Synthesis and Characterization of Poly(1,3-thiazol-2-ylcarbomoyl) Methyl Methacrylate: Its Metal Complexes and Antimicrobial Activity Studies

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ABSTRACT: Poly(1,3-thiazol-2-yl-carbomoyl) methyl methacrylate [poly(TCMMA)] is prepared in dimethyl sulfoxide using 2,2'-azobisisobutyronitrile as an initiator at 60°C. Poly(TCMMA) is characterized by IR and ¹H-NMR spectroscopic techniques. Cadmium(II), copper(II), and nickel(II) chelates of poly(TCMMA) were synthesized. An elemental analysis of the polychelates suggests a metal/ ligand ratio of 1:2. The polychelates are further characterized by IR and magnetic susceptibility measurements. The thermal properties of the polymer and metal chelates are also discussed. The molecular weights of the poly(TCMMA) are determined by the gel permeation chromatography tech-

INTRODUCTION

Recently, anchoring chelating ligands to polymer supports for the preparation of immobilized transitionmetal complexes has been an active field of research.¹ A number of polymer-bound chelating ligands, including polydentate amines, crown ethers, and porphyrins, have been reported.^{2–5} Polymeric Schiff base chelates based on 2-hydroxy-5-vinylbenzaldehyde have been investigated.⁶ The synthesis of polymers containing reactive functional groups has been an active field of research in polymer science, because it provides an approach to a subsequent modification of the polymer for the required application. The synthesis and properties of polymers having photocrosslinkable α , β -unsaturated carbonyl groups,^{7,8} chelating ligands,^{9–11} UV stabilizers,^{12–15} and so forth, have been reported. A wide variety of investigations such as preconcentration and separation of metal ions, semiconductivity, redox reactions, biomedical applications, and so forth, have been carried out using polymers with metal-chelating groups. Polymer complexes structures and thermal stabilities have been of particular interest.^{16,17} The incorporation of metal ions in

nique. The antimicrobial activities of the polymer and metal chelates are tested against Staphylococcus aureus COWAN I (bacteria), Escherichia coli ATCC 25922 (bacteria), Listeria monocytogenes SCOTTA (bacteria), Bacillus subtilis LMG (bacteria), Enterobacter aeroginosa CCM 2531 (bacteria), Klebsiela pneumania FMCS (bacteria), Candida albicans CCM 314 (Mayo yeast), and Saccharamyces cerevisiae UGA 102 (Mayo yeast). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3244-3251, 2003

Key words: poly(1,3-thiazol-2-yl-carbomoyl) methyl methacrylate; metal-polymer complexes; radical polymerization; thermal properties; antimicrobial activities.

polymers not only affects their physical characteristics, like strength, but also their chemical activity.¹⁸ The synthesis and studies of a series of poly Schiff base ligands and their metal complexes have been presented in earlier communications.^{19,20}

The synthesis and biological activities of complexes of thiosemicarbazides have continued to attract attention since Domagk first reported the anticancer activity of thiosemicarbazide.^{21–23} The potential biological activity of compounds containing sulfur and nitrogen may be responsible for this increased interest. West et al., in their attempts to establish structure-biological activity relationships, have studied numerous transition-metal etherocyclic thiosemicarbazones.²⁴ Thiazole and its derivatives have biological significance (e.g., they are found in the vitamin B_1 molecule and in coenzyme cocarboxylase).²⁵ The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activities and as intermediates in the synthesis of antibiotics and dyes.²⁶ Various thiazole derivatives have shown herbicidal, antiinflamatory, antimicrobial, or antiparasitic activity.²⁷ However, the syntheses and physiochemical properties of (1,3-thiazol-2-yl-carbomoyl) methyl methacrylate (TCMMA) and their derivatives have not been reported thus far. These compounds seem to be suitable candidates for further chemical modifications and may be pharma-

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cologically active and useful ligands in coordination chemistry and polymer chemistry.

The present article reports the synthesis and characterization of poly(TCMMA) and its metal chelates with Cd(II), Cu(II), and Ni(II). The spectral, magnetic, and thermal properties; the type of chelation of the ligand; and the geometry around the metal center are discussed. In addition, the antimicrobial activities are tested against several microorganisms.

EXPERIMENTAL

Materials

2-Aminothiazole, chloroacetylchloride, and metal salts (E. Merck) were used as received. Sodium methacrylate was purchased from Aldrich. We synthesized TCMMA according to the literature.¹⁵ All solvents were analytical grade and were purified by standard procedures, where appropriate.

