

## Synthesis of New Polyester-Amides from Polyvinyl Alcohol and Convert Some of Them to Polyester-Imide

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### Abstract

New fifteen polymers were prepared by modification of polyvinyl alcohol; these polymers were prepared by two steps. The first step was included reaction 1 mole of poly vinyl alcohol with 1mole of adipoyl chloride to produce ester-acid chloride polymer .Second step was included reaction the produced polymer in step one with different amines to obtained new ester-amide polymers .Four of them were reacted with acid chloride (acetyl chloride and benzoyl chloride) in DMF to produces ester imide polymers in third step. All these polymers have different physical properties which may be used in different applications. The prepared polymers were characterized by FTIR, <sup>1</sup>HNMR spectroscopy, and by measuring their melting points, softing points, solubilities.

Keywords: poly ester-amide, poly ester –imide, polyvinyl alcohol.

### Introduction

Poly (vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer, because of it is non toxic, non cinogenic and bioadhesive, PVA has been used for various biomedical applications<sup>1</sup>. In additional to the biological activities PVA is used in practical applications because of its easy preparation, excellent chemical resistance, and physical properties.<sup>2</sup>

PVA can be modified to ester polymers by many methods. Polyesters are one of the most versatile synthetic polymers. They are widely used commercially as fibers, plastics, and coatings<sup>3,4,5</sup>. They are heterochain macromolecules that possess carboxylate ester groups as integral components of their polymer backbones.

On the other hand polyamides represent a class of high performance usually formed by the reaction of diamines and diacylchloride. These polymers have found use in a wide variety of applications since they possess many desirable characteristics, such as good process ability, good mechanical properties, good thermal stability, and chemical resistance<sup>6,7</sup>.

Imide is a functional group consisting of two carbonyl groups bound to nitrogen. In chemical industry, many imides are monomers used to make polyimides. The imides most commonly used for this are based on aromatic dicarboxylic acids of moderately high molecular weight such imides contain a heterocyclic.

Aromatic polyimides are well accepted as high performance polymer materials for their excellent mechanical strength and high thermal stability and balanced mechanical and electric properties<sup>(8-12)</sup>.

Therefore, it was thought to be of interest to combine two of the above-mentioned ester and amide or imide groups together in a polymeric framework to give new polymers which may be used in different application. In this research includes preparing of ester –acid chloride polymers through the reaction of acid chloride with polyvinyl alcohol, the produced polymers were modified to ester –amide by reaction with different amines to yield ester –amide polymers. Then four of them; in third step; were reacted with acid chloride in DMF as a solvent to produce polyester imide As shown in scheme (1).

### Experimental

1. Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus.
2. Infrared spectra were recorded on (FT-IR) infrared spectrophotometer as KBr disc in Baghdad University, College of Science, Chemistry Department.
3. Softening point were determined by using Reichert Thermovar with Reichert-Jung Temperature Controller.

4.  $^1\text{H-NMR}$  Spectra were recorded on Shimadzu and tetramethyl silane as internal standard in Ahl-Albate- University in Jordon.

### 1-Preparation of poly[vinyl(acid chloride adipate)]<sup>13</sup> (1)

(1mol.) of poly vinyl alcohol was placed in 20 ml DMF, bolt –head flask was provided with a reflux condenser and dropping funnel. The flask was cooled in ice and the (1mol.) of adipoyl chloride was introduced into the dropping funnel ,acotton wool (or calcium chloride )guard tube was insert into the mouth of the funnel .The adipoyl chloride was added drop wise (45mintes) to the polyvinyl alcohol with frequent shaking .The ice was removed and refluxed for 1\2 hr. The product was poured into the water, washed with a little sodium bicarbonate, washed with water then with ethanol and purified by dissolving it in DMSO and reprecipitating from ethanol.

### 2- Preparation of ester –amide polymers<sup>14</sup>(2a-k)

A mixture of ester –acid chloride polymer (0.1mol) and pure amine (0.1mol) in dimethyl formamide (DMF) 25 ml was refluxed for (8-12) hrs. The mixture was shaken with excess of dilute HCl to remove amine and its salts. The product was washed with 5-10ml of water, and the solid separated was filtered and purified by dissolving in suitable solvent (DMSO) and reprecipitating from another solvent such as (water, ethanol, acetone THF,CHCl<sub>3</sub>).

### 3-preparation of poly [vinyl (N- phenyl substituted phenyl imidyl) a dipate]<sup>15</sup> (3a-c)

A mixture of poly [vinyl (N- Substituted phenyl )amido adipate] (0.02mole) and 0.004gm. sodium hydroxide was dissolve in 10ml DMF and Benzoyl chloride (0.02mole) was added in round flask provided with reflux condenser, then the mixture was refluxed for (6-8) hrs .The product was washed with water then with benzene and purified by dissolving the product by DMSO and reprecipitating from

another solvent such as (acetone, THF , benzene).

### 4-preparation of poly [vinyl (N-n- propyl methyl imidyl) adipate] (6-10)<sup>16,3j</sup>

A mixture of poly [vinyl (N-n- propyl) amido adipate] (0.01mol) and acetyl chloride (0.01mol) in dimethyl formamide (DMF) 25ml was refluxed for 6hrs. After cooling the excess of solvent was removed under vacuum and the solid separated was filtered and purified by dissolving in suitable solvent (DMSO) and reprecipitating from another solvent ethanol.

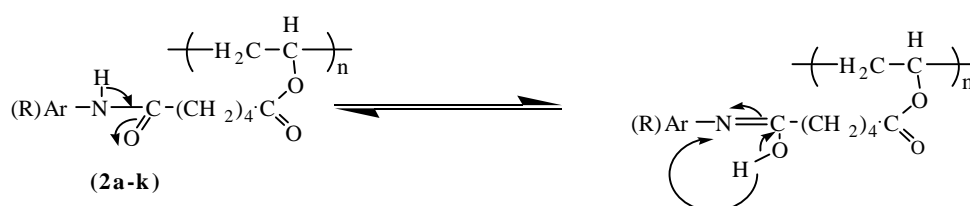
### Results and Discussion

The first included synthesis of polyester – acid chloride was achieved from reaction of (1 mole) poly vinyl alcohol with (1mole) adipoyl chloride in DMF Scheme (1).

The FTIR spectrum of poly [vinyl(acid chloride) adipate] showed the absorption at 1700  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  ester group, 1730  $\text{cm}^{-1}$  for carbonyl acid chloride  $\nu(\text{C=O})$ , and 810  $\text{cm}^{-1}$  due to  $\nu(\text{C-Cl})$ .

