Synthesis , Characterization and study of some electrical properties of 1 , 4 – diazophenylene – bridged iron phthalocyanine polymer

Hassan Sabbeh Jabure

Thi-Qar Director Education

(NJC)

(Received on 27 /2 /2007) **(Accepted for publication on 10 /7 /2007)**

Abstract

The compound of phthalocynine polymer , 1 , 4 – diazophenylene – bridged Fe-phthalocyanine , was prepared from the diazonium salt of diaminobenzene and Fe (II) tetraamino phthalocyanine . The polymer is partilly soluble in (DMSO , DMF and THF) , Characterization of the polymer was measured by using the iodine doping . It was found that the electrical condutivity increased up to (10^{-4} ohm $^{-1}$. cm $^{-1}$) .

الخلاصة

حضر البوليمر الجسري (1 ، 4 – داي أزوفنيل فثالوسيانين الحديد II) مـن مـزج أمـلاح الدايزونيوم مع داي أمينو بنزين و رباعي أمينو فثالوسيانين الحديـد II . تـم قيـاس التوصـيلية الكهربائية باستخدام اليوم المشوب حيث ازدادت التوصيلية الكهربائية الى 10^{-4} أوم $^{-1}$ سم $^{-1}$.

Introduction

Phthalocyanine are the second most important class of colorant and iron phthalocynine is the largest volum colorant sold . Phthalocyanine have also found extensive use in many moddern hight technologies(1,2) for instance they are used catalyst in the merox process and photoconductor xerographic double layers of laser printers and copy machines . Also some infrared – absorbing phthalocyanines cover many important high technical applications including the phthalocyanine therapy cancer , optical data storage and reverse storable absorbers . Phthalocyanine in polymer phases is part of macromolecular metal complexes . Several authors have described the synthesis of phthalocanine polymer (3) .

From phthalocyanine polymer have better performance characteristics than phthalocanine complexes from the structure point of view , the marcrocyclic compounds in polymer phases are subdivided into three types (4,5) .

1. Phthalocyanine is bound to polymer backbond by interaction between the metal of the phthlocyanine and a polymer doner ligand or via statics interaction between a charged phthalocynine and a charged polymer chain . They are mainly investigated for their activity in catalysis or photocatalysis .

2. The ligand phthalocyanine is part of a polymer network or chain like in this study . these polymers are insoluble in organic solvents , but exhibit good thermal stability high electrical conducivity and good catalytic or electrochemical activity .

3. The metal ion in the core of the phthalocyanine ligand is part of a polymer chain . The stacking of Phthalocyanines to high electrical conductivity of the polymers.

The present study deals with the synthesis and characterization of 1 , 4 – diazothenylene – bridged Fe-phthalocyanine polymer and the preliminary of it's electrical properties .

Experimental

A. Chemical Materials

$FeCl_2$, urea, 3–nitrophthalic acid , Ammonium Molybdate, nitrobenzene , methanol , $Na_2S.9H_2O$, $NaNO_2$, HCl , Aceticanhydrid, 1 , 4 – dinitrobenzen and CH_3COONa , DMSO, 3-nitrophthalic anhydried was synthesized according to ref. (6).

B. Instruments :

FT-Infrared spectrometer made shimadzu model (Pye -unicam Sp3 – 300 S) in the range (4000 – 500 cm^{-1}) was used .

U.V- Visible spectrometer was recorded on thermosupertonic Iteelios V (4. 60) was used .

Electrical conductivity (Voltmeter , power supply , resistance , temperature recorder , and measured sample cell) was used under vacuum in department of chemistry , college of Sciences .

