

Synthesis, Characterization, and Antimicrobial Properties of New Polystyrene-Bound Schiff Bases and Their Some Complexes

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ABSTRACT: This study investigated the antimicrobial properties of polymer-bound Schiff bases and their Cu(II) and Ni(II) complexes. Novel polystyrene oligomer-bound Schiff bases (FMPS-Sch) were prepared from (4-formyl-3-methoxyphenoxymethyl)polystyrene (FMPS) with cycloalkylaminothiophene derivatives and their Cu(II) and Ni(II) complexes have been synthesized and characterized. All these substances have been examined for antibacterial activity against pathogenic strains; *Bacillus cereus*, *Listeria*

monocytogenes, *Pseudomonas putida*, *Escherichia coli*, *Salmonella typhi* H, *Brucella abortus*, *Shigella dysenteriae* type 10, *Micrococcus luteus* and antifungal activity against *Candida albicans*. Most of the studied compounds were found effective against bacteria studied and yeast. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1796–1803, 2012

Key words: polymer-bound Schiff bases; cycloalkylaminothiophene; antimicrobial activities

INTRODUCTION

One of the major challenges in medical and drug delivery is to develop materials containing sulfur. A drug containing sulfur is an antibacterial agent because it is a competitive inhibitor of an enzyme catalyzed reaction using *p*-aminobenzoic acid in the synthesis of folic acid.¹ Low molecular weight antimicrobial agents suffer from some disadvantages due to short-term antimicrobial ability. To overcome problems associated with the low molecular weight antimicrobial agents, antimicrobial functional groups can be introduced into polymer molecules.

Some polymers have been widely used as biomaterials because of their biocompatibility. Biomaterials loaded with drugs are used in the treatment of some diseases and to prevent the infection. On the other hand, the bioactive materials provide a strong bond with the bone, which avoids undesirable micro-movements of the implant and ensure the bone integration.²

Many macromolecules have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields like, waste water treatment, recovery of trace metal ions, nuclear chemistry, and antimicrobial agent.^{3–5} Many macromolecules have been developed and showed excellent disinfecting and antibacterial activities. Researchers developed polymeric macromolecules with antibacterial properties which were proved to be more efficient than antibacterial monomer.^{6–8} Therefore, there is a considerable interest in the synthesis and characterization of these macromolecules. However, the drug resistances against antibacterial agents may pose a problem in their use with medical purpose.⁹ The problem could be overcome by the preparation of metal complexes, using a process of chelation with the coordination of transition metal ions. It is well known that N, S, and O atoms play a key role in the coordination of metals. Schiff bases have N atoms as their basic elements. Schiff base derivatives containing donor atom can act as good chelating agents for the transition of metal ions.¹⁰ Metal chelates play an essential role in the chemistry of living matter. It has been known that copper metal contributes to redox reactions in organisms. The functional importance of Copper ion is redox interaction with thiol-containing molecules.¹¹ Nickel plays numerous roles in the biology. For example, urease which is a metalloenzyme (an enzyme which assists in the hydrolysis of urea) contains nickel.

The goal of this study was to evaluate the antimicrobial properties against various pathogenic bacteria

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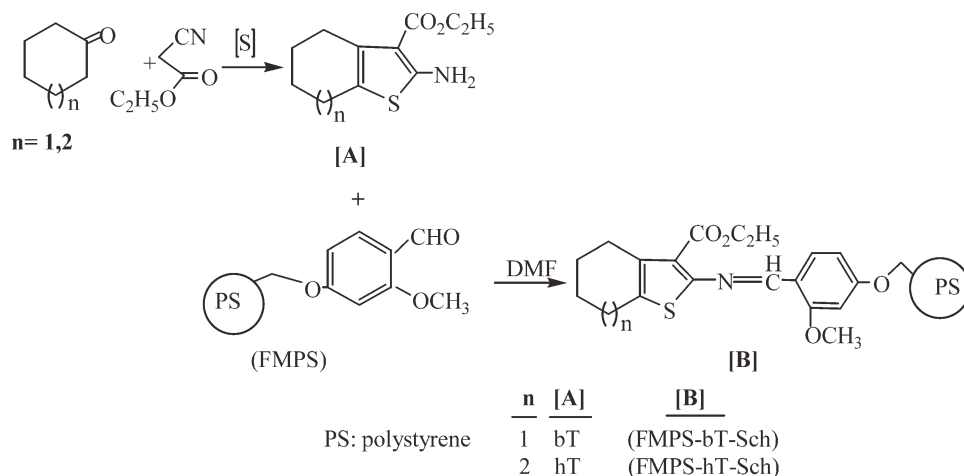


Figure 1 Synthesis of Schiff bases.

of new polymer-Schiff bases having sulfur and their Cu(II) and Ni(II) complexes. Cycloalkylaminothiophene derivatives were synthesized by Gewald et al. methods¹² (Fig. 1). And then, two Schiff bases prepared from cycloalkylaminothiophene and (4-formyl-3-methoxyphenoxy methyl) polystyrene and their Cu(II) and Ni(II) complexes were synthesized and characterized.