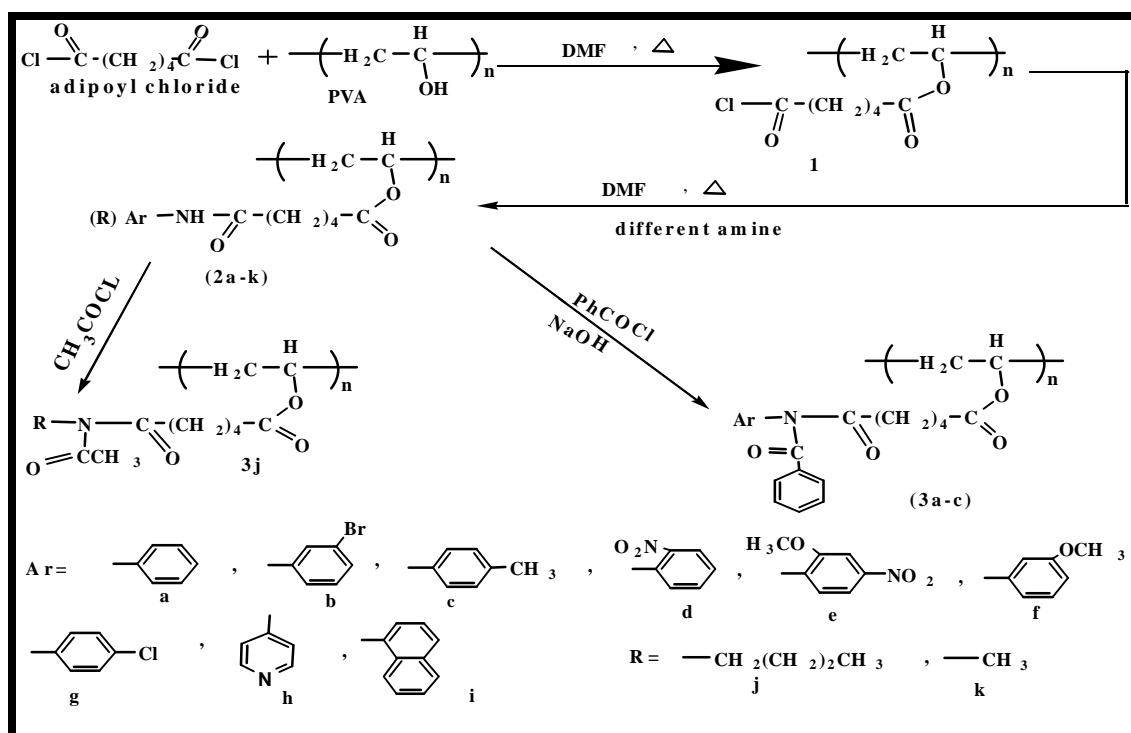
Poly ester-amides were prepared through the reaction of poly ester –acid chloride with different amine in same solvent. The structures of poly ester –amides (2a-k) were confirmed by physical properties which are listed in Table (1). FTIR spectra showed the absorptions at region (3360-3433)  $\text{cm}^{-1}$  due to (N-H)group,(1735-1700)  $\text{cm}^{-1}$  for  $\nu(\text{C=O})$  ester,(1666-1604)  $\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  amide, (1610-1500)  $\text{cm}^{-1}$  due to  $\nu(\text{C=C})$ aromatic, (3116-3000)  $\text{cm}^{-1}$  for  $\nu(\text{C-H})$  aromatic), (2993-2761)  $\text{cm}^{-1}$  due to  $\nu(\text{CH})$  aliphatic and absorption of 1490  $\text{cm}^{-1}$  due to nitro group ( $\text{NO}_2$ ) all these regions are listed in Table (5).

The  $^1\text{H-NMR}$  spectra of poly ester –amide (2a, 2f, 2g, 2h) showed singlet signal at ( $\delta$ 8- $\delta$ 8.3) ppm which was assigned to one proton of  $-\text{NHCO}-$  group and one singlet signals at (11.3-12)ppm assigned to one protone of tautomeric state and signals at (7.1-6.5) ppm assigned to ( $\delta\text{Ar-H}$ )all these regions are listed in Table ( 6 ).



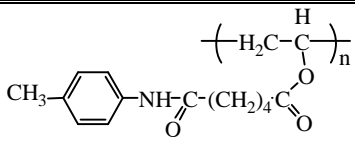
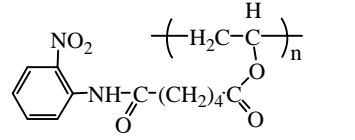
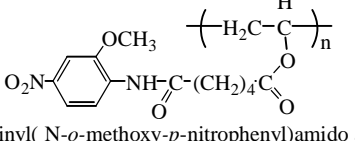
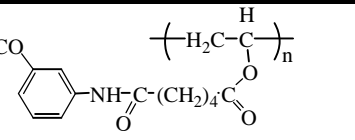
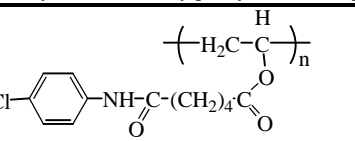
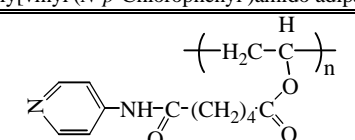
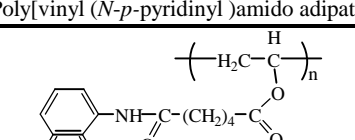
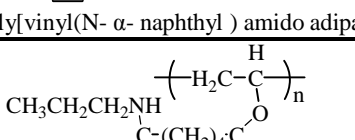
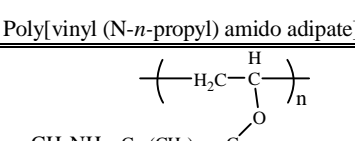
The third step included the reaction of prepared poly ester-imides (3a-c) was prepared from reaction of poly ester-(N-substituted phenyl) (2a-c) amides with Benzoyl chloride in NaOH. Structure of these polymers (3a-c) were confirmed by physical properties which are listed in Table (2) The FTIR Spectra showed stretching band at  $(1750-1728) \text{ cm}^{-1}$  for ester carbonyl (C=O),  $(1670-1635) \text{ cm}^{-1}$  for imide carbonyl (C=O) and showed the disappearance of (NH) bond in some prepared

polymers and the (N-H) bond decreased in the other prepared polyimides all these regions are listed in Table (5). The poly [vinyl (N-*n*-propyl methyl imidyl) adipate] 3j was prepared from reaction of poly [vinyl (N-*n*-(propyl)amido adipate] 2j with acetyl chloride and refluxed for 6hr. in DMF. The physical property of this compound was list in Table (2). And the solubilities of all prepared compounds are listed in Table (3).

