

PREPARATION AND CHARACTERIZATION  
OF SOME POLYALKYLARYLAMINES

تحضير وتوصيف بعض مركبات عديد الكيل آريل الأمينات  
By

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خلاصة: أمكن الحصول على نواتج عديد الكيل آريل الأمينات مع كميات محددة من كلور سبيد القمدير ( الشنائي ) ، بتفاعل ١ ، ٢ - شنائي كلوريد إيثان مع ميثان - فينيلين شنائي الأمين وبارا - فينيلين شنائي الأمين و { ، ٣ - شنائي أمينو شنائي الفينيل فـس وجود حمض الهيدروكلوريك والكحول الميثيلي كمذيب .  
وأمكن الحصول أيضا على عديد ( كلورو ميثيلين - شبه - ٤ ، ٤ - شنائي الأمتين شنائي الفسل ) من تفاعل الكلوروفورم والبيرين بطريقة متناقة . وتم إثبات تركيب المركبات الناتجة باستخدام طيف الأشعة تحت الحمراء والأشعة السينية .  
وعند تفاعل هذه النواتج مع محاليل مائية لكربونات الأمونيوم أعطت هيدروكلوريدات الكيل آريل أمين المتفاعلة وأخرى التحليل الحراري لهذه المركبات .

ABSTRACT- Adducts of polyalkylarylamines with stoichiometric amounts of stannous chloride were obtained by the reaction of 1,2-dichloroethane with m-phenylenediamine, p-phenylenediamine and 4,4'-diaminodiphenyl in the presence of hydrochloric acid and stoichiometric amounts of stannous chloride in methanol as a solvent. Also, adduct of poly (chloromethyne-co- 4,4'-diaminodiphenyl) was obtained from the reaction of chloroform and benzidine by similar method. The structure of these adducts was confirmed by IR spectroscopy, as well as X-ray diffractometry. These adducts when reacted with aqueous solution of ammonium carbonate gave the corresponding polyalkylaryl-amine hydrochlorides. Also thermal analysis of these adducts were carried out .

## I. INTRODUCTION

The different methods for synthesis of alkylarylamines were investigated. Huerman and Hemmerich [1] reported that the synthesis of alkylarylamines by the reaction of aromatic amines with alcohols required a pressure of 80 bar and a high temperature (280°C). Other methods require the reactions of alkyl chlorides with aromatic amines in the presence of catalysts: lithium amide [2], complex of lithium with naphthalene [3], and ion exchange resin [4]. Also, 2-substituted benzimidazoles or imidazoles have reacted with alkyl iodide in the presence of potassium hydroxide [5] to give the corresponding alkyl imidazole derivatives. Recently, Studnicki [6-11] concluded that the chloroalkylarylamines were prepared by the reaction of polychloroalkanes with aromatic amines in the presence of catalytic amounts of stannous chloride and hydrochloric acid in methanol as solvent at 50-60 °C.

The growing interest in using alkyarylamines as corrosion inhibitors [11] of stainless steel in concentrated hydrochloric acid prompted us to undertake the title investigation. The aim of this work was to obtain adducts of polyalkylarylamines with stoichiometric amounts of  $\text{SnCl}_2$ . Further, these adducts were reacted with ammonium carbonate to give polyamine hydrochlorides which will be examined as polyelectrolytes for water treatment in our next investigations.

## 2. EXPERIMENTAL

### 2.1-Synthesis :

#### Adducts of polyalkylarylamines with $\text{SnCl}_2$ (I-IV) :

The adduct of poly (ethylene-co-p-phenylenediamine) with  $\text{SnCl}_2$ , (I), was prepared by reaction of 1,2-dichloroethane with p-phenylenediamine in the presence of hydrochloric acid and stoichiometric amount of  $\text{SnCl}_2$  in methanol as solvent. Thus, 250  $\text{cm}^3$  of methanol and p-phenylenediamine (68.6 gm, 0.5 mol.) were placed in 1000  $\text{cm}^3$  flask equipped with a reflux condenser and stirrer. Concentrated hydrochloric acid (250  $\text{cm}^3$ ) was added dropwisely into the flask, then metallic tin (146 gm) was added slowly at 77°C and at this temperature the substrates were stirred for 1 hr. 1,2-Dichloroethane (44  $\text{cm}^3$ , 0.56 mol) was added slowly at 53°C and at this temperature the content of the flask was stirred for two hours. After cooling, product (I) was precipitated.

