New Antimicrobial Polyurea: Synthesis, Characterization, and Antibacterial Activities of Polyurea-Containing Thiosemicarbazide–Metal Complexes

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ABSTRACT: A novel class of polymer–metal complexes was prepared by the condensation of a polymeric ligand with transition-metal ions. The polymeric ligand was prepared by the addition polymerization of thiosemicarbazides with toluene 2,4-diisocyanate in a 1 : 1 molar ratio. The polymeric ligand and its polymer–metal complexes were characterized by elemental analysis, thermogravimetric analysis, Fourier transform infrared spectroscopy, and ^{13}C-NMR and ^{1}H-NMR spectroscopy. The geometries of the central metal ions were determined by electronic spectra (UV–visible) and magnetic moment measurement. The antibacterial activities of all of the synthesized polymers were investigated against *Bacillus subtilis* and *Staphylococcus aureus* (Gram positive) and *Escherichia coli* and *Salmonella typhi* (Gram negative). These compounds showed excellent antibacterial activities against these bacteria with the spread plate method on agar plates, and the number of viable bacteria were counted after 24 h of incubation period at 37°C. The antibacterial activity results revealed that the Cu(II) chelated polyurea showed a higher antibacterial activity than the other metal-chelated polyureas. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3305–3312, 2008

Key words: metal–polymer complexes; NMR; thermal properties

INTRODUCTION

Since the discovery of manmade polymers, continuous efforts have been made to make polymers more stable, increase their mechanical and chemical strengths, and make them durable in the environment. Now, it is time to meet the challenges for the synthesis of biomedical materials. The use of antimicrobial polymers offers promise for enhancing the efficacy of some existing antimicrobial agents and minimizing the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging the lifetime of the antimicrobial agents. Also, polymeric antimicrobial agents have the advantage that they are nonvolatile and chemically stable and do not permeate through skin. Therefore, they can reduce losses associated with volatilization, photolytic decomposition, and transportation. In the field of biomedical polymers, infections associated with biomaterials represent a significant challenge to the more widespread application of medical implants. Polymers containing metal ions have found widespread applications in the biomedical field and as catalysts in organic synthesis, nuclear chemistry, the preconcentration and recovery of trace metal ions, pollution control, hydrometallurgy, polymer drug grafts, and wastewater treatments.[1–4] Thiosemicarbazides are of considerable interest because of their chemistry and ability to form stable chelates with essential metal ions and their potentially beneficial biological activities, such as antitumor, antibacterial, antiviral, and antimalarial activities.[5–13] The potential biological activity of compounds containing sulfur and nitrogen may be responsible for this increased interest. Toluene 2, 4-diisocyanate (TDI) is an extremely reactive chemical with amino and hydroxyl groups that form polyurea and polyurethane, respectively.[14] TDI also interacts with the amino group of proteins, DNA, and RNA (*in vitro*) and, results from a combination with the primary amide and the amino group to form polyurea. A series of polymer–metal complexes have been synthesized in our laboratory that are used as antimicrobial materials in biomedical fields such as antimicrobial coating materials.[15–17] To continue our efforts, in this study, we synthesized a novel polymeric

ligand (polyurea) and its polymer–metal complexes with transition-metal ions. All the of the synthesized polymers were characterized by various techniques, such as elemental analysis, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and ^{13}C-NMR and ^{1}H-NMR spectroscopy. The antibacterial activities of these compounds were tested against *Bacillus subtilis* and *Staphylococcus aureus* (Gram positive) and *Escherichia coli* and *Salmonella typhi* (Gram negative) with the shaking flask method, where 25-mg/mL concentrations of each compound were tested against 10^5 cfu/mL bacterial solutions.

EXPERIMENTAL

Materials and bacterial strains

Thiosemicarbazide, TDI, and all of the solvents were purchased from S. D. Fine Chemical, Ltd. (Mumbai, India), and the solvents were recrystallized from methanol before use. All of the other chemicals were used as received. Tryptic soy agar was purchased from Difco Laboratories (Lawrence, KS). It contained 15.0 g of a pancreatic digest of casein, 5.0 g of an enzymatic digest of soybean meal, 5.0 g of sodium chloride, and 15.0 g of agar. Tryptic soy broth (TSB) was also purchased from Difco Laboratories. It contained 17.0 g of a pancreatic digest of casein, 3.0 g of an enzymatic digest of soybean meal, 2.5 g of dextrose, 5.0 g of sodium chloride, and 2.5 g of dipotassium phosphate. The bacterial strains used for the antimicrobial activity tests included *S. aureus* (IFO 2340), *B. subtilis* (IFO 24370), *S. typhi* (IFO 3807), and *E. coli* (IFO 3628). The strains were kept at $-80°C$ in a freezer.

