

## Synthesis of New Polymers Derived from Poly (vinyl Chloride) and Study Their Biological Evaluation

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**Abstract:** Poly(vinyl chloride) (PVC) was modified with phthalyl and 1,3,4-thiadiazole binding units in a three steps reaction. First, five phthaloyl amino acids [1-5] was prepared by heating a mixture of finely grounded phthalic anhydride and appropriate amino acid. Second, Reaction of compounds [1-5] with thiosemicarbazide in the presence of POCl<sub>3</sub> afforded five new 1,3,4-thiadiazole compounds [6-10]. Third, Five modified PVC-polymers containing 1,3,4-thiadiazole and phthalyl groups in the repeating units were synthesized through the reaction of compounds [6-10] with PVC in THF solvent. Finally, the structures of the all synthesized compounds were characterized by spectral (IR and UV) analysis, CHNS, melting point for organic compounds and softening point for polymers; the results indicated the expected structures of these compounds. The prepared compounds were tested for their antimicrobial activities.

**Key words:** Poly(vinyl chloride), 1,3,4-thiadiazole, spectral studies, biological activity

### INTRODUCTION

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research (Chen et al. 2008). A number of ligands including polydentate amines, crown ethers, phosphines and bipyridines have been bound with mainly polystyrene divinylbenzene copolymers (Gustafsson et al. 2003; Genhua and Pan 2005). These studies are mostly concerned with ion-binding and catalytic aspects. Very little information appears to exist as to whether, and to what extent, such organic compounds can influence the properties of the macromolecule. Recently, scientists were able to modify PVC by introduction aromatic and heterocyclic moieties through halogen displacement reaction. PVC, thus modified, showed improved overall photochemical stability (Yousif et al. 2007). The facial chlorine displacement from PVC indicated the possibility on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes (Aliwi et al. 2005). This article will describe the synthesis and biological evaluation of 1,3,4-thiadiazole and phthalyl groups as a pending groups into the repeating unit of PVC polymer.

### MATERIALS AND METHODS

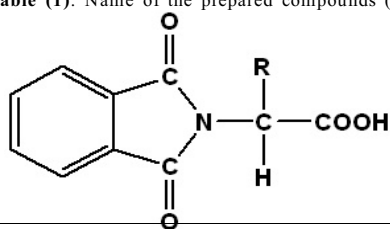
#### *(Step1) Synthesis of (2-phthalimidyl)-carboxylic Acid [1-5]:*

A mixture of (0.06 mole) of appropriate amino acid and (0.06 mole, 2.22 g) of finely grounded phthalic anhydride was heated for (30 min) with stirring in oil bath at 145-150 °C. After cooling, the solid material was dissolved in (40 ml) of hot methanol, the filtrate solution was diluted with (40 ml) of water, and the product allowed to crystallize slowly to give the titled product. The physical data are listed (Tables 2).

#### *Syntheses of [1-phthalimidyl -1-(2-amino -1,3,4-thiadiazol-5-yl)-1-(Substituted)]-methane. [6-10]:*

A mixture of appropriate 2-(phthalimidyl)-carboxylic acid (0.002 mole), thiosemicarbazide (0.002 mole, 0.18 g), phosphoroxchloride (5 ml) was refluxed gently for (3 hr.), after cooling; water was added (50 ml). The mixture was refluxed for (4 hr.), and filtered. The filtrate was neutralized with potassium hydroxide solution. The precipitate was filtrate and washed with distilled water and crystallized from (ethanol-water) to give the desired title compounds [6-10]. The physical data are listed in Table (4)

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**Table (1):** Name of the prepared compounds (1-5).