Similarly, adducts of poly (ethylene-co-m-phenylenediamine) (II), poly (ethylene-co-4,4'-diaminodiphenyl) (III), and poly (chloromethyne-co-4,4'-diaminodiphenyl) (IV) with  $\text{SnCl}_2$  were prepared by reactions of the corresponding aryldiamines and dichloroalkanes.

#### Polyalkylarylamine hydrochloroides (V-VIII) :

Poly (ethylene-co-phenylenediamine) hydrochloride (V) was prepared by the reaction of adduct (I) with aqueous solution of ammonium carbonate. Thus, adduct (I) (15.45 gm) and ammonium carbonate (40 gm) were placed in a 1000  $\text{cm}^3$  flask equipped with a reflux condenser and stirrer. After adding water (400  $\text{cm}^3$ ) slowly, the mixture was stirred at 60°C for 2 hr. Tin carbonate precipitated as a black precipitate (3.35g) was filtered off and the clear solution was evaporated to dry residue. The dry residue was extracted with 99% ethanol. After evaporating the ethanolic solution, the product (V) was obtained.

Preparations of poly (ethylene-co-m-phenylenediamine) (VI), poly-(ethylene-co-4,4'-diaminodiphenyl) (VII) and poly (aminomethyne-co-4,4'-diaminodiphenyl) (VIII) hydrochlorides were carried out similarly.

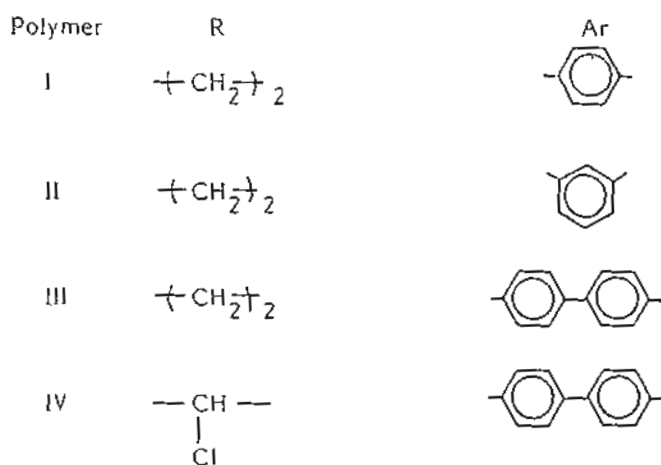
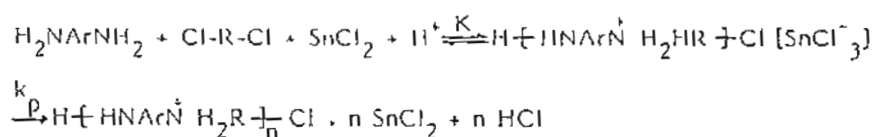
### 2.2- Analysis

The infrared spectra were recorded by a Beckman 4200 Spectrophotometer. The

proton magnetic resonance spectra (in DMSO- $d_6$  as a solvent and using TMS as a zero reference) were obtained at room temperature with a Varian EM-390 spectrometer operating at 90 MHz. X-ray diffractometry data of adducts of polyalkylarylamines with  $\text{SnCl}_2$  were obtained with X-ray diffractometer Siemens D-500, Cu lamp, Ni filter. Thermal analysis was recorded on a Shimadzu DT 30. Thermal Analysis at a heating rate of  $10^\circ\text{C}/\text{min}$ . in  $\text{N}_2$  atmosphere. Tin analysis was carried out by the gravimetric method of Gilman and Rosenberg [12].

