

Short Communication

Study the Electrical Conductivity of Cross-Linked Polymers Doped with LiClO₄

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Three cross-linked polymers (I, II, and III) were prepared in different percent's of triethanol- amine (TEA) to glycerol (G) (TEA: G 1:3, 1:1 and 1:0 respectively) via condensation reaction between TEA and G with fixed amount of maleic anhydride (M). All the polymers were doped with different ratios (1, 5 and 10%) of LiClO₄. Electrical conductivity was measured using guard ring electrode method in temperature range of (298-373K). The result showed that the electrical conductivity increased several orders magnitude with increasing temperature and LiClO₄ concentration.

Keywords: LiClO₄, cross-linked polymers, electrical conductivity, Cross-Linked Polymers

1. INTRODUCTION

Ion containing polymers have been proposed as electrolytes for many solid state electrochemical devices. Over the past few decades important applications have been found in lithium batteries, supercapacitors, electrochromic windows and chemical sensors (1-3).The research and development of solid polymer electrolytes (SPEs) has received a great deal of attention due to the usefulness of these materials in a variety of applications (4-5). Polymer electrolytes are commonly doped with an alkaline salt in order to achieve high ion conductivity, which in general is due to both anions and cations [6]. They are of major interest for a range of applications, for example in battery

technology [7] and electrochromic devices [8] where the metallic cation is the electroactive species. The ionic conductivity of a polymer electrolyte is highly dependent on the concentration of the added salt but it is not clear if the conduction process involves all the ions of the salt [9], since they may be bound to the polymer chains or form neutral ion pair dipoles [10]. However, the incorporation of the dopants into polar organic polymers can induce pronounced changes in various properties of polymers in order to modify and improve its properties [11]. This article will focus on the investigation of the effect of LiClO_4 on the electrical properties of the prepared polymers and studies the electrical properties in pure and doped state at temperatures that ranged 25-100°C.

2. EXPERIMENTAL

2.1. Preparation of polymers I, II and III

Triethanolamine (TEA) was mixed with glycerol (G) for 15 min in 100 ml round-bottom flask equipped with a magnetic stirrer and thermometer. Fixed amount of maleic anhydride (M) was added to the reaction mixture. The reaction vessel was immersed in a sand bath. The temperature slowly increased to 160 °C and maintained at this temperature for 3h. The viscosity of the solution will increase until a crystalline polymer was formed. The final product was washed with water and ethanol for several times. Polymers I, II and III are synthesized by changing the percentage of TEA: G (1:3, 1:1, 1:0) respectively, with maintaining the quantity of the M fixed.

2.2 Solubility

Different solvents like water, methanol, ethanol, dioxane, hexane, carbon tetra chloride and benzene have been used to examine the solubility of the synthesized polymers. The results showed that all polymers are stable [12].

2.3 FTIR measurement

A SHIMADZU 8300 Fourier Transform Infrared Spectrophotometer (FTIR) device was used to measure the infrared spectra using (KBr) in the wave number range (4000-400) cm^{-1} .

2.4 Doping of polymers

The polymer was doped with different ratios of lithium perchlorate (LiClO_4) (1, 5 and 10%) in ethanol to the polymer. The doped polymers were left for seven days to allow LiClO_4 diffuse homogeneously. Doped polymers were dried under vacuum overnight.

2.5 Preparation of the Samples

Powder of polymer samples was pressed under a pressure of 5 ton/cm² for 15 minutes in a circular pellet specimen with a diameter of 2.5 cm and thickness varied from 0.7-2.9 mm. The specimens were pressed at 80 °C. A thin layer of a circular aluminum electrode with a diameter of 1.5 cm was deposited on the both sides of each sample using a coating unit model (Edwards). The deposition of aluminum is done under highly reduced pressure

2.6 Electrical measurements

Three electrode cell or (guard ring electrode method) was used to study the volume resistivity of the polymer. Keithly 614 digital-solid state electrometer was used to measure the resistance. The copper electrodes are provided with two adjustable screws to apply a uniform pressure on the specimens. The specimens are sandwiched between the electrodes; the process is done in a controlled temperature oven (Hereaus electronic). The effect of the dopant on the volume conductivity measurements were achieved in the temperature range (25-100°C).

3. RESULTS AND DISCUSSION

3.1 Polymer synthesis

It is known that condensation reaction of glycerol with maleic anhydride produce hard and rigid polymer [13]. On the other hand, we found that condensation of triethanolamine and glycerol with maleic anhydride produce less hard and rigid polymers (polymer I, II) while the condensation of triethanolamine with maleic anhydride produces polymer (polymer III) tend to be elastic. As in the following chemical reaction scheme (1) for polymer (I and II), and scheme (2) for polymer (III).

