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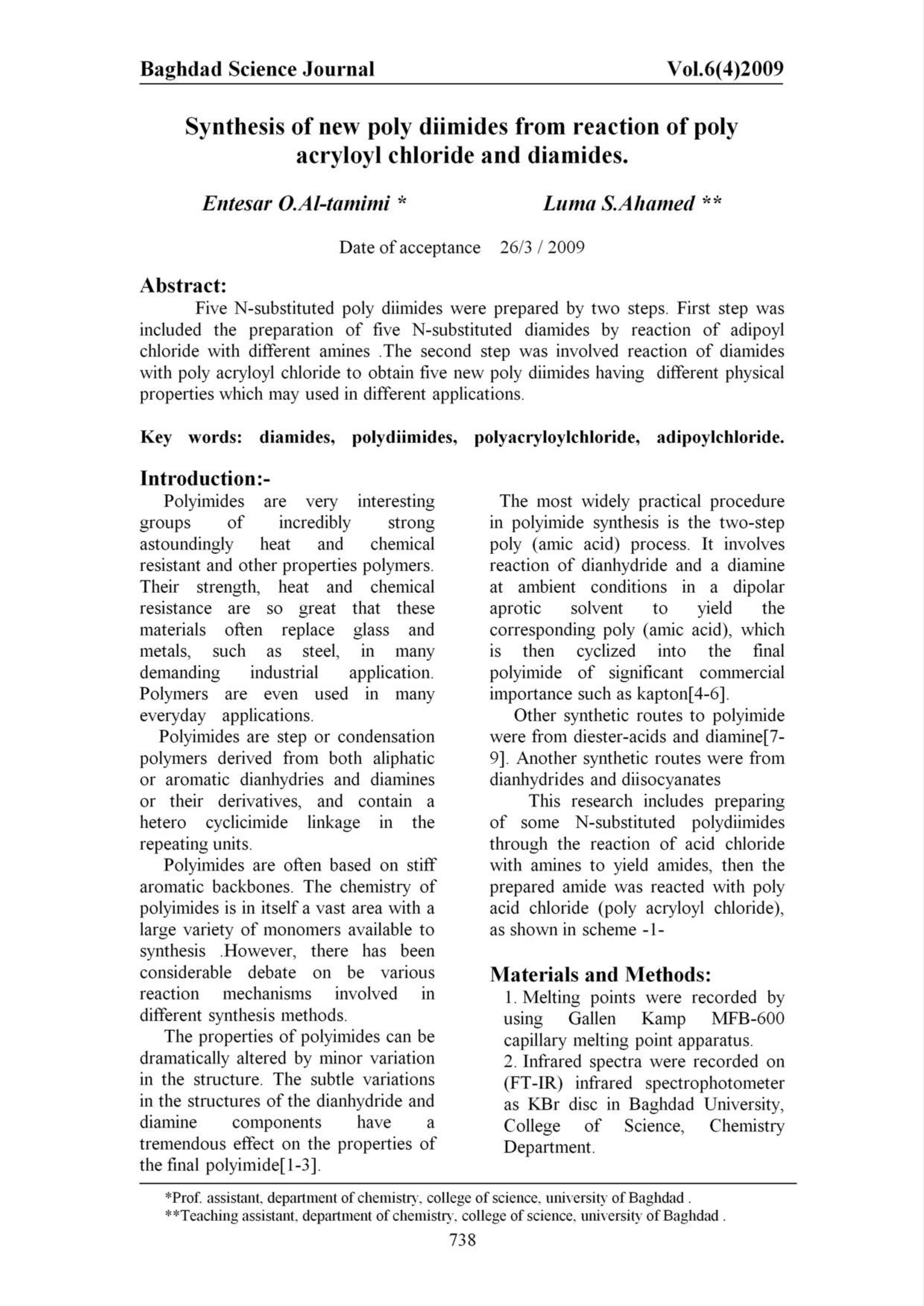

Synthesis of new poly diimides from reaction of poly acryloyl chloride and diamides.

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Abstract:

Five N-substituted poly diimides were prepared by two steps. First step was included the preparation of five N-substituted diamides by reaction of adipoyl chloride with different amines .The second step was involved reaction of diamides with poly acryloyl chloride to obtain five new poly diimides having different physical properties which may used in different applications.

