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Synthesis of Newbis Polymers Derived from Poly Methyl Methacrylate

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Abstract: ***In the present study, new eight polymers of poly methyl methacrylate have been synthesized with three steps. The first method involved direct reaction of different carboxylic acid derivatives with thionyl chloride to give acid chloride (A1-A8), while the second step involved treatment of thiourea with the (A1-A8) in a suitable solvent in the presence amount of (Et_3N) to obtain new compounds (B1-B8). Finally the third step was involved condensation of poly methyl methacrylate with (B1-B8) producing eight new polymethyl methacrylate derivatives. The prepared new compounds and polymers identified by spectral methods (FT-IR,^{1}H-NMR) and measurement some of its physical properties and some specific reaction.***

Keywords: PMMA, acid chloride derivatives, thiourea

1. Introduction

Polyimides have garnered tremendous interest a cross arranges scientific and engineering disciplines. Polyimides are classified as a group of super- engineering plastics owing to their excellent thermal stability [1],and they are a class of representative high- performance and involving aromatic and heterocyclic rings in the main chains are well known as heat- resistant organic materials. However polyimides materials are usually difficult to be processed because of their in fusibility of high temperature and in solubility in most organic solvent [2-3].

These polymers commonly exhibit high thermal stabilities [4] as wellas good mechanical and electronic properties including nonlinear optical and semi conductive characteristics upon dropping making good candidates for use in a variety of optoelectronic applications [5]. Since they can also coordinate to a variety of metal ion, polymer – metal ion interaction be subject of interest for their analytical and technological applications in fields such as environmental,science, industrial separation process and biological researches [6].

2. Material and Methods

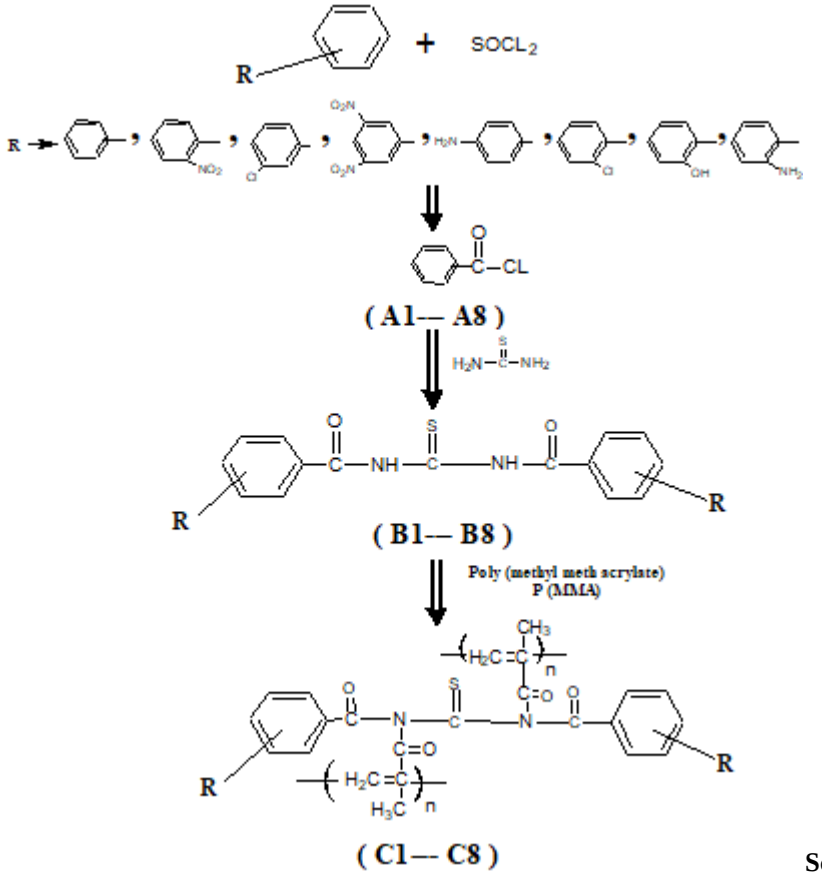
Chemicals employed were of analytical grade and used without further purification. Melting points were determined in Gallen Kamp melting points apparatus and were uncorrected. UV–visible spectra were recorded on shimadzuT60u spectrophotometer using ethanol as a solvent, FT-IR 8400 Fourier transform infrared spectrophotometer as KBr disc. ^{1}H-NMR and ^{13}C- NMR spectra were recorded on Bruker spectroscopy in Ultra shield magnets 300MHz instrument using tetramethylsilanium(TMS) as an inner standard and DMSOd6 as a solvent in Al albayt University in Jordan.

