

Synthesis and Characterization of New Heterocyclic Polymers Contains Two 1, 3, 4- Oxadiazole Rings

تحضير وتشخيص ثلاث سلاسل جديدة من البوليمرات الحاوية على حلقتين غير متجانستين من الاوكسادايازول

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Abstract:-

The synthesis and characterization of new three series of polymers containing two heterocyclic rings 1, 3, 4 – oxadiazole are reported. The molecular structures of the intermediates and target compounds were confirmed by FTIR and ¹H-NMR spectra.

Keywords: 1, 3, 4- Oxadiazole, Polymers, Heterocyclic Polymers.

الخلاصة:-

تم تحضير ثلاث سلاسل جديدة من البوليمرات الحاوية على حلقتين غير متجانستين من 1,3,4-اوكسادايازول. شخصت المركبات والبوليمرات المحضرة بوساطة أطياف الأشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون. وقد أظهرت نتائج التشخيص تطابقاً مع ما تم اقتراحه من صيغ تركيبية للمركبات والبوليمرات المحضرة.

1. Introduction

Heterocyclic chemistry is the largest of the classical divisions of organic chemistry. Heterocyclic compounds are widely distributed in nature, playing a vital role in the metabolism of living cells. Their practical applications range from extensive clinical use to fields as diverse as agriculture, photography, biocide formulation and polymer science. The range of known compounds is enormous, encompassing the whole spectrum of physical, chemical and biological properties [1].

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds [2].

Many series of compounds containing heterocyclic groups have been synthesized, seventeen thiazole polymers were prepared by the poly condensation of bis- α - bromoketones with dithioamides, and the polymers were investigated for preparing heat – resistant fibers and films [3]. Some of the heterocycles compounds use for thermally stable plastics [4].

The electric conductivity was studied for two aliphatic unsaturated polymers with 1, 3, 4 – oxadiazole – 2, 5- diyl units. [5]. with the aim of understanding the influence of heteroatoms in the conduction pathway in organic conducting polymer, the insertions of a nitrogen atom in the main conjugated skeleton were investigated [6]. To help in clarifying the role of the heteroatom in the conduction pathway the preparation and characterization of conjugated polymers based on the thiazole ring were studied [7].

Two reaction routes for the prepare of aromatic poly – 1, 3, 4 – oxadiazoles and poly – 1, 2, 4- triazoles are studied and their influence on the physical properties, i.e., inherent viscosity, glass transition and film integrity [8]. Thermally stable membrane of new aromatic poly – 1, 2, 4- triazoles and poly – 1, 3, 4- oxadiazoles are studied [9].

The similar polymers with conjugated blocks consisting of different types and numbers of rings (benzene, thiophene, 1, 3, 4- oxadiazole) and methylene chains of different length were prepared [10]. A novel approach to synthesize processible, cross – linkable, and thermally stable

heterocyclic polymers (poly oxazolidones) with nonlinear optical properties were investigated [11]. other compounds of montmorillonite – based nano composites of polybenzoxazole were synthesized [12].

The hydrolytic behaviour of polyphenyl -1, 2, 4 – triazine at high temperatures were investigated both experimentally and theoretically [13]. Heterocyclic carbene complexes were prepared containing a pyridyl. These heterogeneous catalysts can be recycled ≥ 14 times with no loss of activity [14].

A new series of Schiff bases containing 1, 3, 4- oxadiazole rings were prepared and biological activity for some of these compounds investigated [15].

The thermal stability of the silicon- containing of polyimides or poly (imide - amide) were studied by prepare thin films, in the range of tens of micrometers thickness [16].

The synthesis and characterizations of new materials incorporating two heterocyclic 1, 3, 4-oxadiazole and 1, 3, 4 – thiadiazole rings have been synthesized, the liquid crystalline properties of compounds derivatives have been extensively researched [17].

In this paper, we report the synthesis and characterization of new three series of polymers containing two heterocyclic 1, 3, 4-oxadiazole rings.

