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
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Synthesis and Antioxidant Activity Screening of New Poly (Imide-Sulfonate) S Have Schiff Base Linkage

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Abstract. A series of new poly (imide-sulfonate)s polyimides involving Schiff base moiety have synthesized via multistep synthesis. The first step involved reaction of pyromellitic anhydride with aniline producing bis (N-phenyl) pyromellitic acid (1) which was subsequently dehydrated to the corresponding bis (N-phenyl) pyromellitimide (2) via fusion method. The synthesized imide (2) reacted with chlorosulfonic acid in the third step to produce bis N-(phenyl) pyromellitimide sulphonyl chloride (3). In the fourth step four diols was synthesized by condensation of 4,4'-methylenedianiline with four hydroxyl substituted aldehydes and ketones producing new diols (4-7) and these in turn were introduced successfully in condensation polymerization with monomer (3) affording the desired new polymers (8-11). The newly synthesized compounds and polymers were characterized through spectral data including FT-IR, ¹H-NMR and ¹³C-NMR. Antioxidant activity of new polymers (8-11) was measured using stable DPPH radicals.

Keywords: poly (imide-sulfonate) s, Schiff base, Antioxidant.

INTRODUCTION

Cyclic imides are an important class of organic compounds, which possess extensive biological activities [1, 2] and have wide range of medical application like anti-inflammatory, analgesic, antitumor, antioxidant and anti-HIV [3-6].

Moreover, polyimides are widely known as promising candidates due to their excellent mechanical, thermal and chemical properties beside good solvent resistance [7-9]. However their limited solubility and infusible nature leads to poor processability and restricted their applications.

To overcome these problems many modifications were performed such as copolymerization or incorporation of bulk or unsymmetrical segments in polymeric chains leading to increase solubility and decrease softening points [10], this in turn develop processability leading to wide spectrum applications [11, 12].

In the present work, a series of new poly (imide-sulfonate) s with incorporation Schiff base component in their chains was synthesized by multistep synthesis. Anti-oxidant activity of these new polymers was evaluated and results indicated that have good antioxidant activity.

EXPERIMENTAL PART

Synthesis of bis(phenyl) pyromellitic acid (1) [11]

Aniline (0.02mol, 1.86g) dissolved in (30mL) dry acetone was added dropwise to (0.01mol, 2.18g) of pyromellitic anhydride dissolve in (30mL) dry acetone.

The resulted mixture was stirred for 3 hour at room temperature then the formed precipitate was filtered, washed with acetone then ether, dried and recrystallized from ethanol.

Synthesis of bis(phenyl) pyromelletimide (2) [10]

Amic acid (1) (0.5gm) was placed in a wide Pyrex tube supplied with a thermometer and immersed in sand bath. The sand bath was heated gradually until the complete fusion of amic acid then sand bath temperature was kept at ten degrees above melting point of the used amic acid for 2 hrs. The fused product was cooled to room temperature and the obtained solid was recrystallized from acetone.

Synthesis of bis N-(phenyl) pyromelletimide sulphonyl chloride (3) [10]

Chlorosulfonic acid (5mL) was added drop wise to (0.005 mol, 1.84g) of bis(phenyl) pyromelletimide during two hours with stirring and keeping temperature at 0°C.

Stirring was continued for eight hours at room temperature then resulting compound was carefully poured into crushed ice with stirring.

The obtained precipitate was filtered, dried, and recrystallized from acetone.

Synthesis of BisSchiff's bases (4-7)

Synthesis of Schiff bases was performed via refluxing the mixture of (0.01mol, 1.98g) of 4,4'-methylenedianiline with (0.02 mol) of aldehyde or ketone dissolved in (25mL) of absolute ethanol with few drops of glacial acetic acid for 6 hours with stirring. The prepared solid was filtered, dried then purified by recrystallization from a suitable solvent.

Synthesis of poly (imide-sulfonate) polymers (8-11)

In a two-neck round bottomed flask equipped with condenser and thermometer a mixture of (0.005 mol) of bisSchiff base (4-7) and (5mL) of pyridine was placed.