Key words: diamides, polydiimides, polyacryloylchloride, adipoylchloride.

Introduction:-

Polyimides are very interesting groups of incredibly strong astoundingly heat and chemical resistant and other properties polymers. Their strength, heat and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial application. Polymers are even used in many everyday applications.

Polyimides are step or condensation polymers derived from both aliphatic or aromatic dianhydries and diamines or their derivatives, and contain a hetero cyclicimide linkage in the repeating units.

Polyimides are often based on stiff aromatic backbones. The chemistry of polyimides is in itself a vast area with a large variety of monomers available to synthesis .However, there has been considerable debate on be various reaction mechanisms involved in different synthesis methods.

The properties of polyimides can be dramatically altered by minor variation in the structure. The subtle variations in the structures of the dianhydride and diamine components have a tremendous effect on the properties of the final polyimide[1-3].

The most widely practical procedure in polyimide synthesis is the two-step poly (amic acid) process. It involves reaction of dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent to yield the corresponding poly (amic acid), which is then cyclized into the final polyimide of significant commercial importance such as kapton[4-6].

Other synthetic routes to polyimide were from diester-acids and diamine[7-9]. Another synthetic routes were from dianhydrides and diisocyanates

This research includes preparing of some N-substituted polydiimides through the reaction of acid chloride with amines to yield amides, then the prepared amide was reacted with poly acid chloride (poly acryloyl chloride), as shown in scheme -1-

Materials and Methods:

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.

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1-preparation of diamides (1-5) [10,11].

(0.1mol) of adipoyl chloride was diluted with 15ml of pure THF, and a solution of 0.2mol of pure amine in 15 -20ml of the same solvent was added until the odor of the acid chloride has disappeared; excess of the amine was not harmful. The mixture was Shaked with excess of dilute HCl to remove amine and its salts. The ethereal layer was washed with 5-10ml of water, and the solvent was evaporated. The amide was recrystallized from dilute ethanol.

2-preparation of poly [diacryl adip di N-substituted diimide] (6-10)[12].

A mixture of poly (acryloyl chloride) (0.2mol) and diamide (0.1mol) in dimethyl formamide (DMF) 25ml was refluxed for (8-10)hrs. After cooling the excess of solvent was removed under vacuum and the solid separated was filtered and purified by dissolving in suitable solvent (DMF, DMSO) and reprecipitating from another solvent such as (water, ethanol, acetone). Conversion of yielded polymers were (50-82 %)

Results and discussion

Synthesis of some new poly N-substituted diimides were achieved from reaction of diamides and poly (acryloyl chloride).scheme-1-

Diamides were prepared through the reaction of adipoyl chloride with two moles of different amines in the same solvent.

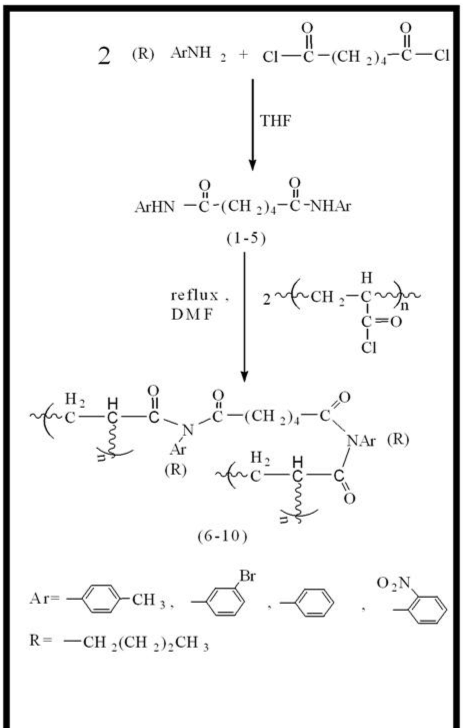
Structures of diamides (1-5) were confirmed by physical properties which are listed in table (1).