EXPERIMENTAL

Materials and physical measurements

All chemicals investigated in the study were reagent grade and were purified when it was necessary. All other materials were reagent grade (Sigma-Aldrich Company, Germany). ¹H-NMR spectra of the ligands and Ni(II) complexes were recorded with a Bruker Spectrospin Avance DPX-400 instrument using TMS as internal standard and CDCl₃ as solvent. Elemental analyses were carried out with an Elementar Micro Vario CHNS instrument. Metal contents were determined by using a Philips PU 9285 atomic absorption instrument at Tubitak, Ankara, Turkey. Electronic spectra were recorded on a Unicam-UV2-100 spectrophotometer in dimethylformamid (DMF). IR spectra were recorded on a Mattson-5000 FTIR instrument in KBr pellets. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymer-Schiff bases and their complexes were recorded by Perkin Elmer-Pyres Diamond model thermal analyzer under nitrogen atmosphere between 30 and 600°C at a heating rate of 10 °C min⁻¹. Magnetic moments were measured at room temperature with MK-1 model Gouy Balance of Christison Scientific Equipment Ltd.

Synthesis of polymer-bound Schiff base (FMPS-Sch)

First Step: Syntheses of 2-Aminothiophenes: General procedure

2-Aminothiophene-3-carboxylic acid ethyl esters [Fig. 1(A)] were prepared according to the procedure

described by Gewald.¹² A mixture of 5.66 g (0.05 mol) ethyl cyanoacetate, 0.05 mol of carbonyl compound, 4.91 g cyclohexanone, and 5.60 g cycloheptanone; respectively for $n = 1$ (bT) and $n = 2$ (hT) 1.60 g (0.05 mol) of sulfur, 4.91 g (0.05 mol) of morpholine, and 15 mL of ethanol was mixed at room temperature. Once an exothermal reaction was observed and the reaction temperature was raised to 50°C, after 1 h, a thick precipitate was obtained. This mixture was poured into the water. The resulting solid was collected and recrystallized from ethanol. For (bT), ¹H NMR (400 MHz, DMSO/TMS): δ (ppm) 1.34 (t, 3H, CH₃), 1.75 (m, 4H, H-14, H-15), 2.70 (m, 4H, H-13, H-16), 4.33 (q, 2H, CH₂), 5.82–6.30 (b, 2H, NH₂). For hT, ¹H NMR (400 MHz, DMSO/TMS): δ (ppm) 1.35 (t, 3H, CH₃), 1.62 (m, 4H, H-14, H-16), 1.85 (m, 2H H-15), 2.84 (m, 4H, H-13, H-17), 4.35 (q, 2H, CH₂), 5.78–6.32 (b, 2H, NH₂).^{12,13}

Second Step: Synthesis of polymeric Schiff-bases

The polymer having Schiff bases were prepared by dropwise with addition of (4-formyl-3-methoxyphenoxy)methyl)polystyrene [(FMPS); 1 g, 100–200 mesh, 1.0–1.5 mmol/g -CHO loading, 1% cross-linked with divinylbenzene (Aldrich)] in hot DMF (15 mL) to a

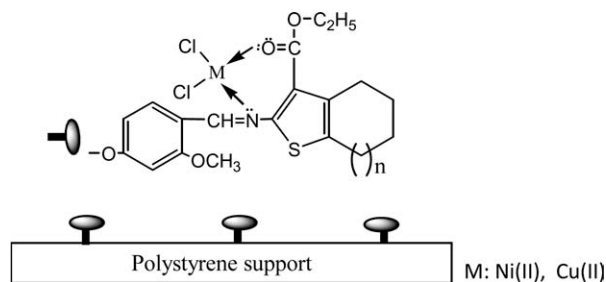


Figure 2 The proposed structures for polymer-bound Schiff-base-M(II) complexes.

solution of cycloalkylaminothiophene derivatives (1.5 mmol, 0.34 g for $n = 1$, 0.36 g for $n = 2$) in DMF (10 mL) while stirring. The stirring was continued until the solution was refluxed to about 3 h later. Then mixture was cooled and was poured into the DMF (~ 100 mL). The resulting solid was collected from DMF [FMPS-Sch; Fig. 1(B)]. The crystalline solid was filtered and dried and kept in desiccator over anhydrous CaCl_2 .

Synthesis of polymer-bound Schiff-base-M(II) complexes (FMPS-Sch-M)

All polymer-metal complexes were prepared by following a general method: DMF solutions of the polymer-bound Schiff-bases (1 g of (FMPS-bT) and 1 g of (FMPS-hT) 1.5×10^{-3} mol loading $-\text{CH}=\text{N}$ in 25 mL and metal salt (0.35 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.20 g CuCl_2) 1.5×10^{-3} mol in 25 mL were mixed and refluxed for 2 h. Then mixture was cooled and was poured into the DMF (~ 100 mL). The resulting solid was collected from DMF (FMPS-Sch-M; Fig. 2). The solid was filtered and dried and kept in desiccator over anhydrous CaCl_2 .