### 3- RESULTS AND DISCUSSION

In the present work adducts of polyalkylarylamines with  $\text{SnCl}_2$  (I-IV) were obtained from the reaction of di- or polychloroalkanes with aromatic diamines in the presence of hydrochloric acid and stoichiometric amounts of stannous chloride as illustrated in Scheme (1).



Scheme (1)

X-Ray diffractometry, Tables (1-4), indicates that aromatic diamines with di- or polychloroalkanes in the presence of  $\text{SnCl}_2$  in methanol give additive products, which contain  $\text{SnCl}_2$  chemically bounded with polyalkylaryamine hydrochlorides. Fig. 1 illustrates the X-ray diffraction pattern of adduct (I) as an example. These results are in agreement with those reported by Studnicki [11]. Table 5 represents the analytical data of adducts of polyamines (I-IV)

and the obtained results agreed well with the calculated values. IR spectra [13] of these adducts shows  $\nu^{+}\text{NH}_3$  at  $2850\text{cm}^{-1}$ ,  $\nu^{+}\text{NH}_2$  at  $2575\text{cm}^{-1}$  and  $\gamma^{+}\text{NH}_3$  at  $1500\text{cm}^{-1}$  and  $\gamma^{+}\text{NH}$  at  $1600\text{cm}^{-1}$ . Fig. 2 illustrate the IR spectrum of adduct (II) as an example. Table 6 shows the thermal analysis data of adducts of polyalkylarylamines with  $\text{SnCl}_2$ . Decomposition of adduct (I) began at  $145^\circ\text{C}$  (the lowest value), but adduct (III) decomposed at  $300^\circ\text{C}$  (the highest value). Fig. 3 illustrates the TG, DTG and DTA curves of adduct (I) as an example.

Table 6 represents the structures and analytical data of the products of the reaction adducts of polyalkylarylamines and  $\text{SnCl}_2$  with aqueous solution of ammonium carbonate. Products of the reaction are polyalkylarylamines hydrochlorides. These products will be, in the next investigations, examined as polyelectrolytes in water treatment. IR spectra [13] of polyalkylarylamines hydrochlorides (V-VIII) show  $\nu^{+}\text{NH}_3$  and  $\nu^{+}\text{NH}_2$  at  $2400\text{-}3600\text{cm}^{-1}$  (broad),  $\gamma^{+}\text{NH}_3$  at  $1500\text{cm}^{-1}$ ,  $\gamma^{+}\text{NH}_2$  at  $1610\text{cm}^{-1}$  and  $\nu^{+}\text{C-N}^+$  at  $1400\text{cm}^{-1}$  (strong). Also, the  $^1\text{H}$  NMR spectrum [14] of neutralized product of polymer (VIII) by ammonium hydroxide to give the corresponding free polyalkylarylamines, showed the aromatic protons (8 H) of two pairs of symmetric signals around  $\delta 7.2$ ,  $6.6\text{ ppm}$  and around  $\delta 7.05$ ,  $6.45\text{ ppm}$  corresponding to two AA' BB' spin system, which may most probably be assigned to proton of two para disubstituted benzene rings, the aliphatic proton (1 H) of multiplet broad peak at  $\delta 4.9\text{ ppm}$  due to C-H and the amino protons (4 H) of broad peak around  $\delta 3.1\text{ ppm}$  corresponding to primary and secondary amino groups. Fig. 4 illustrates the  $^1\text{H}$  NMR spectrum of neutralized product of polymer (VIII) as an example.