General synthesis of acid chloride (A1-A8) [7]

In the around flask substituted benzoic acid (0.002 mol) was dissolve in DMF(10ml) and then be thionyl chloride(0.3mol)added drop by drop with stirring and refluxed for (3-4) hr. The sedimentcooled to room temperature and recrystallized from ethanol to give the desired products. Melting points, yield% data are listed in table (1).

General synthesis of amide (B1-B8)[7].
A mixture of thiourea with (0.001mol) with acid chloride(0.002 mol) using DMF(10ml) as a solvent with (2 drop) of pyridine as catalyst were refluxed for (4-5) hr . The mixture was allowed to cool to room temperature, and the crude mixture was filtered. And the dried precipitate formed was crushed and recrystallized from ethanol. Melting points, yield% data are listed in table (2).

General procedure preparation of polyamides (C1-C8)[1].
To a solution of amide (0.01mole) in THF(25 ml) poly (methyl methacrylate) (PMMA) (0.01 mole) ,and drops of Et_3N were added in (100 ml) round bottom flask. The mixture was refluxed for (6-8) hrs.After cooling themixture solvent was removed. The separated was filtered and purified by dissolving in DMF and re precipitating from water or acetone. All physical properties are recorded in table (3).



Schem 1: Reaction of preparation of polymer

Table 1: Physical properties of synthesized of acid chloride (A1-A8)

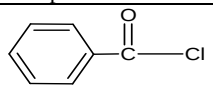
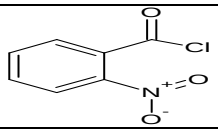
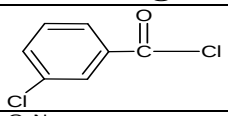
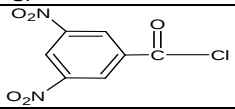
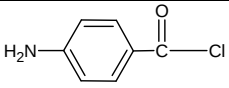
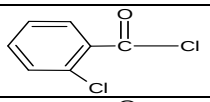
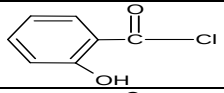
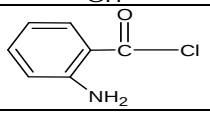
Comp. No.	Compound structure	Melting Point C°	Color	Yield%	Molecular formula	FW
A1		oily	Brown	53.72	C_7H_5ClO	140.567
A2		Oily	Dark brown	67.63	$C_7H_4ClNO_3$	185.565
A3		120-124	Yellow	89.58	$C_7H_4Cl_2O$	175.012
A4		98-111	Yellow	91	$C_7H_3ClN_2O_5$	230.563
A5		Oily	Dark brown	93.2	C_7H_3ClNO	155.581
A6		180-182	Light yellow	91	$C_7H_4Cl_2O$	175.012
A7		Oily	Light yellow	82	$C_7H_5ClO_2$	156.566
A8		193-195	Yellow	95	C_7H_6ClNO	155.581

Table 2: Physical properties of synthesized of amide (B1-B8)

Comp. No.	Compound structure	Melting Point C°	Color	Yield%	Molecular formula	FW.