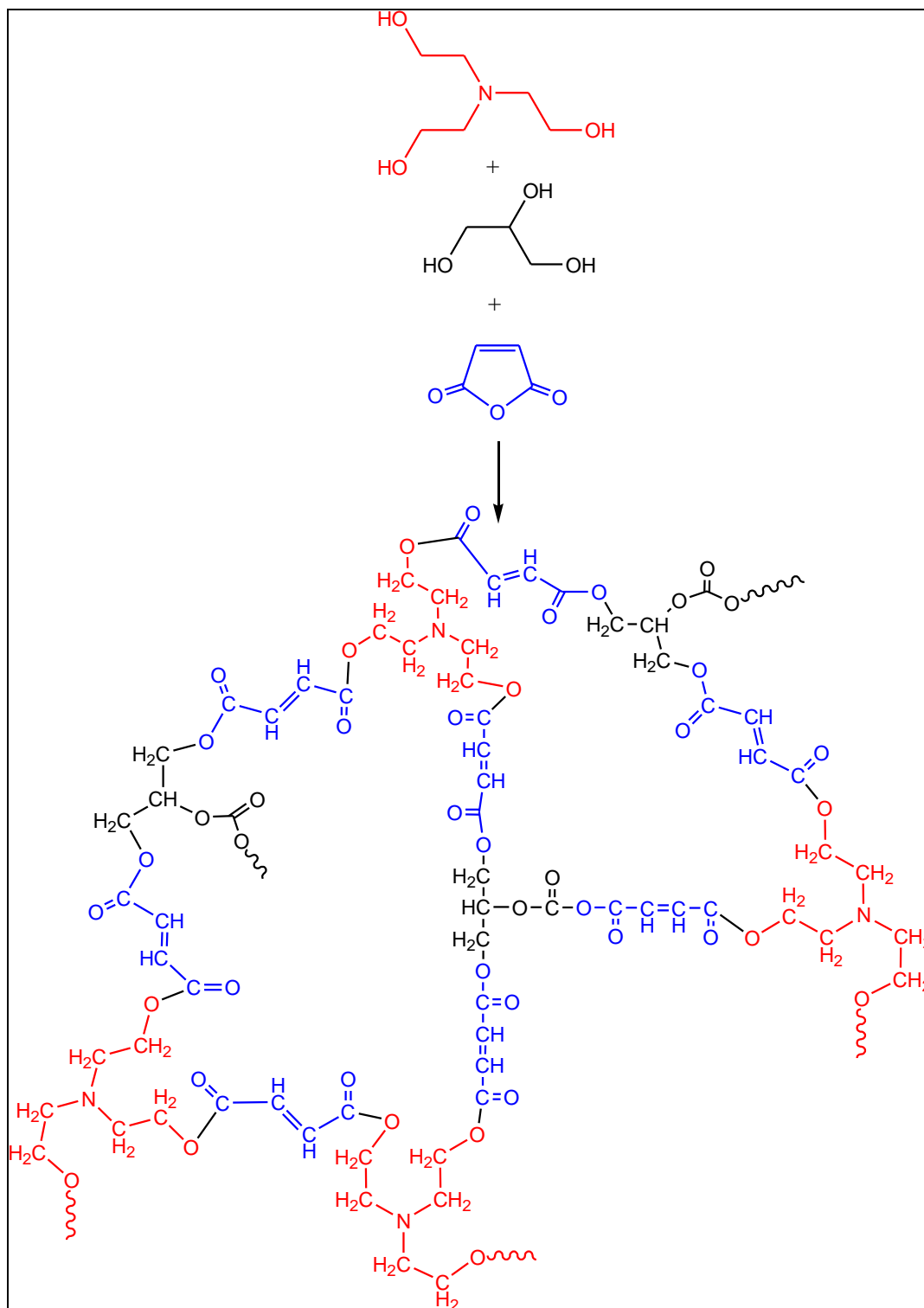
Despite the synthesis of the polymers (I, II and III) are the same, but we believe that polymer III contains more Nitrogen atoms which may play significant role in the electrical conduction.