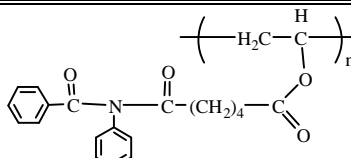
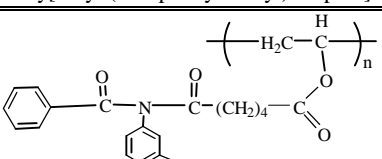
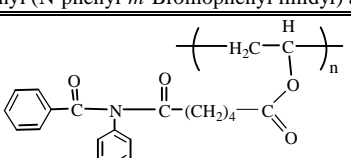
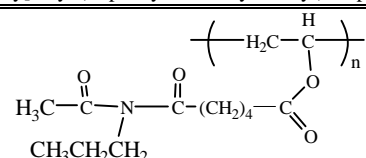


**Table (1)**  
**Physical properties of the prepared poly ester -N-sub.amides.**

Comp. No.	structure	Time reaction hr.	Conv. %	Color	m.p C <sup>o</sup>	s.p C <sup>o</sup>
1	 poly[vinyl(acid chloride)adipate]	1/2	90	black	190	175
2a	 Poly[vinyl (N-phenyl)amido adipate]	12	85	Dark red	-	>300
2b	 Poly[vinyl (N- <i>m</i> -bromo phenyl)amido adipate]	12	60	brown	>300	290

Comp. No.	structure	Time reaction hr.	Conv. %	Color	$m.p$ $C^{\circ}$	$s.p$ $C^{\circ}$
2c	 <p>Poly[vinyl (N-<i>p</i>-toluy)amido adipate]</p>	8	63	Purple	–	260
2d	 <p>Poly[vinyl (N-<i>o</i>-nitrophenyl)amido adipate]</p>	10	60	Brown	–	>300
2e	 <p>Poly[vinyl (N-<i>o</i>-methoxy-<i>p</i>-nitrophenyl)amido adipate]</p>	8	55	Yellow	–	>300
2f	 <p>Poly[vinyl (N-<i>m</i>-methoxy phenyl)amido adipate]</p>	8	65	Red	–	>300
2g	 <p>Poly[vinyl (N-<i>p</i>-Chlorophenyl)amido adipate]</p>	8	60	Dark red	–	>300
2h	 <p>Poly[vinyl (N-<i>p</i>-pyridinyl)amido adipate]</p>	8	68	Dark red	–	>300
2i	 <p>Poly[vinyl (N- <math>\alpha</math>-naphthyl)amido adipate]</p>	8	64	Deep purple	>300	280
2j	 <p>Poly[vinyl (N-<i>n</i>-propyl)amido adipate]</p>	8	75	Dark red	>300	280
2k	 <p>Poly[vinyl (N-methyl)amido adipate]</p>	8	80	Dark red	245	230

**Table (2)**  
**Physical properties of the prepared poly ester – N-sub. Imides.**

Comp. No.	Structure	Time reaction	Conv. %	Color	m.p	s.p
3a	 Poly[vinyl (N-diphenylimidyl) adipate]	6	65	Dark red	–	>300
3b	 Poly[vinyl (N-phenyl-m-Bromophenyl imidyl) adipate]	8	60	Dark red	–	>300
3c	 Poly[vinyl (N-phenyl-P-toluidyl imidyl) adipate]	6	63	Dark purple	–	>300
3j	 Poly[vinyl (N-n-phenyl methyl imidyl) adipate]	6	81	Dark red	–	>300

**Table (3)**  
**Solubility of the prepared polymers.**

Comp. No.	Benzene	DMF	DMSO	THF	Water	CCl <sub>4</sub>	CHCl <sub>3</sub>	Acetone	Cyclohexane
1	Ins.	S.	V.S	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.
2a	P.S	S.	V.S	P.S	Ins.	Ins.	S.	Ins.	Ins.
2b	P.S	S.	V.S	P.S	P.S	P.S	S.	P.S	Ins.
2c	Ins.	S.	V.S	Ins.	Ins.	Ins.	S.	Ins.	Ins.
2d	Ins.	S.	V.S	P.S	Ins.	Ins.	P.S	Ins.	Ins.
2e	Ins.	S.	V.S	Ins.	P.S	P.S	P.S	P.S	Ins.
2f	Ins.	S.	V.S	S.	Ins.	P.S	P.S	P.S	Ins.
2g	P.S	S.	V.S	P.S	Ins.	P.S	S.	P.S	Ins.
2h	P.S	S.	V.S	Ins.	Ins.	Ins.	P.S	P.S	Ins.
2i	Ins.	S.	V.S	Ins.	Ins.	Ins.	Ins.	Ins.	Ins.
2j	Ins.	S.	V.S	Ins.	Ins.	Ins.	P.S	P.S	Ins.
2k	Ins.	S.	V.S	Ins.	Ins.	Ins.	P.S	Ins	Ins.
3a	Ins.	S.	V.S	Ins.	Ins.	Ins.	P.S	Ins	Ins.
3b	Ins.	S.	V.S	Ins.	P.S	Ins.	P.S	P.S	Ins.
3c	Ins.	S.	V.S	Ins.	Ins.	Ins.	S.	Ins.	Ins.
3j	Ins.	S.	V.S	Ins.	Ins.	Ins.	Ins.	P.S	Ins.

V.S = very soluble, P.S = partially soluble, Ins. = insoluble,  
DMF= dimethyl formamide, THF = tetrahydrofuran.

DMSO= dimethyl sulfoxide,

**Table(4)**  
**FTIR absorption ( $\text{cm}^{-1}$ ) of the preparation N-sub. Amides.**

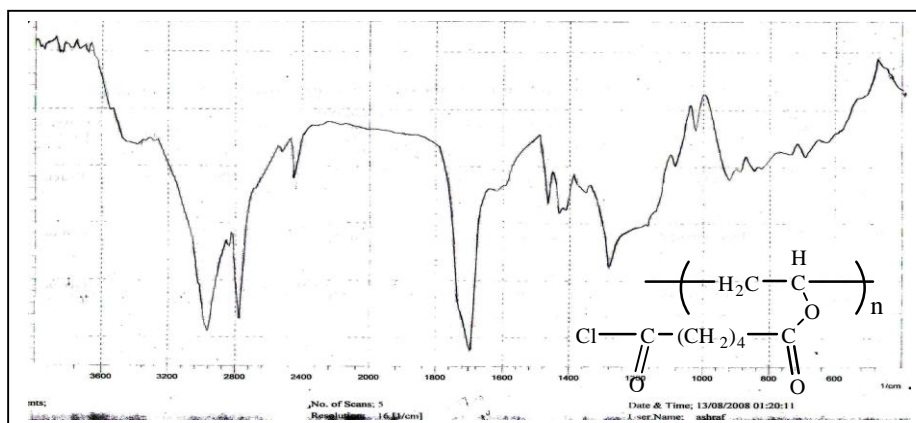
Comp. No.	$\nu$ N-H	$\nu$ C-H Aromatic	$\nu$ C-H Aliphatic	$\nu$ C=O ester	$\nu$ C=O Amide	$\nu$ C=C Aromatic	$\nu$ C-O-C	Other band
1	–	–	2785 2962	1700	–	–	1195	$\nu$ C=O acid 1730 $\nu$ C-Cl 810
2a	3360	3050	2785 2950	1730	1655	1600 1580	1180	–
2b	3409	3000	2993 2777	1728	1627	1575	1180	$\nu$ C-Br 678
2c	3417	3047	2939 2970	1700	1666	1610 1590	1180	–
2d	3379	3085	2869 2962	1720	1627	1566 1512	1180	$\nu$ NO <sub>2</sub> 1490
2e	3433	3116	2931 2869 2761	1728	1627	1500	1180	$\nu$ NO <sub>2</sub> 1427
2f	3394	3070	2939 2869	1728	1604	1570	1195	$\nu$ C-O-C 1040
2g	3433	3020	2939 2869	1728	1635	1500	1180	C-Cl 756
2h	3417	3078	2877 2947	1735	1650	1550	1180	$\nu$ C=N 1525
2i	3425	3078	2947 2877	1735	1643	1512	1180	–
2j	3406	–	2939 2869	1735	1635	–	1180	–
2k	3433	–	2939 2877	1720	1635	–	1150	–