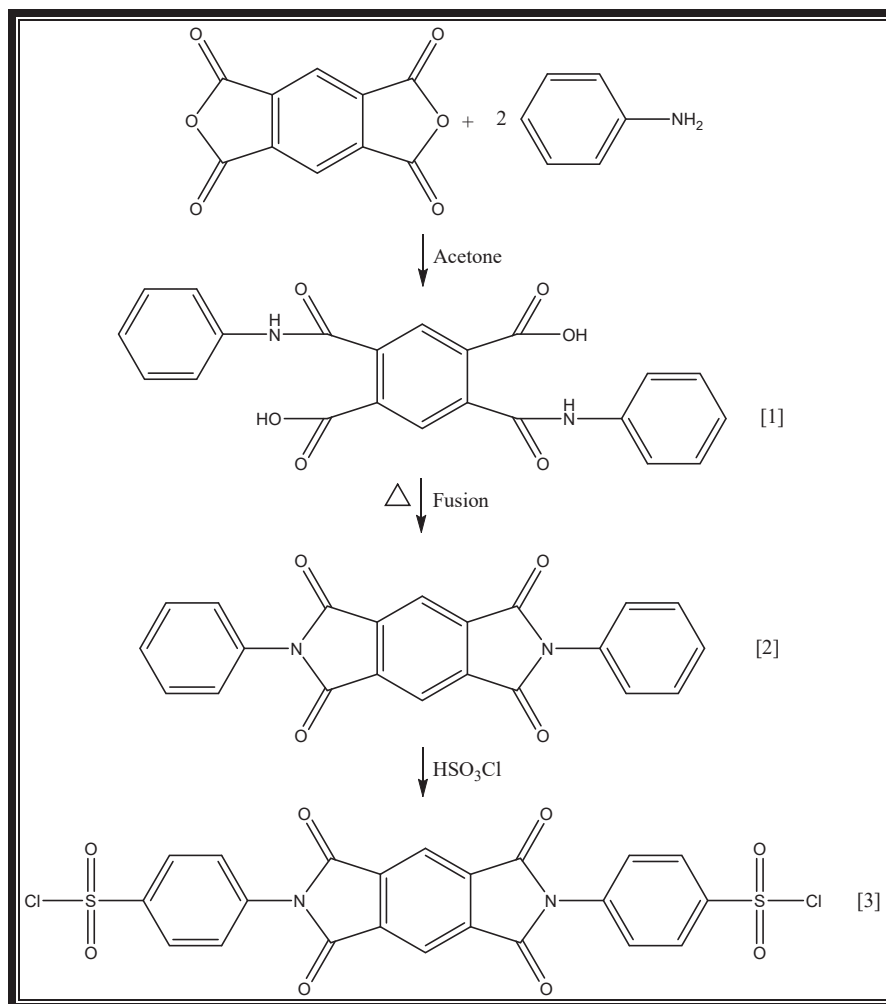
The flask was surrounded via a bath sufficiently cold to lower the temperature of the mixture to 10°C, then bis(phenyl) pyromelletimide sulphonyl chloride (3) (0.005 mol, 2.8g) dissolved in (25mL) THF was added in portions during 30 min. with continuous stirring on magnetic stirrer. The resulted mixture was refluxed for six hours, then cooled to room temperature and pouring on crushed ice with stirring. The obtained precipitate was filtered, washed with cold water, dried, and recrystallized from suitable solvent.

RESULT AND DISCUSSION

Since both cyclic imides and Schiff base belong to a widely used intermediate for synthesis of many types of industrial, pharmaceutical and biological products [13, 14]. This work aims to synthesis of new polymers containing these two important segments (cyclic imide and Schiff base) together beside sulfonate component, each one of these three components have affect physical and mechanical properties of synthesized polymers.

Cyclic imide moiety exhibit the polymer good thermal and mechanical properties, while the presence of Schiff base exhibit flexibility via reducing of crystalline regions and moreover exhibit biological activity and finally sulfonate moiety which exhibit flexibility, reducing softening points and increasing solubility.

The routes for synthesis of target polymers were started from reaction of pyromellitic anhydride (1 mole) with two moles of aniline producing pyromellit amic acid (1) which was introduced in dehydration reaction by fusion in the second step to create the corresponding pyromellitimide (2). In the third step imide (2) reacted with chloro sulfonic acid affording bis N-(phenyl) pyromellitimide sulfonyl chloride (3) as shown in Scheme (1).