Detection of antimicrobial activity

The bacterial subcultures chosen were *Listeria monocytogenes* 4b (ATCC-19115), *Bacillus cereus* sp., *Escherichia coli* (ATCC-1280), *Salmonella typhi* H (NCTC 901.8394), *Pseudomonas putida* sp., *Brucella abortus* (A.99, UK-1995) RSKK-03026, *Micrococcus luteus* ATCC-9341, *Shigella dysenteriae* type 10 (RSKK 1036), and antifungal activity against *Candida albicans* (Y-1200-NIH, Tokyo). The polymer-bound Schiff-base and their complexes were tested for their antimicrobial activity by the well-diffusion method.¹⁴ Each polymer-bound Schiff-base and their complexes was kept dry at room temperature and dissolved (3.5 $\mu\text{g}/\mu\text{L}$) in DMF. DMF was used as solvent and also for control. It was found to have no antimicrobial activity against any of the tested organisms. One percent (v/v) of a 24 h broth culture containing 10^6 CFU/mL was placed in sterile petri dishes. Mueller-Hinton Agar (Merck) kept at 45°C was then poured in to the petri-dishes and allowed to solidity. Then wells of 6 mm diameter were punched carefully by using a sterile cork borer and were entirely filled with the test solutions. The plates were incubated for 24 h at 37°C. On completion of the incubation period, the mean value obtained for the two holes was used to calculate the zone of growth inhibition of each sample.

Bacterial subcultures and antifungal were tested for resistance to eight antibiotics produced by Oxoid Lt., Basingstoke, UK. These were: ampicillin

TABLE I
Analytical and Physical Data for Polymer-Support Schiff Bases Derivatives and Their Complexes

Abbreviation	Chemical formula (^a a :5 for M_{av} , ^b a :4 for M_{h})	χ_{g} (mass susceptibility), color	Elemental analysis found (Calcd) %						^a M_{av} , ^b M_{h}	Polydispersity index (PDI = $M_{\text{w}}/M_{\text{n}}$)
			C	H	N	S	M			
(FMPS-bT-Sch)	(C_8H_8) _a ($\text{C}_{27}\text{H}_{27}\text{SO}_4\text{N}$)	-, Yellow	83.04 (81.95)	7.11 (6.83)	0.89 (1.42)	2.01 (3.26)	-	981, 877	1.11	
(FMPS-hT-Sch)	(C_8H_8) _a ($\text{C}_{28}\text{H}_{29}\text{SO}_4\text{N}$)	-, Yellow	90.12 (82.01)	8.03 (6.94)	0.93 (1.41)	2.24 (3.21)	-	995, 891	1.12	
(FMPS-bT-Sch-Cu)	(C_8H_8) _a ($\text{C}_{27}\text{H}_{27}\text{SO}_4\text{N}$)/ CuCl_2	Paramagnetic, Gray	74.13 (72.04)	7.48 (6.00)	0.78 (1.24)	1.73 (2.87)	4.91 (5.69)	1116, n.o	-	
(FMPS-hT-Sch-Cu)	(C_8H_8) _a ($\text{C}_{28}\text{H}_{29}\text{SO}_4\text{N}$)/ CuCl_2	Paramagnetic, Gray	73.04 (72.21)	6.24 (6.02)	0.93 (1.24)	1.98 (2.83)	4.81 (5.62)	1130, n.o	-	
(FMPS-bT-Sch-Ni)	(C_8H_8) _a ($\text{C}_{27}\text{H}_{27}\text{SO}_4\text{N}$)/ NiCl_2	Diamagnetic, Green	70.16 (69.19)	7.27 (6.04)	1.09 (1.26)	1.91 (2.88)	4.91 (5.22)	1110, 1006	1.10	
(FMPS-hT-Sch-Ni)	(C_8H_8) _a ($\text{C}_{28}\text{H}_{29}\text{SO}_4\text{N}$)/ NiCl_2	Diamagnetic, Green	71.01 (72.59)	7.03 (6.14)	0.87 (1.10)	2.08 (2.85)	4.83 (5.16)	1124, 1020	1.10	

^aAccording to elemental analyses.

^bAccording to ¹H-NMR.

n.o: Not observed.

TABLE II
 $^1\text{H-NMR}$ Chemical Shift (ppm) of the Schiff Bases and Their Ni(II) Complexes

Compound	$-\text{CHO}/-\text{CH}=\text{N}$	c, d, f	b, b', $-\text{OCH}_3$	e	a, a'/g
(FMPS)	10.30/-	8.0-6.2	5.1-4.9, 3.7	3.0, 2.90	1.3-0.8/-
(FMPS-bT-Sch)	-/7.3	7.8-6.3	5.0, 4.8, 3.7	3.0, 2.90	1.3-0.9/2.1-2.8
(FMPS-hT-Sch)	-/7.3	8.0-6.2	4.9-4.7, 3.7	3.0, 2.90	1.2-0.9/2.0-2.8
(FMPS-bT-Sch-Ni)	-/7.4	8.1-6.3	5.1-4.9, 3.7	3.0, 2.90	1.3-0.9/2.1-2.7
(FMPS-hT-Sch-Ni)	-/7.5	8.2-7.2	5.2-4.5, 3.7	3.0, 2.90	0.9-1.2/2.1-2.6

(preventing the growth of Gram-negative bacteria), ofloxacin (entering the bacterial cell and inhibiting DNA-gyrase), nystatin (binding to sterols in the fungal cellular membrane, altering the permeability and allowing leakage of the cellular contents), kanamycin (used in molecular biology as agent to isolate bacteria), sulphamethoxazol (a bacteriostatic antibacterial agent that interferes with folic acid synthesis in susceptible bacteria), amoxycillin (it is β -lactam antibiotic used to treat bacterial infections caused by susceptible microorganisms), chloroamphenicol (it is effective against a wide variety of microorganisms), and ciprofloxacin.

