J Inorg Organomet Polym (2012) 22:1146–1155
DOI 10.1007/s10904-012-9697-5

Polystyrene Containing Carbinolamine/Azomethine Potentially Useful as Antimicrobial Agent: Synthesis and Biological Evaluation

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Received: 19 April 2012 / Accepted: 23 May 2012 / Published online: 17 June 2012

Abstract An investigation of antimicrobial properties of 12 novel modified polymer derived from the condensation reaction of (aminomethyl)polystyrene and four substitute salicylaldehyde (2-hydroxy benzaldehyde, 5-fluoro-2 hydroxy benzaldehyde, 5-fluoro-3-chloro-salicylaldehyde and 5-fluoro-3-methyl-salicylaldehyde) has been carried out and Cr(III) and Ni(II) complexes have been prepared. Modified polymers were characterized by magnetic susceptibility, elemental analyses, and spectral studies. The ^{1}H NMR and ^{13}C NMR spectra analysis of the polymeric carbinolamine/azomethine were determined. In addition, surface morphology and composition were determined by SEM/EDX. Thermo gravimetric analyses of polymers were carried out in nitrogen atmosphere. Antibacterial activities of the polymers attached carbinolamine/azomethine and their complexes were studied by the well-diffusion method against *Listeria monocytogenes 4b*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhi* H, *Brucella abortus*, *Staphylococcus epidermis* sp., *Micrococcus luteus*, *Shigella dysenteria* type 10, *Bacillus cereus, Pseudomonas putida* and antifungal activity against *Candida albicans*.

Keywords Antimicrobial properties · Carbinolamine/azomethine · Polystyrene · Thermal properties · Transmission electron microscop

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1 Introduction

The chemistry of polymer-based complexes of has been receiving significant current attention, because of the biopolymer relevance of the complexes [1]. A large majority of the polymer-based complexes have found wide medicinal applications owing to their potentially beneficial biological (viz. antibacterial and antitumor) activities [2]. Inorganic molecules containing fluorine have been used for a long time as an antitumor agent. But it has side effects such as gastrointestinal toxicity. Therefore, researchers many attempts have been made to obtain polymers having both higher medicinal effectives and lower toxic side effects. Park and at all suggested that fluorine-containing 5-fluorouracil attached to polymers are better antitumor agents than those of other 5-fluorouracil derivatives.

The presence of fluorine group in particular, is recognized in medicinal chemistry as a substituent of distinctive qualities. Because, the presence of fluorine leads to increased lipid solubility, thereby enhancing rates of absorption and transport of drugs in vivo [3]. Therefore, there has been greater effort towards the synthesis of biologically active macromolecule having fluorine group [4]. Antimicrobial polymers have the advantage that they are chemically stable and do not permeate through skin.

Furthermore, they play an important role in reducing the incidences of infections caused by biomaterial implant. Also in relation to antimicrobial polymers containing carbon–nitrogen bond, natural and synthetic polymers with metal moiety proved to exhibit significant antibacterial [5] and antifungal [6] activities.

Encouraged by these observations and in continuation to our previous work in the synthesis of biologically active compounds [7, 8] we synthesized newer polystyrene-bound carbinolamine/azomethine derivatives and their azomethine–Ni(II)/Cr(III)

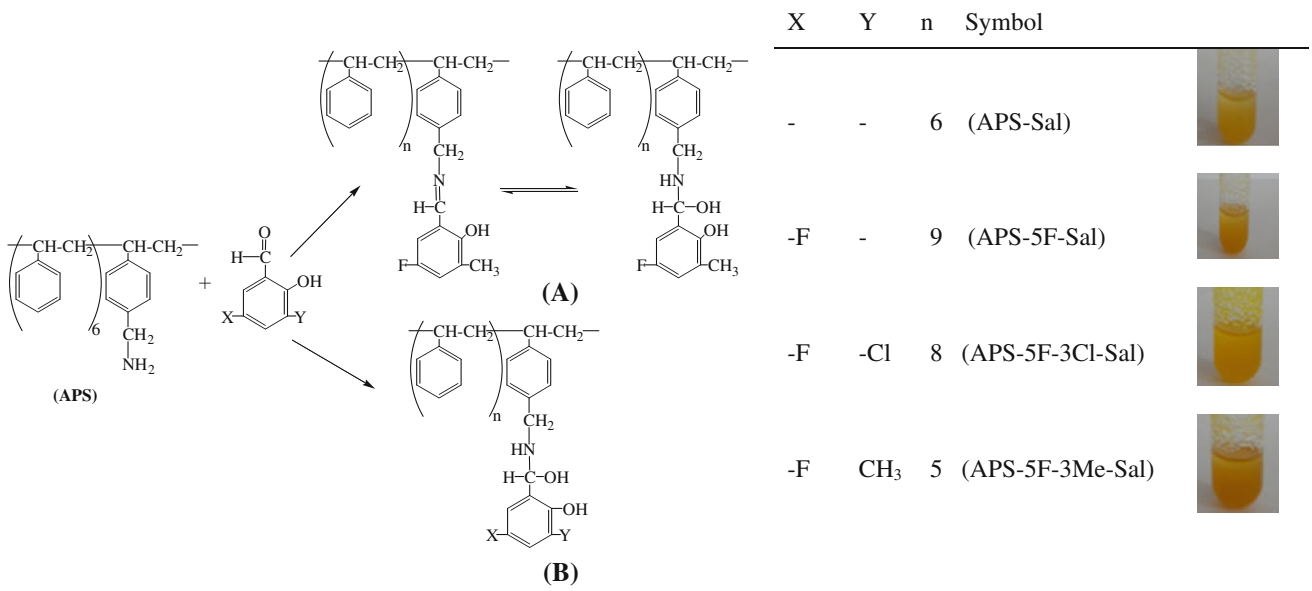


Fig. 1 General representation of the synthesized polymer-bound carbinolamine/azomethine (**A**) and carbinolamine (**B**)