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Table 1 : X-ray diffraction data of adduct (I).

dA°	I/I°	dA°	I/I°	dA°	I/I°	dA°	I/I°
10.281	18.12	5.039	21.74	3.243	8.70	2.600	34.78
10.163	12.32	4.461	13.04	3.198	18.84	2.564	29.71
8.845	30.43	4.171	21.74	3.175	14.49	2.449	22.46
8.672	18.84	3.986	15.94	3.058	17.39	2.411	11.59
7.762	23.19	3.850	37.68	2.988	17.39	2.350	66.67
7.628	25.36	3.786	37.68	2.950	35.51	2.287	10.87
6.511	12.32	3.770	50.72	2.931	39.13	2.186	26.29
6.326	57.97	3.738	100.00	2.831	8.70	1.993	17.39
5.471	18.12	3.590	74.64	2.780	44.20	1.969	33.33
5.405	55.80	3.466	28.26	2.714	14.49	1.859	21.74
5.308	22.46	3.389	34.06	2.698	20.29		

d- interplaner spacing A°. I/I°- relative intensity.

Table 2: X-ray diffraction data of adduct (II)

dA°	I/I°	dA°	I/I°	dA°	I/I°	dA°	I/I°
12.109	14.29	3.067	50.44	2.730	88.31	1.937	45.45
10.782	11.69	3.693	19.48	2.637	19.48	1.841	7.79
8.192	10.39	3.534	9.09	2.564	15.58	1.804	10.39
6.916	44.16	3.440	100.00	2.508	50.65	1.774	20.78
6.194	11.69	3.401	67.53	2.356	14.29	1.743	15.58
5.791	64.96	3.314	10.39	2.309	29.87	1.731	11.69
5.011	44.16	3.100	25.97	2.249	28.96	1.698	22.08
4.646	14.29	3.079	11.69	2.206	18.18	1.678	12.99
4.400	10.39	3.020	44.16	2.191	15.58	1.580	16.88
4.311	12.99	2.894	20.78	2.108	9.09		

Table 3 : X-ray diffraction data of adduct (III).

dA°	I/I°	dA°	I/I°	dA°	I/I°	dA°	I/I°
6.511	4.41	4.114	8.82	3.132	11.52	2.127	8.58
5.791	7.35	3.738	100.00	3.079	40.93	2.103	17.16
5.539	33.82	3.576	7.30	2.898	9.07	1.852	14.71
5.011	6.13	3.209	21.57	2.780	20.34	1.781	5.88
4.210	25.49	3.164	6.37	2.254	7.60	1.427	4.41

Table 4 : X-ray diffraction data of adduct (IV)

dA°	I/I°	dA°	I/I°	dA°	I/I°	dA°	I/I°
5.539	28.44	3.506	4.22	2.988	5.11	2.292	8.00
4.599	6.67	3.440	6.67	2.849	8.44	2.117	6.44
4.461	3.56	3.209	17.33	2.771	10.67	2.103	16.22
4.191	71.11	3.164	30.22	2.747	12.89	2.045	4.89
3.738	100.00	3.121	12.00	2.542	6.00	1.848	7.56
3.590	9.33	3.079	41.56	2.344	4.00		

Table 5 : Analytical data of adducts of polyalkylarylamines (I-IV) with SnCl<sub>2</sub>

Adduct	Molecular formula	N%		Cl%		Sn%	
		Calc.	Found	Calc.	Found	Calc.	Found
I	C <sub>8</sub> H <sub>12</sub> SnCl <sub>4</sub> N <sub>2</sub>	7.05	6.96	35.77	35.45	29.97	29.68
II	C <sub>8</sub> H <sub>12</sub> Sn <sub>2</sub> Cl <sub>6</sub> N <sub>2</sub>	4.77	4.58	36.29	36.02	40.54	40.89
III	C <sub>14</sub> H <sub>16</sub> SnCl <sub>4</sub> N <sub>2</sub>	5.92	5.87	30.02	29.73	25.16	24.91
IV	C <sub>13</sub> H <sub>13</sub> SnCl <sub>5</sub> N <sub>2</sub>	5.67	5.62	35.97	35.67	24.11	24.35

Table 6. Thermal analysis data of adducts of polyalkylarylamines with  $\text{SnCl}_2$  (I-III).