Measurements

The elemental analysis of the polymers was carried out on a PerkinElmer model 2400 elemental analyzer (Waltham, MA) (CDRI, Lucknow). The metal content was determined by complexometric titration against ethylene diamine tetraacetic acid after decomposition with concentrated nitric acid (HNO_3). The FTIR spectra were recorded over the range 4000–500 cm^{-1} on a PerkinElmer infrared spectrophotometer model 621 with KBr pallets. The UV–visible spectra were obtained on a PerkinElmer Lembda EZ-201 spectrophotometer with dimethyl sulfoxide (DMSO) as a solvent, and the magnetic susceptibility measurements of these resins were carried out on a Gouy balance (Malvern, PA) with Hg[Co(SCN)$_4$] as a celebrant. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Jeol SX 300-MHz FX-1000 Fourier transform NMR spectrometer (Oxford, UK) with DMSO as a solvent and tetramethylsilane as an internal standard. The thermal behaviors of the polyurea were determined on a TGA analyzer 2000 (New Castle, DE) in a nitrogen atmosphere at a heating rate of 20°C/min.

### Synthesis

Synthesis of the polymeric ligand

Thiosemicarbazide (9.14 g, 0.1 mol) and TDI (12.5 g, 0.1 mol) were mixed in 60 mL of *N,N*-dimethylformamide (DMF) in a 100-mL, round-bottom flask. The flask was closed with a rubber septum, and the mixture was stirred at 40°C for 24 h. The reaction mixture was evaporated by a rotary evaporator, and the final mixture was cooled and precipitated into deionized water. A solid, light yellow product was obtained; it was dried in a vacuum oven to remove trapped solvents to give the polymeric ligand (polyurea (PU); 14.16 g) at a 73% yield. The polymeric ligand was insoluble in water, methanol, ethanol, and nonpolar solvent but was soluble in tetrahydrofuran, DMF, and DMSO at room temperature.

Synthesis of the polymer–metal complexes

The polymer–metal complexes were synthesized by the mixture of a hot solution of polymeric ligand (0.02 mol) with metal acetate (0.01 mol) in a 100-mL, round-bottom flask at 40°C for 24 h. The reaction mixture was cooled and precipitated into a 75/50 v/v water/acetone mixture. The solid colored product was filtered and then reprecipitated from DMF into ethanol. The solid product was filtered and washed with water and ethanol, respectively. Finally, the product was dried in a vacuum oven to remove trapped solvents; this gave a colored powder of polymer–metal complexes at a 70–75% yield.

Antibacterial assessment

The antibacterial activity tests were performed with the shaking flask method,[18] and the number of viable cells was counted with the spread plate method.[19] *S. aureus, B subtilis, S. typhi,* and *E. coli* were streaked out on tryptic soy agar plates and incubated at 37°C for 24 h. A representative colony was lifted off with a wire loop and placed in 5 mL of TSB, which was then incubated with shaking at 37°C for 24 h. The antibacterial activities of the new polymeric ligand and its polymer–metal complexes were determined by the testing of a 25-mg/mL concentration of the compounds against these two types of bacteria with the aforementioned methods. Only one concentration of these polymers was tested, as these polymers were not soluble in TSB. The polymeric ligand and its polymer–metal complexes were in powder form and were not soluble in water; they formed suspensions when they were mixed with TSB. Each suspension containing antimicrobial agent was mixed with 10^5 cfu of the test organism in a 10-mL culture tube (Falcon). The tubes were incubated at 37°C for 24 h. The test was repeated at least three
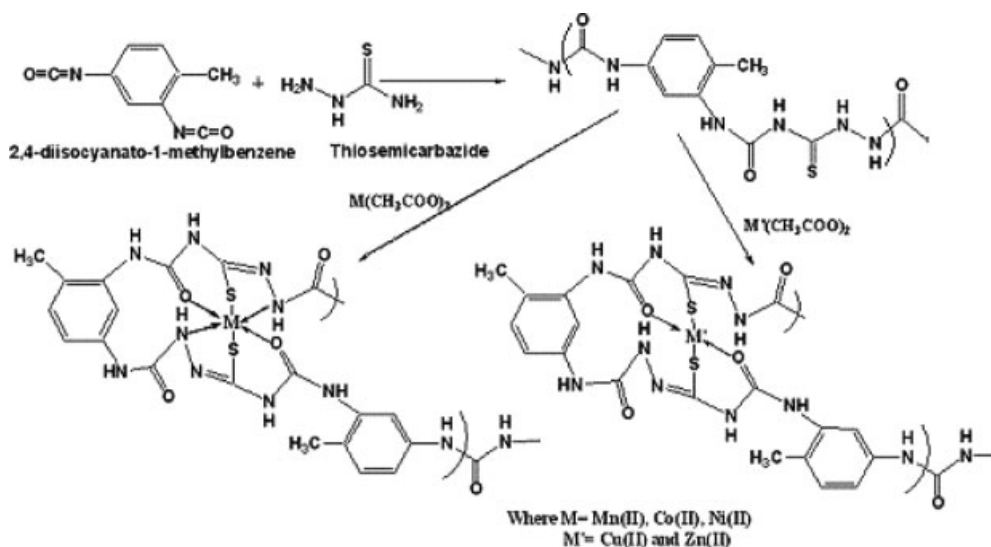
Scheme 1 Synthetic route of the polymeric ligand and its metal complexes.

times for each antimicrobial agent. Samples were taken from each tube and diluted with TSB. The diluted solutions were spread on agar plates, and the plates were incubated at 37°C for 24 h. The number of bacterial cells was calculated by multiplication of the number of colonies by the dilution factors.