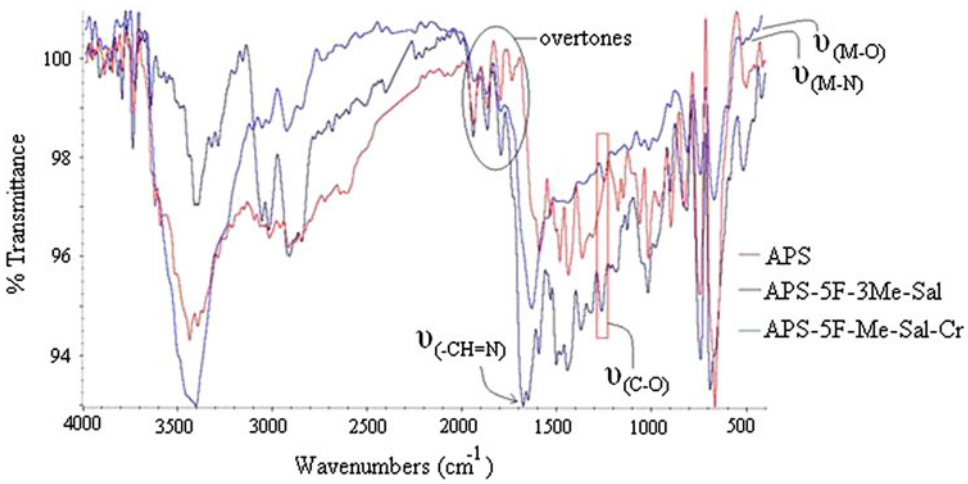


Fig. 2 FTIR spectra of (APS), (APS-5F-3CH_3-Sal), (APS-5F-3CH_3-Sal-Cr)

coordination polymers by facile methods (Figs. 1, 4). Antibacterial and antifungal activities of the prepared compounds have been investigated, and the results showed that some of the synthesized compounds have broad spectrum antibacterial and antifungal activities.

2 Experimental

2.1 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). ^{1}H-NMR spectra of the mofifyed polymers were recorded with a Bruker Spectrospin Avance DPX-400 instrument using TMS as internal standard and DMSO-d_6 as solvent. Elemental analyses were carried out with a LECO, CHNS-932 instrument. Metal contents were determined by using a Philips PU 9285 atomic absorption instrument. Electronic spectra were recorded on a Unicam-UV2-100 spectrophotometer in dimethylformamid (DMF). IR spectra were recorded on a Mattson-5000 FT-IR instrument in KBr pellets. TGA and DSC of the polymer-Schiff bases and their complexes were recorded by Setaram-simultaneous model thermal analyzer under nitrogen atmosphere between 25 and 900 °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. Scanning electron microscopy ofthe

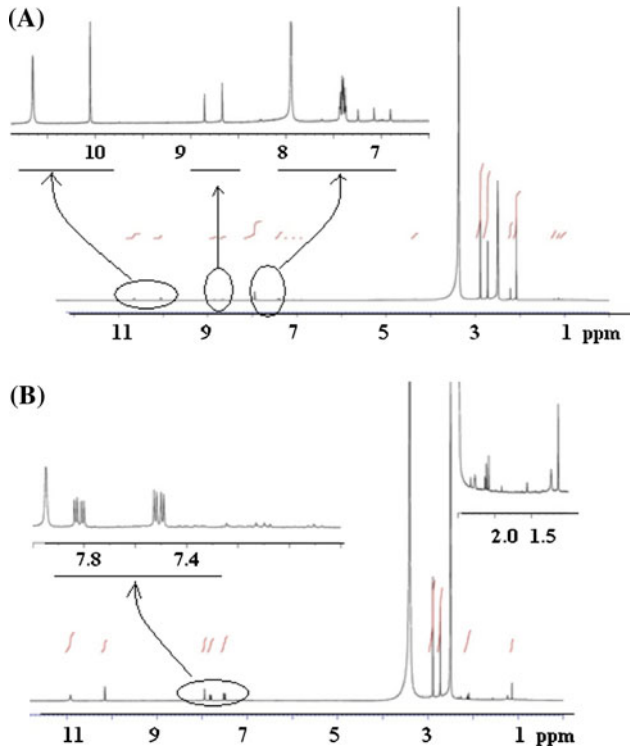


Fig. 3 Carbinolamine form in (APS-5F-3Cl-Sal) (**a**) and carbinolamine/azomethine form in (APS-Sch-5F-3Me-Sal) (**b**)

Au–Pd-coated compounds was done by using a JEOL JEM 100 CX II scanning electron microscope (JEOL, Peabody, MA) equipped with a link analytical system. The electron energy used was 20 keV.

2.2 Synthesis of Polymer Attached Carbinolamine/Azomethine (APS–CA/A)

The polymeric-carbinolamine/azomethine (or Schiff bases) (APS–CA/A) were prepared by reacting of (aminomethyl) polystyrene (APS) (1 g, 100–200 mesh, 0.5–1.0 mmol/g $-NH_2$ loaded, 1 % cross-linked (Aldrich)) in hot DMF (15 mL) with 2-hydroxybenzaldehydes and its derivatives (5-fluoro-2-hydroxy benzaldehyde, 5-fluoro-3-chloro-2-hydroxy benzaldehyde and 5-fluoro-3-methyl-2-hydroxy benzaldehyde; 1.0 mmol) in DMF (10 mL). Aldehyde solutions were slowly added by the drop wise on amine solutions while stirring through 30 min. Then the reaction mixture was boiled and stirred under areflux condenser ca. 3 h, at 70 °C. After the mixture cooling to room temperature, modified polymers were poured into the aceton and washed by adding acetone. The resulting clear yellow product was filtered and dried in the oven and kept with desiccator over anhydrous $CaCl_2$.