FTIR spectra showed the absorptions at region (3301-3247)cm^{-1} due to υ (N-H) group, (1697-1643)cm^{-1} for υ(C=O) amide ,(1595-1496)cm^{-1} due to υ(C=C) aromatic, (3100-3031) cm^{-1} for υ(C-H)aromatic ,(1414-1334) cm^{-1}for υ(C-N),(2950-2860) cm^{-1} due to υ(C-H)aliphatic and absorption of 1427 cm^{-1} due to nitro group (NO_2).All these regions are listed in table(5).

The second step included the reaction of prepared diamide with two mole of poly (acryloyl chloride) in DMF (dimethyl formamide) at reflux temperature in (6-12)hrs.to produce polydiimid .

The structures of (6-10) were confirmed by physical properties which are listed in table (2).

FTIR spectra of compounds (6-10) showed disappearance of absorption band of –NH group at (3301-3247) cm^{-1} which confirmed conversion to N-substituted imide group, and absorption at (1712-1643) cm^{-1} due to υ(C=O) imide, these and other absorptions are listed in table (6).



Scheme-1-

Table (1):Phyiscal properties of the prepared N-sub.diamides

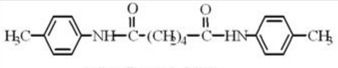
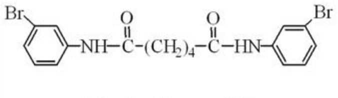
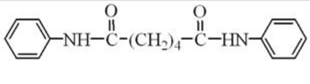
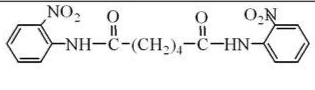
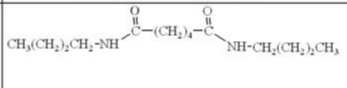
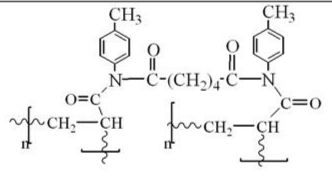
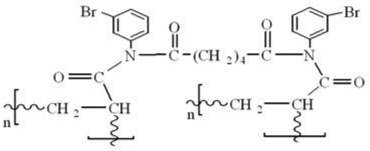
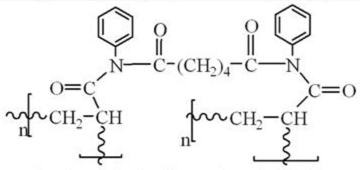
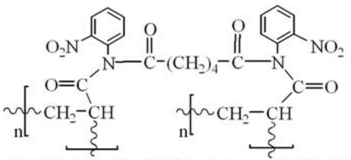
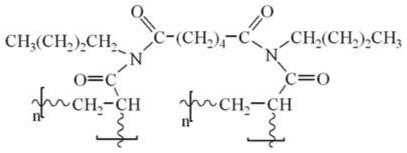
Comp. No.	Compound Structure	m.p C^{O}	Yield %	Color
1	 Adip di-*p*-toluidide	230	85	white
2	 Adip-di m-bromo anilide	110-115	58	gray
3	 Adip-di anilide	220	61	gray
4	 Adip-di *o*- nitro anilide	169-173	52	Yellow
5	 Adip-di *n*- butyl amide	150-152	87	white

Table (2):Phyiscal properties of the prepared poly N-sub.diimides.

Comp. No.	**polymer Structure**	**Time reac. hrs.**	**Conv. %**	**Color**	**s.p.**	**m.p.**
6	 poly[di acryl adip di-{N-(*p*-tolyl)}diimide	6	80	white	160-175	>300
7	 Poly[di acryl adip-di{N-*m bromo*phenyl} diimide]	12	60	gray	180-190	>300
8	 poly[di acryl adip di-{N-phenyl}diimide]	8	63	gray	110-122	>300
9	 Poly[di acryl adip-di{N-*0* nitro phenyl}diimide]	12	50	Yellow	220-230	>300
10	 Poly[di acryl adip-di{N-n-butyl}diimide]	8	82	white	200-210	>300

Conv. = conversion
S.P = softening point
m.p = melting point

Table (3): Solubility of the prepared N-subs. diamide

Comp. .No.	Ethanol	Benzene	CCL4	Acetone	Toluene	DMSO	THF	$CHCl_3$	DMF	Cyclohexane
1	V.S	V.S	P.S	S.	Ins.	V.S	S.	Ins.	V.S	Ins.
2	V.S	V.S	Ins.	V.S	P.S	V.S	V.S	S.	V.S	Ins.
3	S.	S.	Ins.	S.	Ins.	V.S	V.S	Ins.	V.S	Ins.
4	V.S	V.S	P.S	V.S	S.	V.S	V.S	V.S	V.S	Ins.
5	V.S	V.S	Ins.	V.S	P.S	V.S	V.S	V.S	V.S	S.

