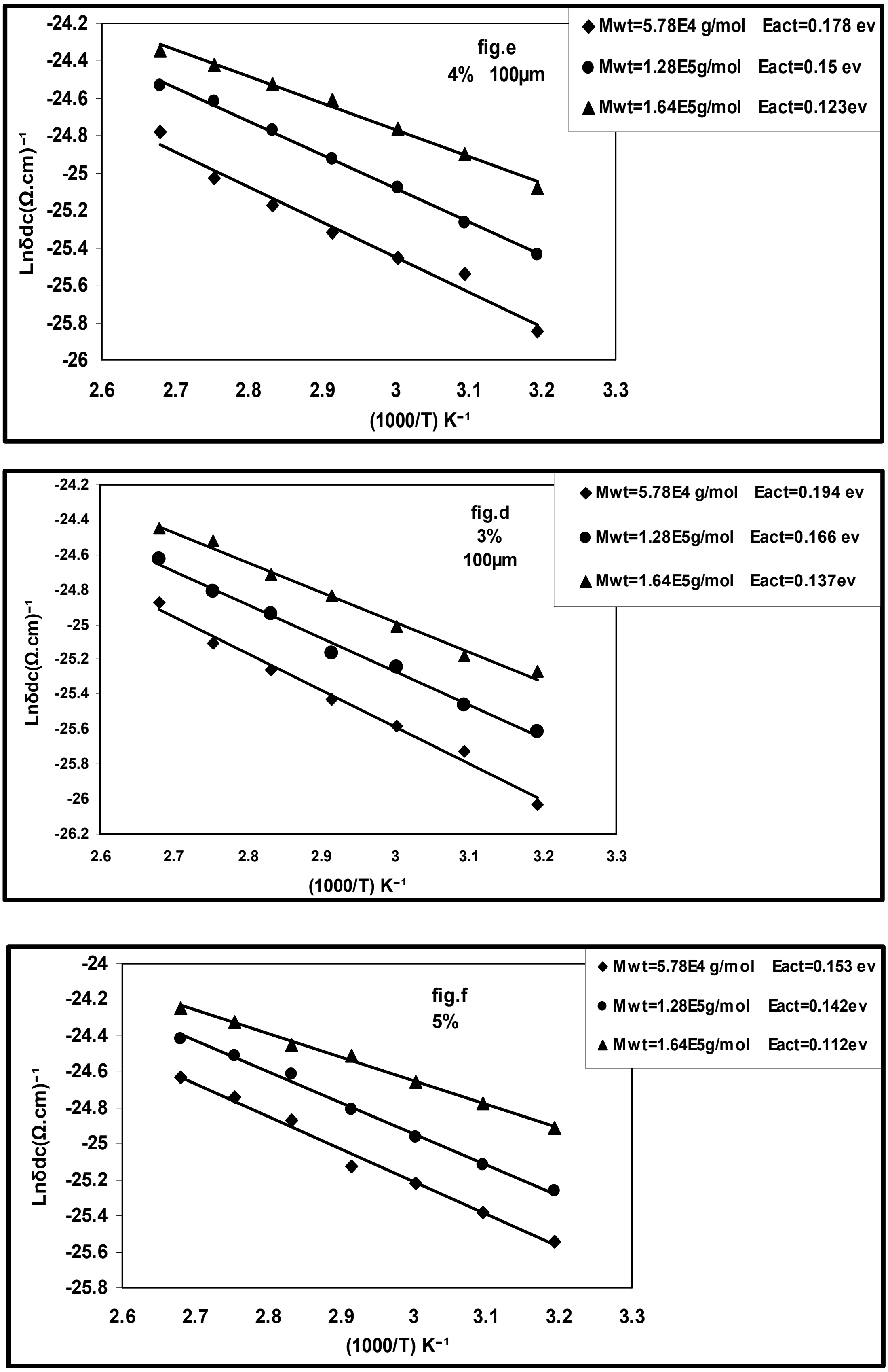


Fig. (4)
Ln δ_{DC} versus 1/T (Arrhenius plot) for PMMA with $TiCl_3$

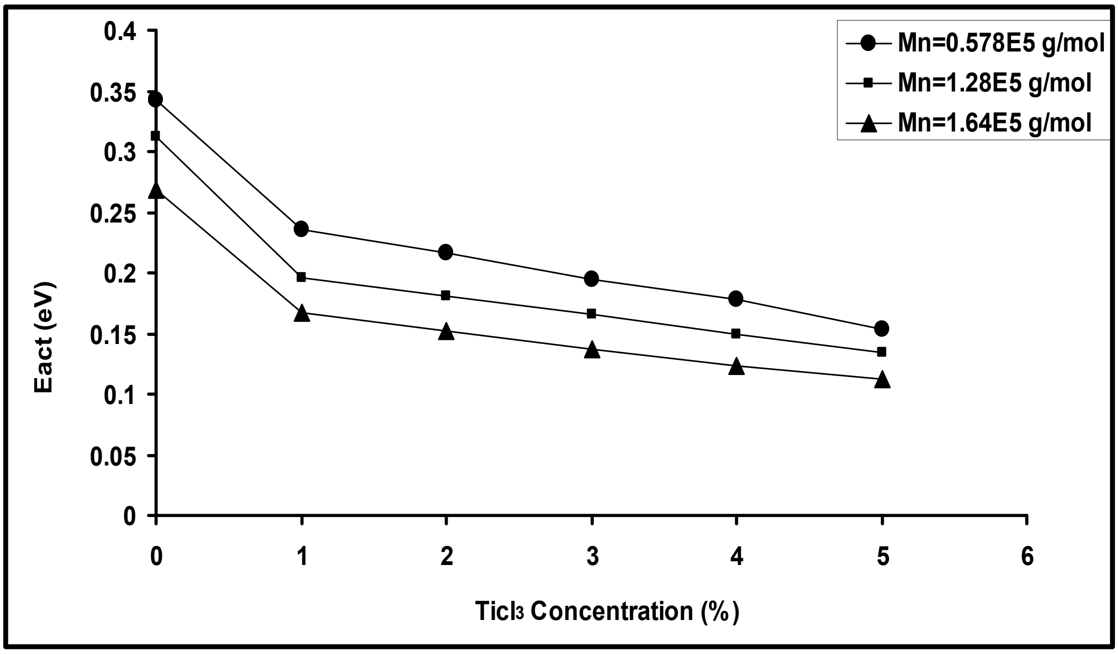


Fig.(5)
Activation energy values with Ticl$_3$ concentration
(different molecular weight)

Table (1)
The Initiator concentration & Viscosity Average Molecular weight of PMMA.

Initiator Concentration mole/ L	Number Average Molecular weight g/ mole
3.2×10^{-2}	0.578×10^{5}
2.0×10^{-2}	1.28×10^{5}
1.2×10^{-2}	1.64×10^{5}

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