Compound number	R group	Name of compound
1	-CH <sub>2</sub> - Ph	2-(phthalimidyl), 3-phenyl propanoic acid
2	-CH <sub>2</sub> -CH <sub>2</sub> -S-CH <sub>3</sub>	2-(phthalimidyl),4-(thioyl) butanoic acid
3	-CH(CH <sub>3</sub> ) <sub>2</sub>	2-(phthalimidyl),2-isopropyl-ethanoic acid
4	-CH <sub>3</sub>	2-(phthalimidyl)- propanoic acid
5	-H	2-(phthalimidyl)-ethanoic acid

**Table (2):** Physical data of compounds [1-5]

Compound number	Color	M. P. °C	%Yield	Found(Calcd.)%			
				C	H	N	S
1	White	168-170	61%	68.11 (69.15)	4.34 (4.44)	4.65 (4.74)	-
2	White	123-124	59%	55.87 (55.90)	5.89 (4.69)	5.46 (5.05)	10.65 (11.48)
3	White	108-110	74%	63.32 (64.36)	5.43 (5.79)	6.45 (5.36)	-
4	White	148-150	58%	60.55 (60.27)	3.88 (4.14)	7.32(6.39)	-
5	White	196-198	48%	59.33(58.54)	3.15(3.44)	7.28(6.83)	-

**Table (3):** Name of the prepared compounds (6-10).

Compoundnumber	R group	Name of compound
6	-CH <sub>2</sub> - Ph	[1-(phthalimidyl)-1-(2-amino 1,3,4-thiadiazol-5-yl)-2-(phenyl)-]-ethane
7	-CH <sub>2</sub> -CH <sub>2</sub> -S-CH <sub>3</sub>	[1-(phthalimidyl)-1-(2-amino 1,3,4-thiadiazol-5-yl)-3-(thioyl)-]-propane
8	-CH(CH <sub>3</sub> ) <sub>2</sub>	[1-(phthalimidyl)-1-(2-amino-1,3,4-thiadiazole-5-yl)-1-(isopropyl)-]-methane
9	-CH <sub>3</sub>	[1-phthalimidyl-1-(2-amino-1,3,4-thiadiazol-5-yl)-]-ethane
10	-H	[1-phthalimidyl-1-(2-amino-1,3,4-thiadiazol-5-yl)-]-methane

**Table (4):** Physical data of compounds [6-10]

Compound number	Color	M. P. °C	%Yield	Found(Calcd.)%			
				C	H	N	S
6	White Yellowish	243-244	42%	60.38(60.70)	4.22(3.60)	15.75(16.66)	8.85(9.53)
7	Pale Yellow	192-195	67%	51.37(50.28)	3.45(4.22)	17.53(16.75)	19.43(19.18)
8	White	186-188	62%	58.47(56.94)	5.35(5.10)	18.44(17.71)	10.34(10.14)
9	Yellow	221-223	55%	53.87(52.52)	4.17(3.67)	21.12(20.43)	11.50(11.69)
10	Off White	268-270	64%	49.43(50.76)	3.54(3.10)	24.53(21.53)	11.22(12.39)

**(Step3): Synthesis of Target Modified Polymers [PI-PV]:**

Appropriate thiadiazole compounds [6-10] (0.04 m mole) was added to (0.25 g) Poly(vinyl chloride) and three drops of pyridine in (25 mL) tetrahydrofuran (THF). The mixture was refluxed for (3 hr.). The modified polymers were filtered, washed with redistilled water, ethanol, and ether then dried under vacuum.

**Table (5):** The Softening point of the modified polymers and PVC

Symbol of the polymer	Color	Softening point (°C)
PI	Colorless	142-146
PII	Yellow brownish	132-137
PIII	Yellow	121-125
PIV	Light Yellow	130-135
PV	Off white	114-118
PVC	Colorless	200-205

#### **Antimicrobial Screening:**

The antimicrobial activities of the compounds were tested against six pathogenic micro organisms (i) *Staphylococcus aureus* (Gram positive bacteria), (ii) *Streptococcus viridans* (Gram positive bacteria), (iii) *Escherichia coli* (Gram Negative bacteria), (iv) *Fusarium oxysporium* (Fungus), (v) *Alternaria alternata* (Fungus), (vi) *Alternaria solani* (Fungus). The culture was maintained by the reported procedure (Atlas et al. 1995). The antimicrobial activity of the extracts was qualitatively determined by a modified disc diffusion method. A lawn of micro-organisms was prepared by pipetting and evenly spreading inoculum (105-106 c.f.u./cm<sup>3</sup>) [c.f.u. colony forming units] onto agar set in Petri dishes, using nutrient agar (NA) for bacteria. Whatman No. 1 filter paper discs of 6 mm diameter were impregnated with the stock solutions of the prepared compounds (100 mg cm<sup>-3</sup>) in DMSO and dried under sterile condition. The dried discs were then placed on the previously inoculated agar surface. The plates were inverted and incubated for 24 h. at 30 °C. Antimicrobial activity was indicated by the presence of clear inhibition zones around the discs.