1-1 Synthesis of Iron (II) tetranitrophthalocyanine

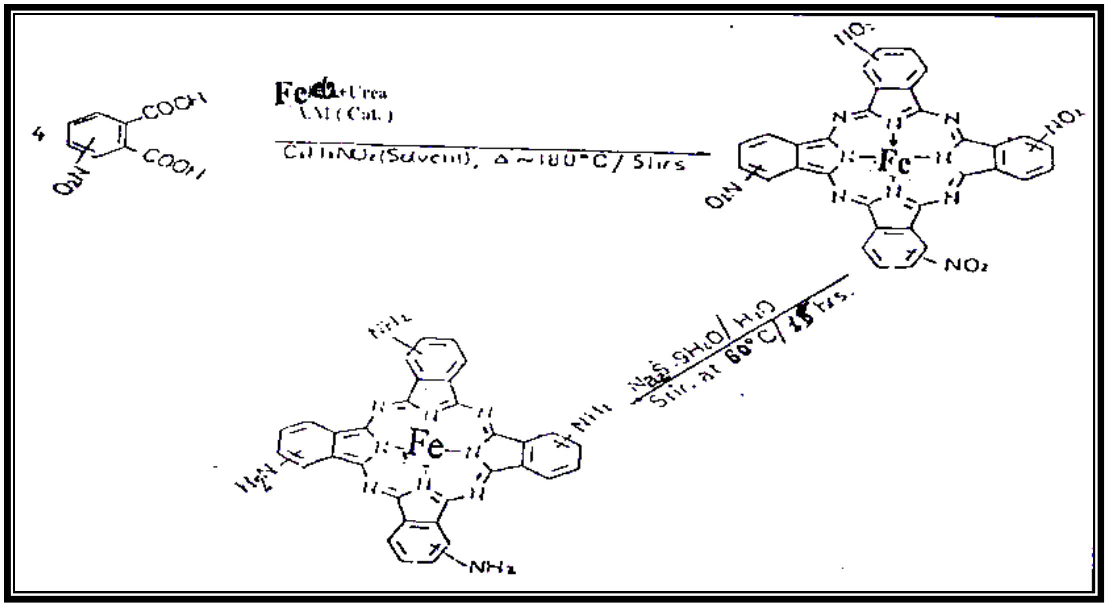
0.5 g (0.005 mole) Iron (II) chloride , 5 . 54 g (0.092 mole) urea , 3.28 g (0.018 mole) nitrophthalicanhydried and 0.075 g of ammonium molybdate were dissolved and mixed with nitrobenzene . After mixing , It was refluxed at (180 – 185 C) for (5 h) . The product was purified in three steps by methanol , (6 m) HCl , (20 %) NaOH Solution , and them washed with hot water . Iron (II) tetranitrophalocyanine shown in the scheme (I) is only one of the possible structural isomers of the complex (6) .

1-2 Synthesis of Iron (II) tetra aminophthalocyanine

4 g (0.005 mole) from nitro compound was dissolved in (100ml) water and 20 g from $Na_2S.9H_2O$ was added . The mixture was stirred under reflux at (60 C) for (18 h) . The solid product separated by □ initroben and treated with 100 ml (1N HCL) and. The product was washed with water to remove the (NaCl , NaOH) .

Iron (I) tetra aminophthalocyanine was filtered and dried at (50C) in a vacuum oven 1 , 4 – □ initrobenzene was prepared by the same procedure (8) .

Shown in the scheme (I) .