**Table(5)**  
**FTIR absorption ( $\text{cm}^{-1}$ ) of the preparation N-sub. Imides.**

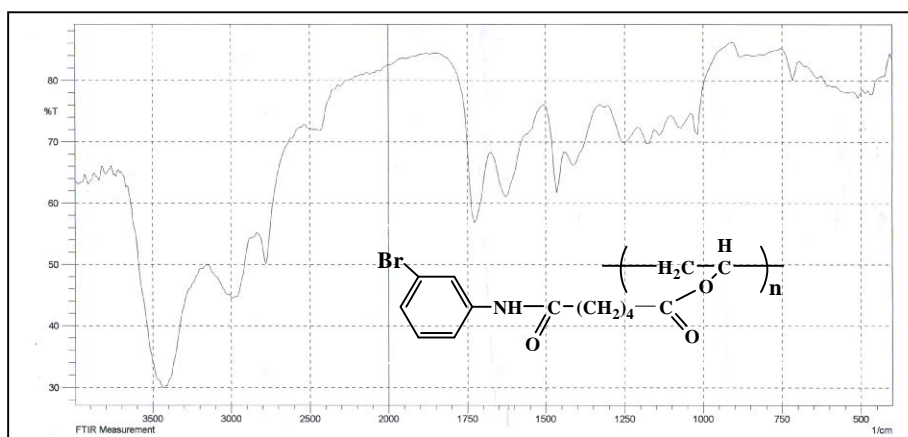
Comp. No.	$\nu$ C-H aromatic	$\nu$ C-H aliphatic	$\nu$ C=O ester	$\nu$ C=O imide	$\nu$ C=C	$\nu$ C-O-C	Other bands
3a	3010	2869 2777	1750	1670	1604	1180	–
3b	3070	2790 2920	1728	1666	1600	1180	$\nu$ C-Br 675
3c	3047	2880 2910	1728	1666	1620 1530	1149	–
3j	–	2939	1740	1635	–	1180	–

**Table (6)**  
 $^1\text{H-NMR}$  spectra for compounds (2a, 2f, 2g, 2h).

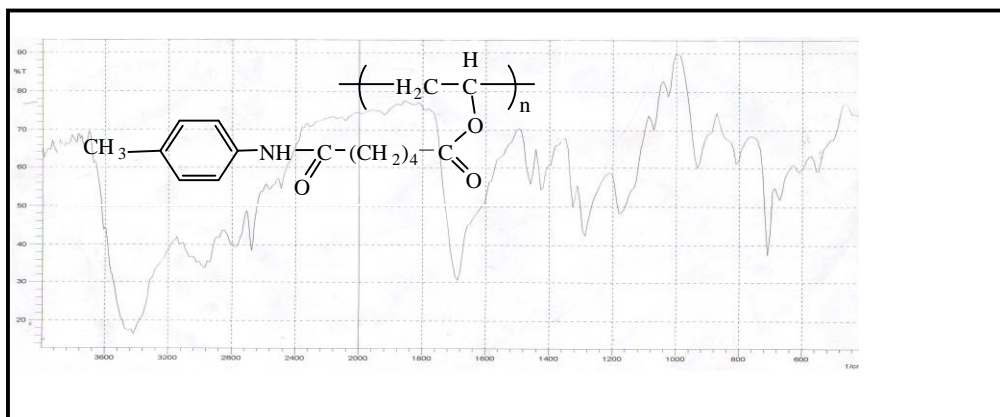
Comp. No.	Fig. No.	$\delta H$ Aliphatic ppm	No. of carbone	$\delta O-H$ totomerizme ppm	$\delta H$ aromatic	$\delta N-H$
2a	16	0.85(s,1H,OH) 1.25(m,1H,CH) 3.4(t,4H,CH <sub>2</sub> ) 2.5(m,4H,CH <sub>2</sub> )	1 2 4,5 3,6	12 (s,1H,OH)	7.1(s,5H)	8.2 (s,1H,NH)
2f	17	0.9(t,2H,CH <sub>2</sub> ) 1.2(m,1H,CH) 2.0(m,4H,CH <sub>2</sub> ) 3.3(t,4H,CH <sub>2</sub> ) 2.5(s,3H,CH <sub>3</sub> )	1 2 4,5 3,6 7	11.3 (s,1H,OH)	7.15 (s, H) 4.4 (t,3H)	8.2 (s, 1H,NH)
2g	18	0.9 (s,1H,OH) 1.8(m,1H,CH) 2.5(m,4H,CH <sub>2</sub> ) 3.3(t,4H,CH <sub>2</sub> )	1 2 4,5 3,6	11.7 (s,1H,OH)	6.6(d,4H)	8.3 (s, 1H,NH)
2h	19	1.3 (t,2H,CH <sub>2</sub> ) 2.5(m,5H,CH,CH <sub>2</sub> ) 3.3 (t,4H,CH <sub>2</sub> )	1 2,5,4 3,6	11.5 (s,1H,OH)	6.5(d,4H)	8 (s, 1H,NH)



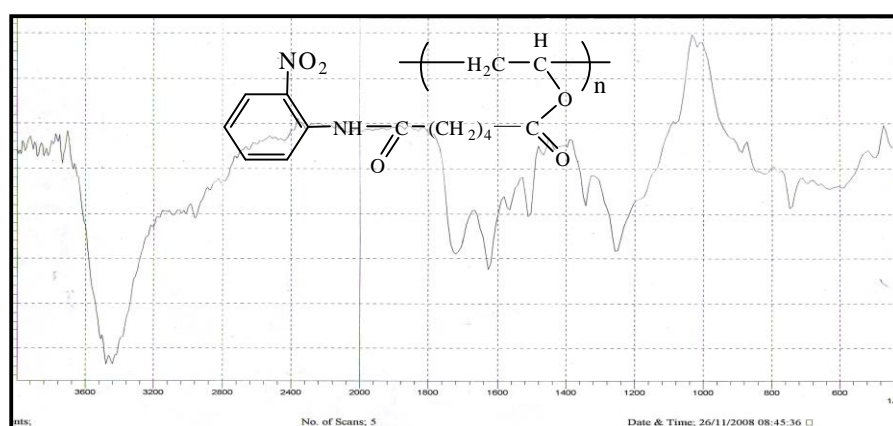
**Fig. (1) FTIR spectrum of resin (1).**