2. Experimental

2.1. Reagents and Technique

All chemicals and solvents were of reagent grade (Aldrich Chemicals Co.) and used without further purification. Infrared spectra were recorded with a Shimadzu 8000 FTIR spectrophotometer in the wave number range $4000-400\text{cm}^{-1}$ with samples embedded in KBr disc (Ibn-Al-Haitham College department of chemistry University of Baghdad). ^1H NMR spectra were obtained with Bruker spectrometer model ultra shield at 300 MHz (Gordon). The compounds were dissolved in DMSO- d_6 solution with the TMS as internal standard

2.2. Synthesis of compounds (I₁, I₂, I₃).

This compound was prepared following the procedure described by Parra et al., [18]. The physical properties and FTIR spectral data of all compounds are summarized in tables (1, 2, 3).

2.3. Synthesis of compounds (II₁, II₂, II₃)

Compound I_{1,2,3} (0.005 mol) and 4- methylbenzoic acid (1.36g, 0.01 mol) were refluxed with phosphorous oxychloride (5 ml) with stirring for 24h and the reaction mixture was then treated with ice- water carefully and made basic by adding concentrated sodium bicarbonate solution. The resulting solid was filtered, washed several times with distilled water, dried and recrystallized from ethanol. The physical properties, FTIR spectral data of all compounds are summarized in Tables (1, 2, 3).

2.4. Synthesis of compounds (III₁, III₂, III₃)

Potassium permanganate (3.33g, 0.021 mol) was added portion wise to a stirred solution of compounds II_{1, 2, 3} in pyridine (16 ml) and water (11 ml) at 70°C. The mixture was then heated with stirring under reflux for 4h. The solvent was evaporated in vacuum, and then distilled water (35ml) was added to the mixture and filtered. The acid III_{1, 2, 3} were precipitated by acidification the filtrate with (2M HCl). It was filtered under suction, washed with water and dried at 100°C and purified by sodium bicarbonate. The physical properties and FTIR spectral data of all compounds III_{1, 2, 3} are summarized in Tables (1, 2, 3).

2.5. Synthesis of compounds (IV₁, IV₂, IV₃)

Compounds III_{1, 2, 3} (0.1 mol) was refluxed with thionyl chloride (5 mL) in presence of 1 drop of DMF for 6h. Unreacted chloride was removed under reduced pressure to precipitate acid chlorides IV_{1, 2, 3}. These compounds are very active and sensitive to the moisture, for this reason is not possible to obtain physical properties and spectral analysis and used without purification.

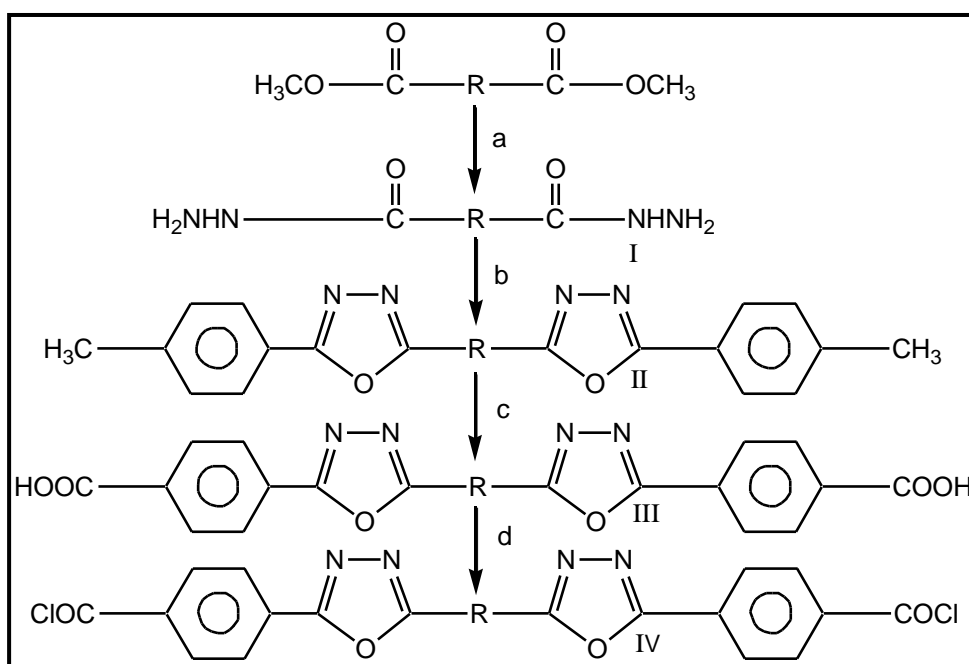
2.6. Synthesis of Polymers (A_{1,2,3}) (AA_{1,2,3}) (E_{1,2,3})