RESULTS AND DISCUSSION

Analytical data and physical properties of the synthesized compounds are summarized in Table I. The analytical data of the complexes correspond well with suggestion of the structure. The weight average molecular weight (M_w) of the polymer and their metal complexes were suggested from this elemental analyses to be 981, 995, 1116, 1130, 1110, and 1124 for (FMPS-bT-Sch), (FMPS-hT-Sch), (FMPS-bT-Sch-Cu), (FMPS-hT-Sch-Cu), (FMPS-bT-Sch-Ni), and (FMPS-hT-Sch-Ni), respectively. Elemental analyses are consistent with a studied polymer. However,

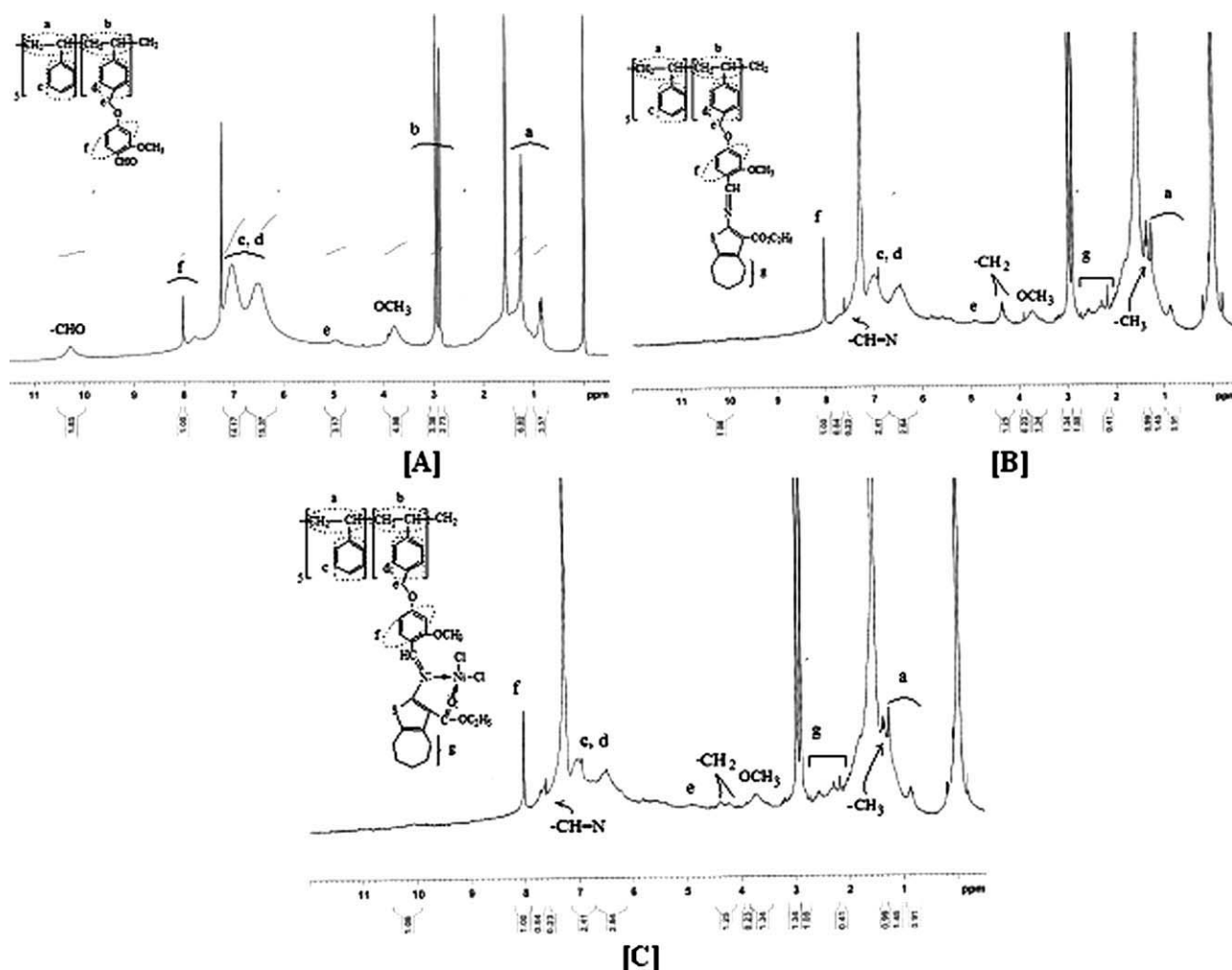


Figure 3 ^1H NMR spectra for FMPS (A), (FMPS-hT-Sch) (B), and (FMPS-hT-Sch-Ni) (C).