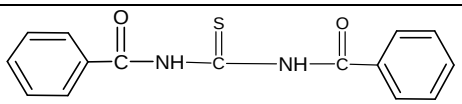
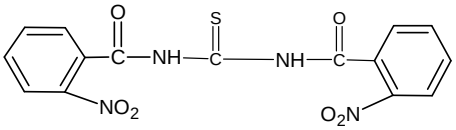
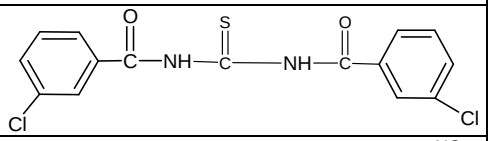
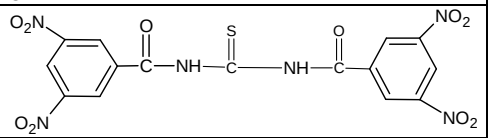
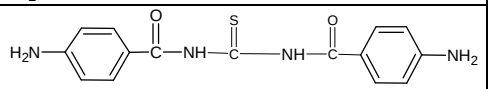
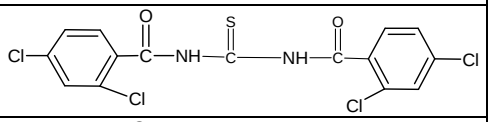
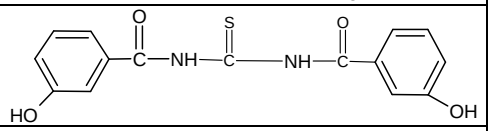
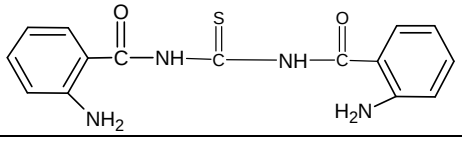
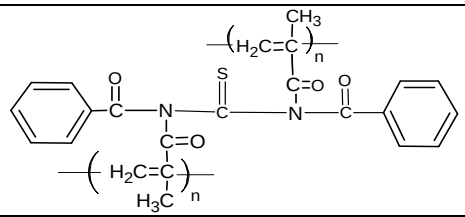
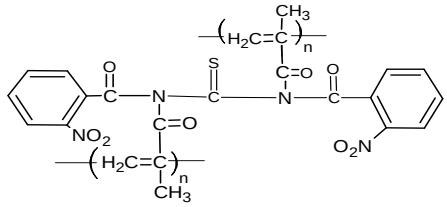
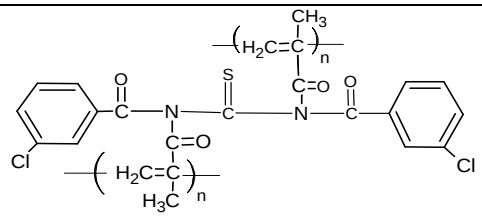
B1		140-144	yellow	75.72	$C_{15}H_{12}N_2O_2S$	284.332
B2		230-233	brown	81.63	$C_{15}H_{10}N_4O_6S$	374.32
B3		192-195	white	63.58	$C_{15}H_{10}Cl_2N_2O_2S$	353.22
B4		171-173	Dark Brown	93	$C_{15}H_8N_6O_{10}S$	464.32
B5		199-203	yellow	73.2	$C_{15}H_{14}N_4O_2S$	314.36
B6		155-158	Light yellow	66	$C_{15}H_{12}N_2O_2S$	422.11
B7		188-191	Yellow	83	$C_{15}H_{12}N_2O_2S$	316.33
B8		162-165	White	60	$C_{15}H_{14}N_4O_2S$	314.36

Table 3: Physical properties of polyamides (C1-C8)

Comp. No.	Compound structure	Melting Point C°	Color	Yield %	Molecular formula	FW
C1		250-260	Brown	75.72	$C_{15}H_{12}N_2O_2S$	284.33
C2		165-175	Faint Yellow	81.63	$C_{15}H_{10}N_4O_6S$	374.32
C3		Oily	Yellow	63.58	$C_{15}H_{10}Cl_2N_2O_2S$	353.22