Table (4): Solubility of the prepared poly N-subs. diimides

Comp. No	**ethanol**	**Benzene**	**CCL4**	**Acetone**	**toluene**	**DMSO**	**THF**	**$CHCl_3$**	**DMF**	**cyclohexane**
6	swell	Ins.	Ins.	Ins.	Ins.	swell	Ins.	Ins.	S.	Ins.
7	swell	Ins.	Ins.	Ins.	Ins.	swell	Ins.	Ins.	S.	Ins.
8	swell	Ins.	Ins.	Ins.	Ins.	swell	Ins.	Ins.	P.S	Ins.
9	swell	Ins.	Ins.	Ins.	Ins.	S.	Ins.	Ins.	swell	Ins.
10	swell	swell	Ins.	swell	Ins.	S.	Ins.	swell	swell	Ins.

Subs. = substituted
v.s = very soluble
p.s = partially soluble
Ins. = insoluble
DMSO= dimethyl sulfoxide
THF = tatrahydrofuran
DMF= dimethyl formamide

Table (5) :FT-IR absorptions (cm^{-1}) of the prepared N-subs.diamides.

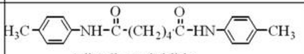
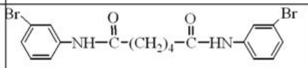
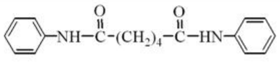
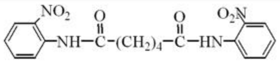
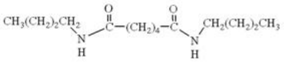
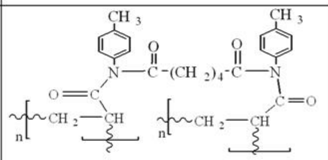
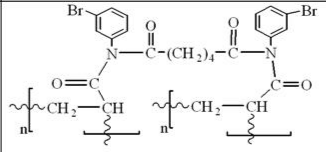
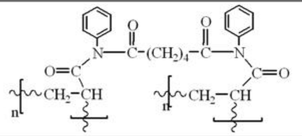
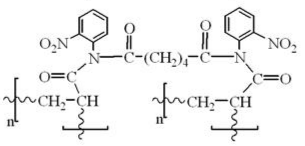
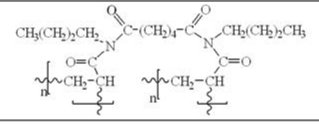
Comp.No.	Comp.Structure	υ N-H	υ C=O Amide	υ C=C Aromatic	υ C-H Aromatic	υ C-H Aliphatic	υC-N	Other band
1	 Adip-di-*p*-toluidide	3301	1658	1595 1519	3050	2923- 2860	1380	
2	 Adip-di m-bromo anilide	3260	1659	1589 1527	3031	2947- 2860	1411	
3	 Adip-di anilide	3247	1658	1596 1550	3070	2939- 2869	1338	
4	 Adip-di *o* nitro anilide	3310	1697	1581 1496	3100	2950 2860	1334	υ C-NO_2 1427
5	 Adip-di *n* butyl amide	3301	1643	-	3100	2945 2869	1350	

Table (6): FTIR absorptions (cm^{-1}) of the prepared N-subs.poly diimides.