Physical measurements

Elemental analyses (C, H, N, S) were performed on a LECO-932 CHNSO elemental analysis apparatus. The IR spectra were recorded using KBr disks (4000-400 cm⁻¹) on a Mattson 1000 S FTIR spectrophotometer. The magnetic susceptibilities were investigated by the Gouy method using Hg[Co(SCN)₄] as a calibrant on a Sherwood scientific magnetic susceptibility balance (model MK 1) at room temperature (20° C); the dia-

magnetic corrections were calculated from Pascal's constants. The ¹H-NMR spectra were recorded on a JEOL FX-90Q spectrometer with CDCl₃ as the solvent and tetramethyl silane as the internal standard. Thermogravimetric (TG) curves were recorded on a Shimadzu TG-50 thermobalance using \sim 5-mg samples. The curves were obtained at a heating rate of 10°C/ min under a dynamic nitrogen flow (5 L h^{-1}); in all cases a 10–500°C temperature range was studied. The metal contents of the complexes were determined by an Ati Unicam (model 929) atomic absorption spectrometer in solutions prepared by decomposing the compounds in concentrated HCI and subsequent dilution with 0.01M HCI. The electronic spectra in the 200–900 nm range were obtained on a CECIL CE 5502 UV-visible spectrophotometer. The weight-average (M_{iv}) and number-average (M_{iv}) molecular weights of the polymer were determined with a Waters 410 gel permation chromatograph equipped with a refractive index detector and calibrated with polystyrene standards.

Monomer synthesis

2-Aminothiazoacetylchloride (compound 1) was prepared by reacting 2-aminothiazole with chloroacetylchloride using small amounts of K_2CO_3 .²⁸ We synthesized TCMMA (compound 2) as follows: a mixture of 2-aminothiazoacetylchloride (1 mol), sodium methacrylate (1.1 mol) in 100 mL of acetonitrile and triethyl-



Scheme 1 The reaction of TCMMA and the free-radical polymerization of the methacrylated product; TEBAC, triethylben-zylammonium chloride.

Analytical and Physical Data of Compounds									
		Yield	Elemental Analyses (%) ^a						
Compound	Color	(%)	С	Н	Ν	S	M ^b	(BM)	
Poly(TCMMA)	White	90	47.79 (47.81)	4.42 (4.38)	12.39 (12.23)	14.16 (14.05)			
Poly(TCMMA)-Cu(II)	Pale green	83	42.06 (41.98)	3.89 (3.68)	10.91 (10.83)	12.46 (12.38)	12.37 (12.25)	1.89	
Poly(TCMMA)-Ni(II)	Pale red	70	42.46 (42.22)	3.93 (3.87)	11.00 (11.04)	12.58 (12.53)	11.54 (11.43)	2.81	
Poly(TCMMA)-Cd(II)	Yellow	70	38.41 (38.33)	3.56 (3.49)	9.96 (9.87)	11.38 (11.29)	19.99 (19.87)	0.00	

^a The calculated (found) values.

^b Values calculated by AAS.

benzylammonium chloride (0.1 mol), and Nal (0.1 mol) as a catalyst were placed in a two-necked roundbottom flask equipped with a magnetic stirrer and thermometer. The mixture was heated to 85°C in a reflux condenser in the presence of 100 ppm hydroquinone as the inhibitor. The reaction was continued for a further period of 24 h. The reaction mixture was cooled to room temperature; transferred to a separating funnel; and washed sequentially with distilled water, 5% NaOH solution, and diethylether. The organic layers were collected and dried over anhydrous MgSO₄ overnight. Diethylether was evaporated and the resulting monomer purified by recrystallization from aqueous ethanol (1:3, 90% yield). The reaction of TCMMA and the free-radical polymerization of the methacrylated product are described in Scheme 1.

Polymerization

TCMMA was polymerized as a 4M solution of dimethyl sulfoxide (DMSO) using 2,2'-azobisisobutyronitrile (AIBN; 1 wt % monomer) as initiator. The monomer, AIBN, and DMSO were placed in a polymerization tube, flushed with nitrogen, sealed, and kept in a thermostat at 60°C. After 18 h, the polymer was precipitated in methanol, redissolved in DMSO, reprecipitated by methanol, filtered, and dried in a vacuum.

Synthesis of polychelates

Poly(TCMMA)-Cd(II), -Cu(II), and -Ni (II) acetate complexes were prepared by dissolving equimolar amounts of poly(TCMMA) and metal salts in DMSO

(25 mL) and refluxing for 18 h. The resulting mixture was precipitated by pouring it into a large excess of distilled water containing ammonium hydroxide (NH₄OH) to remove the metal acetate incorporated in the polymer complexes. The isolated polymer complexes were then filtered, washed with hot water, and dried in a vacuum oven at 40°C for several days. The yield, color elemental analysis results, and characteristic IR bands are given in Tables I and II, respectively.