RESULTS AND DISCUSSION

Chemistry of the polymer and its polymer–metal complex

The polymeric ligand was prepared according to the synthetic route shown in Scheme 1. The nitrogen of thiosemicarbazides has an excess of electrons, so it will react with species that are electron-deficient.

The carbon atom in the isocyanate group is sandwiched between two electronegative elements, oxygen and nitrogen. This carbon is also electron-deficient, so nitrogen donates a pair of electrons to the carbon, and overall, a urea dimer is obtained. These dimers (urea) have amino or amide groups on one the hand and an isocyanate group on the other, so it can react with either a amine or amide or a diisocyanate to form a trimer or a polymer. The polymer–metal complexes were coordinated with polyurea and gave colored polymer–metal complexes, which were insoluble in common organic solvents but soluble in DMSO and DMF. The elemental analysis results of the synthesized compounds were also in a very good agreement with the calculated values and are given in Table I.

TABLE I
Elemental Analysis of the Polymeric Ligand and Its Polymer–Metal Complexes

Compound abbreviation	Empirical formula	Elemental analysis				
		Carbon	Hydrogen	Nitrogen	Sulfur	Metal
PU	$(C_{10}H_{11}N_5O_2S)_x$	45.27	4.18	26.40	12.09	—
		(45.28)	(4.19)	(26.42)	(12.10)	—
PU–Mn(II)	$(C_{20}H_{20}N_{10}O_4S_2{-}Mn)_x$	41.17	3.45	24.00	10.99	9.42
		(41.20)	(3.50)	(24.09)	(10.97)	(9.43)
PU–Co(II)	$(C_{20}H_{20}N_{10}O_4S_2{-}Co)_x$	40.89	3.43	23.84	10.92	10.03
		(40.90)	(3.44)	(23.85)	(10.90)	(10.01)
PU–Ni(II)	$(C_{20}H_{20}N_{10}O_4S_2{-}Ni)_x$	40.90	3.43	23.85	10.92	9.90
		(40.92)	(3.45)	(23.89)	(10.91)	(9.92)
PU–Cu(II)	$(C_{20}H_{20}N_{10}O_4S_2{-}Cu)_x$	40.57	3.40	23.66	10.83	10.73
		(40.58)	(3.42)	(23.67)	(10.84)	(10.75)
PU–Zn(II)	$(C_{20}H_{20}N_{10}O_4S_2{-}Zn)_x$	40.44	3.39	23.58	10.80	11.01
		(40.44)	(3.41)	(23.65)	(10.82)	(10.09)

x = number of repeating units of polymeric chain. The calculated values of metal-to-ligand stoichiometry are listed outside parentheses, and the observed values are listed inside parentheses.

TABLE II
FTIR Spectral Bands with Their Assignments

Assignment	PU	PU–Mn(II)	PU–Co(II)	PU–Ni(II)	PU–Cu(II)	PU–Zn(II)
NH	3240, 3175, 3060(s)	3170, 3060(s)	3170, 3065(s)	3180, 3065(s)	3170, 3065(s)	3170, 3060(s)
CH$_2$	2970–2855(s)	2942–2840(s)	2960–2850(s)	2950–2845(s)	2940–2850(s)	2945–2850(s)
C=O	1680, 1670	1671, 1655(s)	1671, 1655(s)	1670, 1660(w)	1672, 1650(s)	1672, 1657(s)
C=S	1560(s)	—	—	—	—	—
C=N	—	1575(s)	1572(s)	1575(w)	1572(s)	1575(s)
δ(CH)	1480(s)	1470(m)	1465(s)	1465(w)	1475(s)	1470(s)
δ(C—N)	1435(s)	1435(m)	1440(s)	1425(s)	1425(m)	1430(s)
νM-O	—	620(s)	621(s)	590(s)	600(s)	620(b)
νM-N	—	440(w)	435(s)	430(s)	420(m)	438(s)
νM-S	—	380(s)	370(s)	375(s)	380(s)	375(b)

s = strong; vs — very strong; m = medium; b = broad; w = weak.