TABLE III
IR Bands (cm^{-1}) and Electronic Spectral (nm) of Schiff Base and Their Metal Complexes

Compound	$\nu_{\text{ring}}(\text{CH})/\nu_{\text{as}}(\text{CH})$	$\nu_{\text{as}}(\text{CH}_2)/\nu_{\text{s}}(\text{CH}_2)$	$\delta(\text{CH}_2)/\text{Ar-OCH}_3/\nu(\text{C-S-C})$	$\nu(\text{C=O})/\nu(\text{CH=N})/\nu(\text{M-O})/\nu(\text{M-N})$	λ_{max}
(FMPS-bT-Sch)	3082/3027	2923/2856	1404/1391/604	1800/1621/-	225; 258; 264
(FMPS-hT-Sch)	3084/3026	2921/2854	1403/1391/604	1803/1621/-	228; 257; 263
(FMPS-bT-Sch-Cu)	3085/3031	2930/2852	1403/1392/604	1804/1621/517/452	226; 256; 263
(FMPS-hT-Sch-Cu)	3086/3034	2926/2854	1403/1391/604	1804/1621/490/441	227; 258; 264
(FMPS-bT-Sch-Ni)	3082/3032	2926/2852	1404/1392/604	1803/1621/517/452	229; 258; 263
(FMPS-hT-Sch-Ni)	3084/3030	2930/2856	1404/1391	1804/1621/490/441	231; 257; 264

deviations from these values were noted, which may be attributed to the polymeric nature of the coordination polymers.¹⁵ The number average and weight average molecular weights (M_w and M_n) of PAA-Schiff bases and polydispersity index (M_w/M_n) are given in Table I.

¹H-NMR spectra of polystyrene including Schiff bases and their Ni(II) complexes

The ¹H-NMR spectra of polystyrene including Schiff Bases and their Ni(II) Complexes are summarized in Table II. Three signals are found in the regions $\delta = 0.8\text{--}1.3$, $2.7\text{--}3.1$, and $6.2\text{--}7.0$ ppm, which may be assigned to the $-\text{CH}_2-\text{CH}-$ marked with a, $-\text{CH}_2-\text{CH}-$ marked with b and (c,d) protons, respectively (Fig. 3). The ligands give rise to broad signals at $\delta = 7.3$ ppm, which may be attributed to the imine protons ($-\text{N}=\text{CH}-$) of the polymers incorporating Schiff bases. The protons of $-\text{CH}_3$ and $-\text{CH}_2$ of $-\text{CO}_2\text{C}_2\text{H}_5$ group in the Schiff bases are also observed as expected. The aliphatic ring proton signals appear at $\delta = 2.1\text{--}2.8$, $2.0\text{--}2.8$, $2.1\text{--}2.7$, and $2.1\text{--}2.6$ ppm for (FMPS-bT-Sch), (FMPS-hT-Sch), (FMPS-bT-Sch-Ni), and (FMPS-hT-Sch-Ni), respectively. The Ni(II) complexes exhibit signals in the range of $7.4\text{--}7.5$ ppm due to $-\text{CH}=\text{N}$ protons. These signals are observed in the higher field than ligands. The signals ¹H-NMR of Ni(II) complexes are

different from those of the corresponding ligands, suggesting the coordination through oxygen atoms in of $-\text{CO}_2\text{C}_2\text{H}_5$ and azomethine groups. Since Cu(II) complexes are paramagnetic, the ¹H-NMR spectra could not be obtained.

IR, UV-GB spectra and magnetic properties of polymeric Schiff bases and their complexes

The relevant IR spectral assignments of polymers including Schiff bases and their Ni(II) and Cu(II) complexes are given in Table III and corresponding spectra depicted in Figure 4. IR bands in the $3082\text{--}3086$ cm^{-1} , $3026\text{--}3034$ cm^{-1} , $2921\text{--}2930$ cm^{-1} , $2852\text{--}2856$ cm^{-1} , $1403\text{--}1404$ cm^{-1} , $1391\text{--}1392$ cm^{-1} regions are characteristic of $\nu_{\text{ring}}(\text{CH})$, $\nu_{\text{as}}(\text{CH})$, $\nu_{\text{as}}(\text{CH}_2)$, $\nu_{\text{s}}(\text{CH}_2)$, $\delta(\text{CH}_2)$, and Ar-OCH_3 respectively.¹⁶

New three bands appearing at $1800\text{--}1804$ cm^{-1} , 1621 cm^{-1} , and 604 cm^{-1} are assigned to $\nu(\text{C=O})$, $\nu(\text{CH=N})$, and $\nu(\text{C-S-C})$ vibrations, respectively, for the polymeric-Schiff bases.¹⁷ These observations indicate that the cycloalkylaminothiophene derivatives react with the polymer [Fig. 1(A)].