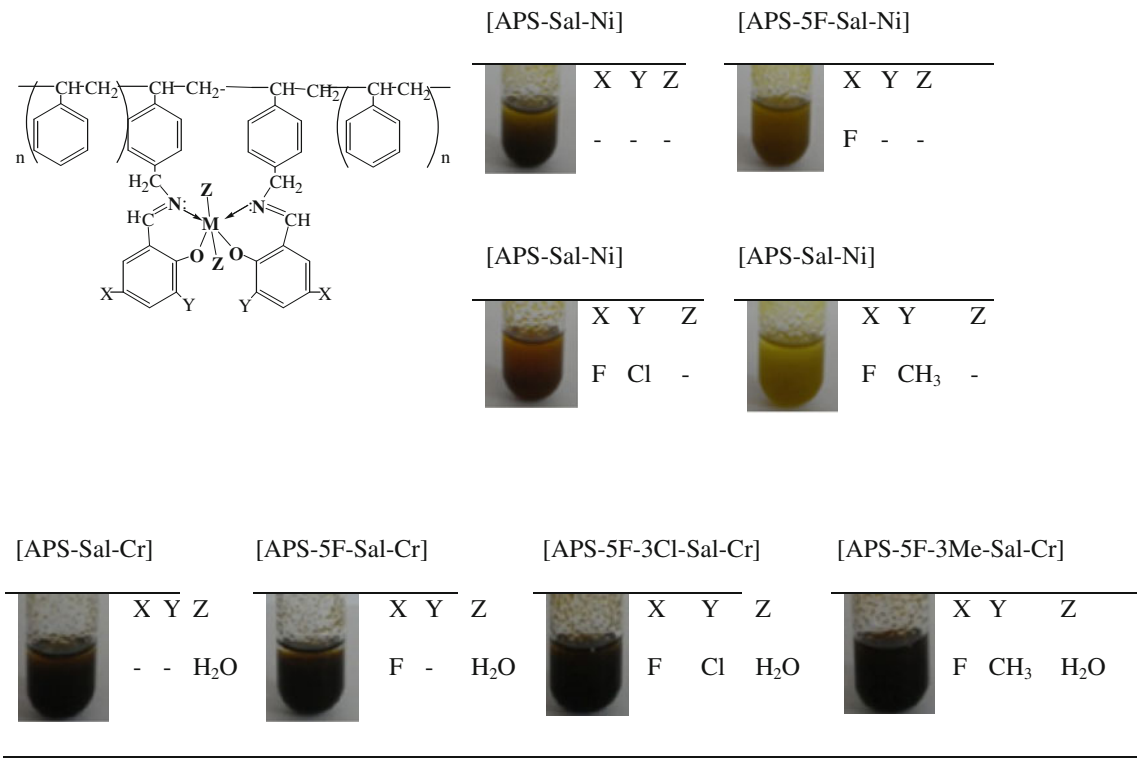


Fig. 4 Imaging in DMF solution and suggestion structure of the synthesized coordination polymer

2.3 Synthesis of Coordination Polymers (APS–A–M)

Metal-containing polymer complexes were synthesized by following a general method. The polymeric-azomethine/carbinolamine (APS–CA/A) were prepared by reacting of (aminomethyl) polystyrene (AMP) (1 g, 100–200 mesh, 0.5–1.0 mmol/g $–NH_2$ loaded 1 % cross-linked (Aldrich)) in hot DMF (15 mL) with 2-hydroxybenzaldehydes and it's derivatives (5-fluoro-2-hydroxy benzaldehyde, 5-fluoro-3-chloro-2-hydroxy benzaldehyde and 5-fluoro-3-methyl-2-hydroxy benzaldehyde; 1.0 mmol) in DMF (10 mL) and were stirred for 2 h under a reflux condenser at 50 °C. Metal salts (1.0 mmol $NiCl_2.6H_2O/CrCl_3.6H_2O$) in DMF (5 mL) were added to upon the mixture through 15 min and mixing process was continued ca. 4 h. Thus metal-containing polymer complexes were obtained (Fig. 4). After the mixture cooling to room temperature, polymeric-Schiff base complexes were poured into the aceton and washed by adding acetone. The resulting solid (clear green/dark yellow) was filtered and dried in a oven.

2.4 Detection of Antimicrobial Activity

The bacterial subcultures chosen were *L. monocytogenes 4b* ATCC19115, *S. aureus* ATCC25923, *E. coli* ATCC1230, *S. typhi H* NCTC-901.8394, *B. abortus* RSKK03026, *S. epidermis* sp., *M. luteus* ATCC 9341, *S. dysenteria* type 10 NCTC 9351, *B. cereus* sp., *P. putida* sp. An antifungal susceptibility test was used by *C. albicans* Y-1200-NIH, Tokyo. The polymers were tested for their antimicrobial activity by the well-diffusion method. Each polymer was kept dry at room temperature and dissolved (0, 15 g/ml) 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. 1 % (v/v) of 24 h broth culture containing 10^6 CFU/ml was placed in sterile petri dishes. Mueller-Hinton Agar (MHA) (15 ml) kept at 45 °C was then poured into the petri dishes and allowed to solidity. Then 6 mm diameter wells 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 three holes was used to calculate the zone of growth inhibition of each sample. Bacterial subcultures and antifungal were tested for resistance to four antibiotics (produced by Oxoid Lt., Basingstoke, UK): Sulphamethoxazole, Ampicillin, Nystatin, Sulbactam.