Characterization

FTIR spectra

FTIR spectroscopy was used for the analysis of the polymeric ligand and its polymer–metal complexes and is illustrated in Table II; it indicated the formation of the expected compounds. The IR spectrum of the polymeric ligand showed bands at 3060, 3175, and 3240 cm^{-1} due to N—H groups, but the band at 3240 cm^{-1} was absent in the polymer–metal complexes, which indicated a loss of protons via thioenolisation.[20] Two strong and sharp bands appeared in all of the synthesized polymers at 2970–2940 and 2850–2840 cm^{-1} because of the asymmetrical and symmetrical stretching vibrations of the —CH$_3$ groups. The peaks at 1680 and 1670 cm^{-1} were assigned to νC=O groups. In the polymer–metal complexes, the peaks at 1680 showed a negative shift of 20–30 cm^{-1}, which indicated bonding through this oxygen of polyurea. The band at 1560 cm^{-1} was observed due to the νC=S group and was absent in the polymer–metal complexes, but the presence of a new band at 1575 cm^{-1} due to νC=N indicated the removal of a hydrazinic proton through thioenolisation and the subsequent participation of thioenolic sulfur in bonding The bands at 3050, 1230, 1480, and 840 cm^{-1} remained unchanged in the polymer–metal complexes. In all of the polymer–metal complexes, the coordination of metal ion to the polymeric ligand was further supported by the appearance of ν M-O, ν M-N, and ν M-S stretching vibrations at the 620–590, 440–420, and 380–375 cm^{-1} regions, respectively.[21,22]

^{13}C-NMR and ^{1}H-NMR spectra

The synthesized polymers were followed by ^{13}C-NMR and ^{1}H-NMR spectroscopy. Figure 1(a,b) shows ^{1}H-NMR spectra of the polymeric ligand and its Zn(II) polychelates. The ^{1}H-NMR spectra of PU showed signals at 2.15 and 6.3–7.4 ppm due to the methyl group and aromatic protons, respectively.[23]

The signals at 3.52, 5.42, 5.63, and 6.12 ppm were assigned to the NH group; the signal at 3.52 disappeared in the case of Zn(II) complexes because of the deprotonation of NH of a hydrazinic proton through thioenolisation. The aromatic signals became broad and less intense because of the drifting of a ring electron toward the metal ions. The ^{13}C-NMR spectra of the polymeric ligand and its Zn(II) polychelate are given in Figure 2(a,b). The ^{13}C-NMR chemical shifts for the methyl CH$_3$ appeared at 16.23 ppm, respectively.[24] The thionyl
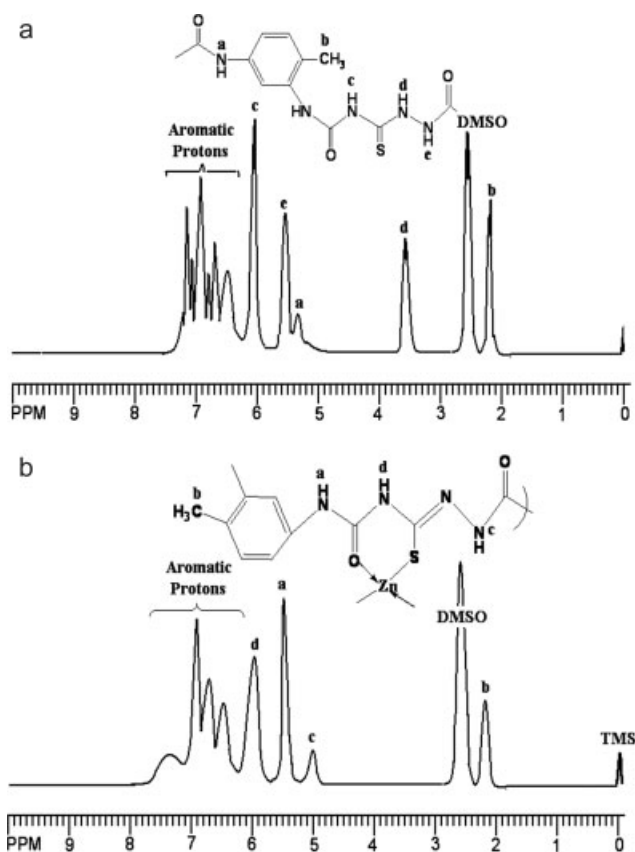