Comp. No.	Comp.Structure	υ C=O Amide	υ C=C Aromatic	υ C-H Aromatic	υ C-H Aliphatic	υC-N	Other band
6		1695	1596 1519	3039	2947 2869	1373	
7		1697	1635 1495	3080	2940 2856	1404	
8		1667	1596 1550	3070	2947 2880	1388	
9		1712	1580 1520	3010	2954	1411	υ C-NO_2 1450
10		1643	-	-	2952 2931	1373	

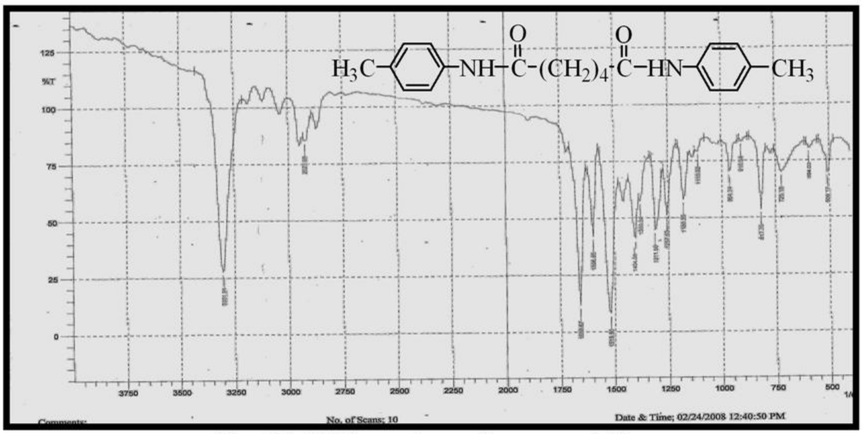


Fig. (1): FTIR spectrum of compound (1)

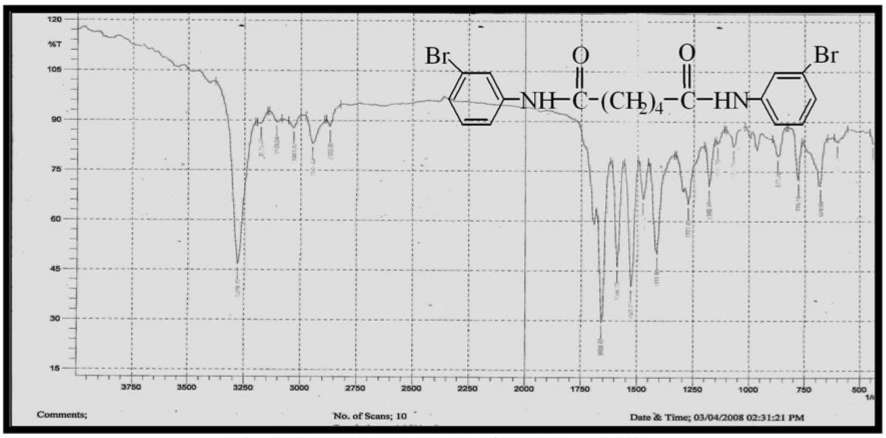


Fig. (2): FTIR spectrum of compound (2)

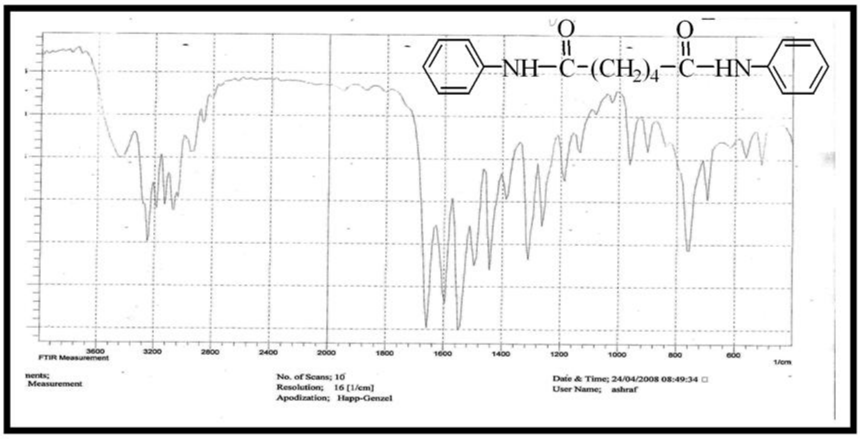


Fig. (3): FTIR spectrum of compound (3)