#### **Instrumentation:**

The percentage compositions of the elements (CHNS) for the compounds were determined using an elemental analyzer CHNS Model Fison EA 1108. Melting points were recorded on a hot stage Gallen Kamp melting point apparatus and were uncorrected. Softening points were determined using thermal microscope (Kofler-method), Reichert thermovar. The FTIR spectra in the -range (4000-400) cm<sup>-1</sup> cut were recorded as KBr disc on FTIR.8300 Shimadzu Spectrophotometer. The Uv-visible spectra were measured using Shimadzu Uv-vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm.

## **RESULTS AND DISCUSSION**

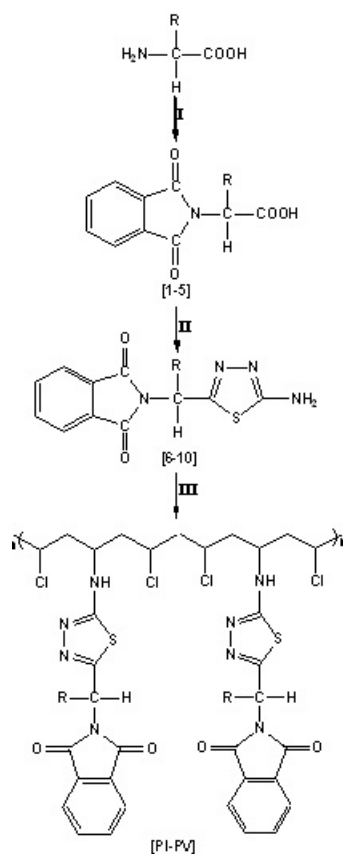
#### **Synthesis and Characterization:**

Poly(vinyl chloride) (PVC) is a polymer of great commercial importance, and it has a variety of applications ranging from containers for blood or urine to cable insulation to packaging materials. One of the most problem in PVC its low thermal and photostability against sunlight, thus, the modification of PVC have intensively been examined in the literature, For instance, it has been shown by our group researcher that the degradation rate of modification (PVC-heterocyclic) are lowerd than unmodified PVC .ie., this modification can have stabilizing effect on the PVC, The covalent modification of PVC for the introduction of heterocyclic units such as (1,3,4-oxadiazole, 1,3,4-thiadiazole, benzothiazole, benzoxazole, benzimidazole) to the polymer main chain can be achieved by nucleophilic substitution reaction of chlorine atoms, Mercapto and amino heterocyclic compounds have been shown to be appropriate modification reagents for this strategy. We have designed a new functional polymeric material by modifying a commercially available polymer (PVC), through introducing 1,3,4-thiadizole and phthalyl units. The synthetic details of the applied strategy for this modification of PVC are shown in Scheme (1).

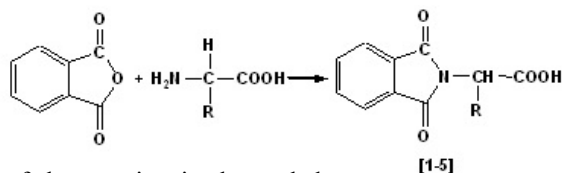
2-(phthalimidyl)-carboxylic acid [1-5] was prepared from nucleophilic addition-elimination reaction of appropriate amino acid and phthalic anhydride by heating.