To stirring solution of (*p*-phenyldiamine, Benzidine, thiodiglycol) (0.0004 mol) in dry pyridine (15ml), at - 5c°, a solution of acid chloride (IV₁, IV₂, IV₃) (0.0002 mol) in dry pyridine 15ml was added dropwise. The stirring was continued for half an hour at -5c° and then overnight at room temperature. The solvent was evaporated. To the residue water distilled (30ml) was added. The precipitate was filtered to give polymers. These polymers purified by sodium hydroxide solution.

3. Results and Discussion

4. 3.1. Synthesis

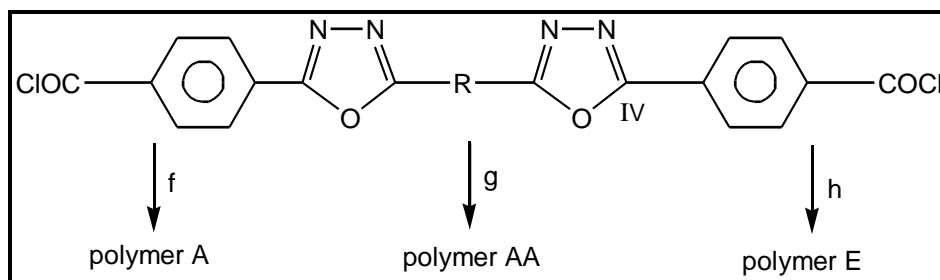
The synthetic routs used for the synthesis of IV compounds in series (1, 2, 3) are outlined in Scheme I.



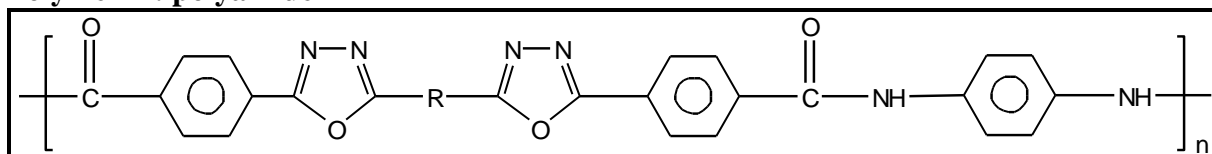
Scheme I: R = 0, (CH₂)₄, 

The synthetic routes of IV compounds, reactions and reagents: (a) Ethanol, NH₂NH₂, H₂O; (b) POCl₃, 4-methylbenzoicacid; (c) KMnO₄, Pyridine H₂O; (d) SOCl₂, DMF.

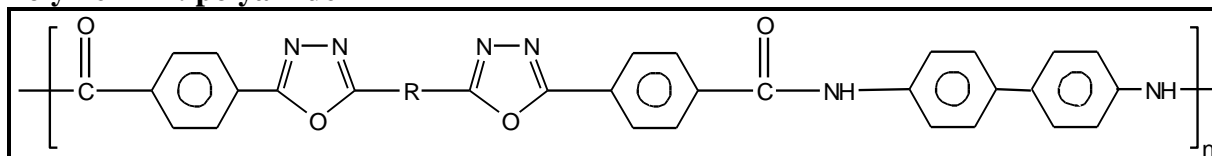
The Synthetic routs for the synthesis of polymers in series (1, 2, 3) are outlined in Scheme II.