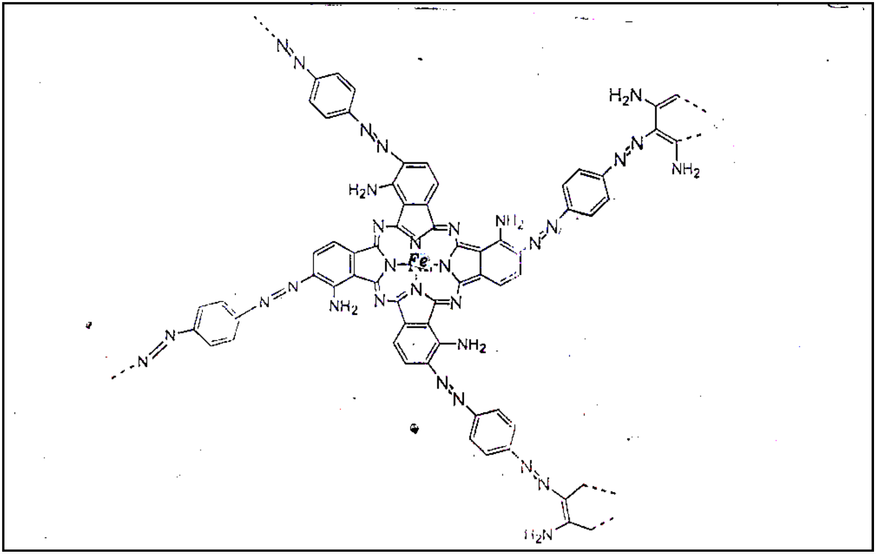
Scheme (1)

1-3 Synthesis of 1, 4 diazophenelyene bridge Fe- phthalocyanine polymer .

Preparation of the diazonium salt was based on piccard's study (9) . 0.54 g of 1 ,4 – diamino benzene .

Was dissolved in a hot mixture of 2 – 4 ml concentrated HCl and 20 ml of water . Temperature was maintained at (0 C) and the solution was tetraazotised by the addition of 0.7 g of $NaNO_2$ in 5 ml of water with in 1 min. The tetraazo solution was left in ice for 5 min and then added to a suspension of 0.5 g Iron (II) tetra amino phthalocyanine and 4 g of crystallized CH_3COONa in 50 ml of water . It was stirred well and allowed of stand (1h) . The resultant mixture was heated up to (80 C) and purification was made by hot water .

Scheme (2) shows only one of the structural isomer of the polymer .



Scheme (2)

Results and discussion :

The synthesis of Iron (II) tetranitrophthalocyanine , Iron (II) tetra aminophthalocyanine and 1 , 4 – diazo phenelyene – bridge Fe – phthalocyanine polymer were confirmed by IR-Spectra(5) taken in KBr. The nitro phthalocyanine complex show characteristic – NO_2 peaks at 1340 cm^{-1} and 1540 $^{-1}$. The characteristic nitro peak at 1340 cm^{-1} disappeared after reduction and the – NH2 stretching peak appeared in the polymer at 3450 cm^{-1} , C – H at 3000 and 749 cm^{-1} , C = C peak at 1602 , 1620 , 1506 , 4173 , 1396 , 937 , 816 , 667 , and 560 , and aryl-N-Peak at 1246 cm $^{-1}$. These peaks are represented in Fig (1) . Fig (2) represent U.V-visible spectra of Iron (II) tetranitrophthalocyanine , Iron (II) tetra aminophthalocyanine and 1 , 4 – diazophenelyene – bridge Fe – phthalocyanine polymer , have been studied with the using of dimethlylsulphoxide . All of they showed the phthalocyanine special two bands , the first at 600 – 700 nm which is called Q-bands and the second one at 300 – 400 nm which is called B-band[5].