These compounds were characterized by their melting points, FTIR spectroscopy and UV-Vis spectroscopy. The main band appeared at (1726-1693) cm<sup>-1</sup> which are assigned as (O=C-N) group, (3001-3112) cm<sup>-1</sup> for C-H aromatic. These bands which proved the conversion of amino acid to compounds [1-5], moreover, compounds [1-5] showed characteristic IR bands at (1772-1749) cm<sup>-1</sup> for (O=C-OH), (3200-3267) cm<sup>-1</sup> for OH, (2918-2971) cm<sup>-1</sup> C-H aliphatic of amino acid, the other bands shown in the Tables (6 to 10).

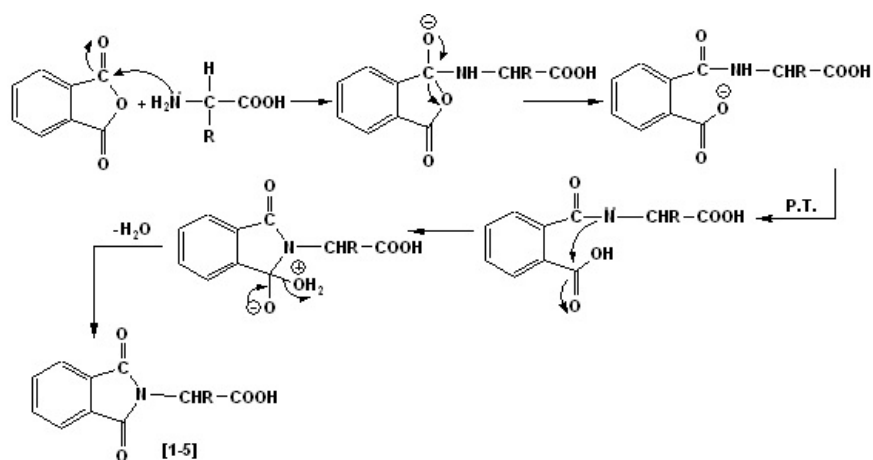
Compounds [1-5] and equivalent of thiosemicarbazide were subjected by cycloaddition reaction by means of POCl<sub>3</sub> leading to the formation of 2-amino-5-(substituted) thiadiazoles [6-10].



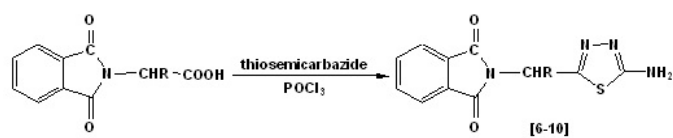
**Scheme (1):** Reagents and conditions: (I) Phthalic anhydride, heat (30 min), (II) Thiosemicarbazide,  $\text{POCl}_3$  (reflux 3 hr.), then water (50 ml) (reflux 4 hr.), (III) PVC, THF, 3drops Pyridine (reflux 3 hr.).