3.2 Polymer characterization

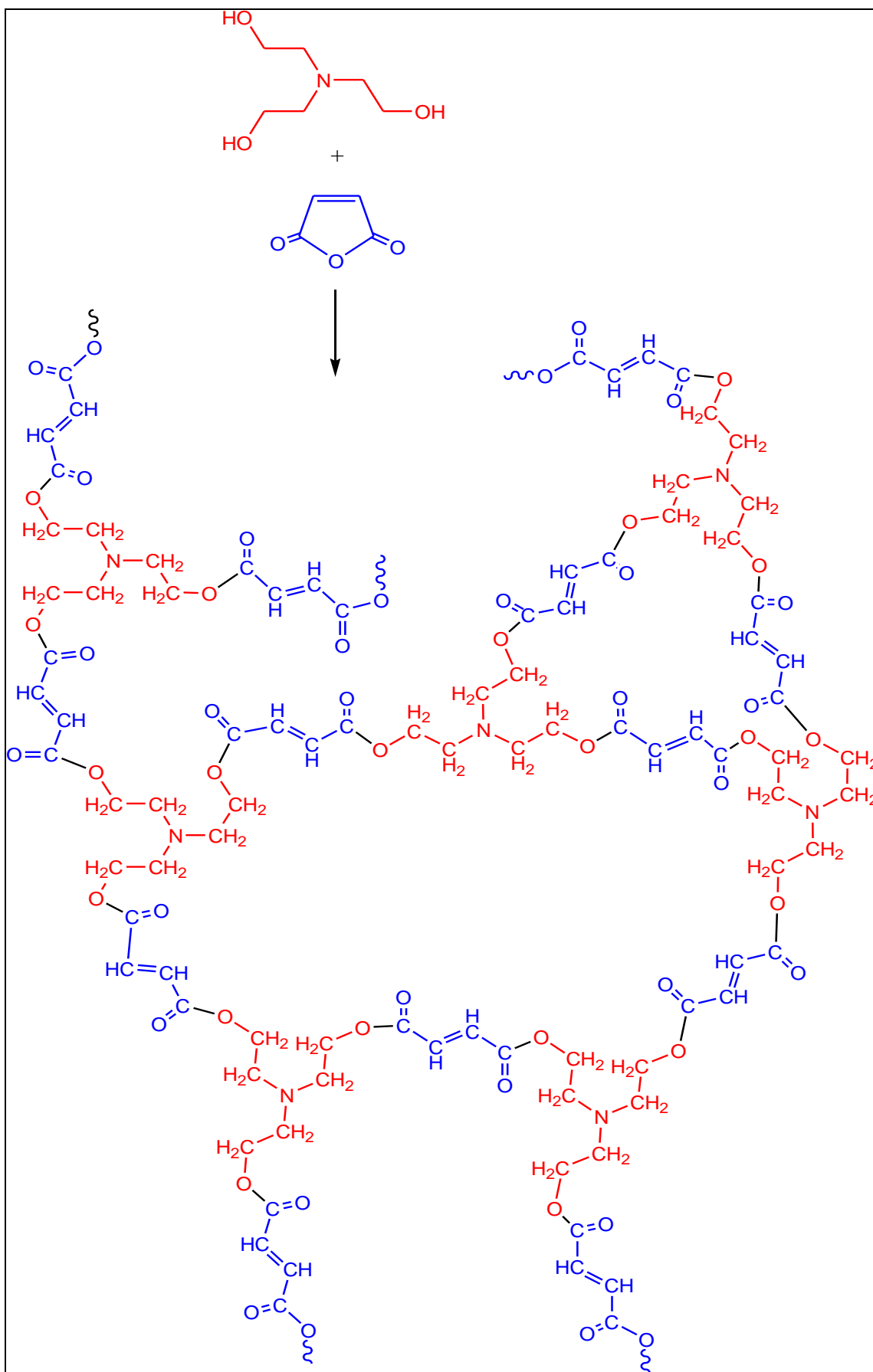
All the prepared polymer are characterized by the difficult solubility in most solvents [13], that because of the high degree of cross linking which prevent the rotation of the bonds and consequently the molecule have high energy barrier to solvation process and for this reason we cannot determine the molecular weight and the degree of polymerization.

However, the polymers [I, II and III] were identified by FTIR spectrum. The FTIR spectrum of polymers [I] and [II] showed the appearance of the characteristic absorption bands at (1732 cm⁻¹) due to the stretching vibration of the (C=O) of the forming ester. A band at (1161 cm⁻¹) was due to the (C-O) stretching of ester and appearance of (C-N) band at (1296 cm⁻¹), a band of (C=C) appears at (1639cm⁻¹)and also a band at (2943cm⁻¹) due to C-H aliphatic.