Figure 1 ^{1}H-NMR spectra of (a) the polymeric ligand (PU) and (b) Zn(II) polychelate [PU–Zn(II)].
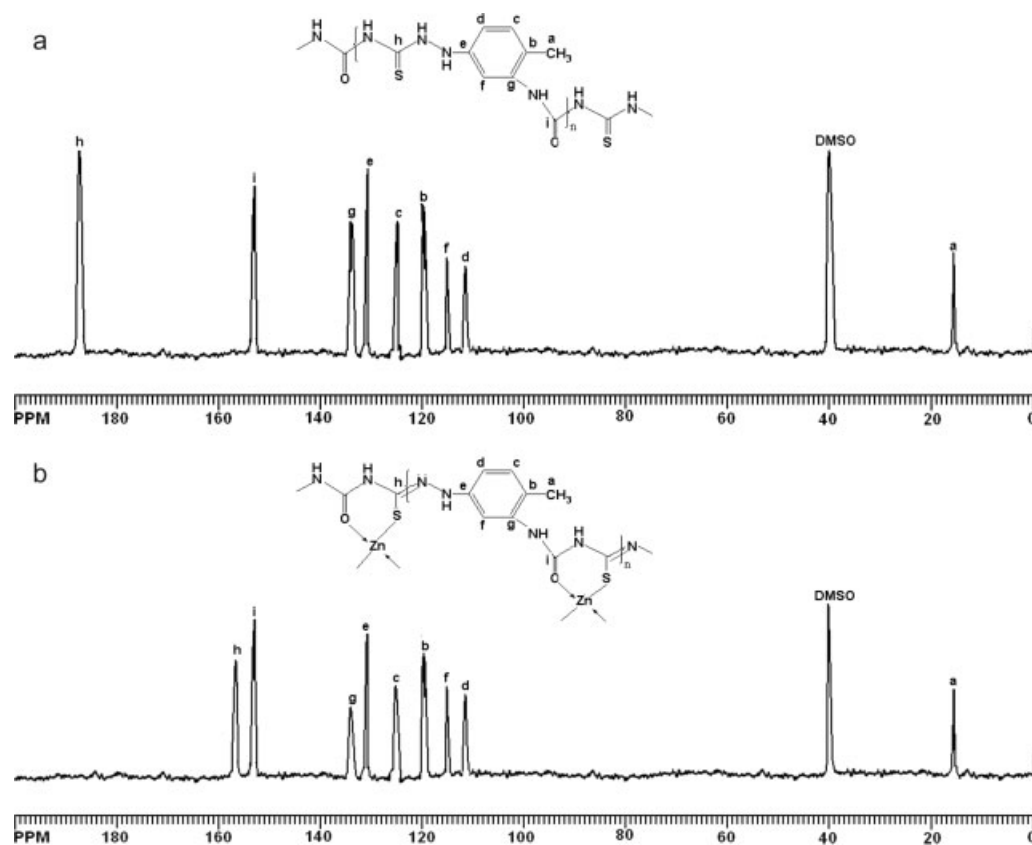
Figure 2 ^{13}C-NMR spectra of (a) the polymeric ligand (PU) and (b) Zn(II) polychelate [PU–Zn(II)].

and carbonyl peaks of the polymeric ligand showed resonance signals at 188.1 and 153.2 ppm. In the polymer–metal complexes, the thionyl peaks shifted from 188 to 156.2, which indicated the formation of the S—C=N group[25] and bonding with metal ions. Six signals at 111.2, 115.3, 125.2, 131.4, and 134.6 ppm were due to the presence of aromatic carbons. The ^{1}H-NMR and ^{13}C-NMR spectra of the PU and PU–Zn(II) showed that the metal ions were attached through the carbonyl group, thionyl group, and hydrazinic nitrogen of the polymeric ligand.

Electronic spectra and magnetic moment

The electronic spectra of all of the synthesized polymers were recorded in DMSO solution. The various crystal field parameters, Dq, B, β, and β^0, were calculated with a known equation, and the values are given in Table III. The magnetic moment of PU–Mn(II) was 5.80 μ_B, which suggested the presence of five unpaired electrons. The electronic spectrum of this complex exhibited three absorption bands at 18,520, 22,760, and 24,540 cm^{-1}, which were

TABLE III
Magnetic Susceptibility and Electronic Spectra and Their Parameters***

Abbreviation	Magnetic moment (μ_B)	Electronic spectral data		10Dq	B	β	β (%)
		Electronic transition (cm^{-1})	Assignment				
PU–Mn(II)	5.80	24,540	$^{4}A_{1g}(G) \leftarrow {}^{6}A_{1g}(F)$	7685	645	.839	17%
		22,760	$^{4}T_{2g}(G) \leftarrow {}^{6}A_{1g}(F)$				
		18,520	$^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g}(F)$				
PU–Co(II)	4.74	19,570	$^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$	9615	810	.842	16%
		16,340	$^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$				
		8,580	$^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$				
PU–Ni(II)	3.12	24,360	$^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$	8840	742	.839	16%
		13,980	$^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$				
		9,020	$^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$				
PU–Cu(II)	1.81	27,580	Charge transfer				
		15,360	$^{2}A_{1g} \leftarrow {}^{2}B_{1g}$				

assigned to the $^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_1)$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)(\nu_2)$, and $^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_3)$ transitions, respectively, which suggested an octahedral geometry.[26] The polymer complex of Co(II) had a magnetic moment of 4.74 μ_B because of four unpaired electrons and showed three bands at 8580, 16,340, and 19,570 cm^{-1} due to the $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_2)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ transitions, respectively.[27] The PU–Ni(II) complex showed three bands at 9020, 13,980, and 24,360 cm^{-1}, which were assigned to the spin-allowed transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)(\nu_1)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)(\nu_2)$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)(\nu_3)$, respectively, which supported the fact that the nickel(II) complex had an octahedral structure.[28] The electronic spectrum of the PU–Cu(II) complex exhibited bands at 15,360 and 27,580 cm^{-1}, which was assigned to $^2A_{1g} \leftarrow {}^2B_{1g}$ and a charge-transfer band that indicated a square planar geometry.[29] Thus, the electronic spectral study further supported the structure proposed for the polymeric complexes.