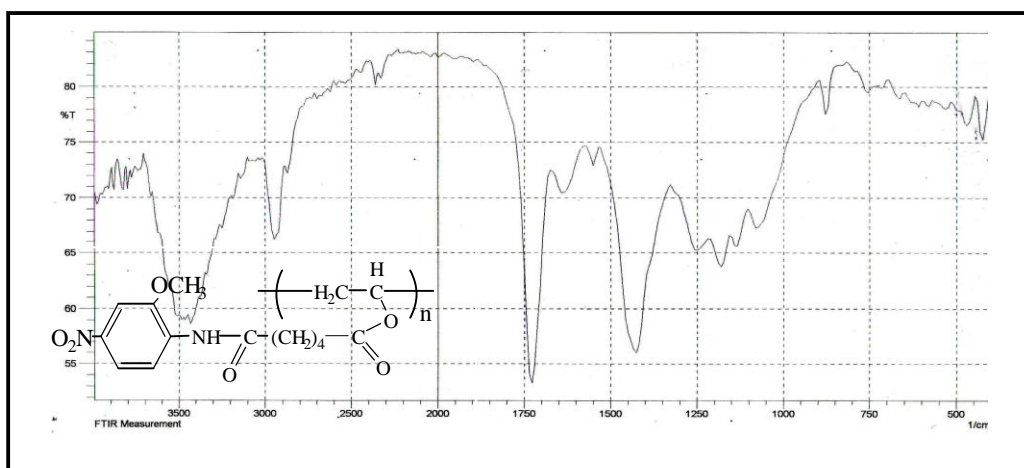
**Fig. (2) FTIR spectrum of resin (2b).**



**Fig. (3) FTIR spectrum of resin (2c).**

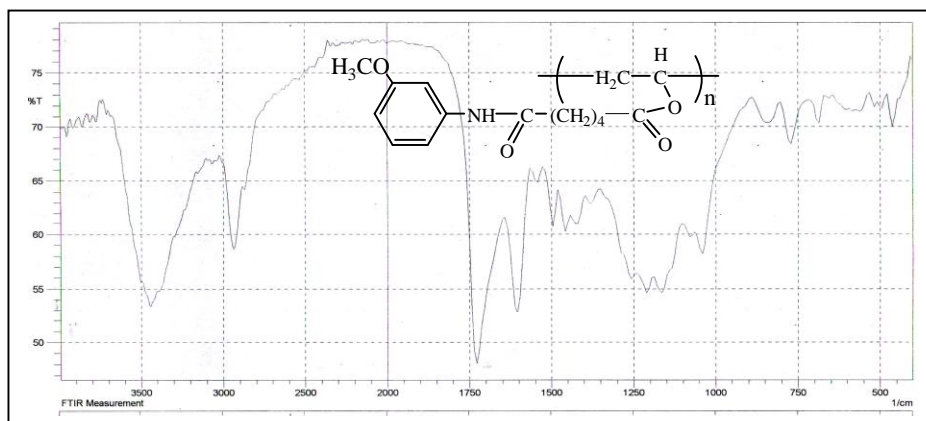


**Fig. (4) FTIR spectrum of resin (2d).**

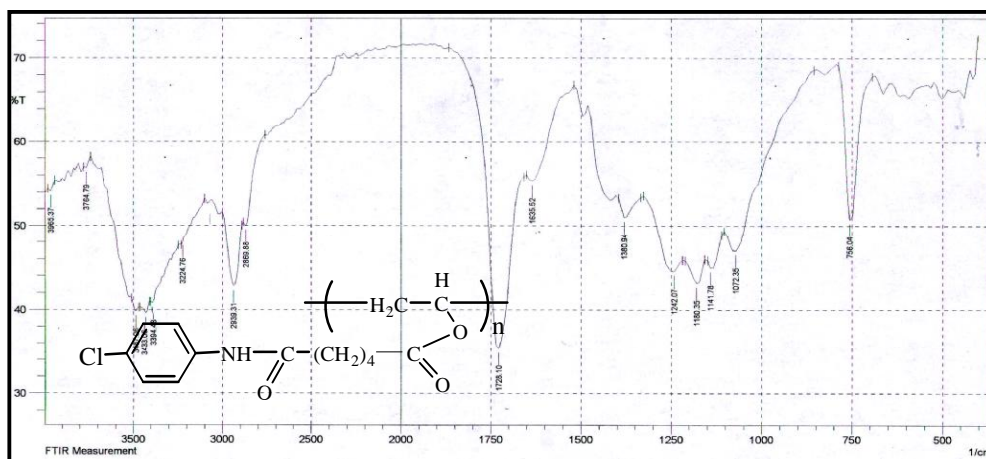


**Fig. (5) FTIR spectrum of resin (2e).**

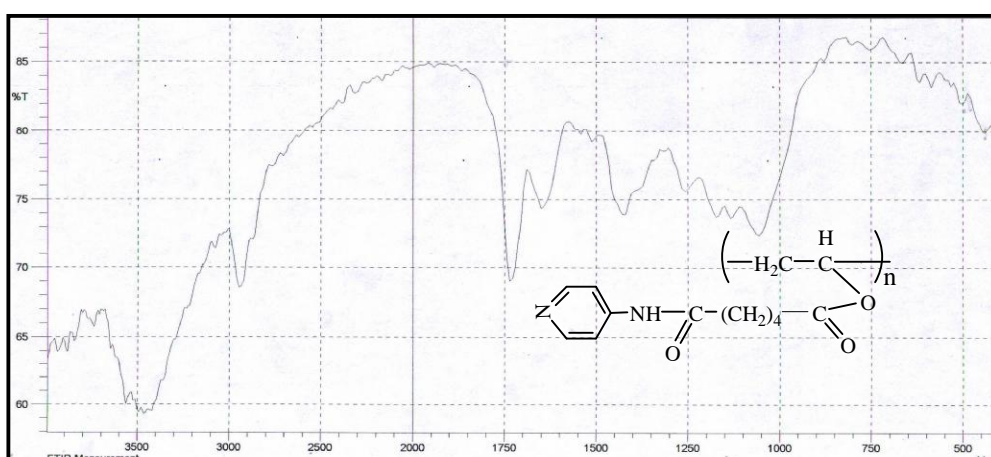




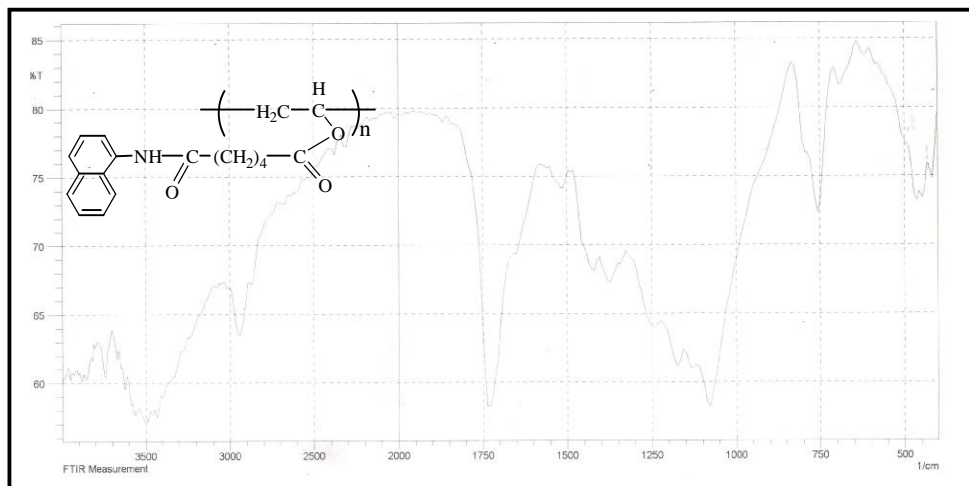
**Fig. (6) FTIR spectrum of resin (2f).**