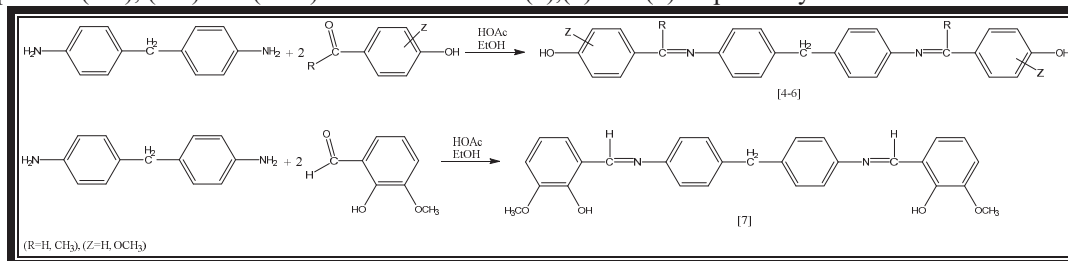


SCHEME (1) route for synthesis of monomer (3)

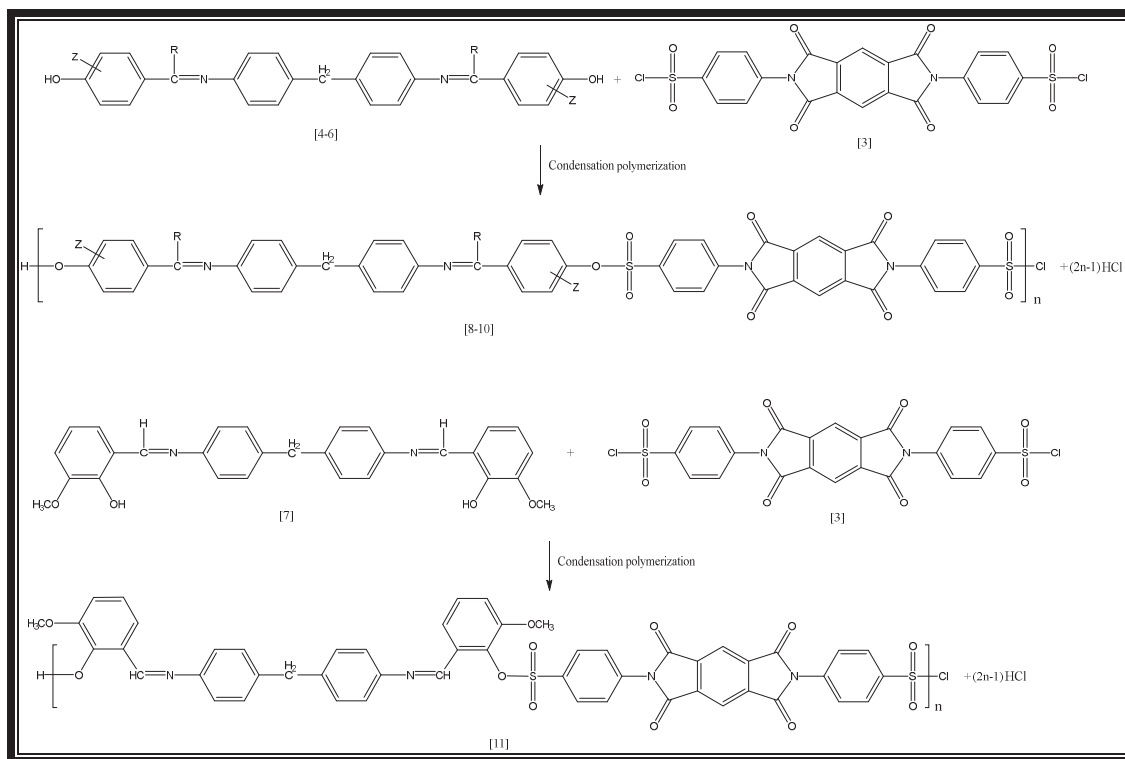
Furthermore, four new diol compounds containing two Schiff base moieties (4-7) were synthesized via condensation reaction of 4,4'-methylenedianiline (1 mole) with (2 mol) of hydroxyl substituted aldehydes or ketones in absolute ethanol in presence of catalytic amount of glacial acetic acid under reflux condition.

New diols (4-7) and compound (3) represent (dinucleophiles) and (dielectrophiles) monomers respectively, thus introducing of monomer (3) in condensation polymerization with new four diols to synthesized new poly(imide-sulfonate)s polymers (8-11) which contain three important parts in their repeating units namely (cyclic imide, Schiff base and sulfonate) segments.