3 Results and Discussion

Analytical data and some of the physical properties of all modified polymers are given in Table 1. The elemental analyses can be considered compatible with the chemical formulas of the compounds due to polymers of different chain lengths [9]. The weight average molecular weight (Mw) was suggested from element analyses.

3.1 IR Spectra of Polymer-Bound Carbinolamine/Azomethine and their Ni(II) and Cr(III) Complexes

The characteristic peaks of IR spectra of (APS) polymer and all modified polymers are given in Table 2. Three overtone peaks showed in 1943, 1873, 1800 cm^{-1} all of modified polymer. For (APS) polymer, the vibrations of primary amine are observed in 3443, 3400 and 1543 cm^{-1}. The regions are characteristic $\upsilon(NH_2)_{asym}$, $\upsilon(NH_2)_{sym}$ and $\delta(NH_2)$, respectively [10]. In the spectra of modified polymers ((APS-Sal), (APS-5F-Sal), (APS-5F-3Cl-Sal), (APS-5F-3Me-Sal)) appearing new bands at 1278, 1269, 1282 and 1239 cm^{-1}, respectively, are assigned to $\upsilon(C–O)_{carbinol\ group}$ stretching vibrations [11, 12]. This situation was evaluated as participation aldehyde to polymer (Fig. 2). Modified polymers with aldehydes have not show imine bands, but coordination polymers including metal have show imine bands. Those imine bands observed between in range of 1630–1634 cm^{-1}. As the reason for this may be the coordination of the metal ion with the pair of electrons on the nitrogen atom in the imine group [13]. Also new weak bands appeared in the 434–475 and 492–506 cm^{-1} region, belonging to υ (M–N) and υ (M–O), respectively. This are confirmed formation of coordinate covalent bond through one nitrogen and phenol oxygen for all modified complexes [14]. Furthermore, IR bands in the 3423–3448, 3005–3043, 2900–2930, 523–76, 682–762 and 523–541 cm^{-1} regions are characteristic of υ (OH) (for Schiff bases-metal complexes), υ (CH) aromatic, υ (CH) aliphatic, υ (CH) buckling out of plane and υ (CH) buckling, respectively.

3.2 ^{1}H-NMR Spectra of Polymer-Bound Carbinolamine/Azomethine

^{1}H-NMR spectra of (APS) polymer and (APS)-including carbinolamine and azomethine are given in Table 3. For (APS) polymer, the signal is observed at 4.25 ppm which assigned to the $-NH_2$. The ^{1}H-NMR signal of the (APS) polymer exhibit two broad signals at 8.00–6.00 and 2.50–1.60 ppm, which are assigned to the –CH of aromatic protons and aliphatic protons, respectively. The ^{1}H-NMR spectra of the (APS-Sal), (APS-5F-Sal), (APS-5F-3Cl-Sal) and (APS-5F-3Me-Sal) signals at 10.90–10.70 and 10.25–10.15 ppm. The downfield shift, which are assigned to the $–CH_{(c.amine)}$ and $–NH_{(c.amine)}$ and protons, respectively (Fig. 3a). (APS-5F-3Me-Sal) compound showed sharp signal at 8.00 ppm, but other studied polymers do not

Table 1 Analytical data and some of the physical properties of modified polymer

Compound	Chemical formula M_w	Colour μ_{eff}, BM	Elemental analysis found (calculated) %				
			C	H	N	Ni	Cr
(APS)	$[(C_8H_8)_{\mathbf{6}}(C_9H_{11}N)]$	Cream	85.35	7.35	1.60		
	757	–	(90.36)	(7.79)	(1.85)		
(APS-Sal)	$[(C_8H_8)_{\mathbf{6}}(C_{16}H_{17}NO_2)]$	Yellow	87.18	7.15	1.62		
	879	–	(87.37)	(7.39)	(1.59)		
(APS-5F-Sal)	$[(C_8H_8)_{\mathbf{9}}(C_{16}H_{16}NO_2F)]$	Yellow	87.09	7.21	1.52		
	1209	–	(87.34)	(7.27)	(1.16)		
(APS-5F-3Cl-Sal)	$[(C_8H_8)_{\mathbf{8}}(C_{16}H_{15}NO_2FCl)]$	Yellow	84.24	6.81	1.45		
	1139	–	(84.28)	(6.94)	(1.23)		
(APS-5F-3Me-Sal)	$[(C_8H_8)_{\mathbf{5}}(C_{17}H_{16}NOF)]$	Yellow	86.72	7.17	1.49		
	789	–	(86.69)	(7.10)	(1.72)		
(APS-Sal-Ni)	$[(C_8H_8)_{\mathbf{11}}(C_{32}H_{28}N_2O_2Ni)]$	Green	86.25	7.12	1.43	0.03	–
	1674	Diamagnetic	(86.02)	(6.93)	(1.67)	0.04	
(APS-5F-Sal-Ni)	$[(C_8H_8)_{\mathbf{13}}(C_{32}H_{26}N_2O_2F_2Ni)]$	Khaki	85.28	7.02	1.45	0.03	–
	1918	Diamagnetic	(85.09)	(6.77)	(1.46)	0.04	
(APS-5F-3Cl-Sal-Ni)	$[(C_8H_8)_{\mathbf{18}}(C_{32}H_{24}N_2O_2F_2Cl_2Ni)]$	Light brown	84.40	6.87	1.39	0.03	–
	2507	Diamagnetic	(84.24)	(6.70)	(1.12)	0.02	
(APS-5F-3Me-Sal-Ni)	$[(C_8H_8)_{15}(C_{34}H_{30}N_2O_2F_2Ni)]$	Pistachio green	85.82	7.08	1.44	0.03	–
	2154	Diamagnetic	(85.79)	(6.96)	(1.30)	0.04	
(APS-Sal-Cr)	$[(C_8H_8)_{\mathbf{13}}(C_{32}H_{30}N_2O_3ClCr)]_3$	Naphtha green	84.77	6.99	1.57	–	0.01
	5788.5	3.02	(84.58)	(6.94)	(1.45)		0.01
(APS-5F-Sal-Cr)	$[(C_8H_8)_{\mathbf{10}}(C_{32}H_{28}N_2O_3F_2ClCr)]_3$	Naphtha green	81.74	6.78	2.48	–	0.01
	4960.5	3.06	(81.28)	(6.53)	(1.69)		0.02
(APS-5F-3Cl-Sal-Cr)	$[(C_8H_8)_{\mathbf{12}}(C_{32}H_{26}N_2O_3F_2Cl_3Cr)]_2$	Naphtha green	80.23	6.58	2.02	–	0.01
	3861	2.67	(79.56)	(6.32)	(1.45)		0.01
(APS-5F-3Me-Sal-Cr)	$[(C_8H_8)_{\mathbf{13}}(C_{34}H_{32}N_2O_3F_2ClCr)]_4$	Naphtha green	83.82	7.13	1.98	–	0.01
	5980.5	3.41	(83.07)	(6.82)	(1.40)		0.02