Polymer I	TEA + G + M (TEA:G)=(1:3)
Polymer II	TEA + G + M (TEA:G)=(1:1)
Polymer III	TEA + G + M (TEA:G)=(1:0)



Scheme 1. The suggested structure of polymers II



Scheme 2. The suggested structure of polymer III

Also, the FTIR spectrum of polymer [III] shows the appearance of the band at (1732 cm^{-1}) due to $\nu(\text{C}=\text{O})$ of ester. A band at (1161 cm^{-1}) was due to the (C-O) stretching of ester and appearance of (C-N) band at (1288 cm^{-1}), a band of (C=C) appears at (1639 cm^{-1}) and also a band at (2943 cm^{-1}) due to C-H aliphatic.

3.3 Electrical conductivity

It is known that the conductivity of traditional semiconductors like silicone and germanium increased with increasing temperature and that was because of the increasing charge carriers in the conduction band. Many researches have proved that, generally; polymers exhibit a similar electrical conductivity behavior depending on temperature to that of semiconductors.

The relation between the effect of temperature and the electrical conductivity for all polymers (I, II and III) in the pure and doped state are shown in figures 1-4. The results clearly showed that there is a significant increase in the electrical conductivity (reduction in the electrical resistance) with increasing of temperature from 25 to $100\text{ }^{\circ}\text{C}$ in a behavior similar to that of semiconductors [14-15].

The prepared polymers differ in their structure and contain different percent of nitrogen and oxygen atoms. The presence of these atoms in the polymeric chains enhances the interaction between the polymer and the dopants and consequently enhances the conductivity of the polymer.

Polymer III showed higher conductivity than polymer II and I due to high percent content of these atoms (figures 1). Length of the chains in polymers II is greater than polymer III so the increase in the length of the chains and their motions could increase the conductivity of the polymer As reported by Xi & Tang [16].

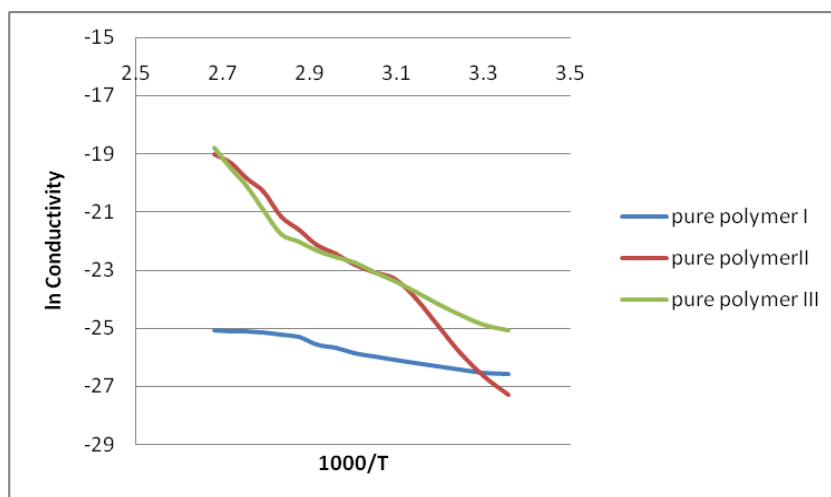


Figure 1. Plot of conductivity vs $1000/T$ for the pure polymers

From figures 2, 3 and 4, doping of the polymers with different ratios of LiClO_4 cause a dramatic increase in the conductivity of the polymers, this increase is due to small size of Li atom which make it diffuse within the matrix of the polymer, this fact was enhance when the ratio of doping

of the polymers is increase. The variation of conductivity for doped polymers of different LiClO_4 concentrations as a function of temperature shows that all sample conductivity is increase with increasing temperature characteristic of semi conducting materials this behavior can be related to segmental motion as a result of increasing temperature.

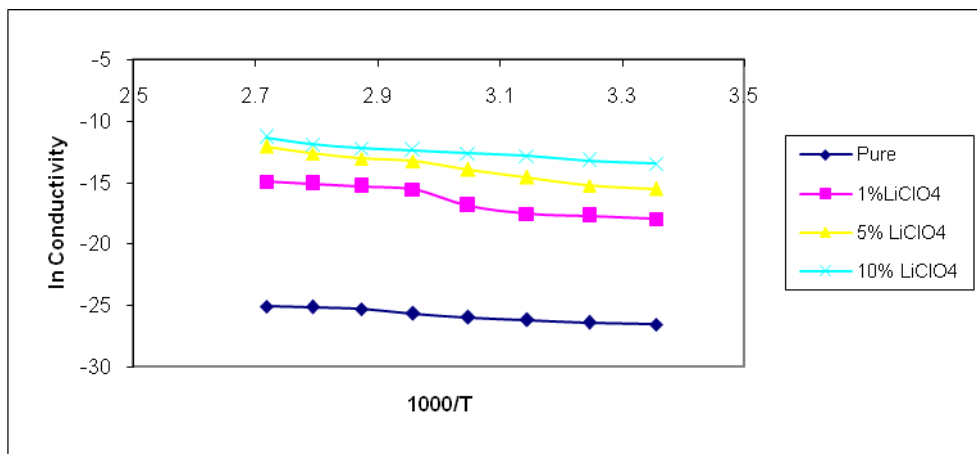


Figure 2. Plot of conductivity vs 1000/T for pure and doped polymer (I)