Preparation of microbial cultures

The microorganisms used in the study were provided by the culture collection of the Microbiology Laboratory of Biological Sciences (University of Firat). In this work, Staphylococcus aureus COWAN I (bacteria), Escherichia coli ATCC 25922 (bacteria), Listeria monocytogenes SCOTTA (bacteria), Bacillus subtilis LMG (bacteria), Enterobacter aeroginosa CCM 2531 (bacteria), Klebsiela pneumania FMCS (bacteria), Candida albicans CCM 314 (Mayo yeast), and Saccharamyces cerevisiae UGA 102 (Mayo yeast) were used to investigate the bacteriological and antifungal activities of a polyligand and its transition-metal complexes.

Bacteria strains were nourished in nutrient broth (Difco) and yeasts in malt extract broth (Difco) and incubated for 24 and 48 h, respectively. According to the disk diffusion method, bacterias were inoculated on Mueller Hinton agar (Oxoid) and yeasts on Saburoud dextrose agar. The polyligands (50 ppm) and their complexes (100 ppm) were dissolved in absolute ethanol and absorbed on sterile paper antibiotic disks that were previously inoculated. The prepared samples were left for 1 h at 4°C. The bacteria samples were

TABLE II IR Spectral Data of Polyligand and Its Complexes

	-			-		
Compound	ν (C==O,ester)	ν(N—H)	ν(CH3)—ν(CH ₂)	ν(C==N)	ν(C—S—C)	ν(C—S)
Poly(TCMMA)	1740	3186	2975–2928	1590	660 s	987 vs
Poly(TCMMA)-Cu(II)	1725	np	2978-2928	1580	655 s	985 vs
Poly(TCMMA)-Ni(II)	1725	np	2976-2925	1580	655 s	985 vs
Poly(TCMMA)-Cd(II)	1725	np	2975-2925	1580	655 s	985 vs

s, strong; vs, very strong; np, not present

	• • • • • • • • • • • • • • • • • • •	
Solvent	λ_{\max} (nm)	$\mu_{\rm eff}$ (B.M.)
DMSO DMSO DMSO	250, 315 247, 270 (sh), 350 (sh), 500 245, 295, 500 (sh), 650 (sh)	1.89 2.81
DMSO	248, 332 (sh), 438, 630	Dia
	Solvent DMSO DMSO DMSO DMSO DMSO	Solvent λ_{max} (nm) DMSO 250, 315 DMSO 247, 270 (sh), 350 (sh), 500 DMSO 245, 295, 500 (sh), 650 (sh) DMSO 248, 332 (sh), 438, 630

TABLE III Characteristic UV-Vis Bands of Polyligand and Complexes

sh, shoulder; Dia, diamagnetic complex; μ_{eff} , magnetic moment; B.M., Bohr magneton.

incubated at 32°C for 18-24 h, and the yeast samples were incubated at 25°C for 72 h. Ethyl alcohol absorbed disks were used for the control only. The resulting inhibition zones on the plates were measured (mm). The data reported in Tables III and IV are the average data of three experiments.

RESULTS AND DISCUSSION

Characterization of monomer and its polymer

The FTIR spectra of the monomer and its polymer are shown in Figure 1. The IR spectrum of the homopolymer shows absorption bands at 3186, 1740, and 1710 cm^{-1} that are due to --NH and C==O (ester and amide) groups, respectively. In the spectrum of the polyligand, the other most characteristic absorptions are at 1590 cm⁻¹ [ν (C=N) in the thiazole ring] and 655 cm⁻¹ [ν (C-S-C) in the thiazole ring]. The bands at 3186 and 1710 cm⁻¹ disappear when the homopolymer is dissolved in DMSO and four absorption bands are observed at 1600, 1540, 1475, and 1420 cm^{-1} that are attributed to $v_{asym+sym}$ (C==C) and C==N vibrations.

In order to identify the structure of compound 2, the ¹H-NMR spectra were recorded in CDCI₃. The ¹H-NMR spectra of compound 2 have the characteristic resonances corresponding to the general formula. These data are also in agreement with the molecular structure given in Scheme 2.

The ¹H-NMR spectrum of compound 2 (Fig. 2) exhibited the corresponding proton signals at 1.9 ppm that are due to CH₃ and at 5.0 ppm that are due to OCH₂. The signals at 7.0–7.7 ppm are attributed to the =CH— in the thiazole ring. The signals at 6.2 and 5.7 ppm are attributed to the olefinic ($C=CH_2$) protons. The signals at 9.1 ppm are attributed to the NH proton. Poly(TCMMA) can be represented by the two tautomeric forms in Scheme 2.