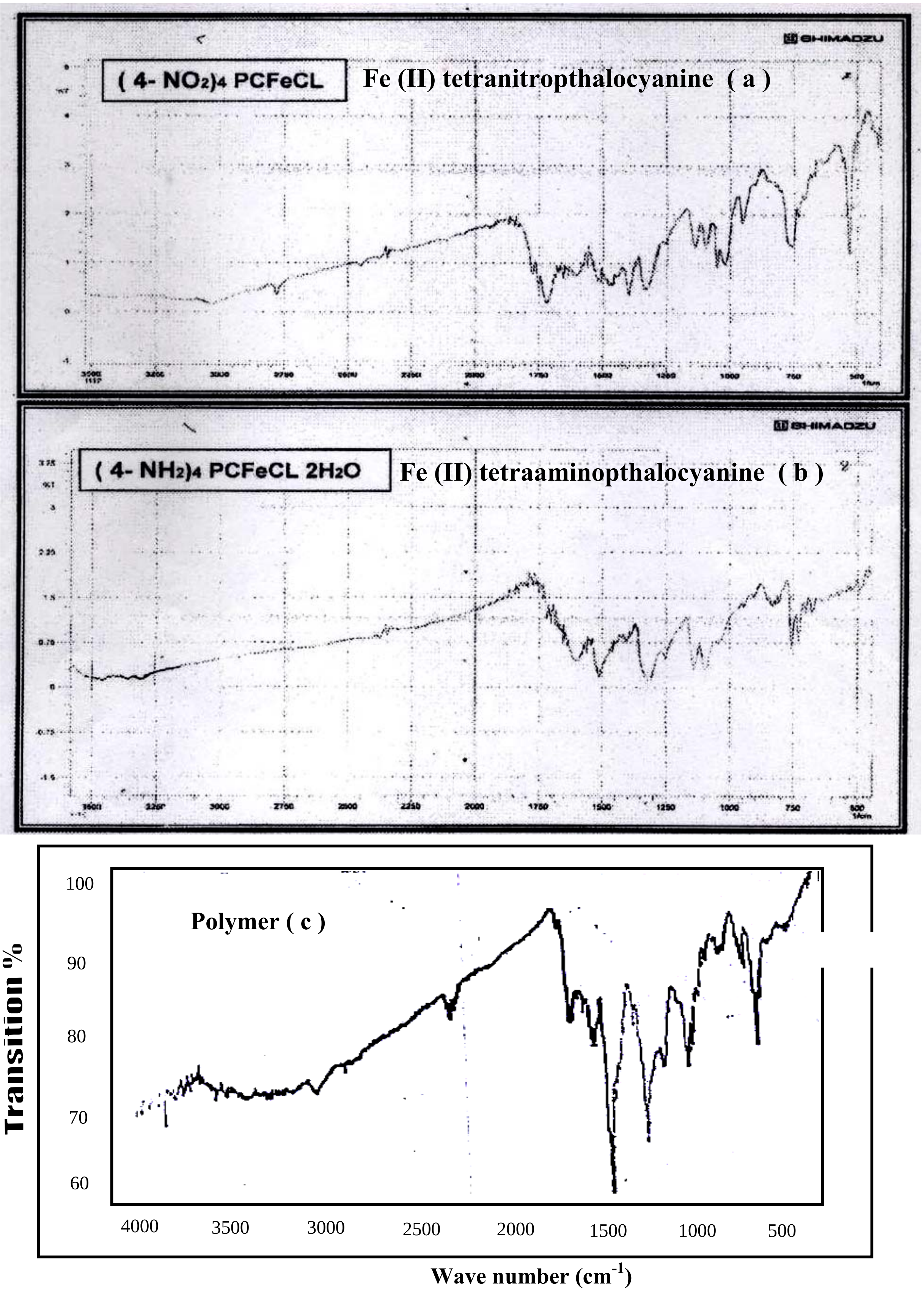
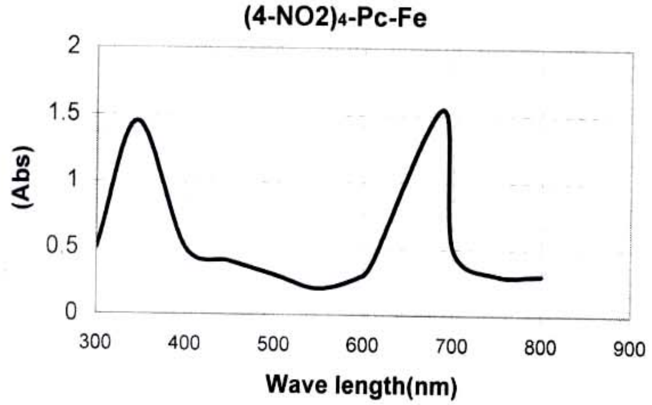
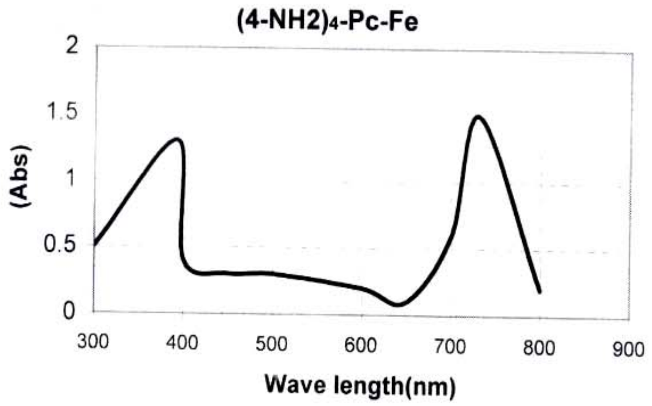