Synthesis of new diols (4-7) and new polymers (8-11) are shown in Schemes (2) and (3) while physical properties of compounds (1-3), (4-7) and (8-11) are listed in Table (1),(2) and (3) respectively.



SCHEME (2) route for synthesis of monomers (4-7)



SCHEME (3). route for synthesis of polymers (8-11)

The new polymers showed low softening points and good solubility in many organic solvents including (THF, DMF, DMSO, acetone, dioxane and hot chloroform and insoluble in petroleum ether, diethyl ether, ethanol, methanol and n-hexane.

These physical properties provide the opportunity for wide spectrum of potential applications for these polymers.

Table 1. Physical properties for compounds (1-3)

Comp. No.	Compound structure	Color	Melting point °C	Yield %	Recrystallization solvent
1		White	345-348	81	Ethanol
2		Pale yellow	311-313	85	Acetone
3		Off-white	250 dec.	77	Acetone

Table 2. Physical properties for compounds (4-7)

Comp. No.	Compound structure	Color	Melting point °C	Yield %	Recrystallization solvent
4		Yellow	240-242	83	Ethanol
5		Yellow	71-73	94	Ethanol
6		Orange	58-60	80	Acetone
7		Orange	132-135	84	Acetone

Table 3. Physical properties for compounds (8-11)

Poly. No.	Compound structure	Color	Softening point °C	Conv. Ratio %	Recrystallization solvent
8		Yellow	180-190	85	Chloroform
9		Dark red	163-180	81	Chloroform
10		Orange	215-222	79	Chloroform
11		Orange	160-173	71	Chloroform

Chemical structures of prepared compounds and polymers were confirmed by using FT-IR, ¹H-NMR and ¹³C-NMR spectral data.

FT-IR spectrum of bis amic (1) has showed absorption bands at (3479, 3409) cm⁻¹, (1690) cm⁻¹ and (1637) cm⁻¹ which are due to ν(O-H) carboxyl, ν(N-H) amide, ν(C=O) carboxyl and ν(C=O) amide respectively [15].

FT-IR spectrum of bis imide (2) exhibited two points first disappearance of ν(O-H) carboxyl, ν(N-H) amide, ν(C=O) carboxyl and ν(C=O) amide absorption bands and appearance of two new absorption bands at (1782) cm⁻¹ and (1724) cm⁻¹ due to asym. and sym. ν(C=O) imide indicating success of imide formation.

FT-IR spectrum of compound (3) display the appearance of two new absorption bands at (1361) cm⁻¹ and (1186) cm⁻¹ which are due to asym. ν(SO₂) and sym. ν(SO₂) indicating success of compound (3) formation.

FT-IR spectral data are listed in Table (4).

Moreover FT-IR spectra of new diols (4-7) presented clear absorption bands at (3311-3477) cm⁻¹ and (1600-1623) cm⁻¹ which are due to ν(O-H) phenolic and ν(C=N) imine.

Details of FT-IR spectral data of diols (4-7) are listed in Table (5).

¹H-NMR spectrum of diol (5) showed singlet signal at (σ=3.68) ppm that resulted from two (CH₃) protons and singlet signal at (σ=4.92) ppm that resulted from (-CH₂-) protons [16] other signals appeared at (σ=6.5-7.98) ppm and (σ=10.47) ppm which are belong to aromatic protons and (OH) proton respectively.

¹³C-NMR spectrum of compound (5) displayed signals at (σ=26.24) ppm and (σ=35.81) ppm are assigned to two (CH₃) and (-CH₂-) carbons. Other signals appeared at (σ=113.55-146.34) ppm and (σ=161.97) ppm triggered by aromatic carbons and (C=N) carbons respectively.

¹H-NMR spectrum of diol (7) displayed signal at (σ=3.88-3.91) ppm, (σ=4.91) ppm and (σ=6.55-7.48) ppm which are assigned to two (OCH₃) protons, (-CH₂-) protons and aromatic protons, while signals belong to (-CH=N-) imine protons and (OH) protons appeared at (σ=9.03) ppm and (σ=13.44-13.48) ppm respectively.

¹³C-NMR spectrum of diol (7) exhibited signals at (σ=35) ppm and (σ=55.81) ppm which are caused by (-CH₂-) and (OCH₃) carbons while signals at (σ=113.88-150.51) ppm and (σ=162.83-163.08) ppm are assigned to aromatic carbons and C=N carbons.