Thermal analysis

Figure 3 shows the TGA thermograms of all of the synthesized polymers, and the data are tabulated in Table IV. The initial 2–3% weight loss for the polymeric ligand was at 130–160°C; this decomposition was mainly due to the loss of absorption of water and other solvents. Above 200°C, a rapid weight loss was observed in the polymeric ligand, and 40% of weight was lost up to 350–400°C. The ligand was decomposed completely into a volatile substance. After the loss of absorbed water or solvent, the polymer–metal complexes showed a two-step degradation, where the first step was faster than the second. This may have been due to the fact that the noncoordinated part of the complexes decomposed first, whereas the actual coordinated part of all of the polymer–metal complexes decomposed later.[30] The results of TGA reveal that the polymer complex of
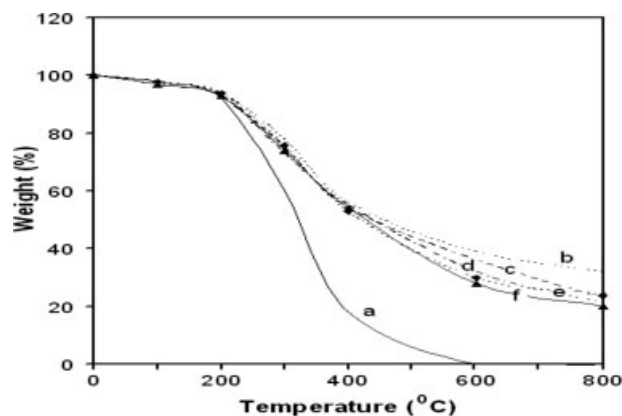
Figure 3 TGA thermograms of the polymeric ligand and its polymer–metal complexes.

TABLE IV
Thermal Behaviors of the Polymeric Ligand and Its Polymer–Metal Complexes

Material	Temperature (°C) corresponding to a weight loss of					
	100	200	300	400	600	800
PU	98	92	60	18	0	0
PU–Mn(II)	97	93	74	54	28	20
PU–Co(II)	98	93	73	53	30	21
PU–Ni(II)	98	94	76	53	30	24
PU–Cu(II)	98.2	94	78	56	39	32
PU–Zn(II)	98.5	93	75	54	36	23

Cu(II) was comparatively more thermally stable than the other complexes. The thermal stability of PU–Cu(II) was higher than those of the others because of the higher stability constant of Cu(II) ions. The order of stability on the basis of thermal residual weight at 800°C appeared to be PU–Cu(II) > PU–Zn(II) > PU–Ni(II) > PU–Co(II) > PU–Mn(II). This order matched Irving–Williams order of stability for complexes of divalent metal ions.[31]