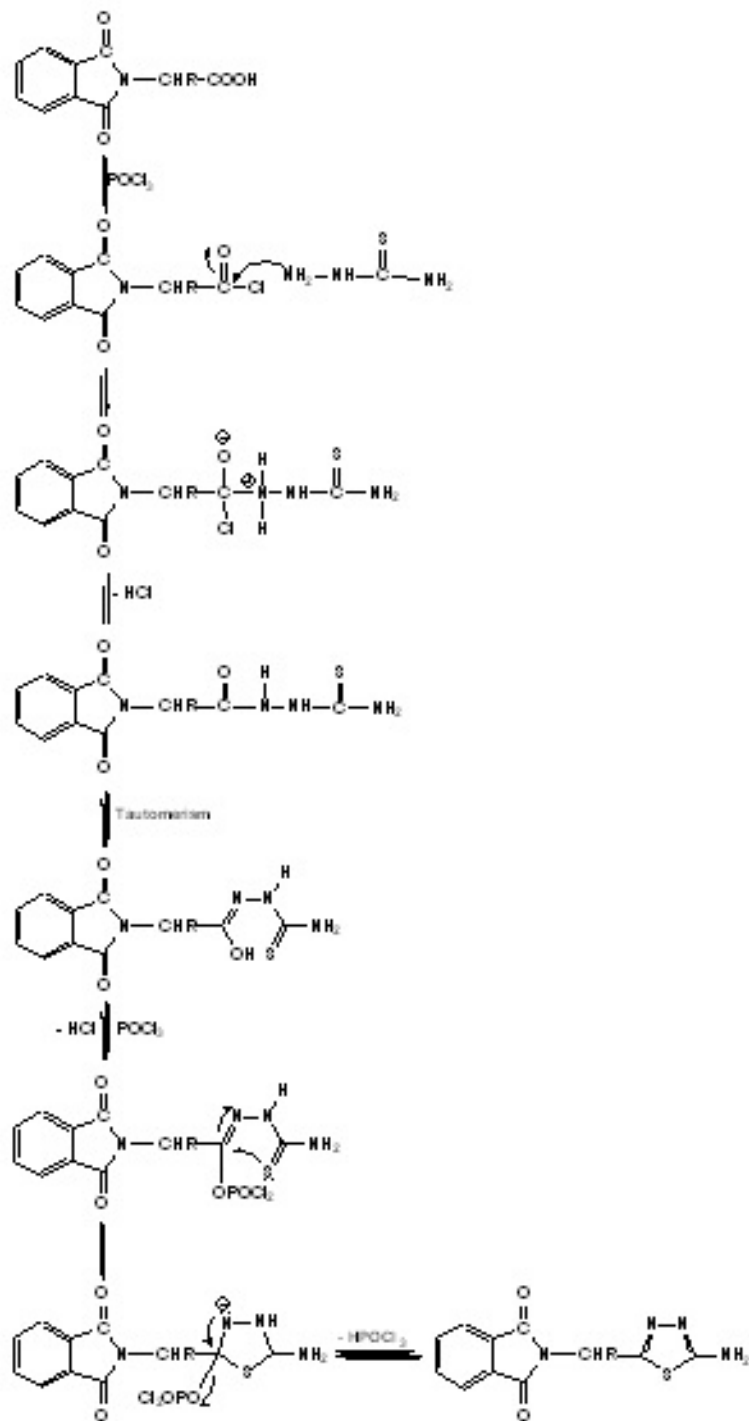
The proposed mechanism of the reaction is shown below



**Scheme (2)**



The proposed mechanism of the above reaction is shown in Scheme (3)



Scheme (3)

**Table (6):** Characteristic absorption bands of 2-(phthalimidyl), 3-phenyl propanoic acid compound

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3267	O-H stretching	3030	C-H stretching of benzene ring
2927	C-H stretching aliphatic	1749	C=O stretching
1697	O=C-N stretching	1458	C-H bending of CH <sub>2</sub>
1074	C-H bending in plane	632	C-H bending out-of-plane

**Table (7):** Characteristic absorption bands of 2-(phthalimidyl),4-(thioly) butanoic acid compound

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3200	O-H stretching	2923	C-H stretching aliphatic asym.
2856	C-H stretching aliphatic sym.	1748	C=O stretching
1706	O=C-N stretching	1460	C-H bending of CH <sub>2</sub>
1396	C-H bending of CH <sub>3</sub>	1078	C-H bending in plane
1018	C-H bending in plane	630	C-H bending out-of-plane

**Table (8):** Characteristic absorption bands of 2-(phthalimidyl)- propanoic acid compound

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3228	O-H stretching	3112	C-H stretching of benzene ring
2962	C-H stretching aliphatic of -CH-	2927	C-H stretching aliphatic asym. of -CH <sub>3</sub>
2871	C-H stretching aliphatic sym. of -CH <sub>3</sub>	1766	C=O stretching
1693	O=C-N stretching	1465	C-H bending of CH <sub>3</sub>
1089	C-H bending in plane	648	C-H bending out-of-plane

**Table (9):** Characteristic absorption bands of 2-(phthalimidyl)-ethanoic acid compound.

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3255	O-H stretching	3001	C-H stretching of benzene ring
2918	C-H stretching aliphatic	1755	C=O stretching
1695	O=C-N stretching	1344	C-H bending of CH <sub>3</sub>
1018	C-H bending in plane	1072	C-H bending in plane
623	C-H bending out-of-plane		

**Table (10):** Characteristic absorption bands of 2-(phthalimidyl),2-isopropyl-ethanoic acid compound

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3100	C-H stretching of benzene ring	2985	C-H aliphatic stretching
1772	C=O stretching	1728	O=C-N stretching
1415	C-H bending of CH <sub>3</sub>	1085	C-H bending in plane
1068	C-H bending in plane	622	C-H bending out-of-plane

Compounds [1-5] and equivalent of thiosemicarbazide were subjected by cycloaddition reaction by means of POCl<sub>3</sub> leading to the formation of 2-amino-5-(substituted) thiazoles [6-10].

