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Effect of Acidic Dopants properties on the Electrical Conductivity of Poly aniline

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Abstract

Polyaniline was doped with different halogenic acids. The electrical conductivity of the doped polymers shows significant affects of the counter ions of the dopant on the conductivity. It was appeared that the electron affinity of the counter ion is the dominating factor. The results show that the electrical conductivity will increase with increasing the dopants concentration. The percolation point was also investigated; it was shown that the electron affinity of the counter ion of the dopant plays the major effect on this point.

Keywords: Polyaniline, electrical conductivity

Introduction

Poly aniline is the oldest type of conductive polymers .It was one of the most versatile conjugated polymers .The basic chain structure exist in three oxidation states (1) which can be chemically doped (2) . In the emeraldine base form, poly aniline is rendered conductivity through doping by protonic acids. The doping or protonation occurs by a general reaction of poly aniline with protonic acids in the form H M , where M is the counter ion (3) . The process that transforms insulating polymers to conductors is through the formation of charge transfer complexes between the electron donor or electron acceptor and the polymers (4).The doped polymer backbone becomes positively or negatively charged with dopant forming oppositely charged ions (5) . It was suggested that poly aniline is reversibly doped in to three forms: A reduced forms; Radical cation intermediate forms; and Oxidized form,poly aniline is stable in the aqueous solution for all these three forms. The radical cation form is highly conductive. The oxidized forms, however, are insulating (6,7,8) . Doping poly aniline with derivatives of sulfonic acid will increase the ionic conductivity to about $10^{-3}\ \Omega^{-1}$ (9) . The aim of this work is to find the effect of the counter ions resulted from doping by protonic acids on the conductivity of poly aniline, whereby the charge carrier will be carried according to the type of the dopant used.

Experimental

Chemicals

All chemicals and reagents were purified according to the normal methods (10).

Preparation of polyaniline:

15 ml of pured aniline was dissolved in 600ml(1M)HCl in around bottom flask .After cooling the solution to 5ºc ,a solution of [28.2gm ammonium persulphate in300ml(1M)HCl]was added drop wise for 15min.with stirring. The mixture was stirred for 2 hrs at 5ºc , filtered and the precipitant was washed 4times with 100ml of 1M HCl , then transferred to a beaker containing 400ml of 1M HCl with continuous stirring for 4hrs.then filtering and drying of the product for 48hrs.at room temperature. The result of fine green crystals of polyaniline doped with HCl .To obtain pure undoped polyaniline, washing the doped polymer with (0.1M) ammonium hydroxide for 3hrs was carried then the polymer was filtered and dried.

Doping process

Doping with HCl:

Specimens with 2 cm diameter and (0.6-0.8 cm) thickness from the pure polyaniline are prepared under 5 ton/cm^2 pressure. The specimen is doped with HCl through exposing the polymer film to the vapor of(37%) HCl for different time intervals to obtain different percent of doping.

Doping with HF, HI:

Polyaniline specimens doped with(48%) HF,(56%) HI have been achieved by following the same sequence of doping with HCl.

Doping with HBr:

Polyaniline specimens doped with (48%)HBr were accomplished by immersing the pure polyaniline specimen in HBr for different times to obtain different percent of doping.

Electrical conductivity measurements:

The electrical conductivity of the pure and doped polymers were measured using the standard 3-probe DC technique according to ASTM method (ASTM, 1981) **(11)** .

Results And Discussions

The volume conductivity of the pure and undoped polyaniline were measured using three probe cell (11). The influence of the amount percent of dopant material on the conductivities of polyaniline is shown in table (1). It is clear that the conductivity of polyaniline increases as the concentrate of the dopant material increases.

It was noted that the highest conductivity of polyaniline doped with HBr is equal to $4.6x10^{-7}$ ohm^{-1}.cm^{-1} at 4% of doping level, while the highest conductivity in doping with HCl was $1.3x10^{-7}$ ohm^{-1}.cm^{-1} via 5% of doping in contrast the maximum conductivities reaches 2.2 $x10^{-8}$ohm^{1}.cm^{-1} and 1.9 $x10^{-8}$ ohm^{-1}.cm^{-1} by doping with 5% of HF and HI respectively.Many factors effects the electrical conductivity of polymers have been investigated. The number and mobility of the charge carriers, which can be correlated with the chemical composition, are the main factors.Doping polyaniline with protonic acids will produce a charge carrier formed between the polymer chains and the proton H^+.As a result the maximum conductivity of poly aniline via doping with different types of protonic acids will follow the order:

HBr > HCl > HF > HI

It was noticed from our results that the electrical conductivity depends also on the type of the counter ion of the dopants moieties (Br^-, Cl^-, F^-, and I^-). The counter ion may affects the mobility of the charge carriers. In compairing the results with many physical properties (table 2) , it was clearly observed that the conductivity increase with increasing electron affinities and with decreasing the thermal conductivity of the counter ions , except deviations in the properties of Br^- ion , while the covalent radios or atomic radios have no correlations with the electrical conductivities .The deviations' in the case of Br^- ion can be explained by the experimental errors , whereby the doping with HBr is made by immersing the specimen in solution of HBr , as a result the water of the acid solution will behave also as a doping agent and increase the conductivity(12).Figure (1).The exponential increase of conductivity with increased doping concentration is a well known phenomenon, the doping proceeds heterogeneously inside and at the surface of the morphological subunits of the polymers. At low levels, single individual particles are transfored firstly to become conductive ones. Charge transport cannot take place as long as these particles are still isolated by the surrounding unreacted particles .This point was appeared at significant concentrations of dopant , a jump in conductivity must be observed at a point which is known as the percolation point.The effect of counter ion was clearly observed in Figure (1). Table (3) shows the percolation point for different dopants.

Table (1): Electrical conductivities of polyaniline (σ ohm^{-1}.cm^{-1}) doped with different acids concentrations

Doped with:	1%	2%	3%	4%	5%
HF $x10^{-9}$	0.877	1.994	7.43	17.99	22.40
HCl $x10^{-9}$	10.56	38.74	59.87	87.05	130.82
HBr$x10^{-9}$	0.169	14.3	449.5	462.5	463.8
HI $x10^{-9}$	o.049	0.081	0.149	11.42	19.83

These results are clearly demonstrating the effects of the electron affinities of the counter ion (table 2) , which is compatible with the maximum conductivities of the doped polymers , except the deviations with Br^- ion.

Table (2): physical properties of dopants:

	Atomic radios(M)	Covalent radios (M)	Thermal conductivity w cm k	Electro-negativity (Pauling)	Electron affinities K cal gm
F	$0.75x10^{-10}$	$0.72x10^{-10}$	$2.7x10^{-4}$	3.98	79.5
Cl	$0.97x10^{-10}$	$0.99x10^{-10}$	$8.0x10^{-5}$	3.16	83.3
Br	$1.12x10^{-10}$	$1.14x10^{-10}$	$1.22x10^{-3}$	2.96	77.5
I	$1.32x10^{-10}$	$1.33x10^{-}10^{-10}$	$4.45x10^{-3}$	2.66	70.6

Undoped polyaniline $2.68x10^{-11}$ σ ohm^{-1}.cm^{-1}

Table (3): Percolation points appeared at different dopants concentrations

Dopant	HBr	HCl	HF	HI
Dop.percent w/w %	2	4	3	4

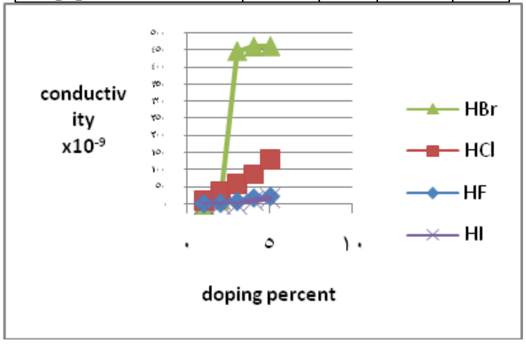

Figure (1) Effect of dopants concentration on electrical conductivity polyaniline

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تأثير خواص المشوبات الحامضية على التوصيلية الكهربائية للبولي انيلين

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الملخص

حضر البولي انيلين وشوب بمجموعة من الحوامض الهالوجينية . حيث اوضحت الدراسة تاثير الايون المرافق للمشوب على التوصيلية الكهربائية وتبين ان الالفة الالكترونية للايون المرافق لها التاثير الاساسي على التوصيلية.كما اوضحت النتائج ان التوصيلية الكهربائية تزداد بزيادة تركيز المشوب . وتم التحقق من نقطة الانقلاب حيث ان الالفة الالكترونية للايون المرافق في المشوب كان لها التأثير الأساسي على قيمة هذه النقطة .