Antimicrobial assessment

The screening of all of the polymers for antibacterial activity were tested against *S. aureus* and *B. subtilis* (Gram positive) and *S. typhi* and *E. coli* (Gram negative) bacteria, respectively. The shaking flask method was used here to determine the antimicrobial activities of the polymeric ligand and its polymer–metal complexes. According to this method, each antimicrobial agent (25 mg/mL) was mixed with a certain number of bacteria (1×10^5 cfu/mL) in a flask (culture tube), and the flask was incubated at 37°C for 24 h. Then, a 100-μL sample was taken from each tube and spread onto agar plates. The agar plates were incubated at 37°C for 24 h, and the number of viable bacteria on the plates was counted at the end of the incubation period. The number of viable bacteria and the percentage reduction of the number of bacteria are shown in Figure 4. Table V shows the minimum inhibitory concentrations (MICs) evaluated by the conventional spread plate method. The two figures for each strain indicate the range of MICs; the growth of the bacterium cloud was seen as visual colonies below the lower concentration limit of MICs, whereas as no colonies were observed above the higher limit. Consequently, the exact MICs were supposed to lie between these two values. A general trend is shown in Table V that the Cu(II)-chelated polymer complexes were more active than the other metal-chelated polymers complexes. Also, all of the polymer–metal complexes were more active then the polymeric ligand. The lethal action of isocyanate biocides is an outcome of their ability to
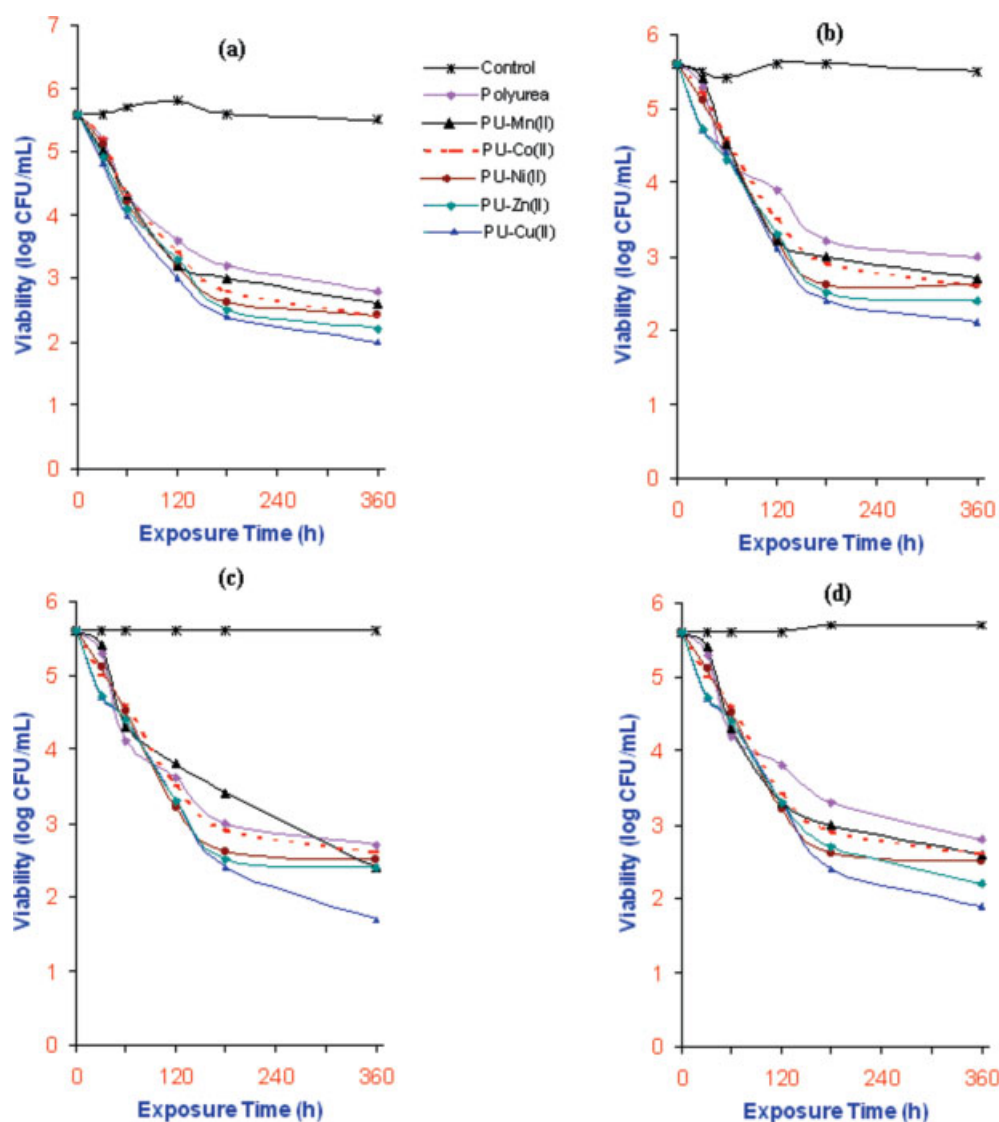
Figure 4 Antimicrobial activity against (a) *E.coli,* (b) *B. subtilis,* (c) *S. aureus,* and (d) *S. typhi.* [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

inhibit microbes. Isocyanate is an extremely reactive chemical, which interacts with protein, DNA, and RNA as a results of a combination with the primary amide and with the amino groups, although the phenol group binds little polyurea. Isocyanate also reacts extensively with nucleic acid (e.g., the DNA of the bacteriophage T2). Low concentrations of isocyanate are sporostatic and inhibit germination. It is difficult to pinpoint accurately the mechanism(s) responsible for isocyanate-induced microbial inactivation. Clearly, its interactive, and crosslinking properties must play a considerable role in this activity. Polymer–metal complexes are not dangerous to eukaryotic cells at low concentrations. The new polymer-containing metal complexes were not expected to be toxic to humans; however, a toxicity study for these polymers should be carried out before their use *in vivo*. Although allergies may be

developed for the diisocyanate, in general, this should not be a concern for the diisocyanate-based polymers, which cause fewer allergic responses compared to diisocyanate monomers. However, this

TABLE V
Antibacterial Activity of the Polymeric Ligand and Its Metal Complexes

Abbreviation	MIC (µg/mL)[a]			
	E. coli	*B. subtilis*	*S. aureus*	*S. typhi*
PU	275–350	275–350	>450	>500
PU–Mn(II)	220–350	220–350	260–350	230–422
PU–Co(II)	220–350	220–350	>500	230–422
PU–Ni(II)	220–325	200–325	275–325	230–422
PU–Cu(II)	200–300	200–275	140–226	140–220
PU–Zn(II)	215–325	200–275	150–226	230–350

[a] As determined by the spread plate method.

issue should also be clarified before any internal use of these polymers.