The azomethine and carbonyl bands in the IR spectra of the complexes appear in the range $1639\text{--}1631$ cm^{-1} and $1773\text{--}1778$ cm^{-1} , somewhat lower than observed for the (FMPS-bT) and (FMPS-hT-Sch). These indicate that the azomethine nitrogen and the oxygen of the carbonyl group are

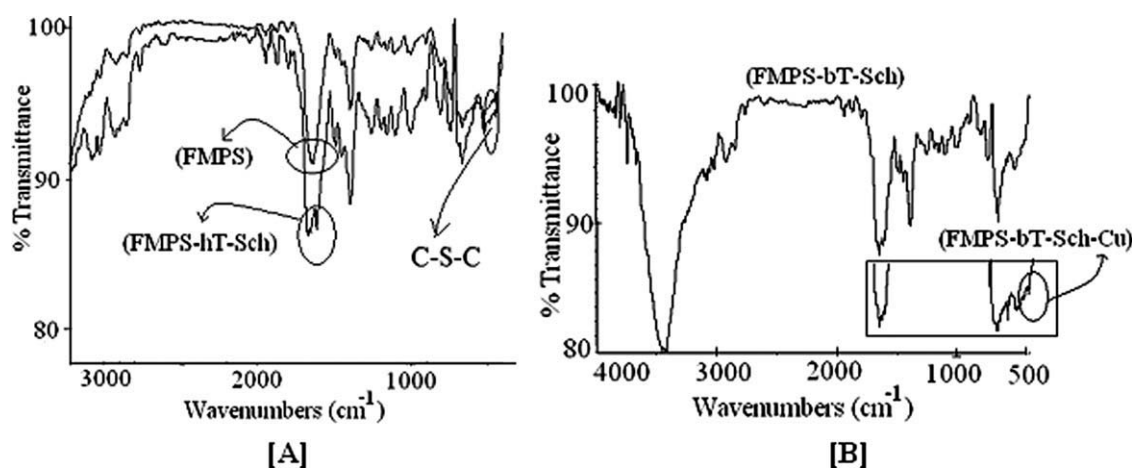


Figure 4 FTIR spectrum of studied polymer.

TABLE IV
TGA and DCS Results of Schiff Base and Their Metal Complexes

No	Compound	Thermally decomposed				DSC Results		
		T_i	$T_{1/2}$	T_{max}	T_f	Residue at 900°C (wt %) 10.7	Glass transition temperature (T_g) (°C)	Endothermic transition temperature (°C)
I	(FMPS-bT-Sch)	353	410	408	447	10.7	110	410
II	(FMPS-hT-Sch)	354	403	407	435	9.8	114	371
III	(FMPS-bT-Sch-Cu)	353	412	409	440	9.3	115	272
IV	(FMPS-hT-Sch-Cu)	364	411	410	436	11.4	120	407
V	(FMPS-bT-Sch-Ni)	350	360	410	433	9.9	112	404
VI	(FMPS-hT-Sch-Ni)	354	364	409	442	10.5	107	408

coordinated to metal ion. All complexes exhibit a $\nu(\text{C}-\text{S}-\text{C})$ thiophene ring frequency and $\text{Ar}-\text{OCH}_3$ that are almost unshifted relative to the Schiff base-polymer (634 cm^{-1} , 1391 cm^{-1}), suggesting that the sulfur atom of thiophene ring and the oxygen of group $\text{Ar}-\text{OCH}_3$ is not coordinated.¹⁶ Furthermore, the appearance of new small bands at $452-441\text{ cm}^{-1}$ and $517-490\text{ cm}^{-1}$ can be assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$, respectively.¹⁸ Thus, it appears that the metal(II) ions are bonded to the polymer through

one nitrogen and carbonyl oxygen in the polymeric complexes, and that the base acts as a neutral bidentate ligand.

The observed low magnetic moments for the tetrahedral complexes compared with the values for the distorted octahedral complexes may be taken as additional evidence for the presence of tetrahedral geometry around the Cu(II) ion. For the Ni(II) complexes, the effective diamagnetic moment was measured as 0.06 BM.¹⁰