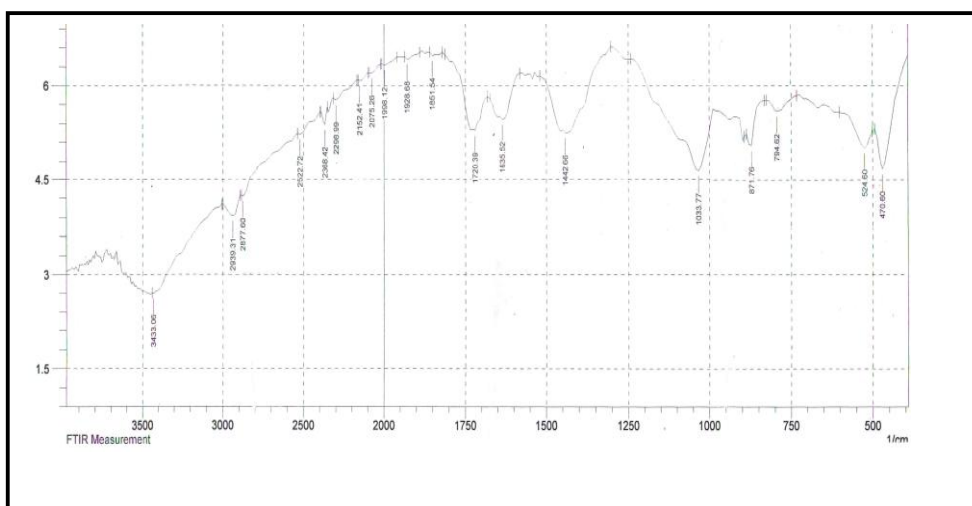
**Fig. (7) FTIR spectrum of resin (2g).**



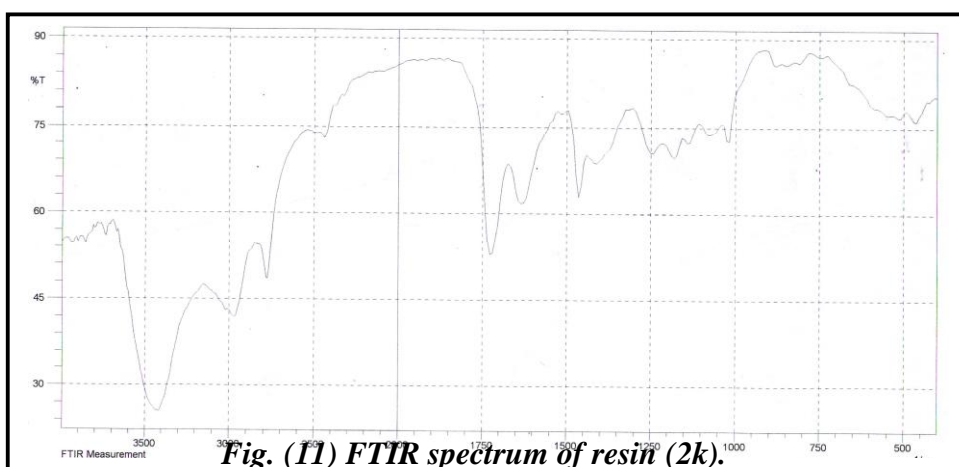
**Fig. (8) FTIR spectrum of resin (2h).**



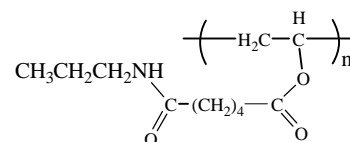
**Fig. (9) FTIR spectrum of resin (2i).**



**Fig. (10) FTIR spectrum of resin (2j).**



**Fig. (11) FTIR spectrum of resin (2k).**



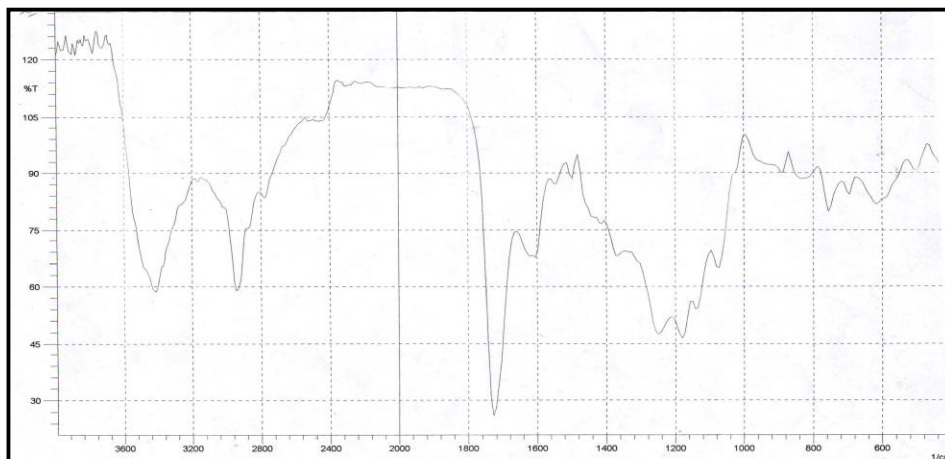


Fig. (12) FTIR spectrum of resin (3a).