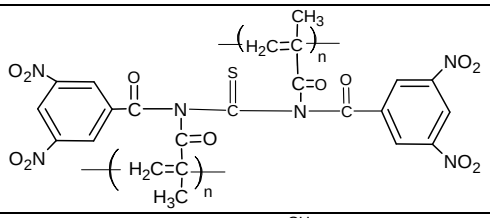
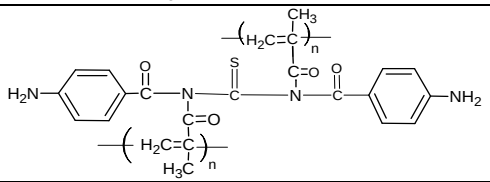
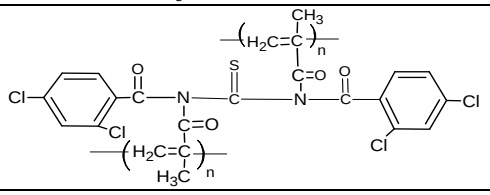
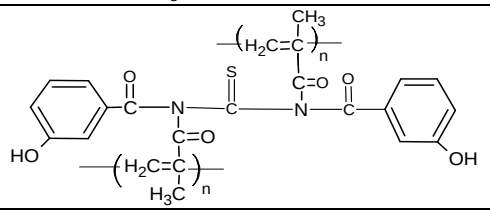
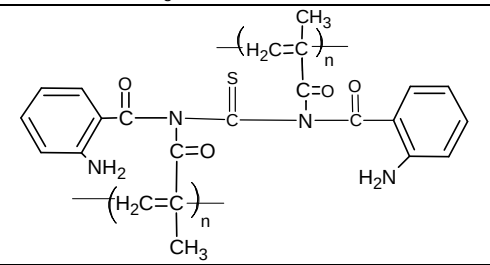
C4		Oily	Brown	93	$C_{15}H_8N_6O_{10}S$	464.32
C5		126-135	Orange	73.2	$C_{15}H_{14}N_4O_2S$	314.36
C6		Oily	Dark Orange	66	$C_{15}H_{12}N_2O_2S$	175.01
C7		235-242	Light yellow	83	$C_{15}H_{12}N_2O_2S$	156.56
C8		Oily	Yellow	60	$C_{15}H_{14}N_4O_2S$	314.36

Table 4: FT-IR spectral data for some functional group for all product compounds (B1-B8)

Comp. No.	υ (C-H) Aromatic cm^{-1}	υ (N-H)	υ (C-N)	υ (C=O)	υ (C-S)	υ (C=C)	Others
B1.	3182-3024	3387	1315	1616	667	1531	-
B2.	3005-3170	3394	1257	1720	694	1616	υ (NO_2) 1354,1531
B3.	3032-3197	3302	1303	1693	621	1612	υ (C-Cl) 1063
B4.	3035-3186	3375	1404	1635	725	1620	υ (NO_2) 1350,1543
B5.	3024	3270	1465	1683	732	1604	υ (NH_2) 3329
B6.	3030	3402	1471	1701	771	1587	υ (C-Cl)1024
B7.	2960	3375	1410	1670	690	1612	υ(OH) 3460
B8.	3024	3213	1415	1651	790	1577	υ(NH_2) 3383

Table 5: FT-IR spectral data for some functional group for all product compounds (C1-C8)

Comp. No	υ (C-H) Aromatic cm^{-1}	υ (C-H) Aliphatic cm^{-1}	υ (C=O)	υ (C-S)	υ (C=C)	υ (C-N)	Others
C1	3111	2987-2954	1714	617	1635	1475	-
C2.	3075	2881-2956	1765	626	1668	1394 -	υ (NO_2) 1357,1460
C3.	3140	2953-2997	1732	752	1635	1436	υ (C-Cl) 1149
C4.	3109-3174	2950	1728	635	1635	1456	υ (NO_2) 1348,1544
C5.	3104	2939	1735	650	1640	1399	υ (NH_2) 3400

C6.	3040	2889-2947	1676	746	1558	1454	υ (C-Cl) 1056
C7.	2953-2983	2887	1699	698	1651	1465	υ(OH) 3450
C8.	3024	2781	1685	617	1616	1465	υ(NH_2) 3421