No	extremum DTA (°C)	extremum DTG (°C)
I	145, 165, 230, 390, 370, 415, 450	145, 165, 230, 255, 275, 305, 370, 415
II	205, 240, 255, 355, 475	240, 340, 475, 700
III	300, 345, 375, 680, 720, 755, 780	300, 325, 345, 355, 400, 455

Table 7. Structure and analytical data of polyalkylarylamines hydrochlorides (V-VIII).

Product	Structure	N %		Cl %	
		Calc.	Found	Calc.	Found
V	$\left[ \text{HN} - \text{C}_6\text{H}_4 - \text{NH} - (\text{CH}_2)_2 \right]_n \cdot 2n \text{HCl}$	13.53	13.35	34.30	33.83
VI	$\left[ \text{HN} - \text{C}_6\text{H}_3 - \text{NH} - (\text{CH}_2)_2 \right]_n \cdot 2n \text{HCl}$	13.53	15.41	34.30	34.51
VII	$\left[ \text{HN} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{NH} - (\text{CH}_2)_2 \right]_n \cdot 2n \text{HCl}$	9.89	9.83	25.09	24.86
VIII	$\left[ \text{HN} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{NH} - \underset{\text{NH}_2}{\text{CH}} \right]_n \cdot 2n \text{HCl}$	14.79	14.58	25.00	23.76