CONCLUSIONS

A new polymeric ligand (PU) was synthesized by addition polymerization. The polymeric ligand was also coordinated with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) to give polymer–metal complexes. All of the synthesized polymers showed excellent antimicrobial activities against *S. aureus*, *B. subtilis*, *S. typhi*, and *E. coli*. These results indicate that the polymer–metal complexes showed more antibacterial activity than the polymeric ligand. In the polymers metal complexes, the Cu(II)-chelated polymers showed more activity and more thermal stability then other polymers because of their higher stability constant. Because these agents are relatively stable at high temperatures, they can be used for medical and biomaterial applications requiring thermal sterilization.

References

1. Warshawasky, A. In Synthesis and Separation Using Functional Polymers; Wiley: New York, 1998.
2. Alelah, A.; Moet, A. Functionalized Polymers and Applications; Chapman & Hall: London, 1990.
3. Mathew, B.; Pillai, V. Eur Polym J 1994, 30, 61.
4. Diab, M.; El Sonbati, A.; Ghoniem, M. Acta Polym 1989, 40, 545.
5. Dhumwad, S. D.; Gudasi, K. B.; Goudor, T. R. Indian J Chem A 1994, 33, 320.
6. Hall, I. H.; Chen, S. Y.; Barnes, B. J.; West, D. X. Met Based Drugs 1999, 6, 143.
7. Bermejo, E.; Carballo, R.; Castineiras, A.; Dominguez, R.; Liberta, A. E.; Maichle-Mossmer, C.; West, D. X.; Naturfosch, Z. Met Based Drugs 1999, 54, 777.
8. Perez, J. M.; Matesanz, A. I.; Marin-Ambite, A.; Navarro, P.; Alonso, C.; Souza, P. J Inorg Biochem 1999, 75, 255.
9. Reddy, K. H.; Reddy, P. S.; Babu, P. R. J Inorg Biochem 1999, 77, 169.
10. Kelly, P. F.; Slawin, A. M. Z.; Soriano-Rama, A. J Chem Soc Dalton Trans 1996, 53, 1.
11. West, D. X.; Padhye, S. B.; Sonawane, P. B. Struct Bonding 1991, 76, 1.
12. Liberta, A. E.; West, D. X. Biol Met 1992, 5, 121.
13. West, D. X.; Liberta, A. E.; Padhye, S. B.; Chikate, R. C.; Sonawane, P. B.; Kumbhar, A. S.; Yerande, R. G. Coord Chem Rev 1993, 123, 49.
14. Jaykumar, R.; Rajkumar, A.; Nagendarn, R.; Nanjundan, S. J Appl Polym Sci 2002, 85, 1194.
15. Nishat, N.; Ahamd, S.; Ahamad, T. J Appl Polym Sci 2006, 101, 1347.
16. Ahamad, T.; Kumar, V.; Nishat, N. Polym Int 2006, 55, 1398.
17. Nishat, N.; Ahmad, S.; Raisuddin, A. T. J Appl Polym Sci 2006, 100, 928.
18. Moon, W.; Kim, J. C.; Chung, K.; Park, E.; Kim, M.; Yoom, J. J Appl Polym Sci 2003, 90, 1797.
19. Merianos, J. J. Disinfection, Sterilization and Preservation, 4th ed.; Lea & Febiger: Philadelphia, 1991.
20. Braibanti, A.; Dallavalle, F.; Pellinghel, M. A.; Loprati, E. Inorg Chem 1968, 7, 1430.
21. Mostafa, M. M.; Hamid, A. F.; Elasmy, A. A. Transition Met Chem 1981, 6, 303.
22. Nishat, N.; Ahamad, T.; Haq, M. M.; Kumar, V. J Coord Chem 2007, 60, 85.
23. Silverstein, R. M.; Basler, G. C.; Morrill, C. T. Spectrometric Identification of Organic Compounds, 5th ed.; Wiley-Interscience: New York, 1991; p 220.
24. Ju-Yeon, L.; Eun-Ju, P. Bull Korean Chem Soc 2001, 22, 753.
25. Ibrahim, Y.; Alaaddin, C. Transition Met Chem 2003, 28, 399.
26. Cotton, F.; Wilkinson, G.; Murillo, C.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; Wiley-Interscience: New York, 1999.
27. König, E. Structure and Bonding; Springer-Verlag: Berlin, 1971; p 175.
28. Patel, Y.; Shah, J. Ind J Chem A 1985, 24, 8000.
29. Bhave, N. S.; Aswar, A. S. Asian J Chem 1992, 4, 65.
30. Bhave, N. S.; Aswar, A. S. Colloid Polym Sci 1991, 269, 54702.
31. Irving, H.; Williams, R. J. J Chem Soc 1993, 3192.