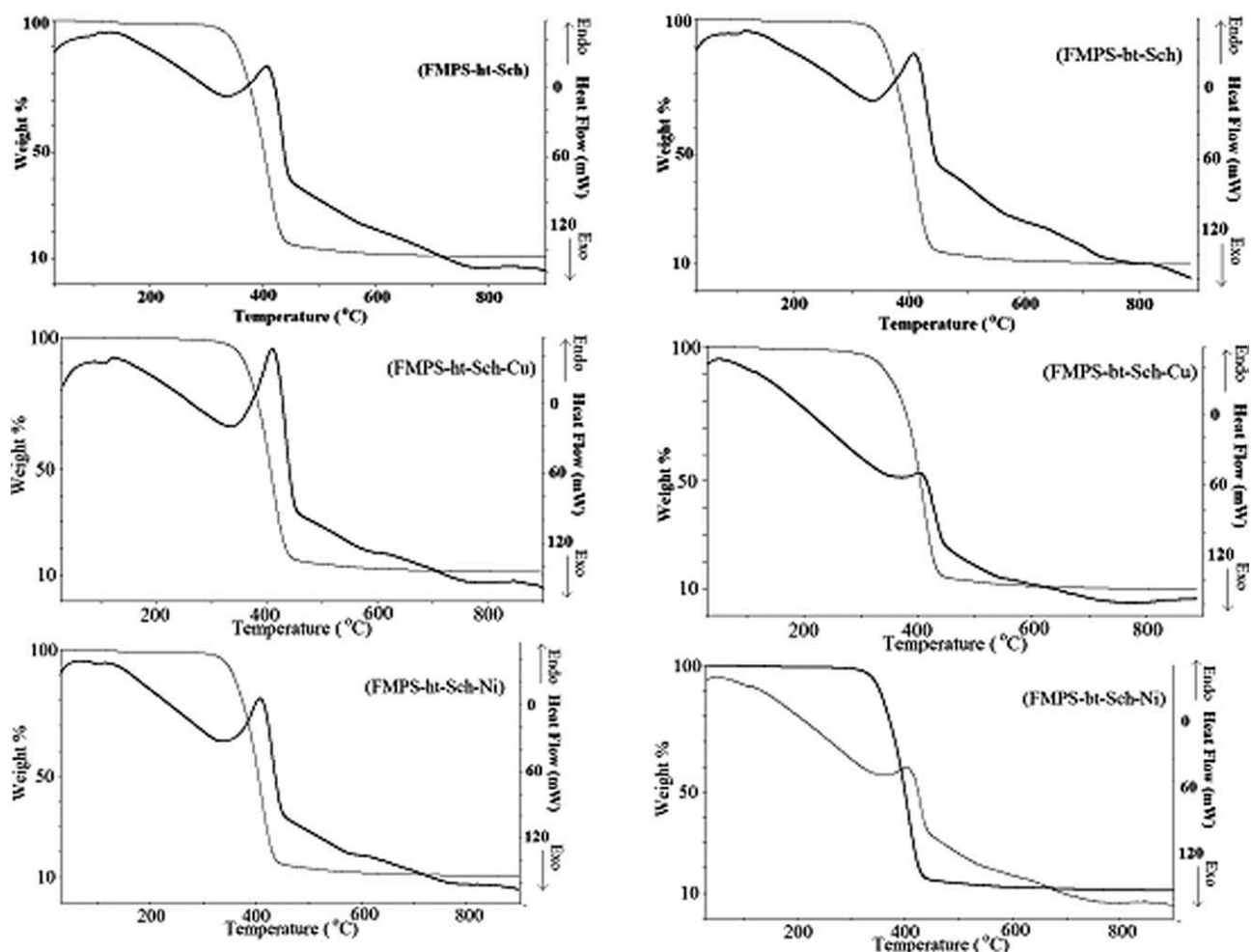


Figure 5 TGA and DSC curves for polymer matrix.

TABLE V
Biological Activity Schiff Bases, Complexes (3.5 $\mu\text{g}/\mu\text{L}$) and Standard Reagents (*Diameter of Zone of Inhibition (mm))

Compound	Gram (+)			Gram (-)				Yeast	
	<i>B. cereus</i>	<i>L. monocytogenes</i> 4b	<i>M. luteus</i>	<i>P. Putida</i>	<i>E. coli</i>	<i>S. typhi</i> H	<i>Br. Abortus</i>	<i>Sh.dys</i> <i>tip 10</i>	<i>C. albicans</i>
(FMPS-bT-Sch)	16	15	19	15	20	14	15	13	22
(FMPS-hT-Sch)	12	13	15	18	14	20	–	–	20
(FMPS-bT-Sch-Cu)	–	–	–	16	16	20	–	20	16
(FMPS-hT-Sch-Cu)	15	12	16	15	15	22	14	17	25
(FMPS-bT-Sch-Ni)	13	13	13	17	16	13	12	15	20
(FMPS-hT-Sch-Ni)	16	16	19	19	18	19	24	15	25
Standard reagents name									
K30	– ²⁷	15	27 ²⁷	14	25	20	–	20 ²⁷	–
AMP10	– ⁰	16	33 ³⁰	8	10	11	–	10 ³³	–
C30	– ²⁸	18	24 ²⁹	12	30	19	–	18 ³³	–
CIP5	– ⁸	17	20 ³²	20	25	23	–	24 ³³	–
AMC30	– ¹	22	21 ²⁷	15	14	19 ³¹	–	19 ²⁷	–
SKT25	–	11	20	18	18	17	–	18	–
OFX 10	30	–	–	–	–	–	–	–	–
NYS100	–	–	–	–	–	–	–	–	20

The electronic spectra (in DMF) for the polymeric Schiff-bases and their metal complexes are given in Table II. The higher-energy bands in the region 225–231 nm may be assigned to π - π^* transitions of the aromatic rings. The medium-energy bands in the region 264–256 nm may be attributed to n - π^* transitions of the heteroatom groups.

Electronic spectra of the Cu(II) complexes are similar and they present one broad absorption band within the 694–893 nm range which is assigned to a d - d transition expected of Cu(II) complexes compounds in tetragonal distorted octahedron due to Jahn Teller distortion. Tetrahedral Cu(II) complexes often give broad bands resulting from several overlapping bands or where the bands are resolved up to three close bands. This clearly indicates a tetrahedral environment around Cu(II) ion.¹⁹ For Ni(II) complexes, absorption at 478 nm, which is assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, is consistent with a D_{4h} symmetry about the metal.