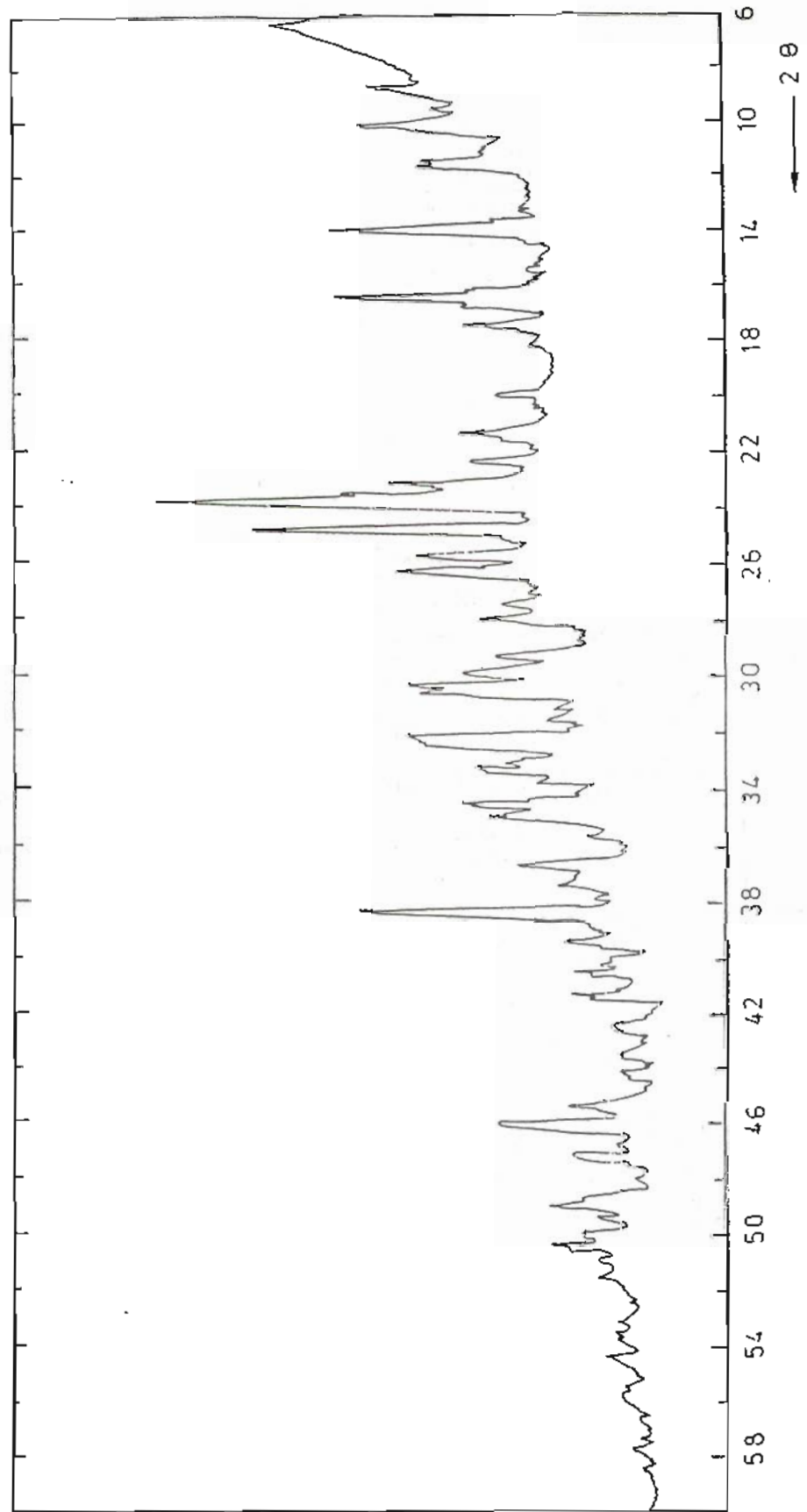


Fig.(1): x-Roy diffraction pattern of adduct (I).