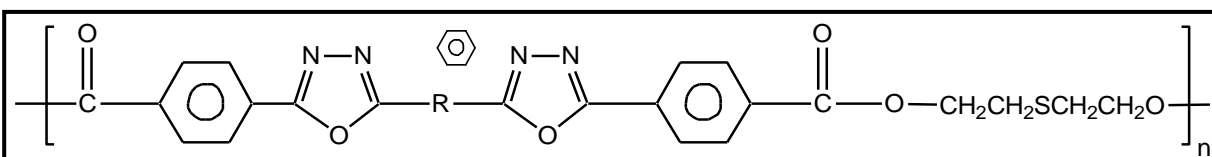
Polymer A: polyamide



Polymer AA: polyamide



Polymer E: polyester



Scheme II: R = 0, (CH₂)₄,

The synthetic route of polymers, reactions and reagents:

(a) Pyridine, *p*-Phenylenediamine; (b) Pyridine, Benzidine; (c) Pyridine, Thiodiglycol.

The first step of the scheme 1 is the synthesis of hydrazide in good yield from reaction of ester [R = 0, (CH₂)₄,] with excess of hydrazine hydrate in ethanol [18]. The hydrazide compounds (I_{1, 2, 3}) and 4 – methyl benzoic acid could be smoothly cyclicly dehydrated by boiling in phosphorus oxychloride to obtained the oxadiazole compounds (II_{1, 2, 3}) in good yields, the ¹HNMR spectrum of compound II₁ shows the methyl group at δ2.5 ppm and phenyl group at δ 7.4 – 8.0 ppm. This analysis of this compound is good evidence which correspond to the structure of suggested compound.

The oxidation reaction of methyl group in compounds of series (1, 2, 3) using potassium permanganate in pyridine gives compounds (III_{1, 2, 3}). The structures of these compounds were confirmed by their higher melting points and FTTR spectral data tables (1, 2, 3).The FTIR spectrum for the compound III₃ shows broad O – H stretching absorption in the region (3304 – 2391 cm⁻¹) as was as the C = O absorption at (1687 cm⁻¹).

The compounds (IV_{1, 2, 3}) were converted to the corresponding acid chloride by refluxing with thionyl chloride in presence of few drops of DMF. These compounds are very active and sensitive to the moisture, for this reason is not possible to obtain their physical properties and spectral analysis and without purification

Finally, the polymers (A_{1, 2, 3}) (AA_{1, 2, 3}) (E_{1, 2, 3}) were synthesized by reaction of compounds (IV_{1, 2, 3}) with (*p*-phenylenediamine, benzidine, thiodiglycol) respectively to yield a new three series of polymers (A_{1, 2, 3}) (AA_{1, 2, 3}) (E_{1, 2, 3}). The structures of these polymers were characterized

by spectral data (FTIR and $^1\text{H-NMR}$). These analysis are consistent with their proposed structures, (see Tables1, 2, 3).in the FTIR spectra of polymer A₂ a marked rise in the carbonyl frequency is observed (1697 cm^{-1}) this is due to the unsaturation adjacent to the C – O group.

The HNMR spectrum of polymer E, for example shows a broad

peak at δ 4.45 ppm to the group of $\text{O}=\text{C}-\text{OCH}_2$ polymer and a doable peak at δ (2.8 – 3.2) ppm to the OCH_2 SCH_2 groups. And appearances of peaks at δ 7.35 – 8.4 ppm for the aromatic hydrogen are good evidence for the structures given to the polymer.

5. 4. Conclusions

New three series of polymers {poly amides (A, AA), polyester E} containing two heterocyclic rings 1, 3, 4- oxadiazole have been prepared.

The chemical structures of these compounds were examined by FT- IR and $^1\text{H-NMR}$ spectroscopies. The results are in agreement with the considered molecular structure.

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Table(1): The Physical Properties, FTIR Spectral Data Of Compounds In Series 1 ($R = 0$).

No.	Name of Compound	M.P. °C	Yield %	FTIR Characteristic Bands (V/cm^{-1})		
I₁	Oxalohydrazide	251	90	C = O 1680		
II₁	5,5̄-di-p-tolyl-2,2̄-bi(1,3,4-oxadiazole)	192	87	C = N oxadiazole 1612	C – H ali. 2922	C – O – C sym. & asym 1184 – 1288
III₁	4,4̄-([2,2̄-bi(1,3,4-oxadiazole)]-5,5̄-diyl)di benzoic acid	> 300	80	1614	C = O 1693	O – H 2924 – 2546
IV₁	4,4̄-([2,2̄-bi(1,3,4-oxadiazole)]-5,5̄-diyl)di benzoyl chloride			-	-	-
	Polymer A ₁	> 300		1610	1649	N – H 3300
	Polymer AA ₁	> 300		1612	1649	3302
	Polymer E ₁	> 300		1610	1716	3400

Table (2): The Physical Properties, FTIR Spectral Data Of Compounds In Series 2 ($R = (CH_2)_4$).