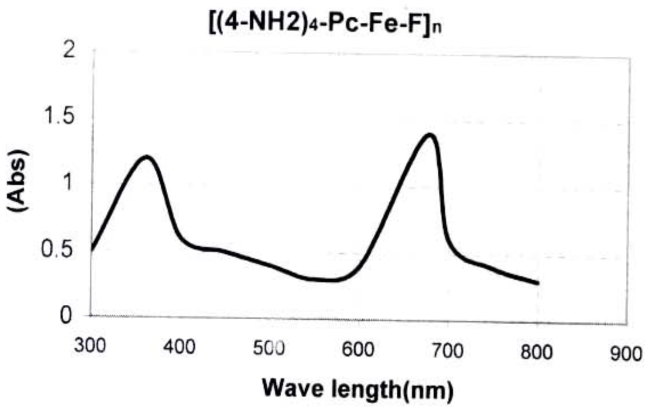
Figure (1) . Infrared spectrum of compounds a , b , c



Fe (II) tetranitropthalocyanine (a)



Fe (II) tetraaminopthalocyanine (b)



Polymer (c)

Figure (2) .u-v , v- visible spectrum of compounds a, b, c

Electrical conductivity :

The electrical properties of phthalocyanine and related compounds defend very much up on the morphology of the Macrocyclic systems to achive good semiconducting or even conducting properties .

Doping of the polymer iodine was acheaved by the dissolved of polymer in ccl4 and stirrer at (70 C) for (72 h) , after that the polymer doping was filtered and dried in vaccum oven at (50 C) .

The maximum conductivity of the doped polymer samples is (3–52x10^{-4} ohm^{-1} cm^{-1}) . it increases conductivity of conjugated by forming ions (10) .

Conclusions :

1 , 4 – diazophenelyene – bridge Fe phthalocyanine polymer was synthesized and characterized . The problem in dissolving phthalocyanine polymer makes their characterization or in some cases impossible .

The present of (- N = N -) bond was proven by FT-IR absorption band at around 1400 cm^{-1} and shoulder formation at around 690 nm in the UV-Visb Spectrum . The low conductivity of the polymer was increased up to 10^{-1} ohm^{-1} cm^{-1} by doping with iodine and the values of (E) and ( ) were calculated to the polymer and iodine – doped polymer that it’s showed in table (1) .

Table (1) shown the values of Δ E and

Sample	E (ev)	6 (ohm^{-1} cm^{-1})
Polymer	0.247	1.841 x 10^{-4}
Iodine – doped polymer	0.0254	6.112 x 10^{-4}

The conductivity was increased to the peroximity of distance between the energy levels which was ralated reversally with the value of conductivity .

