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Effect of Polymeric Chain Flexibility on Electrical Conductivity of Aromatic Polyesters

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ABSTRACT

Two types of aromatic polyesters were prepared by polycondensation of terephthaloyl dichloride with 2,7-dihydroxy naphthalene (polymer 1) and bis(4,4′-di-α-naphthoyl) methane (polymer 2). The electrical conductivity of polymer 2 is larger than that of polymer 1. The reason is the polymers chain mobility. The effect of doping by ferric chloride and temperature on electrical conductivity was studied. It was noticed that the doping process increased the conductivity of polymer 1 more than polymer 2. The temperature well increase the electrical conductivity of purred polymer in a manner that the activation energy of polymer 2 is larger than that of polymer 1.

Keywords: polyester, aromatic, electrical conductivity.

تأثير مرونة السلسلة البوليمرية على التوصيل الكهربائي للبولي استرات الاروماتية

الملخص

حضر نوعين من البولي استرات الاروماتية عن طريق البلمرة التكثيفية للترفثاويل داي كلوريد 7,2-ثنائي هيدروكسي نفثالين (بوليمر I) ومع بس(4,4-ثنائي –α -نفثويل)ميثان (بوليمر II).

إن التوصيلية الكهربائية للبوليمر II كانت اكبر من التوصيلية الكهربائية للبوليمر I وقد عزي السبب إلى مرونة السلاسل في البوليمر. درس تأثير التشويب بواسطة كلوريد الحديديك، لوحظ أن كفاءة عملية التشويب في زيادة التوصيل الكهربائي للبوليمرI اكبر من II.

إن زيادة درجة الحرارة تزيد من التوصيل الكهربائي للبوليمرات النقية بحيث لوحظ أن مقدار طاقة التنشيط للبوليمر II اكبر من البوليمر I.

INTRODUCTION

Conductive polymers are the most recent generation of polymers. In the late 1950’s Organic semiconductors became the focus of investigations. The synthesis of electrically conductivite polymers with conjugated -C=C- bonds requires the controlled coupling of a large number of monomers.

Experimental studies (Goo, Smith and Heeger,1991) have established that, for conducting polymers, the electrical properties and the mechanical properties are improved together in a correlated manner. The increasing in both conductivity and modules is resulted from increasing uniaxial orientation, improved packing and enhanced interchain interaction.

Electrical conductivity in polymers results from the existence of charge carriers and the ability of those carriers to move. In principle broad π-electrons hand widths can lead to relatively carrier mobilities (Heeger et al.,1988).

Little (Little,1964) showed that an aromatic and heterocyclic group in polymer exhibiting electrical conductivity of 0.5 s/cm.

Aromatic polyesters are characterized by their inherent flame retardance, resistence to UV, and has good electrical properties. It can use to be semiconductor components. Polyesters consisting of bisphenol A and aromatic dicarboxylic acid are amorphous and shows an electrical conductivity ranged from 10^{-16} Scm^{-1} at room temperature to 10^{-11} Scm^{-1} at 520k (Serin, Cankurtaran and Yilmaz,2003),whereas the activation energy was found around 1.6 ev.

The interruption of chain conjugation of aromatic polyester by aliphatic groups shows an increasing in electrical conductivity (Shehab and Khattab, 2001) . The reason responsible for this finding is the increasing in chain mobility due to the presence of aliphatic segments.

Iodine doping of copoly phenylene vinylene-aliphatic ester has been enhanced the electrical conductivity to about 10^{-2} Scm^{-1} (Yang and Karaz, 1994) . The aliphatic ester group added to poly phenylene vinylene is to make the chain more flexible and increase the conductivity . These studies make us sure that the molecules containing an ester and aromatic rings groups are considered to be dopable and consequently conducting. In our work we shall study the effect of aromaticity content and its ordering in the polymer chain on the electrical conductivity of the polyester.

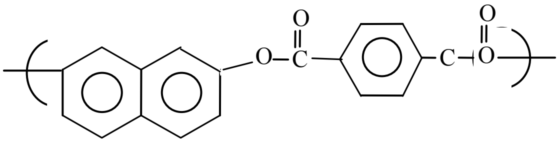
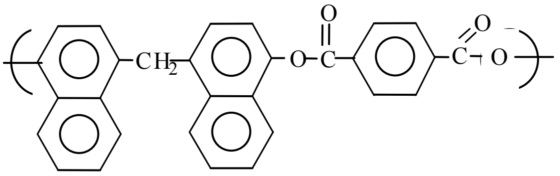
EXPERIMENTAL

Chemicals and Reagents:

All chemicals were purified by known methods (Perrin,Amarego and Perrin,1980). Terephthaloyl dichloride (TPC) was prepared by refluxing terephthalic acid with an excess amount of thionyl chloride in presence of some drops of dimethyl formamide.

Synthesis of polymers:

Two polyester have been prepared by solution process polymerization using terephthaloyl dichloride condensed with equimolar of two types of aromatic diol according to known methods (Gadoye, Paurathnam and Nadkarni). Polymer 1 was prepared by reaction of TPC with 2,7-dihydroxynaphthalene, while polymer 2 was prepared with bis-(4,4′-di α-naphloyl)methane.