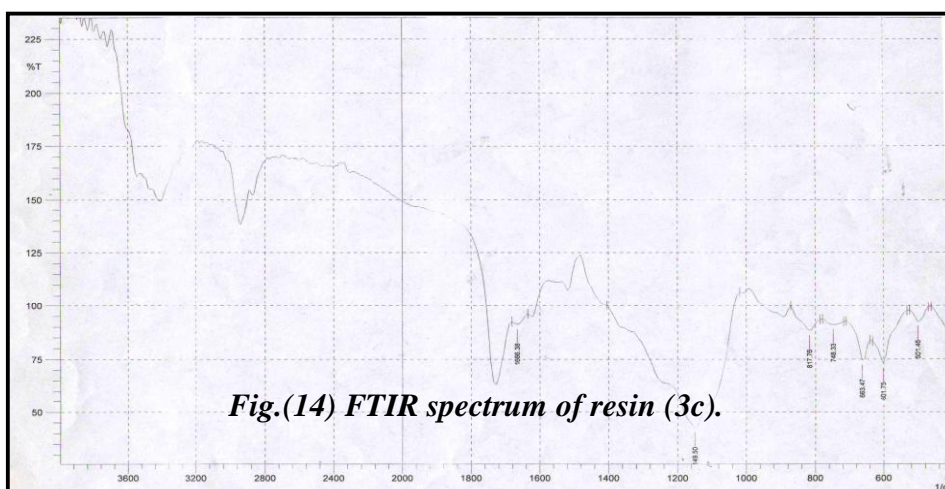
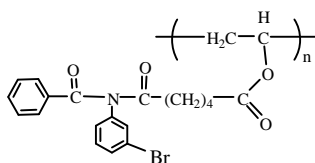
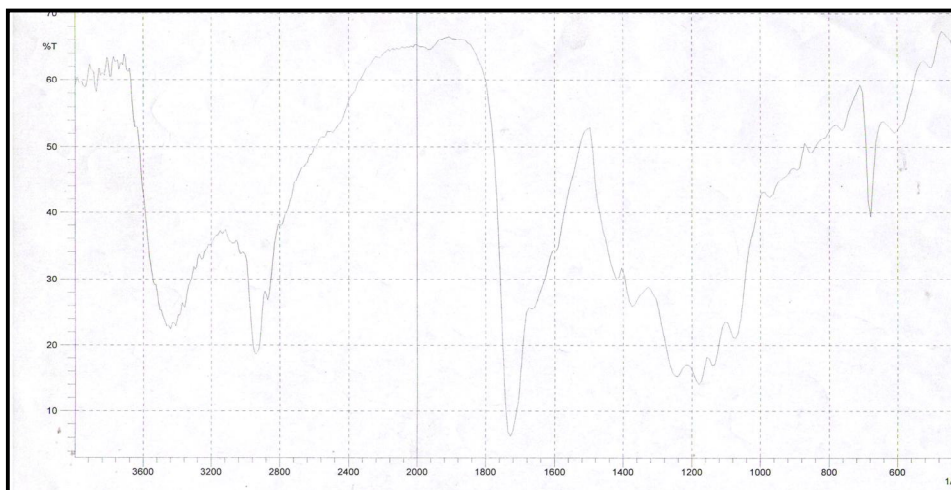
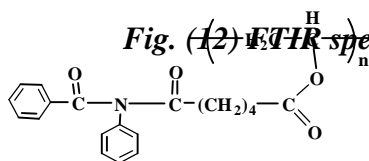
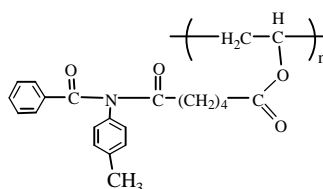


Fig.(14) FTIR spectrum of resin (3c).



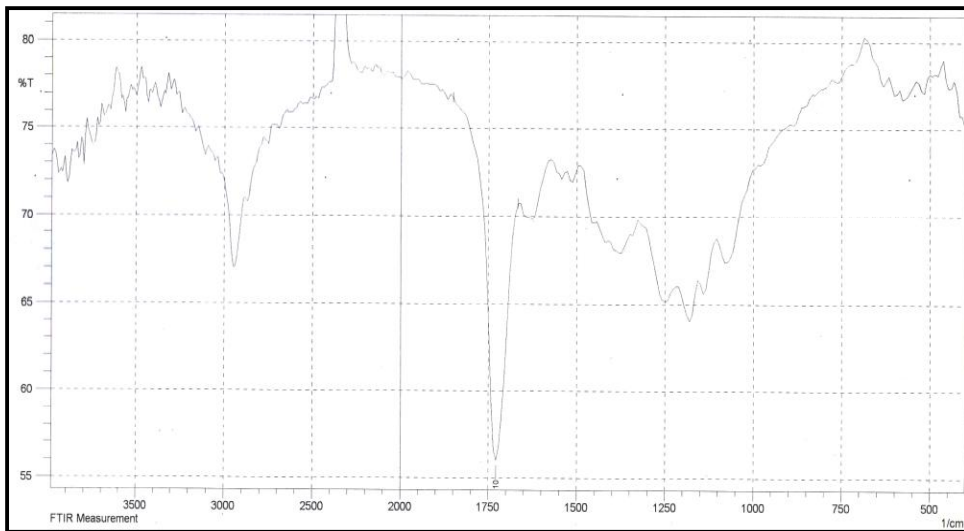


Fig. (15) FTIR spectrum of resin (3j).