The structures of the compounds were established on the basis of their melting points, FTIR and UV-Vis spectroscopy. The FTIR spectra of the compounds give the evidence for the formation of 1,3,4-thiadizole compounds through the appearance of the bands at (3342-3423) cm<sup>-1</sup> v asym. (NH<sub>2</sub>), (3174-3282) cm<sup>-1</sup> v sym. (NH<sub>2</sub>), (1602-1622) cm<sup>-1</sup> C=N. These bands which proved the conversion of compounds [1-5] to compounds [6-10] and these compounds have more characteristic IR bands at (1722-1710)cm<sup>-1</sup> O=C-N, other bands showed in the Table (11 to 15).

**Table (11):** Characteristic absorption bands of [1-(phthalimidyl)-1-(2-amino 1,3,4-thiadiazol-5-yl)-2-(phenyl)-]ethane compound.

IR spectral(cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3410	NH <sub>2</sub> stretching v asym.	3282	NH <sub>2</sub> stretching v sym.
2925	C-H stretching aliphatic asym	2856	C-H stretching aliphatic sym
1710	O=C-N stretching	1606	C=N stretching

**Table (12):** Characteristic absorption bands of [1-(phthalimidyl)-1-(2-amino 1,3,4-thiadiazol-5-yl)-3-(thioly)]-propane compound.

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3423	NH <sub>2</sub> stretching v asym.	3263	NH <sub>2</sub> stretching v sym.
3103	C-H stretching of benzene ring	2922	C-H stretching aliphatic
1710	O=C-N stretching	1620	C=N stretching
1093	C-H bending in plane	644	C-H bending out-of-plane

**Table (13):** Characteristic absorption bands of [1-phthalimidyl]-1-(2-amino-1,3,4-thiadiazole-5-yl)-1-(isopropyl)-]methane compound.

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3342	NH <sub>2</sub> stretching v asym.	3174	NH <sub>2</sub> stretching v sym.
2925	C-H stretching aliphatic asym.	2858	C-H stretching aliphatic sym.
1710	O=C-N stretching	1614	C=N stretching
1070	C-H bending in plane	661	C-H bending out-of-plane

**Table (14):** Characteristic absorption bands of [1-phthalimidyl]-1-(2-amino-1,3,4-thiadiazol-5-yl)-]ethane compound.

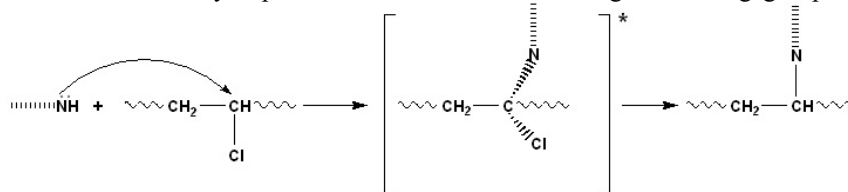
IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3365	NH <sub>2</sub> stretching v asym.	3276	NH <sub>2</sub> stretching v sym.
3128	C-H stretching of benzene ring	2925	C-H stretching aliphatic asym.
2856	C-H stretching aliphatic sym	1710	O=C-N stretching
1602	C=N stretching	1031	C-H bending in plane
717	C-H bending out-of-plane		

**Table (15):** Characteristic absorption bands of [1-phthalimidyl]-1-(2-amino-1,3,4-thiadiazol-5-yl)-]methane compound.

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3392	NH <sub>2</sub> stretching v asym.	3263	NH <sub>2</sub> stretching v sym.
3093	C-H stretching of benzene ring	1722	O=C-N stretching.
1622	C=N stretching	621	C-H bending out-of-plane

Modified PVC polymers (PI-PV) were prepared by the reaction of [6-10] with equivalent moles of PVC in THF.