show signals. The spectra strongly suggest that in solution the carbinolamine and Schiff bases forms remain as two dominant species for (APS-5F-3Me-Sal) (Fig. 3b). Similar carbinolamine–azomethine forms has not been previously reported in other polymer-bound azomethine studies. The signals are found in the regions 8.00–7.45, 7.95–7.34, and 1.46–2.98 ppm which are described to aromatic protons of poly(styrene), aromatic protons of aldehyde and aliphatic –CH and $–CH_3$ protons of poly(styrene) for modified polymer.

3.3 UV–vis Spectra of Polymer-Bound Carbinolamine/Azomethine and Their Ni(II) and Cr(III) Complexes

The electronic spectra of polymer-bound carbinolamine/azomethine and their Ni(II) and Cr(III) complexes are given in Table 2. UV–vis spectra of all compounds were taken in DMF. The band observed in 266–255 nm and 306 nm which may be considered to $\sigma \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transition of–NH_2 for (APS) respectively. The energy bands in the region 341–306 nm be assigned to $n \rightarrow \pi^*$ transitions of the –NH for all modified polymers. In addition, the band observed in 421 nm which may be considered to $n \rightarrow \pi^*$ transition of –CH = N for (APS-5F-3Me-Sal) [15]. This case may be due to the carbinolamine and azomethine forms remain as two dominant species for (APS-5F-3Me-Sal). Furthermore, absorption violence showed an increase in with complexation. The lower bands in the region 324–342 nm may be assigned to charge transfer transition which anticipated due to forbidden d–d transitions for square plane Ni(II) complexes. And the lower bands in 545–405 nm are assigned to charge transfer transitions for octahedral coordinated Cr(III) complexes [16]. Chromium (III) complexes of (APS-Sal), (APS-5F-3Cl-Sal) and (APS-5F-3Me-Sal) shows two bands in the region 398–418 nm and 283–306 nm, respectively. The peak ca 400 nm and 290 corresponds to the $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) electronic transition respectively. In the UV-GB spectrum of [APS-5F-Sal-Cr] complexes have

Table 2 Important IR vibration frequencies (cm^{-1}) and UV–visible spectrum values (nm) of APS and modified polymers

Compound	ν (O–H) ν(C–O)	ν $(C–H)_{aliphatic}$ ν $(C–H)_{aromatic}$	ν $(NH_2)_{asym,\ sym}$ ν (CH = N)	ν (M–O) ν (M–N)	$N \rightarrow \pi^*_{(C–N)}$, $\pi \rightarrow \pi^*_{(C=N)}$ d → d
(APS)	–	2921, 2852	3443, 3400	–	306 (0.262), –
	–	3060, 3021	–	–	–
(APS-Sal)	3,413	2921, 2852	–	–	320 (1.340), –
	1,278	3060, 3021	–	–	–
(APS-5F-Sal)	3,413	2921, 2852	–	–	320 (0.183), –
	1,269	3060, 3021	–	–	–
(APS-5F-3Cl-Sal)	3,413	2921, 2852	–	–	341 (2.633), –
	1,282	3060, 3021	–	–	–
(APS-5F-3Me-Sal)	3,413	2921, 2852	–	–	331 (1.828), 421 (0.803)
	1,239	3060, 3021	–	–	–
(APS-Sal-Ni)	3,421	2921, 2856	–	486	324 (0.639), no
	1,278	3060, 3026	1,630	443	–
(APS-5F-Sal-Ni)	3,421	2921, 2860	–	–	335 (0.435), 420 (0.093)
	1,256	3065, 3026	1,631	–	–
(APS-5F-3Cl-Sal-Ni)	3,421	2921, 2856	–	473	334 (0.258), 421 (0.081)
	1,226	3060, 3026	1,634	438	–
(APS-5F-3Me-Sal-Ni)	3,421	2921, 2852	–	482	342 (0.128), 430 (0.087)
	1,260	3060, 3030	1,634	447	–
(APS-Sal-Cr)	3,421	2921, 2856	–	473	324 (0.346), no
	1,256	3065, 3026	1,632	431	405 (0.032), $^4A_{2g} \rightarrow {}^4T_{1g}$
(APS-5F-Sal-Cr)	3,413	2921, 2860	–	491	317 (0.621), 325 (0.605)
	1,252	3056, 3026	1,638	442	407 (0.535), $^4A_{2g} \rightarrow {}^4T_{1g}$
					545 (0.059), $^4A_{2g} \rightarrow {}^4T_{2g}$
(APS-5F-3Cl-Sal-Cr)	3,413	2921, 2852	–	508	327 (0.846), 348 (0.513)
	1,256	3065, 3034	1,640	473	407 (0.330), $^4A_{2g} \rightarrow {}^4T_{1g}$
(APS-5F-3Me-Sal-Cr)	3,413	2934, 2856	–	489	318 (1.033), 402 (0.867)
	1,260	3065, 3026	1,637	442	428 (0.108), $^4A_{2g} \rightarrow {}^4T_{1g}$

no no observed

three bands at 545, 407 and 283 nm, respectively. The peak at 545, 350 and 290 nm corresponds to the $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) electronic transition respectively.