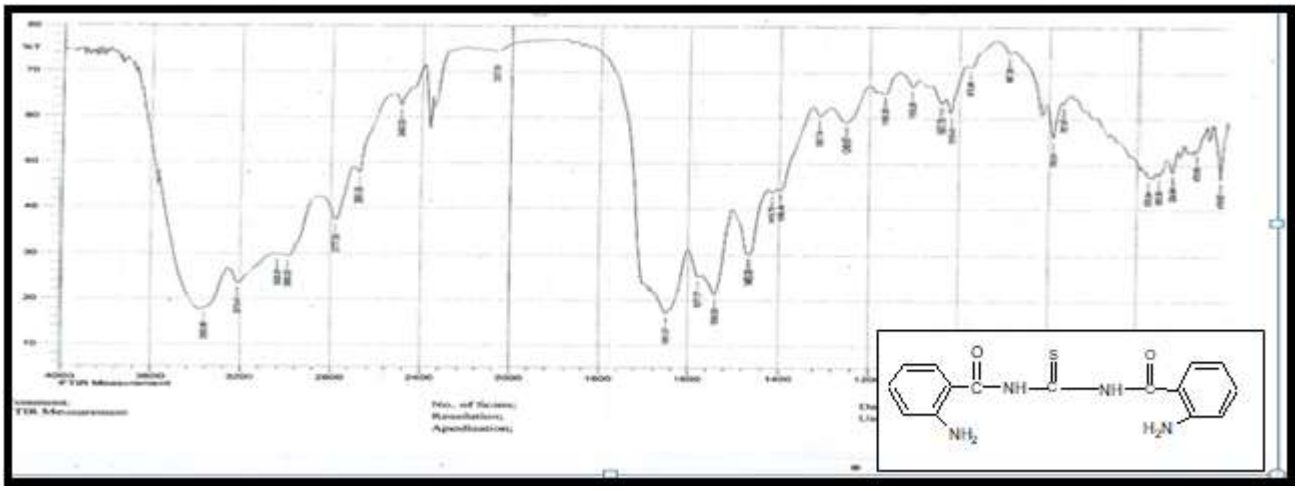


Figure 1: FT-IR spectrum of compound (B8)

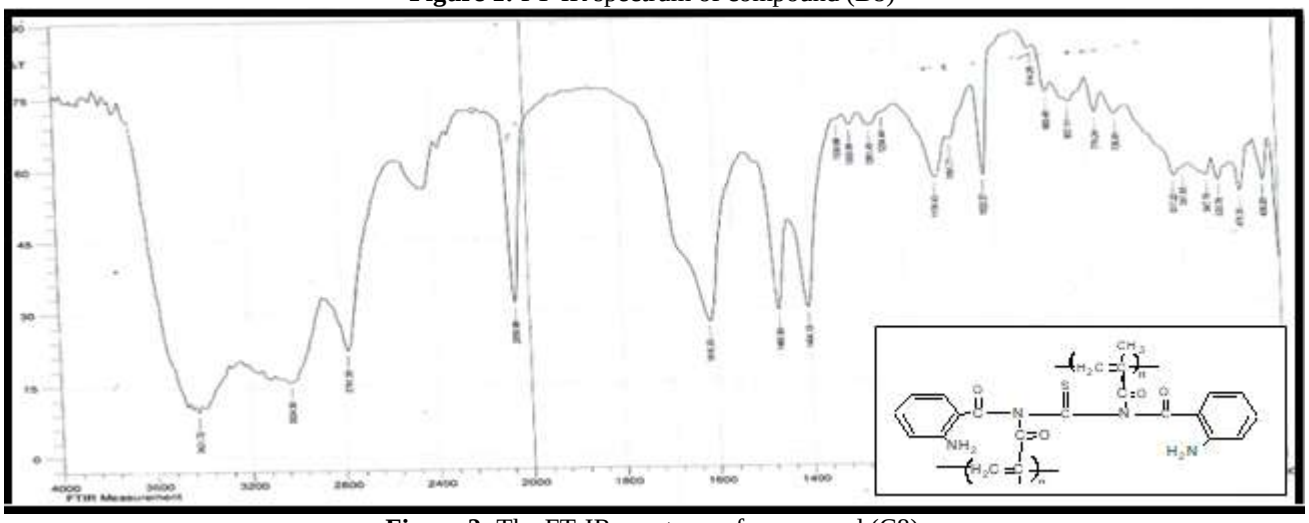
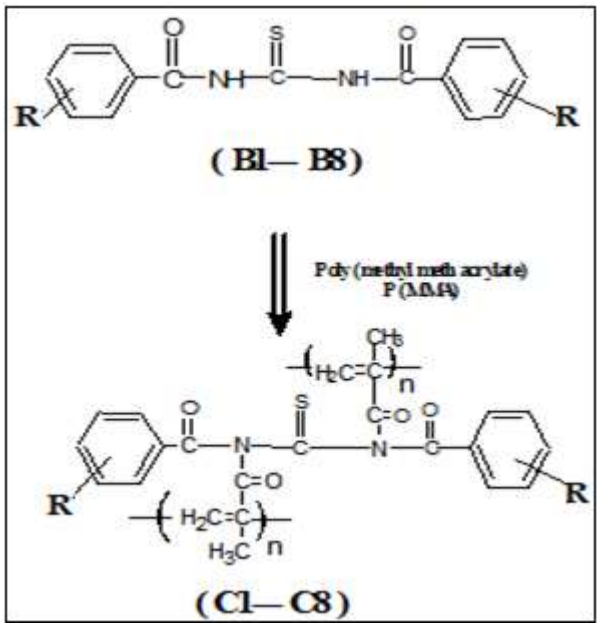