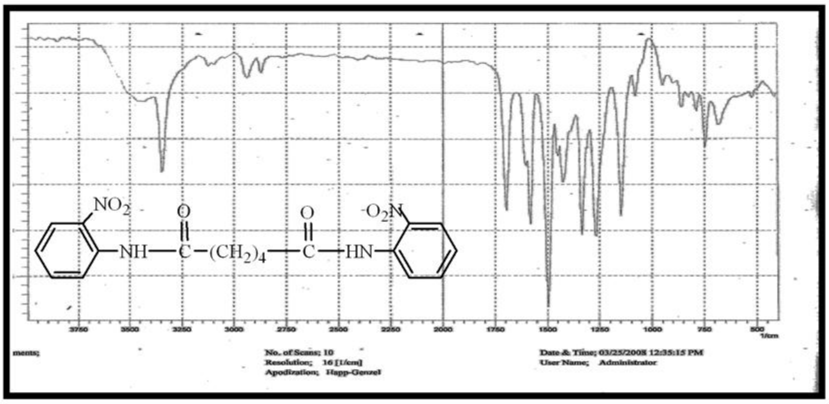


Fig. (4): FTIR spectrum of compound (4)

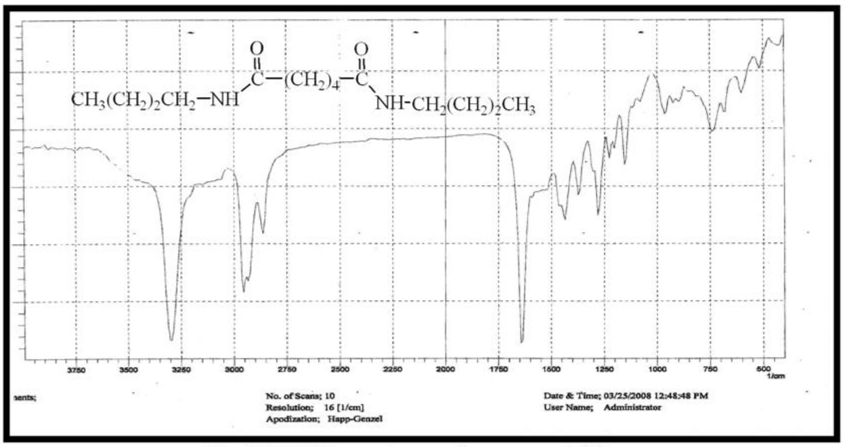


Fig.(5):FTIR spectrum of compound (5)

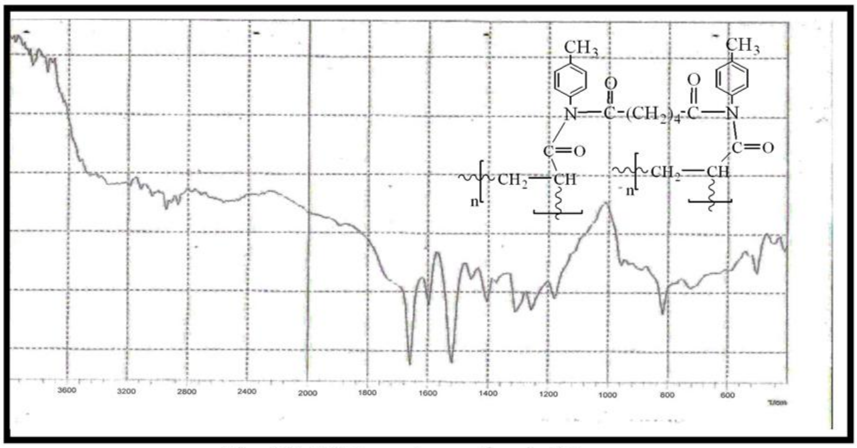


Fig. (6): FTIR spectrum of resin (6)

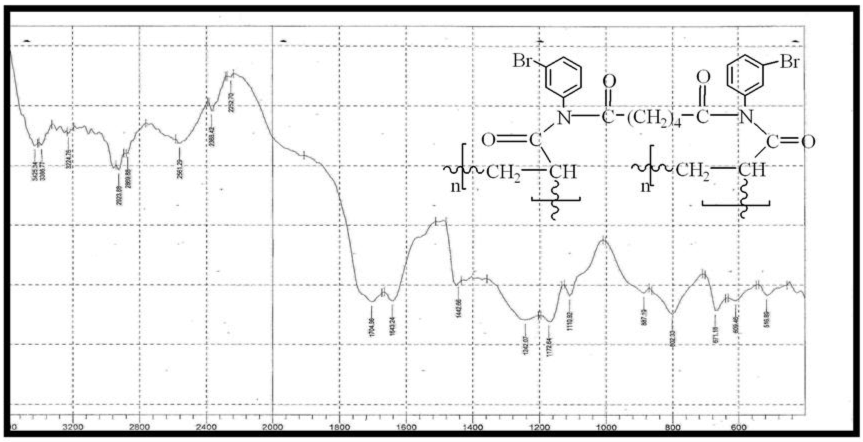


Fig. (7): FTIR spectrum of resin (7)