3.4 Magnetic Susceptibility of Polymer-Bound Ni(II) and Cr(III) Complexes

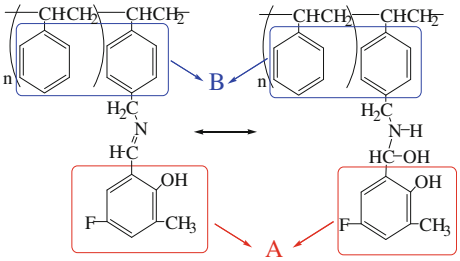
Measurements of magnetic susceptibility of metal-containing azomethine polymers are summarized in Table 1. Ni(II) complexes of polymer-bound azomethine polymers [APS-Sal-Ni], [APS-5F-Sal-Ni], [APS-5F-3Cl-Sal-Ni] and [APS-5F-3Me-Sal-Ni] found to be diamagnetic. This reason suggested Ni(II) complexes are square plane. Absorption at 340 nm, which is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, is consistent with a D_{4h} symmetry about the metal [17]. Measurements of magnetic susceptibility of [APS-Sal-Cr], [APS-5F-Sal-Cr], [APS-5F-3Cl-Sal-Cr] and [APS-5F-3Me-Sal-Cr] complexes are determined 3.02, 3.06, 2.67 and 3.41 respectively. According to the results, thought to be an octahedral structure in complexation.

3.5 Thermal Stability of Polymer-Bound Carbinolamine/Azomethine and Their Ni(II) and Cr(III) Complexes

TGA and DTA thermograms: The TGA and DTA thermograms for polystyrene attached carbinolamine/azomethine and their complexes were recorded in N_2 atmosphere, and the percent weight loss and the corresponding temperature range are given in Table 4. The TGA thermogram of all polymer-Bound carbinolamine/azomethine and their Ni(II) and Cr(III) complexes exhibits a one-step weight in the range of 370–450 °C. The values of T_i, T_{max}, $T_{1/2}$ and T_f are 384, 416, 414 and 446 °C, respectively for (APS-Sal). Initial (T_i), maximum and finally (T_f) decomposition temperature of (APS-Sal) is higher than (APS-5F-Sal), (APS-5F-3Cl-Sal) and (APS-5F-3Me-Sal). According to

Table 3 ^{1}H-NMR chemical shift (ppm) of the APS and modified polymers

Position	(APS)	(APS-Sal)	(APS-5F-Sal)	(APS-5F-3Cl-Sal)	(APS-5F-3Me-Sal)
–OH/–NH	–/3.80–4.20*	10.70/10.25	10.70/10.25	10.90/10.15	10.64/10.05
–CH = N	–	–	–	–	8.85
$(–CH)_B$	8.20–7.10	8.00–7.70	8.00–7.80	7.83–7.48	7.95–7.37
$(–CH)_A$	–	6.70–7.00	6.70–7.10	7.45–7.55	6.90–7.25
$(–CH,–CH_2,$ $–CH_3)_{alif}$	1.60–2.50	1.10–2.90	1.15–2.85	1.10–2.90	1.00–2.90



* NH_2 chemical shift values belonging to APS

Table 4 TGA/DTA results and elemental composition of modified polymer by XPS

Compound	Thermally decomposed									Elemental composition (by XPS)					
	TGA				DTA										
	T_i	$T_{1/2}$	T_f	Loss of mass at 900 °C (wt %)	1.	2.	3.	4.	5.	C	O	F	Cl	Ni	Cr
(APS)	378	413	443	91	33	110	167	303	407	97.22					
(APS-Sal)	384	414	446	91	39	111	175	418	–	97.05	2.30				
(APS-5F-Sal)	380	417	447	93	80	143	420	–	–	96.82	2.14	0.46			
(APS-5F-3Cl-Sal)	375	418	446	89	39	118	171	418	–	94.50	2.20	0.77	1.44		
(APS-5F-3Me-Sal)	357	396	435	92	36	107	164	404	–	97.93	1.77	0.30			
(APS-Sal-Ni)	382	418	443	86	36	118	168	425	–	94.82	2.41			1.38	
(APS-5F-Sal-Ni)	370	414	439	91	36	107	171	421	–	94.65	1.98	0.59		1.48	
(APS-5F-3Cl-Sal-Ni)	386	421	446	86	36	107	168	421	–	91.56	3.09	0.66	2.14	2.11	
(APS-5F-3Me-Sal-Ni)	377	417	445	91	43	130	170	423	–	96.09	1.64	0.49		1.44	
(APS-Sal-Cr)	370	415	443	82	36	107	168	418	–	94.42	1.74				1.06
(APS-5F-Sal-Cr)	386	421	446	84	36	107	171	207	425	88.42	2.29	0.50	4.24		1.55
(APS-5F-3Cl-Sal-Cr)	381	422	444	79	81	147	179	422	–	90.91	1.47	0.68	3.36		1.70
(APS-5F-3Me-Sal-Cr)	380	417	450	86	37	104	167	424	–	93.65	2.12	0.70	1.27		1.07

T_i temperature of inital degradation, $T_{1/2}$ temperature of half degradation, T_f temperature of finally degradation

this result that (APS-Sal) is much thermally stable. And the highest decomposition temperature (T_i: 386, T_f: 455; T_i: 386, T_f: 455) has a [APS-5F-3Cl-Sal-Ni] and [APS-5F-Sal-Cr] among metal-containing modified polymers. In addition, due to absence of any mass loss until region where to the 100 °C temperature change in the TGA curves, can be evaluated as there is not crystal water in structure of modified polymers [17].