No.	Name of Compound	M.P. °C	Yield %	FTIR Characteristic Bands (V/cm^{-1})		
I ₂	Adipohydrazide	194	88	C = O 1631		
II ₂	1,4-bis(5-(<i>p</i> -tolyl)-1,3,4-oxadiazol-2-yl)butane	> 300	86	C = N Oxadiazole 1618	C – H ali. 2922	C – O – C sym. & asym. 1180 – 1244
III ₂	4,4̄-(5,5̄-(butane-1,4-diyl)bis(1,3,4-oxadiazole-5,2-diyl)) di benzoic acid	> 300	85	1614	C = O 1685	O – H 3066 – 2549
IV ₂	4,4̄-(5,5̄-(butane-1,4-diyl)bis(1,3,4-oxadiazole-5,2-diyl)) di benzoyl chloride			-	-	-
	Polymer A ₂	> 300		1616	C – H ali. 2924	N – H 3397
	Polymer AA ₂	> 300		1615	2924	3381
	Polymer E ₂	> 300		1612	1670	3422

Table (3): The Physical Properties, FTIR Spectral Data Of Compounds In Series 3 ($R =$ ).

No.	Name of compound	M.P. °C	Yield %	FTIR Characteristic Bands (V/cm^{-1})		
I ₃	Terephthalohydrazide	> 300	85	C = O 1693		
II ₃	1,4-bis(5-(<i>p</i> -tolyl)-1,3,4-oxadiazole-2-yl) benzene	> 300	83	C = N oxadiazole 1610	C – H ali. 2924	C - O – C sym. & asym. 1182 – 1271
III ₃	4,4̄-(5,5̄-(1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)) di benzoic acid	> 300	80	1614	C = O 1687	O – H 3066 – 2542
IV ₃	4,4̄-(5,5̄-(1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)) di benzoyl chloride			-	-	-
	Polymer A ₃	> 300		1620	1691	N – H 3400
	Polymer AA ₃	> 300		1612	1664	3402
	Polymer E ₃	> 300		1612	1662	3425

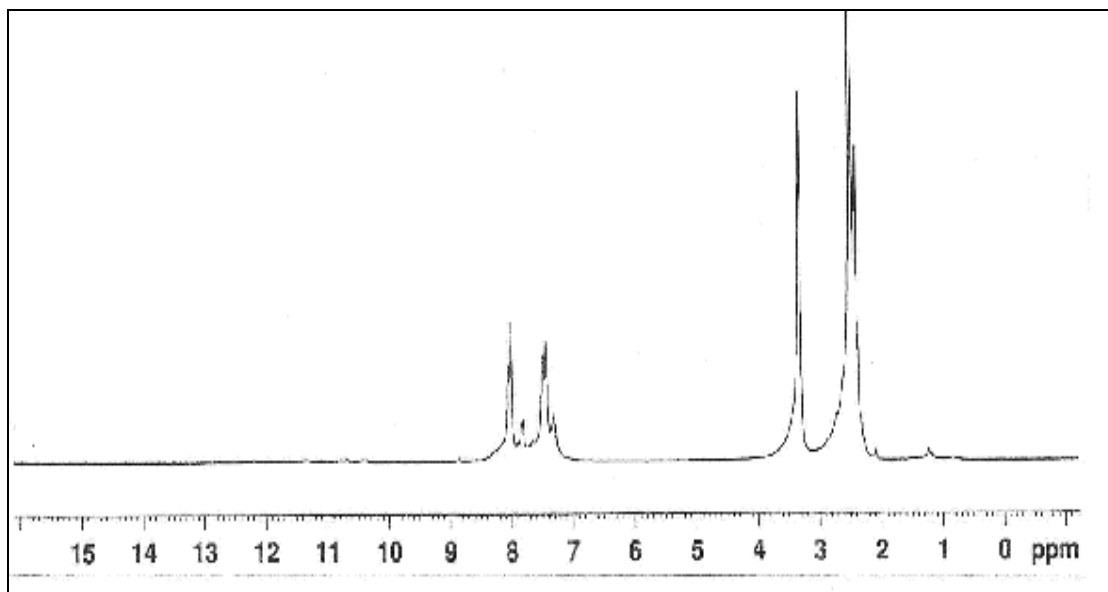


Figure (1):¹HNMR Spectrum for Compound II₁.