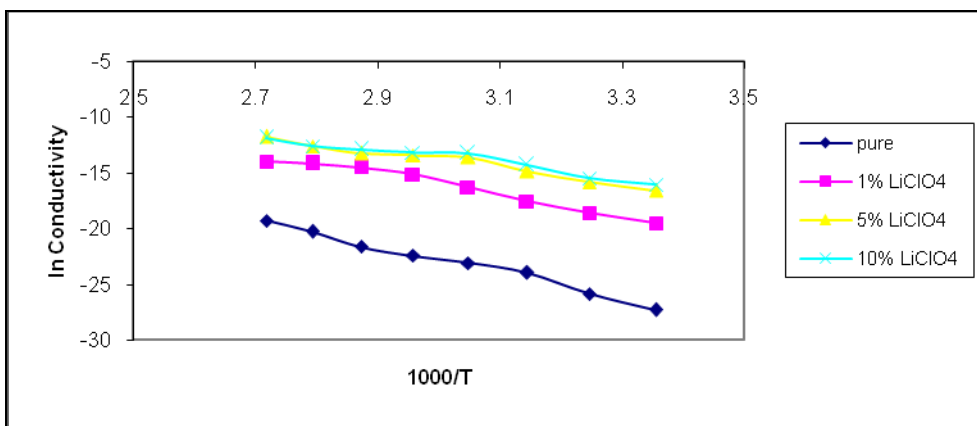


Figure 3. Plot of conductivity vs 1000/T for pure and doped polymer (II)

Table 1. Activation energy for polymers in the pure and doped state

LiClO ₄	Activation energy e.v.		
	Polymer I	Polymer II	Polymer III
0%	0.0228	0.0101	0.0084
1%	0.0062	0.0041	0.0053
5%	0.0024	0.0029	0.0048
10%	0.0012	0.0024	0.0035

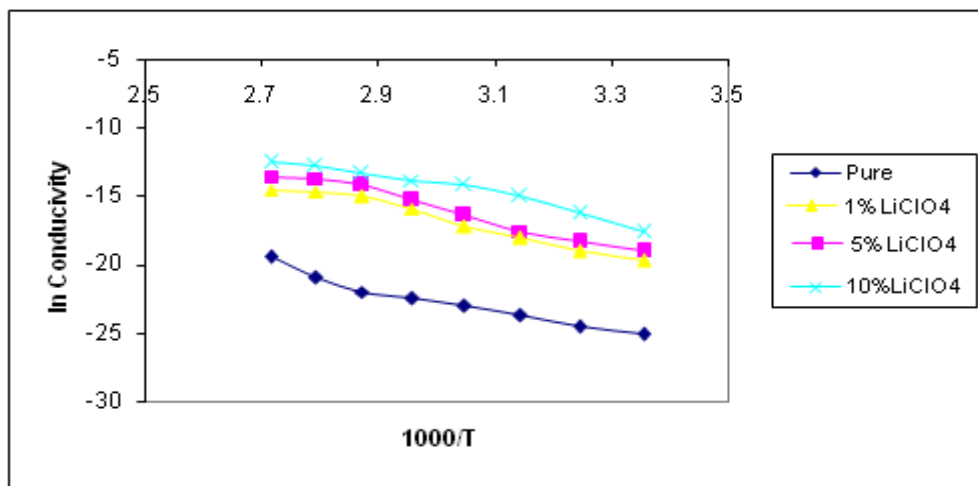


Figure 4. Plot of conductivity vs 1000/T for pure and doped polymer (III)

The activation energy also calculated by using Arrhenius equation, table 1 indicate that 1% LiClO₄ sample have higher activation energy while 10% LiClO₄ has lower activation energy value.

4. CONCLUSION

The structure of polymer has a great effect on its electrical properties, the conductivity is increase with increasing the concentration of LiClO₄ and as the temperature increase the conductivity is increase too in a behavior similar to the semiconducting materials.

ACKNOWLEDGEMENTS

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