Figure 2: The FT-IR spectrum of compound (C8)

3. Results and Discussion

Poly imides are important family of organic compounds that posse's wide spectrum of biological activities [8]. The present work involved three steps, first step include preparation of new eight acid chloride (A1-A8) were prepare by reaction of different substituted benzoic acid with thionyl chloride [9] in DMF. The synthesis of these compounds was carried out lined in scheme (1) and the physical properties for these compounds including melting point and yield as shown in table (1). Structures ofthe prepared were confirms by FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectrum of compound (A8) showed clear absorption band at (3062, 2939, 1701 and 1049) cm^{-1} attributed to υ (C-H aromatic), υ (C-H aliphatic), υ (C=O) and υ (C-Cl) respectively. The ^{1}H-NMR spectrum of compound (A5) showed the single at (8.5-8.7) ppm attributed to (NH_2) proton, and multiple signal at (7.26-7.51) ppm due to aromatic protons as shown in fig.(3).The second strategy used in work involved building of new amides (B1-B8) by reaction of acid chloride (A1-A8) which prepared in first step with thiourea the synthesis of these compounds was carried out lined in scheme (1) and these compounds were identified by FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectrum of compound (B8) showed clear absorption band at (3213,3024 and 1651) cm^{-1}due to υ (N-H), υ (C-H aromatic) and υ (C=O) amide and respectively. And disappearance the absorption of υ (C-Cl) groups shown in fig.(1),Also in the^{1}H-NMR spectrum of compound (B5) showed the single at (5.45) ppm was attributed to (N-H) proton, and multiple signal at (7.16-7.41) ppm due aromatic protons and single at (8.61-8.93) ppm due to (NH_2)protons as shown in fig.(4). Moreover, In order to obtain poly imides (C1-C8) the amides (B1-B8) were subjected to another nucleophilic substitution by treating with poly methyl methacrylate (PMMA) using triethylamine (Et_3N) as a catalyst [10], as shown in the following equation [11]:-



Scheme (2)

TheFT-IR spectrum of compound (C8) (see fig.(2)) showed the disappearance of amide bands (N-H) at (3455) cm^{-1} and appearance of band at (1685, 3024, 2781and 1465) cm^{-1} attributed to υ (C=Oamide) , υ (C-H aromatic), υ (C-H aliphatic) and υ(C-N) respectively. All these bands are listed in table (5), while the ^{1}H-NMR spectrum of compound (C1) showed different characteristic singles,two multiple (3.03 and 3.75) ppm assigned for ethylene (acryl) protons and multiple single at (7.141, 8.21) ppm to aromatic protons and singlet at (1.12, 1.71) ppm due (CH_3) protons as shown in fig.(5). Also the 1H-NMR spectrum of compound (C3) showed different characteristic singles at (4.29 and 4.49) ppm assigned for ethylene (acryl) protons and multiple single at (7.51- 8.11) ppm to aromatic protons and singlet at (1.21) ppm due (CH_3) protons. Thecompound (C5) showed four different characteristic singles, two multiple (2.64 and 3.03) ppm assigned for ethylene (acryl) protons and multiple single at (7.61, 7.72) ppm to aromatic protons and singlet at (8.61, 8.87) pmm due (NH_2) protons and singlet at (1.62) pmm due (CH3) protons as shown in fig.(6).