FT-IR spectra of polymers (8-11) showed either disappearance or reducing in ν(O-H) absorption band this point beside the presence of ν(C=O) imide, ν(C=N) imine and ν(SO₂) absorption bands all these proved success of

polymerization process. Spectra presented absorption bands at (1774-1780) cm^{-1} , (1722-1726) cm^{-1} , (1600-1658) cm^{-1} , (1311-1367) cm^{-1} , (1367-1369) cm^{-1} and (1120-1170) cm^{-1} which are due to asym. $\nu(\text{C}=\text{O})$ imide, sym. $\nu(\text{C}=\text{O})$ imide, $\nu(\text{C}=\text{N})$ imine, $\nu(\text{C}-\text{N})$ imide, asym. $\nu(\text{SO}_2)$ and sym. $\nu(\text{SO}_2)$ respectively [16].

FT-IR spectral data of polymers (8-11) are listed in Table (6).

TABLE 4. FT-IR spectral data (cm^{-1}) for compounds (1-3)

Comp. No.	$\nu(\text{O}-\text{H})$ $\nu(\text{N}-\text{H})$	$\nu(\text{C}-\text{H})$ Arom.	$\nu(\text{C}=\text{O})$ Acid	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{O})$ Amide	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$ Imide	$\nu(\text{SO}_2)$ asym.	$\nu(\text{SO}_2)$ sym.
1	3479	3089	1690	-	1637	1596	-	-	-
	3409	3053							
2	-	3060	-	1782	-	1502	1396	-	-
				1724					
3	-	3049	-	1782	-	1591	1409	1361	1186
				1728					

TABLE 5. FT-IR spectral data (cm^{-1}) for compounds (4-7)

Comp. No.	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{H})$ Arom.	$\nu(\text{C}-\text{H})$ Aliph.	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	Other
4	3471	3026	2960	1604	1581	p-sub.
	3419		2881			835
5	3375	3033	2906	1600	1579	p-sub.
	3311		2835			837
6	3427	3040	2950	1623	1587	p-sub.
	3409		2891			817
7	3477	3075	2997	1620	1512	-
	3448		2885			

TABLE 6. FT-IR spectral data (cm^{-1}) for polymer (8-11)

Poly. No.	$\nu(\text{C}-\text{H})$ Arom.	$\nu(\text{C}-\text{H})$ Aliph.	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$ Imide	$\nu(\text{SO}_2)$
8	3060	2958	1774	1654	1579	1311	1369
		2831	1722	1600			1170
9	3097	2906	1780	1658	1598	1315	1367
		2835	1726	1658			1120
10	3062	2956	1774	1654	1589	1313	1369
		2850	1724	1654			1161
11	3095	2929	1776	1652	1569	1367	1367
		2837	1726	1614			1159

$^1\text{H-NMR}$ spectrum of polymer (8) presented signals at ($\sigma=4.18$) ppm, ($\sigma=7.04-9.04$) ppm and ($\sigma=9.9$) ppm which are attributed to ($-\text{CH}_2-$) protons, aromatic protons and imine protons respectively [17].

¹³C-NMR spectrum of polymer (8) showed signals at ($\sigma=34.20$) ppm, ($\sigma=115.08-148.06$) ppm, ($\sigma=162.32-163.32$) ppm and ($\sigma=164.89-165.37$) ppm which are assigned to (-CH₂-) carbon, aromatic carbons, (C=N) imine carbons and (C=O) imide carbons respectively.

¹H-NMR spectrum of polymer (9) exhibited signals at ($\sigma=2.87$) ppm and ($\sigma=3.02$) ppm triggered by two (CH₃) protons and signals at ($\sigma=4.07$) ppm and ($\sigma=6.97-8.95$) ppm triggered by (-CH₂-) protons and aromatic protons.

¹³C-NMR spectrum of polymer (9) presented signals at ($\sigma=26.25-30.73$) ppm and ($\sigma=34.29-35.76$) ppm belong to two (CH₃) carbons and (-CH₂-) carbons.

Signals at ($\sigma=115.11-148.12$) ppm, ($\sigma=161.97-162.29$) ppm and ($\sigma=165.38-167.28$) ppm which are generated by aromatic carbons, (C=N) imine carbons and (C=O) imide carbons respectively.