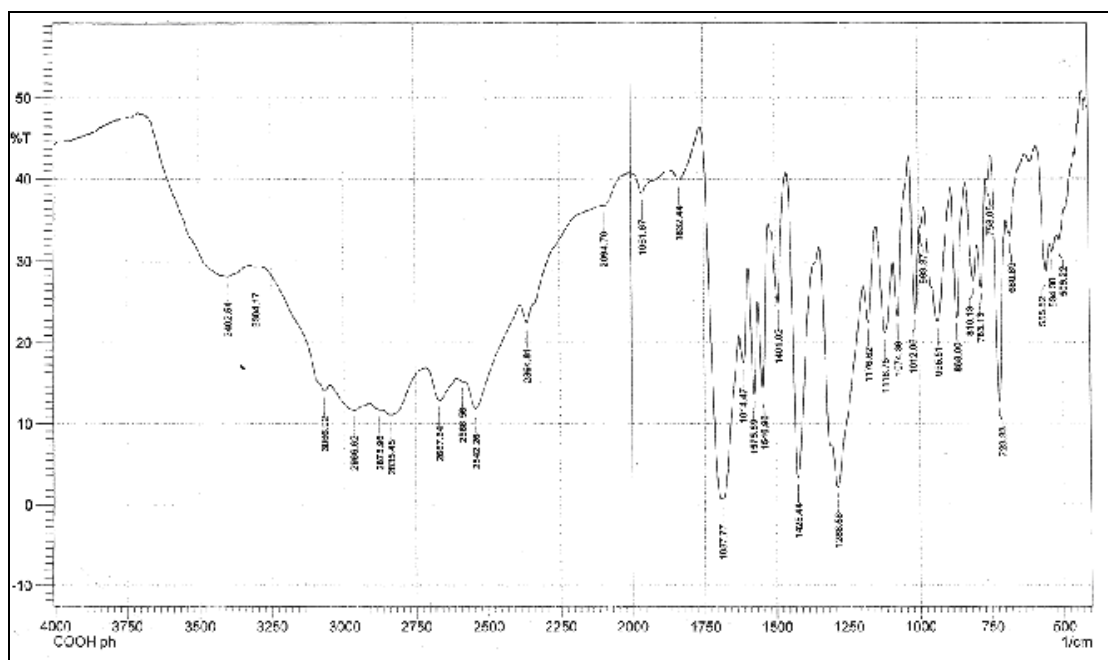


Figure (2): The FTIR Spectrum for Compound II₃

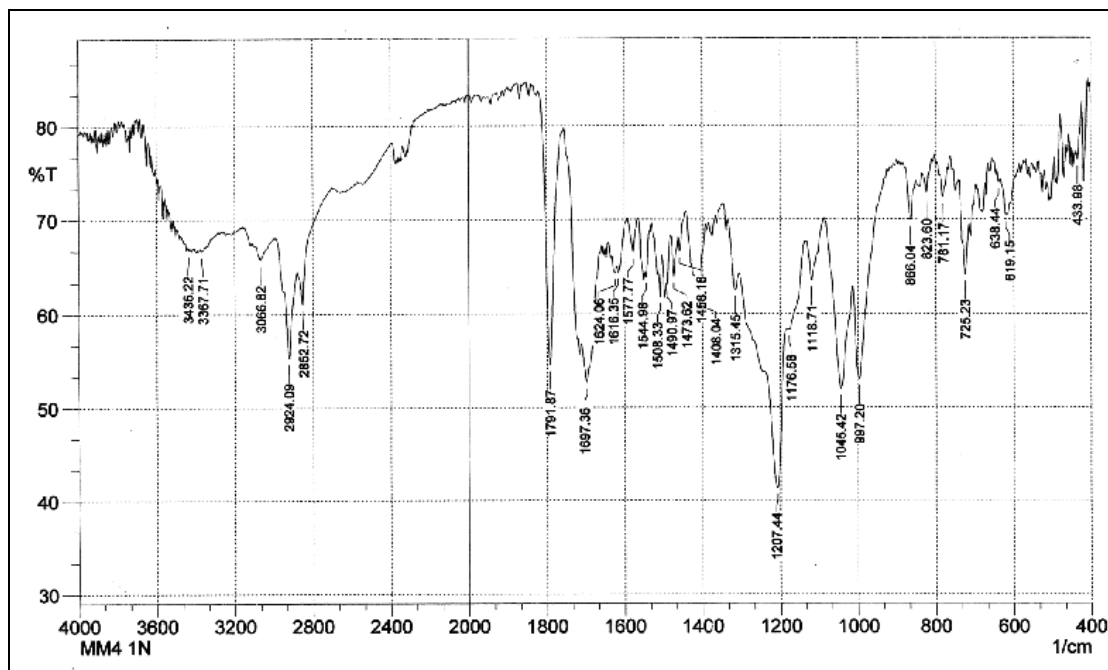