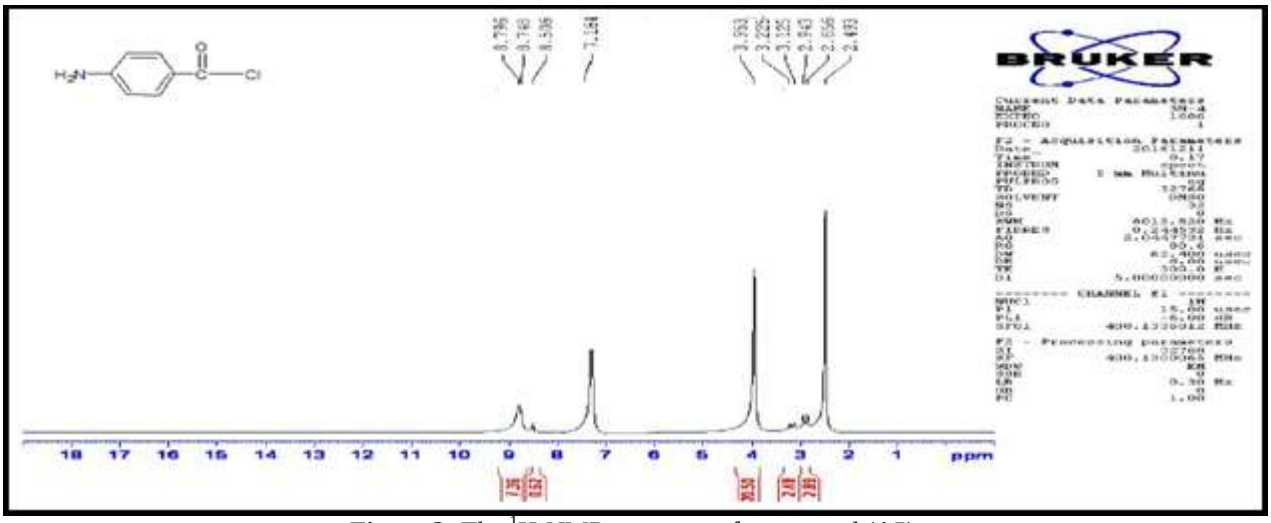


Figure 3: The ^{1}H-NMR spectrum of compound (A5)

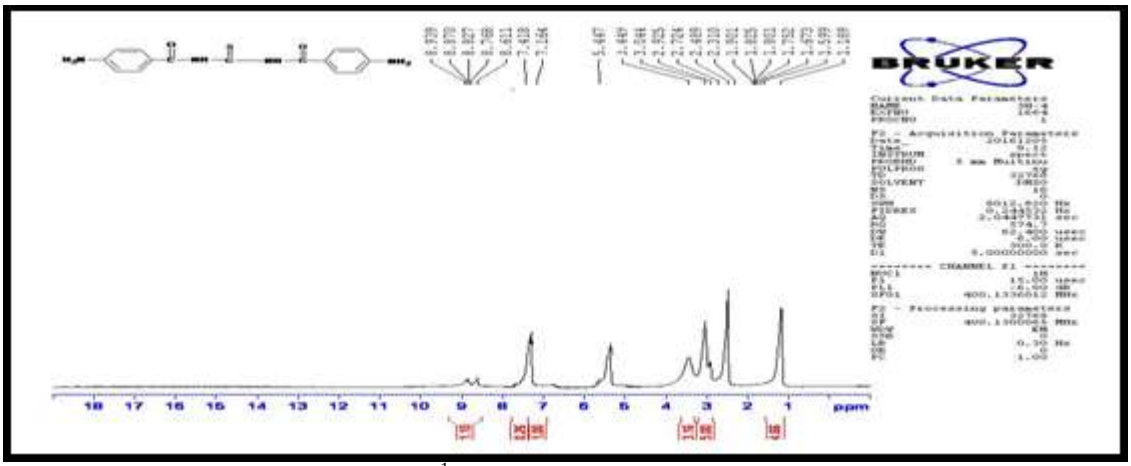


Figure 4: The ^{1}H-NMR spectrum of compound (B5)