The reaction was initiated by the nucleophilic attack of (N) atom on the carbon carrying chlorine atom in the polymeric chain followed by departure of chloride anion as a good leaving group.



The successful modification of PVC with 1,3,4-thiadiazole and phthalyl group can be demonstrated by FTIR spectroscopy. These compounds clearly revealed the three characteristic vibrations of the C=O, C=N, N-H of the 1,3,4-thiadiazole and phthalyl groups, The most common bands are tabulated in Table (16 to 21).

**Table (16):** Characteristic absorption bands of Modified polymer [PI]

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3200	N-H stretching	1714	O=C-N stretching
2920	C-H stretching of aliphatic	1616	C=N stretching
2858	C-H stretching of (CH <sub>2</sub> ) polymer	613	C-Cl stretching

**Table (17):** Characteristic absorption bands of Modified polymer [PII]

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3186	N-H stretching	1716	O=C-N stretching
2922	C-H stretching of aliphatic	1650	C=N stretching
2854	C-H stretching of (CH <sub>2</sub> ) polymer	613	C-Cl stretching

**Table (18):** Characteristic absorption bands of Modified polymer [PIII]

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3298	N-H stretching	1712	O=C-N stretching
2923	C-H stretching of aliphatic	1614	C=N stretching
2856	C-H stretching of (CH <sub>2</sub> ) polymer	613	C-Cl stretching

**Table (19):** Characteristic absorption bands of Modified polymer [PIV]

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3280	N-H stretching	1712	O=C-N stretching
2922	C-H stretching of aliphatic	1608	C=N stretching
2854	C-H stretching of (CH <sub>2</sub> ) polymer	613	C-Cl stretching

**Table (20):** Characteristic absorption bands of Modified polymer [PV]

IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
3290	N-H stretching	1714	O=C-N stretching
2918	C-H stretching of aliphatic	1615	C=N stretching
2856	C-H stretching of (CH <sub>2</sub> ) polymer	615	C-Cl stretching

**Table (21):** Characteristic absorption bands of PVC polymer

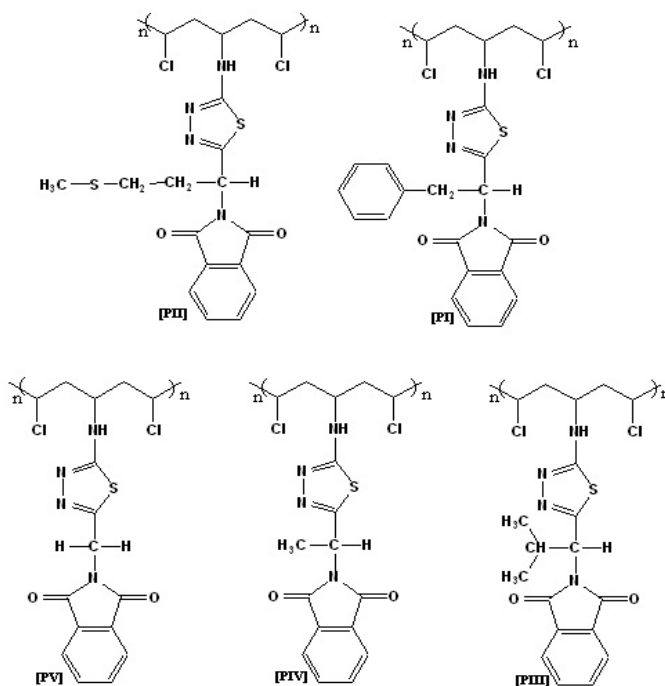
IR spectral (cm <sup>-1</sup> )	Assignment	IR spectral (cm <sup>-1</sup> )	Assignment
2970	C-H stretching of -CH-	1429	C-H bending of CH <sub>2</sub> polymer
2910	C-H stretching asym. of -CH <sub>2</sub>	615	C-Cl stretching
2860	C-H stretching sym. of -CH <sub>2</sub>		