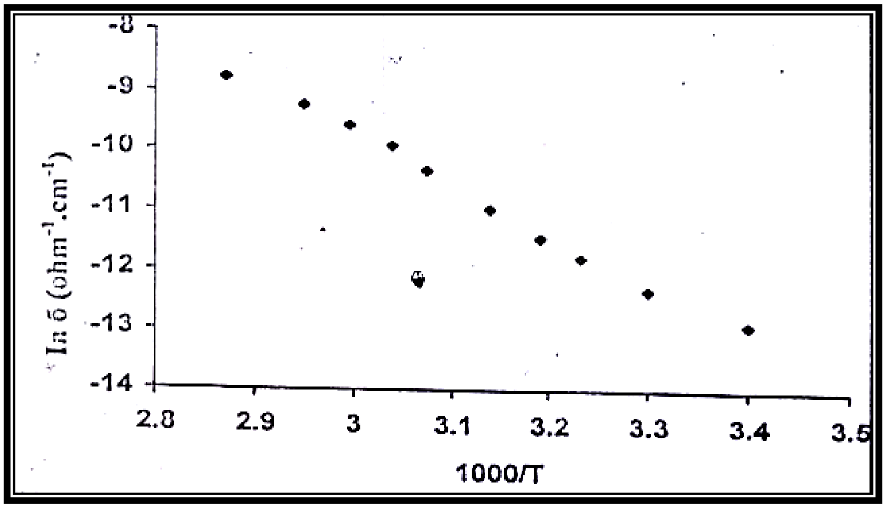


Fig (3) Conductivity of 1 , 4 – diazophenylene – bridged Fe – Phthalocyanine polymer

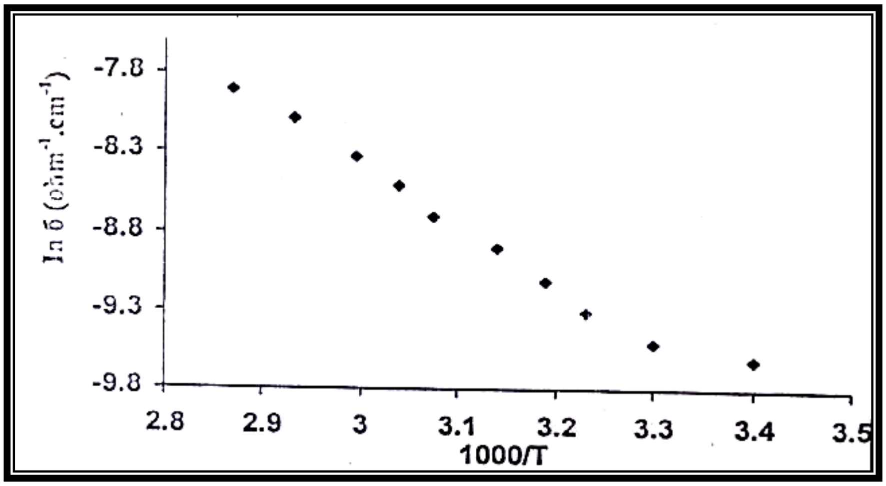


Fig (4) Conductivity of iodine – doped 1 , 4 – diazophenylene – bridged Fe – Phthalocyanine polymer

References :

1- Thami, T. Simon , J. and Jaffrezic , N ; ***Bull Soc. Chem Fr ;*** 1996,**133**,762

2- Boas, J , F. Feilding, P.E.and mockoy,A. G; ***Aust. J. Chem***.; 1974, **27** ,7 .

3- Gregory P . ; ***J . Purphyrins phthalocyanines*** ; 2000, **4**, 432.

4- Lezonff ,C.C.; ***phthalocyanines:*** Properties and Applications 1999,**2** ,59 .

5- Somani , P. R ; ***Materials chemistry and physies*** .; 2002 , **77** , 117 .

6- Vogel , H. ; ***Practieal organic chemistry***.,1969,**9**,1076 .

7- Nuchter,M. Microsynth synthesis Application Notes , 2001.

8- Vogel , H. ; ***Practical organic chemistry*** ,1969,**9** , 837.

9- Piccord , ***J. Am . Chem . Soc***.1926, **48** **,** 2878 **.**

10-Wohrle,D.; ***Adv.Polymer.Sc***i.1983, **50**,46.