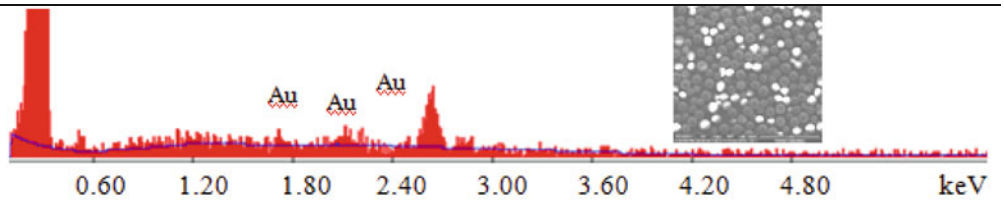
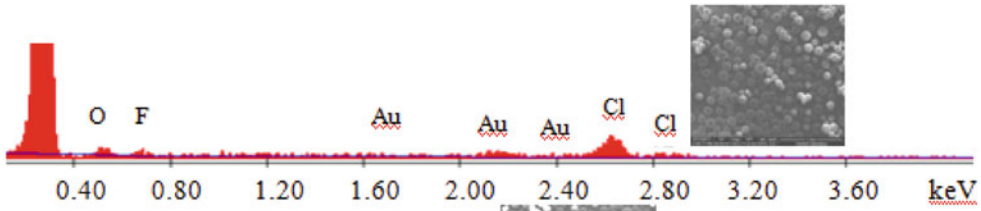
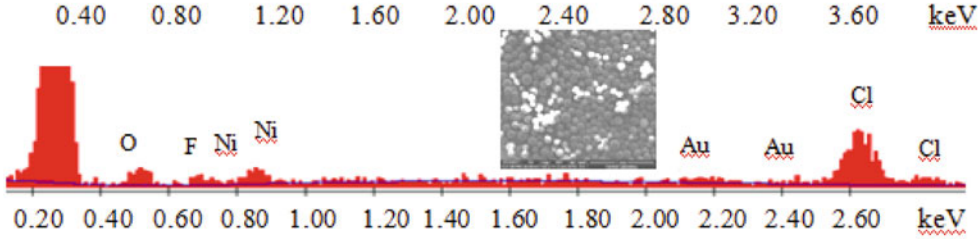
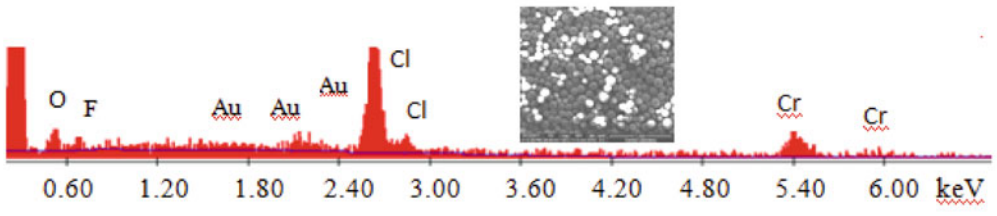
The DTA thermograms of studied polymeric have four endothermic peaks except (APS), (APS-5F-Sal) and (APS-5F-Sal-Cr). The endothermic curve are observed in between 33 and 80 °C, 104 and 147 °C, 164 and 175 °C and 207–425 °C are in the between 33 and 425 °C for studied polymeric carbinolamine/azomethine and their 1. step, 2. step, 3. step and 4. step, respectively.

The DTA thermogram of the (APS-5F-Sal) shows three endothermic peak 80, 143 and 420 °C, in contrast to the DTA thermogram of the (APS-5F-Sal-Cr) which shows five endothermic decomposition peak.

3.6 Scanning Electron Microscopy and EDX Analysis

SEM images of APS and modified polymers shown in Table 5. SEM images of modified polymers were not markedly different from those of APS. This image indicates that protects structure are of modified polymers from

Table 5 SEM imaging (mag 120×) EDX spectra of APS and selected modified polymers

Compound	
(APS)	
(APS-5F-3Cl-Sal)	
[APS-5F-3Cl-Sal-Ni]	
[APS-5F-3Me-Sal-Cr]	

(APS). Table 4 presents the elemental compositions of synthesized (APS-Sal), (APS-5F-Sal), (APS-5F-3Cl-Sal) and (APS-5F-3Me-Sal) and their complexes as obtained from EDX analysis. EDX is not the technique of choice for analyzing polymers. Because intensities of the carbon atom is often erratic in modified polymers. However, an EDX spectrum gives an excellent elemental analysis for all elements in the periodic sable above beryllium in modified polymer. In Table 4 shows that hydrogen atoms are not taken into account composition of all studied polymer. EDX analysis shows the presence of metal ions (Ni(II) and Cr(III)) in the prepared coordination polymer. The combined information from SEM and EDX indicate the genuine modified polymer formation with aldehyde group and metal ions.