TGA and DSC

Thermal analysis results of polymers are given in Table IV and corresponding curves depicted in Figure 5. (FMPS-bT-Sch) and (FMPS-hT-Sch) complexes are thermally decomposed in a step. According to initial decomposition temperature (T_i), (FMPS-hT-Sch-Cu) matrix had the highest decomposition temperature (364°C), whereas that of (FMPS-bT-Sch-Ni) composite had the lowest (350°C). The I–VI complexes are thermally stable up to 127, 121, 120, 107, 147, and 121°C, respectively. In the decomposition process of the I–VI complexes, the mass losses corresponded to absorption H_2O or CH_3OH leaving in the first

stages of the decomposition. Mass loss under 150°C corresponds to the absorbed volatile molecules and low molecular weight segments in polymer matrix.¹⁰

The DSC results for the polymeric Schiff-bases and their metal complexes are given in Table IV. The DSC curves observed for the polymer matrix are shown in Figure 5. An endothermic heat flow due to the glass transition is seen around 110, 114, 115, 120, 112, and 107°C.²⁰ The endothermic peaks present transitions between 272 and 410°C arising due to the removal of some fragment ($-\text{CH}_2\text{CH}-$, $-\text{CH}=\text{N}-$, OCH_3 , or $\text{CO}_2\text{C}_2\text{H}_5$) in polymer matrix.

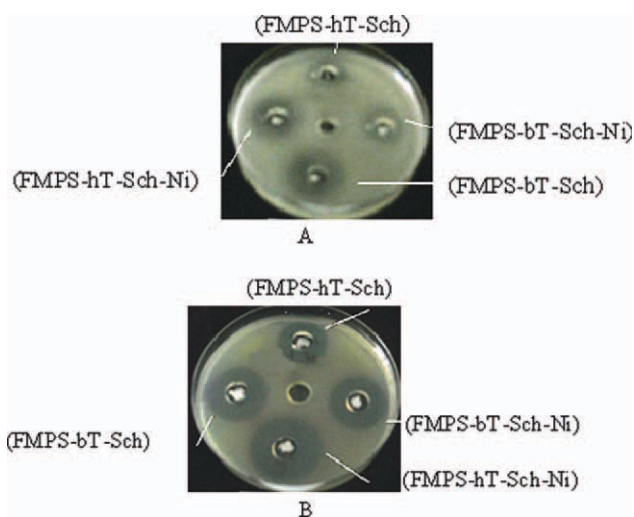


Figure 6 Biological activity pictures of (FMPS-hT-Sch), (FMPS-bT-Sch), and their Ni(II) complexes (A: for *E. coli*, B: for *C. albicans*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Biological activity of polymer-bound Schiff-base and their complexes

The ligands and their complexes were screened for antimicrobial activity in DMF solvent as a control. The compounds were tested with the same concentrations in DMF solution (3.5 $\mu\text{g}/\mu\text{L}$).

All the synthesized compounds exhibited varying degree of inhibitory effects on the growth of different tested strains (Table V). All of the compounds were active against *P. putita*, *E. coli*, *S. typhi* H, and *C. albicans*. All synthesized compounds showed moderate activity against *B. cereus*, *L. monocytogenes*, and *M. luteus*, except (FMPS-bT-Sch-Cu). (FMPS-bT-Sch-Cu) complex was inactive Gram (+). As shown in Table V, Cu(II) and Ni(II) complexes of (FMPS-hT-Sch) showed a significant activity against *C. albicans*.

B. abortus is a Gram-negative bacterium that causes premature abortion of a cattle fetus. What makes this bacterium so dangerous is that it is zoonotic, that is it can be transferred from an animal to a human host and still remain pathogenic.²¹ In humans this disease causes both acute and chronic symptoms, but can be treated with antibiotics. This research indicates that (FMPS-bT-Sch) and their complexes active against *B. abortus* (Table IV). (FMPS-hT-Sch) and its Cu(II) complex were inactive in *B. abortus*. Generally, the Ni(II) complexes are more potent bactericides than the Cu(II) complexes except *S. typhi* H and *Sh. dys* tip 10.

Ligands show more activity than their metal complexes (Fig. 6). This enhancement in activity depends on some factor. Some important factors such as the nature of the metal ion, nature of the ligand, geometry of the complexes, hydrophilic, and lipophilicity have influence on antibacterial activity.²² The antibacterial activity of these compounds was also compared with seven commercial antibiotics, namely, kanamycin, sulphamethoxazol, chloroamphenicol, ampicillin, amoxicillin, ciprofloxacin, and nystatin. It was seen that the compounds studied were as effective as the antibiotics mentioned above.^{23–29}

CONCLUSIONS

Two novel Schiff bases with polystyrene oligomer-support and their Ni(II) and Cu(II) complexes have been prepared, characterized, and tested for their

antimicrobial activities. The material exhibited very good antimicrobial activity against a wide range of microorganisms. The synthesized compounds were as effective as the antibiotics mentioned.

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