The ultraviolet-visible spectrophotometry technique is used to characterize the prepared compounds in (DMSO) as a solvent and the polymers in tetrahydrofuran (THF) as a solvent. The ultraviolet visible electronic spectra of the prepared compounds and modified polymers showed an absorption bands could be attributed to the p @ p\* electronic transitions, these transitions are assigned in relevance to the structures of compounds and polymers. As shown in Table (22). The increase of the absorbance in the Uv-Vis range for samples containing prepared compounds or modified PVC compared with (PVC) can be explained by the formation of conjugation double bonds (band corresponding to the p @ p\* transition) in these modified polymers resulting from introducing an aromatic 1,3,4-thiadiazole and phthalyl rings. Thus, shifting the absorbance to longer wavelengths (i.e the bathochromic effect) is good evidence that modification were formed in our PVC and compounds. Moreover, the broadening in the bands caused by the presence of other chromophores such as (C=N, etc) which absorb in the above region and this overlapping bands make the interpretation of the results difficult.

**Table (22):** Electronic spectra of the prepared compounds.

Compound	Absorption Bands (nm.)	Compound	Absorption Bands (nm.)	polymer	Absorption Bands (nm.)
1	296, 263	6	288, 246	PI	265
2	293,261	7	260, 238	PII	281, 263
3	294, 263	8	266, 246	PIII	236
4	295, 259	9	272, 312	PIV	263
5	294, 261	10	282, 246	PV	260

On the basis of the preceding discussion, the structure of the complexes suggested as follows:



**Antimicrobial Results:**

Preliminary screening for antimicrobial activities of the stock solutions of prepared compounds corresponding were performed qualitatively using the disc diffusion assay. Antimicrobial activities were measured from the diameter of clear inhibition zones caused by compounds. (Table 23).

**Table (23):** Quantitative antimicrobial assay results [MIC ( $\mu\text{ cm}^{-3}$ )].

compounds	<i>Staphylococcus aureus</i>	<i>Streptococcus viridans</i>	<i>Escherichia coli</i>	<i>Fusarium oxysporium</i>	<i>Alternaria alternata</i>	<i>Alternaria solani</i>
1	13	14	13	3	4	4
2	15	17	26	17	18	16
3	16	11	13	18	25	23
4	12	12	5	8	-	11
5	12	18	20	23	11	15
6	21	26	27	15	21	15
7	16	5	21	22	19	12
8	22	32	27	43	-	14
8	25	21	23	14	15	7
10	22	13	15	16	18	11
PI	32	33	25	25	22	33
PII	35	43	41	32	12	15
PIII	33	35	27	38	22	36
PIV	16	24	22	12	15	13
PV	15	22	26	31	22	25

**REFERENCES**

- Aliwi, M., E. Yousif, A. Otaiwi, 2005. Synthesis and photochemical study of some metal complexes of poly(vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole. *Iraqi Journal of polymers*, 10(1): 53-64.
- Atlas, M., E. Alfres, P. Brown and C. Lawrence, 1995. *Laboratory Manual Experimental Microbiology*, Mosby - Year Book.
- Chen, Y., Y. Song, Y. Zhang and Lang, 2008. A tricobalt(II) coordination polymer incorporating in situ generated 5-methyltetrazolate ligands. *Inorganic Chemistry Communications*, 11: 572-575.
- Genhua, Z. and C. Pan, 2005. Preparation of star polymers based on polystyrene or poly(styrene-b-N-isopropyl acrylamide) and divinylbenzene via reversible addition-fragmentation chain transfer polymerization. *Polymer*, 46: 2802-2810.
- Gustafsson, B., M. Hakansson, S. Jagner, 2003. "Complexes between copper(I) chloride and polydentate aromatic amines". *Inorganica Chimica Acta*, 350: 209-214.
- Yousif, E., A. Hameed and E. Bakir, 2007. Synthesis and photochemical study of of poly(vinyl chloride) - 1,3,4-oxadiazole and 1,3,4-thiadiazole, *Journal of Al-Nahrain University(Science)*, 10(1): 7-12.