3.7 Biological Activity of Studied Polymer

The (aminomethyl) polystyrene and modified poly(styrene) were screened for antimicrobial activity in DMF solvent as a control substance. The compounds were tested with the same concentrations in DMF solution (0.15 g/ml). All the synthesized compounds and antibiotic exhibited varying degree of inhibitory effects on the growth of different tested strains (Table 6; Fig. 5). APS was inactive in all of studied bacteria except *B. abartus* and *C. albicans*. All of studied polymer was inactive in *Sh.dys. typ 10* and *M. luteus* whereas all of them was active *C. albicans* except (APS-Sch-5F-3Me-Sal). *B. abartus* is dangerous bacterium. It is a gram-negative bacterium that causes premature abortion of a cattle fetus. It can be transferred from an animal to a human host. In humans this disease causes both acute and chronic symptoms, but can be treated with antibiotics. This research indicates that (APS-Sch-5F-3Cl-Sal-Cr) coordination polymer is more active against *Br. abortus* than other studied polymer (Table 6). In this study, the Cr(III) coordination polymers are more potent bactericides than the Ni(II) coordination polymer. Furthermore, the antibacterial activity of these compounds was also compared with four commercial antibiotics, namely, Sulphamethoxazole, Ampicillin, Sulbactam and Nystatin. It was

Table 6 Antimicrobial activity of studied compounds (0.15 g/ml) and standard reagents (diameter of zone inhibition (mm))

	APS	And	It's	Derv.	With aldehyde	Ni(II) complexes				Cr(III) complexes			
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Gram (+)													
Sh. dys. typ 10	–	–	–	–	–	–	–	–	–	–	–	–	–
P. putida	–	16	11	–	–	–	–	14	12	12	15	–	–
S. typhi H	–	–	11	–	–	–	–	–	14	20	–	–	15
Br. abortus	12	12	14	–	15	13	15	12	12	13	–	16	–
L. monocytogenes 4b	–	–	14	11	–	–	12	–	–	12	–	14	12
B. cereus	–	–	15	16	–	–	15	–	–	–	–	14	–
Gram (−)													
S. aureus	–	–	–	18	–	–	14	–	–	–	12	13	14
S. epidermis	–	11	11	14	–	17	15	12	15	12	11	12	–
M. l uteus	–	–	–	–	–	–	–	–	–	–	–	–	–
E. coli	–	15	–	10	–	–	13	–	–	14	11	13	–
Yeast													
C. albicans	13	21	25	–	14	20	24	13	20	20	18	16	15
DMF (control)	–	–	–	–	–	–	–	–	–	–	–	–	–

Positive control	*S. aureus*	*L. monocytogenes*	*E. coli*	*S. typhi H*	*Br. abortus*	*C. albicans*	
SXT25	24	11	18	17	–	–	SXT25, Sulphamethoxazol 25 μg;
AMP10	30	16	10	11	–	–	AMP10, Ampicillin 10 μg;
NYS100	–	–	–	–	–	20	NYS100, Nystatin 100 μg;
SCF	–	–	–	–	12	–	SCF, Sulbactam (30 μg)

1. (APS) **2.** (APS-Sal) **3.** (APS-5F-Sal) **4.** (APS-5F-3Cl-Sal) **5.** (APS-5F-3Me-Sal) **6.** (APS-Sal-Ni) **7.** (APS-5F-Sal-Ni) **8.** (APS-5F-3Cl-Sal-Ni) **9.** (APS-5F-3Me-Sal-Ni) **10.** (APS-Sal-Cr) **11.** (APS-5F-Sal-Cr) **12.** (APS-5F-3Cl-Sal-Cr) **13.**(APS-5F-3Me-Sal-Cr)

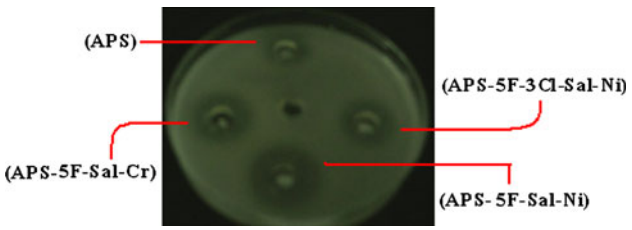


Fig. 5 Imaging of antimicrobial affectivities of (APS), (APS-Sch-5F-Sal-Cr), (APS-5F-3Cl-Sal-Ni), (APS-5F-Sal-Ni) against to *C. albicans*

seen that the synthesized compounds were effective as the antibiotics mentioned.

4 Conclusions

In summary, a range of modified polymers have been prepared for preliminary screening as antimicrobial agents. Novel coordination polymers were prepared, including salicylaldehyde and its derivatives with fluoro at the five position. Square planer and octahedral geometries have been proposed for Ni(II) and Cr(III) coordination polymer with the help of various physicochemical studies like IR, UV, TGA/DTA, magnetic susceptibility, elemental analyses and SEM/EDX. Carbinolamine and azomethine structure have been proposed for modified aldehydes polymer from ^{1}H-NMR spectra. We know that carbinolamines can be stabilized by electron-withdrawing groups attached to the tetrahedral carbon [18, 19]. In this study, carbinolamine structures may be stabilized due to attached polystyrene. In the IR spectra of modified polymers appearing new or new weak bands show that Schiff bases and coordination polymers were synthesized. Free modified polymer and their metal complexes were screened against various bacteria and fungi to access their potential as antimicrobial agents. The antimicrobial data shows that the Cr(III) complexes are superior to the free modified polymer and their Ni(II) complexes. Furthermore, this result indicates that studied polymers are active as sulphamethoxazole, ampicillin, sulbactam and nystatin. This study demonstrated the in vitro antibacterial activity of modifed polymer, which may have potential biomedical applications owing to their antibacterial properties.

Acknowledgments This work was supported by the Gazi University Research Fund (Project number: 05/2010-75) and Ahi Evran Unıversity, grant No: FBA-11-27-2011.

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