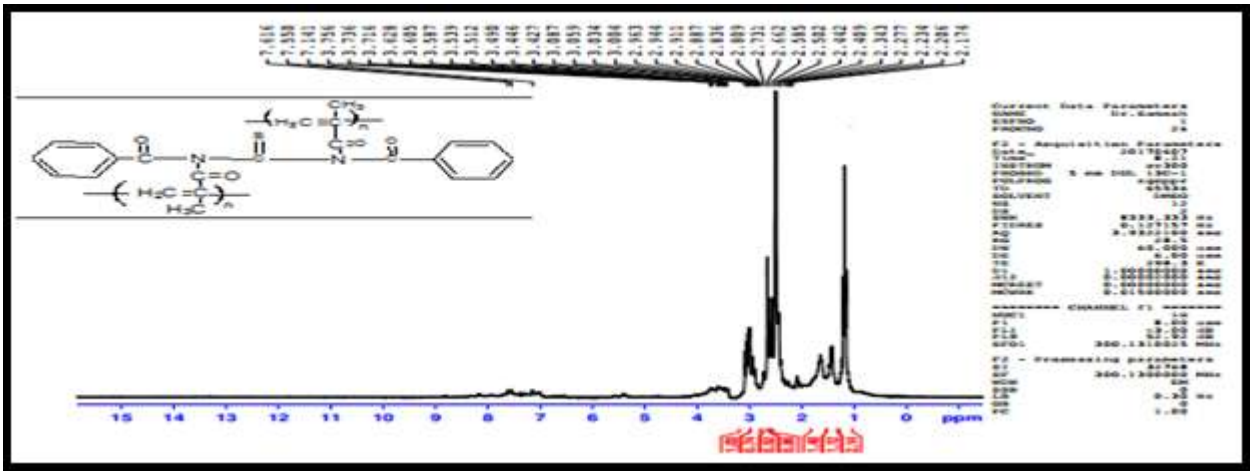


Figure 5: The 1H-NMR spectrum of compound (C1)

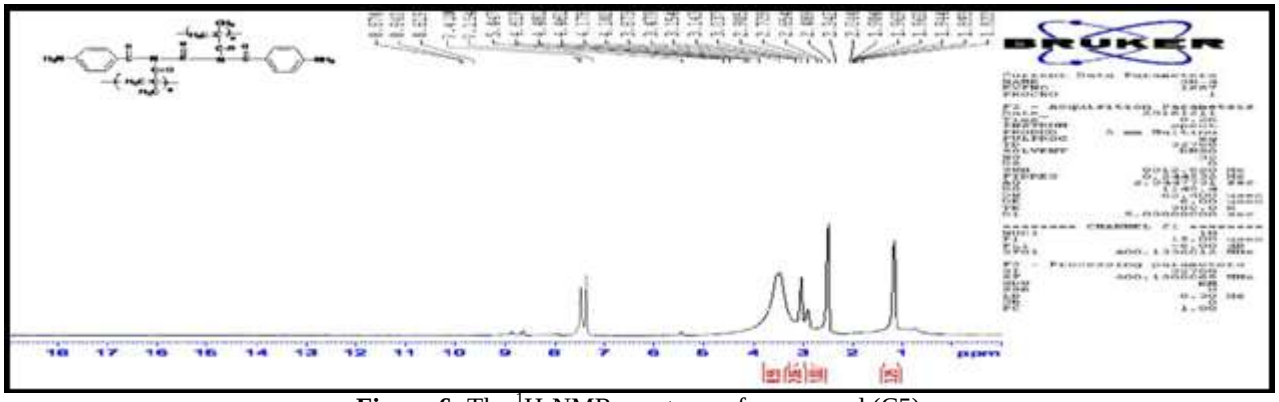


Figure 6: The ^{1}H-NMR spectrum of compound (C5)

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