Figure (3): The FTIR Spectrum for Polymer A₂

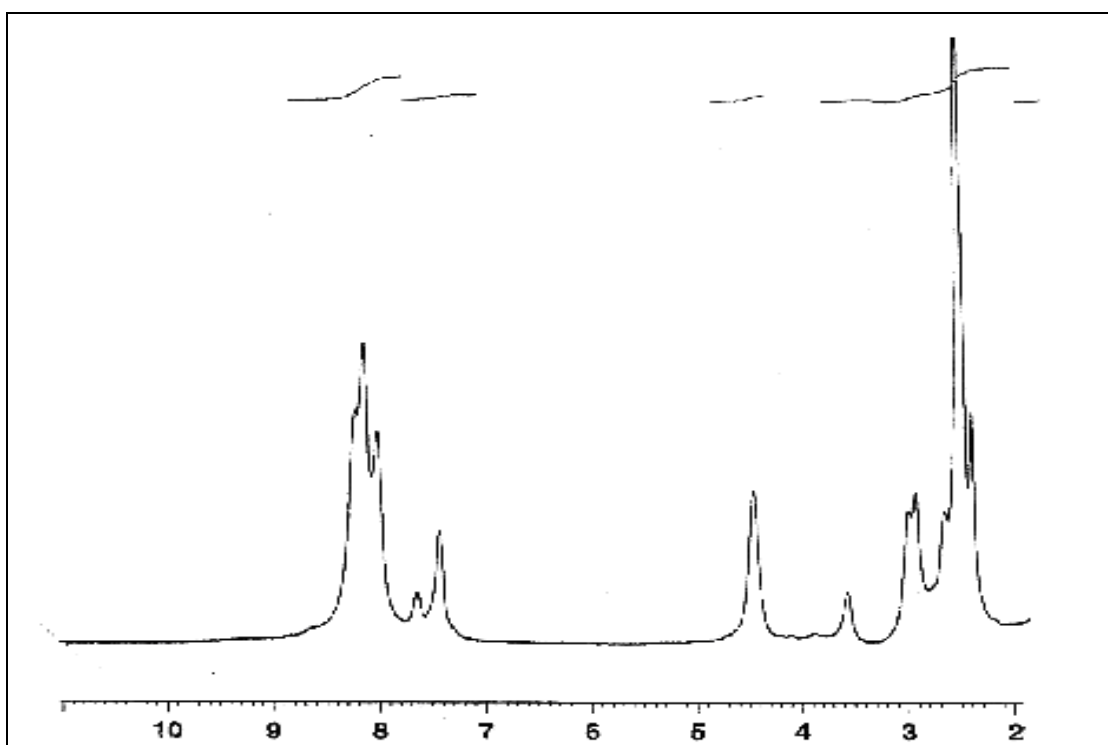


Figure (4): The ¹H NMR Spectrum for Polymer E₁