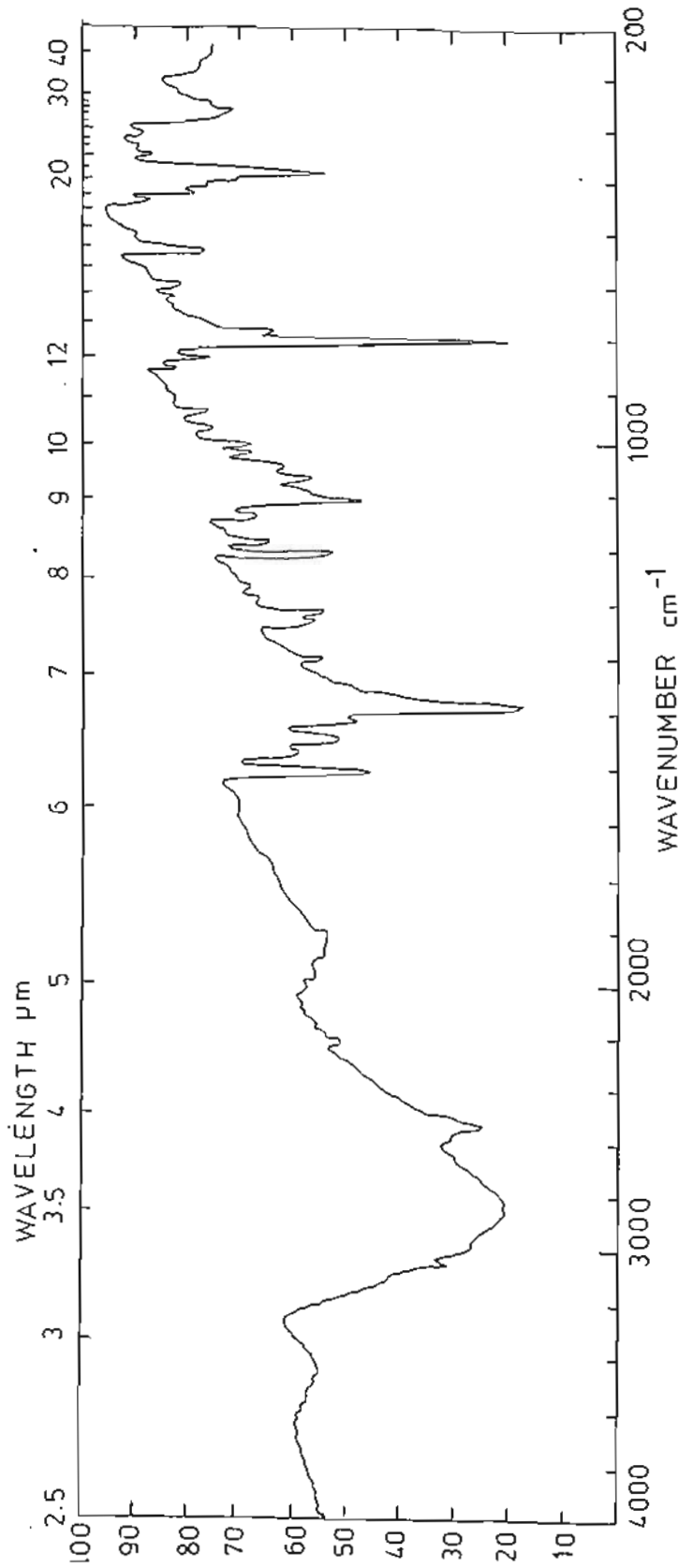


Fig.(2): IR Spectrum of adduct (II)

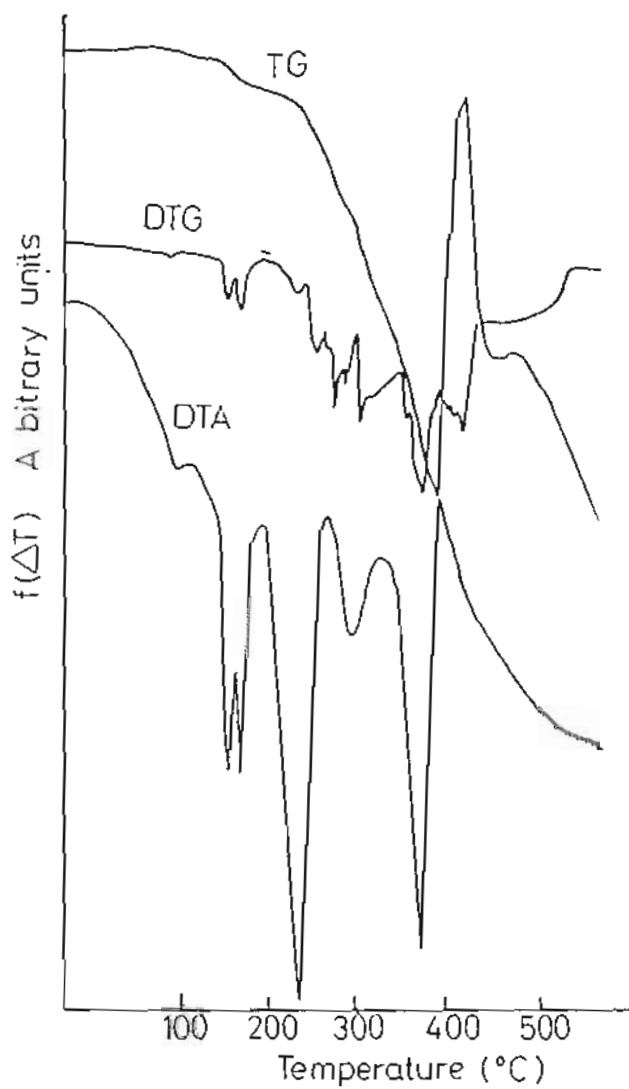


Fig. (3): TG, DTG and DTA curves of adduct (I).