Polymer No.	Structure
1	
2	

Doping:

The doping process was complished by mixing the polymer sample with different mole ratio of ferric chloride as a dopants at room temperature.

Preparation of specimens:

Circular pellet specimens were prepared from the pured and doped polymer samples, put under a pressure of 7-10 ton/cm^2. The diameter of the pellet was 2 cm with thickness varied from 0.6-2 mm.

Electrical measurements:

The volume conductivity was measured by using a three probe cell according to the equation (ASTM 1981):

$$\sigma = \frac{Id}{AE}$$

Were I is the output current (Amp.) when a step voltage E (volt) is applied, d is the specimen thickness (cm), A is the effective area of the measuring electrode (cm^2).

RESULTS AND DISCUSSION

Preparation of polymers:

A low temperature polycondensation of TPC with two types of diols by using solution process was depended in this work. Fig 1 and 2 (table 1)shows the FTIR spectra of the investigated polymers.

Polymer 1 represents the polyester of TPC with 2,7-dihydroxy naphthalene, where a complete conjugation of double and single bond is present. In polymer 2 the conjugation was interrupted by methylene group.

Conductivity measurements:

The volume conductivity of the prepared polymers have been measured at room temperature. The numerical values of these conductivities σ are listed below.

Polymer No.	**σ s/cm**
1	13.77×10^{-12}
2	21.42×10^{-11}

Table 1: IR spectra of polymers 1 and 2

polymer	**C = O streching**	**C— O ester sym.**	**asym.**	**Aromatic C—H bending**	**Aliphatic C — H bending**
1	1724	1235	1077	1575	
				1507	
				1408	
				1379	
2	1717	1286	1076	1512	1234
				1447	1201
				1409	1145
				1384	

It was known that the delocalization of charges through aromatic rings and ester groups enhances the conductivity of the polymers (Maier et al.,1989).

The results shows that polymers 2 has a larger conductivity than polymer 1 by one order of magnitude. This can be explained by that the interruption of conjugation in the chain of polymer 2 by methylene group will increase the chain mobility and enhancing the conductivity. Most probably the increase in chains mobility will enhances the conductivity through decreasing the viscosity and increasing the rate of diffusion of charge carriers and interchain collision.

Effect of Doping on Conductivity:

The delocalization of electrons a long the conjugated chains and their jumping from one chain to another through the dopant molecules will represent the process by which charges are transported through the polymeric material.

The metal ion of the dopant ferric chloride has an empty d-orbital, so it was an electron acceptor, in accordance the polymeric chain with an aromatic rings and ester group deals as an electron donor. The efficiency of dopant is related to its ability to form some type of complexes (charge transfer complexes) (Shirakaw, Lowis and Mac Diarmid,1977) with the unsaturation units in the polymer chain. These complexes are the charge carrier and they are responsible of the electrical conductivity in polymer. Increasing the concentration of these complexes will increase the conductivity.

The studies polymers are doped with different mole ratio of ferric chloride. The electrical conductivities have been increased by many order of magnitude as shown below.

Polymer No.	$FeCl_3$ /mole ratio	σ /s.cm^{-1}
1	0	13.77×10^{-12}
	2	6.86×10^{-11}
	4	3.48×10^{-8}
	5	7.11×10^{-5}
2	0	21.42×10^{-11}
	0.5	14.76×10^{-11}
	2	2.86×10^{-9}
	4	11.88×10^{-8}
	5	10.12×10^{-8}

It was noticed that the conductivity of polymer 1 is more enhanced than polymer 2 by doping. It can be suggested that the chain mobility of polymer 2 is reduced more than polymer 1 due to polymers-dopant interactions, so the unsaturation units a long the chain is play the main role of increasing the conductivity where's polymer 1 is dominate.

Temperature effect on conductivity:

The electrical conductivity in semiconductor is increased with increasing temperature. This is due to an increase in the population of electrons in the conduction band (Giffith and Rearndon, 1985).

The changes in conductivities of pure polymers 1 with temperature and the activation energy ΔE of the conduction process is listed below.

Temp./K	286	328	349	369	**ΔE/e.v.**
σ/S.cm^{-1}	13.77×10^{-12}	27.54×10^{-12}	34.43×10^{-12}	41.32×10^{-12}	0.1215

From these results, it has been shown that there is a systematic increase of electrical conductivity with temperature relase. The percent effect of temperature on conductivity can be estimated by calculating the activation energy of this process. The activation energy is most likely belong to chain mobilities (Shehab and Khatta,2001). In another hand, there are no significant effect of temperature on electrical conductivity 0f polymer 2. The conductivity is likely to be almost constant at about ($2o\times10^{-11}$ to 29×10^{-11}) S.cm^{-1} in temperature range between (280-373) K^{o}. This can be explained by that the chain of polymer 2 with -CH_2- group between two naphthalene is more flexible than polymer 1.The chain mobility of polymer 2 is less sensitive to temperature than polymer 1.

The effect of temperature on conductivity of the doped polymers are difficult to interpret. We think that temperature changes may cause some reactions between that dopants and the polymer that gives rise to confusing results.

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