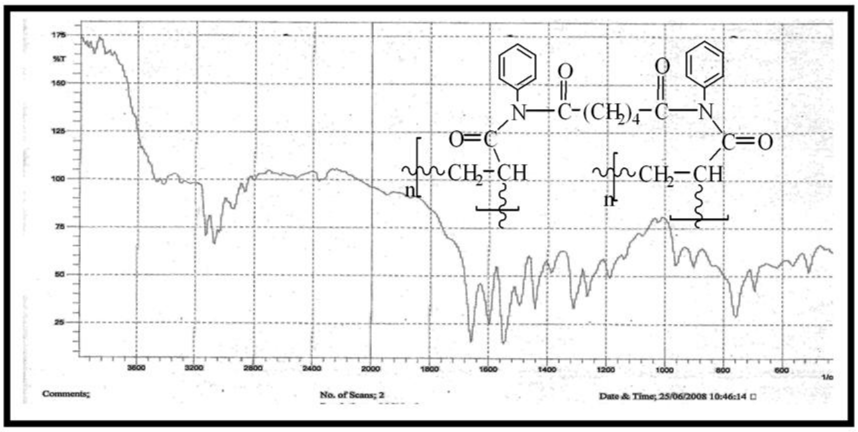


Fig. (8): FTIR spectrum of resin (8)

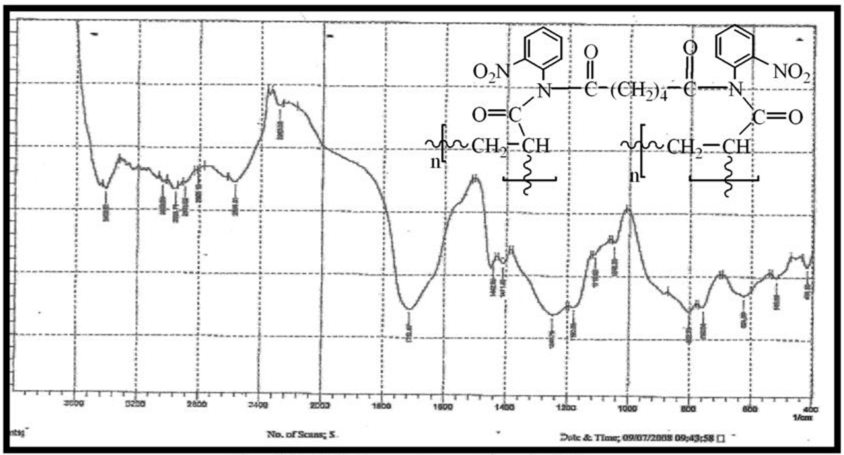


Fig. (9): FTIR spectrum of resin (9)

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تحضير بولي ثنائي ايمايدات جديدة من تفاعل بولي كلوريد الاكريلويل مع مركبات ثنائي اميد

انتصار عبيد التميمي* ***لمى سامي احمد ****

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**كلية العلوم/ قسم الكيمياء /جامعة بغداد

الخلاصة :-

تم تحضير خمس بوليمرات جديدة من نوع ثنائي الايمايد وتضمن هذا التحضير خطوتين ، الخطوة الاولى تحضير خمس مركبات من نوع ثنائي الامايدات من تفاعل كلوريد الاديبويل مع امينات مختلفة .اما الخطوة الثانية فتضمنت مفاعلة ثنائي الامايد مع بوليمر كلوريد الاكريلويل ليعطي بوليمرات من نوع ثنائي الاميدات ذات مواصفات فيزيائية جديدة مماسمح باستخدامها في تطبيقات مختلفة.