¹H-NMR spectrum of polymer (10) displayed signals at ($\sigma=3.95$) ppm and ($\sigma=4.01$) ppm belong to two (OCH₃) protons and (-CH₂-) protons.

Other signals at ($\sigma=7.08-8.65$) ppm and ($\sigma=9.03$) ppm which attributed to aromatic protons and imine proton respectively.

¹³C-NMR spectrum of polymer (10) exhibited signals at ($\sigma=34.5$) ppm, ($\sigma=55.52-56.09$) ppm, ($\sigma=110.57-153.0$) ppm, ($\sigma=162.29$) ppm and ($\sigma=165.38-167.27$) ppm which are assigned to (-CH₂-) carbon, (OCH₃) carbons, aromatic carbons, (C=N) imine carbons and (C=O) imide carbons respectively.

¹H-NMR spectrum of polymer (11) displayed signals at ($\sigma=3.93-3.99$) ppm, (4.13) ppm, (7.01-8.67) ppm and (9.04) ppm which are attributed to two (OCH₃) protons, (-CH₂-) protons, aromatic protons and imine protons respectively.

¹³C-NMR spectrum of polymer (11) showed signals at ($\sigma=34.17$) ppm, ($\sigma=55.82-56.04$) ppm, ($\sigma=115.49-150.53$) ppm, ($\sigma=163.07$) ppm and ($\sigma=164.87-165.38$) ppm which are triggered by (-CH₂-) carbon, two (OCH₃) carbons, aromatic carbons, (C=N) imine carbons and (C=O) imide carbons respectively.

ANTIOXIDANT ACTIVITY

Antioxidant activity of the newly synthesized polymers (8-11) was measured by using stable DPPH radicals with minor adjustments according to Tailor, C. S. [18].

New polymers (8-11) were used to investigate the scavenging activity. Two different concentrations (10 μ g/mL and 25 μ g/mL) for each polymer were used and every sample was mixed with DPPH solution and then completes the volume to one particular mL using ethanol. Ascorbic acid was used as a positive control.

The decline in absorbance was measured at 517 nm.

Scavenging activity was measured according to the equation formula below [19].

(Scavenging % = (Absorbance of control – absorbance of sample / absorbance of control) X 100%)

Figure (1) indicated change of % scavenging value with sample concentration.

Findings were showed that polymer samples have a good scavenging % activity. Besides it is noticeable that there is a linear relationship between scavenging % value of studied samples and their concentration where increasing of concentration has led to clear increasing in % scavenging value.

The results indicated that the tested polymers exhibit a good antioxidant activity.

TABLE 7. Scavenging values of polymers (8-11)

Polymer No.	% scavenging value at (10 μ g/mL)	% scavenging value at (25 μ g/mL)
8	30	55
9	52	90
10	40	75
11	48	82

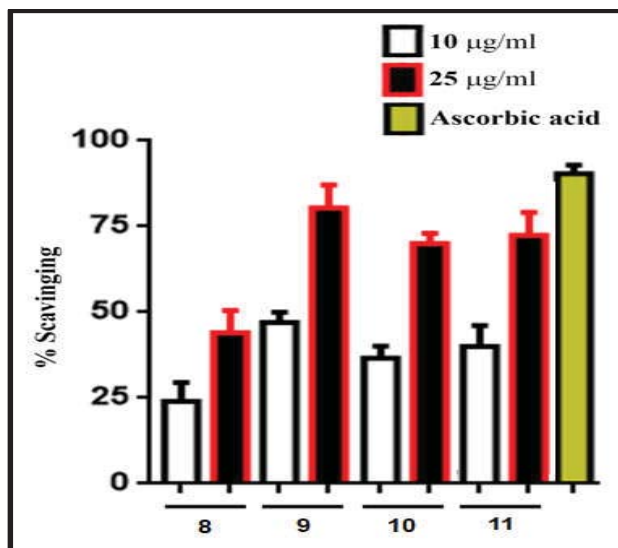


FIGURE 1. Scavenging activity of polymers (8-11)

CONCLUSIONS

This study has shown that new synthesized polymers have a good solubility in different organic solvents. Additionally, these polymers have a good prospect to apply in many applications; one of these applications is antioxidant. The new polymers have good antioxidant activity compared with ascorbic acid which was used as a standard antioxidant.

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