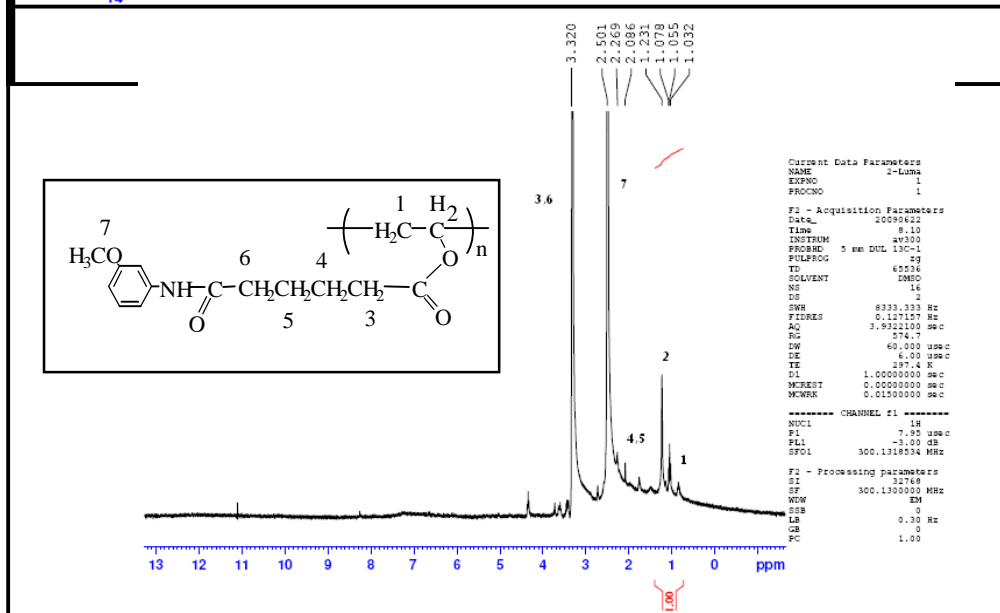
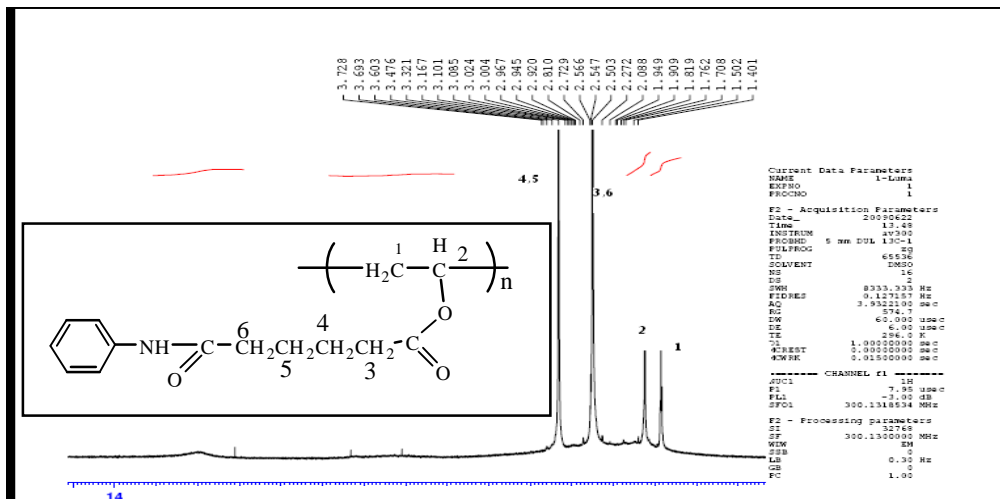
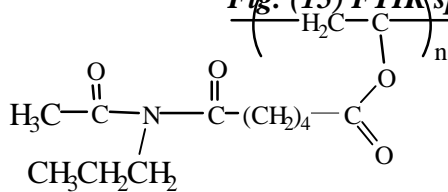
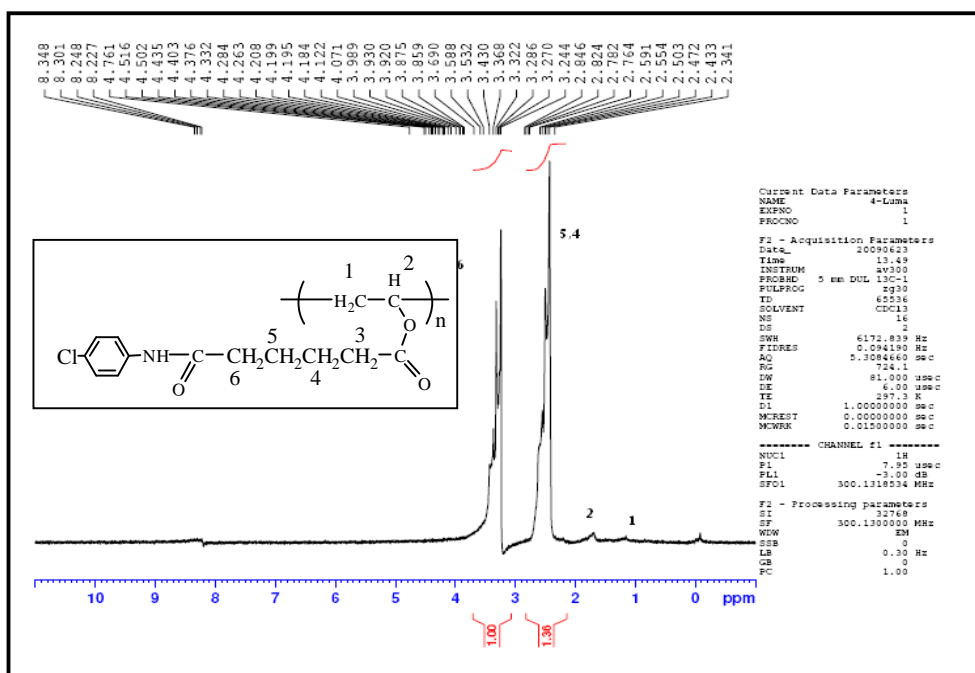
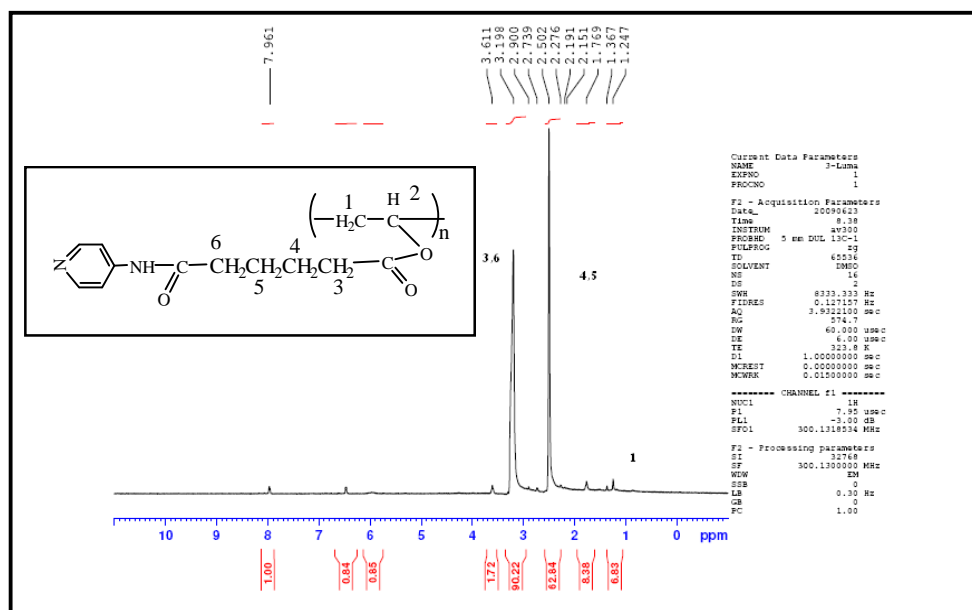


Fig. (17) <sup>1</sup>H NMR spectrum of resin (2f).

Fig. (18) <sup>1</sup>H NMR spectrum of resin (2g).Fig. (19) <sup>1</sup>H NMR spectrum of resin (2h).

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## الخلاصة

في هذا البحث تم تحضير 15 بوليمر جديد من تحويل بوليمر الكحول الفايئيلي، حضرت هذه البوليمرات بخطوتين، الخطوة الاولى تضمنت تحضير بوليمر استر - كلوريد حامض ابتداء من بولي فانيل الكحول بتفاعل 1مول منه مع 1 مول من كلوريد الاديوبيل، الخطوة الثانية تضمنت تفاعل البوليمر الناتج من الخطوة الاولى مع امينات (ارماتية واليفاتية) مختلفة ليعطي بوليمرات جديدة حاوية على مجاميع استر امايد متدلوية، اربعة من هذه البوليمرات تم تحويلها بخطوة ثالثة الى بوليمرات استر - امايد جديدة بتفاعلها مع كلوريد الحامض (كلوريد الاستيل وكلوريد البنزويل). في مذيب ال DMF. هذه البوليمرات المحضرة ذات مواصفات فيزيائية جديدة مما قد يسمح لها باستخدامها في تطبيقات مختلفة. تم تشخيص هذه البوليمرات باستخدام اطياف NMR, FTIR وقياس درجات الانصهار ودرجات التلين والذوبانية.

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