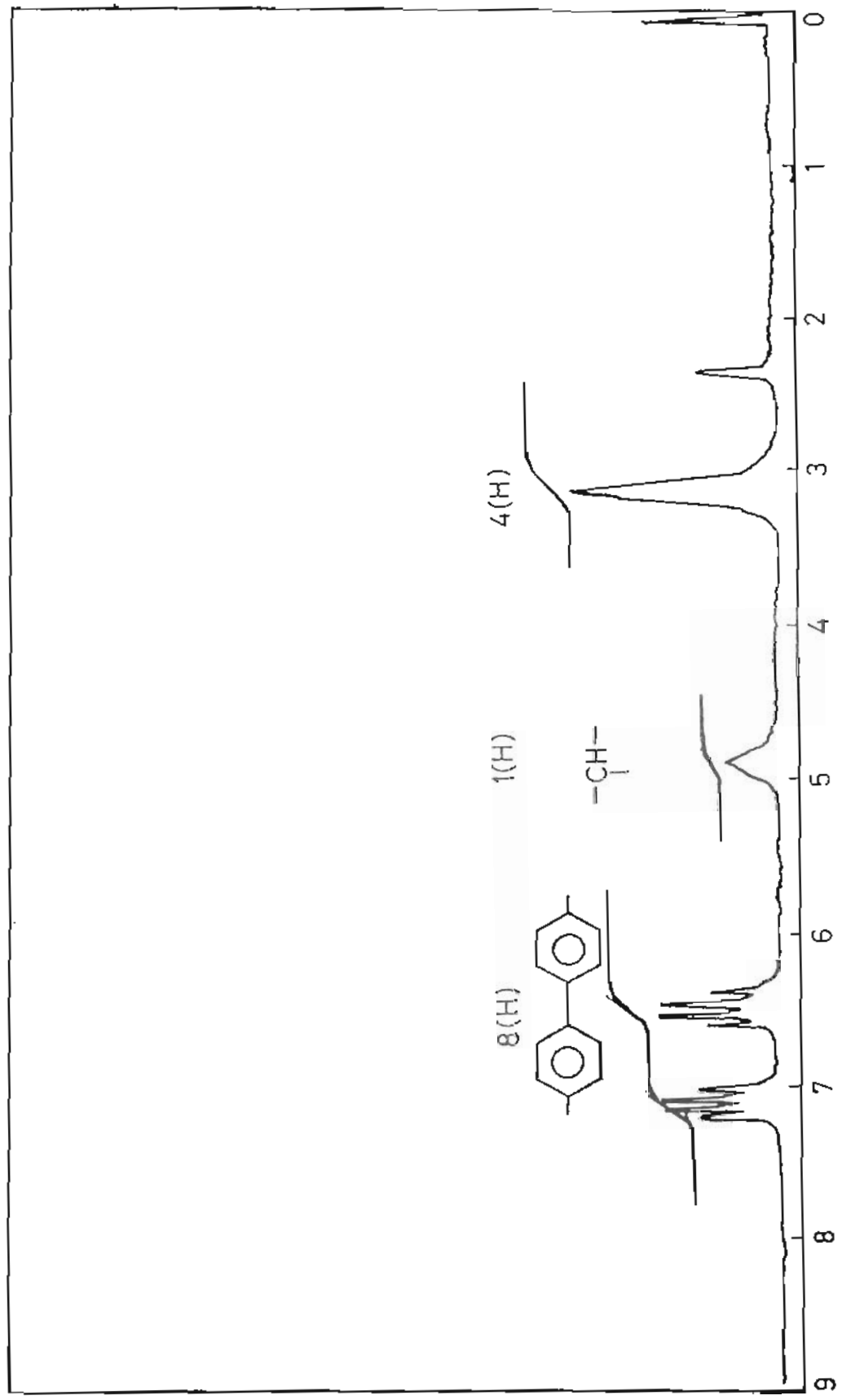


Fig. 4.  $^1\text{H}$  NMR spectrum of neutralized product of polymer VIII.