Molecular weights

The weight-average (M_w) and number-average (M_n) molecular weights and the polydispersity indexes (M_w/M_n) of poly(TCMMA) are measured by gel permeation chromatography (GPC) technique. The GPC system calibrated with polystyrene in tetrahydrofuran (THF) showed that the M_w of the poly(TCMMA) was 72,000 and the M_n was 41,500. The polydispersity index (PDI) for poly(TCMMA) is 1.73. The PDI indicates that the TCMMA radicals are likely to undergo termination by disproportionation. The theoretical values of the M_w/M_n values for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively.²⁹

Characterization of polymer complexes

All the polymer complexes are intensely colored, stable in air, and insoluble in common organic solvents. The polymer was soluble in DMSO, DMF, acetone, diethylether, and THF. It was insoluble in nonpolar and hydroxy solvents like benzene, toluene, methanol, ethanol, water and CHCl₃, CH₂Cl₂, and so forth. The IR spectra of the polymer complexes show new bands and shifts of the characteristic bands. In the Cu(II) complex, the IR spectrum shows a lowering of the OH

Antimicrobial Effects of Monomer, Polyligand, and Its Complexes									
	E.c.			E.a.			C.a.	S.c.	
	S.a.	ATCC	L.m.	B.s.	CCM	K.p.	CCM	UGA	
Compound	COWAN	25922	SCOTTA	LMG	2531	FMCS	314	102	
ТСММА	_	7	_	_	_	_	_		
Poly(TCMMA)	_	_	_	_	_	6	_		
Poly(TCMMA)-Cu(II)	8	11	15	9	14	10	10	11	
Poly(TCMMA)-Ni(II)	10	9	10	_	10	12	_	_	
Poly(TCMMA)-Cd(II)	—	—	—	—	9		8	_	

TADLE IN

Compound concentration = 50 μ g/disk; (—) the compounds have any activity against the microorganism.

100 80 а 60 40 20 %T 100-80 b 60 40 20 0 1000 500 4000 3000 2000 wavenumbers (cm⁻¹)

Figure 1 FTIR spectra of TCMMA (spectrum a) and poly-(TCMMA) (spectrum b).

stretching frequency by about 10–15 cm⁻¹, indicating that the OH group is involved in the coordination. The bands that appear at 415 and 435 cm⁻¹ are due to the C—C out of plane deformation vibration in the polyligand. The new bands at 470 and 412 cm⁻¹, which are absent in the TCMMA homopolymer, are tentatively assigned to $\nu_{(M-O)}$, $\nu_{(M-N)}$, respectively.^{30,31} The IR absorptions of aliphatic groups of the polyligand appear at 2975–2927 cm⁻¹, and the positions of these groups were not changed in the case of complexes.

Although IR spectral studies have been employed in investigations of complexes, such studies have been strictly empirical and have proved of little use in solving stereochemical problems. In the present study, an attempt has been made to understand the mode of coordination of the metal ion with the polyligand system. The presence or absence and the shift of certain bands in the polychelate spectrum have been



Figure 2 ¹H-NMR spectra of TCMMA.

utilized to arrive at the nature of the coordination. The macromolecular chelate imposes a severe constraint around the donor site because of the presence of bulky groups, which is further aggravated by the fact that these systems usually adopt a coiled structure.

The strong bands observed at 3186 cm⁻¹ for the polyligand can be attributed to the ---NH--- group vibration. The HNC=O group vibrations of the free polyligand occur at 1710 cm⁻¹. In the IR spectra of the complexes, this band was not observed at the same frequencies and the same intensities. In addition, the ester carbonyl group vibrations of the free polyligand occur at 1740 cm⁻¹. In the IR spectra of complexes, this band is shifted to 1725 cm⁻¹. These results indicate that the N=C-OH group was highly affected by complexation. The free polyligand and band at 1165 cm⁻¹ can be attributed to the C—OH group vibration.³² In the metal complexes this band is shifted to higher frequencies, indicating coordination of oxygen to the metal atoms. In the IR spectra of polychelates (Table II) the absence of a broad band at 3200-3000 cm⁻¹ indicates the cleavage of the hydrogen bond, deprotonation of the hydroxy oxygen, and its coordination to metal ions.^{33,34} The marked shifts toward high frequency of the hydroxy C—O vibration in polychelates indicate the involvement of the oxygen of hydroxy C—O in bonding with metal ions.³⁵

From the IR spectral studies, the elemental analysis of the polychelates, and the structure of the polyli-



Scheme 2 The molecular structure of compound 3.



Figure 3 TGA curves of the polymer and polychelates heated in nitrogen at a heating rate of 10° C/min.

gand, it appears that the chelation of metal ions may be occurring between two groups from different polymeric chains as shown in the structure below.



The elemental analysis has shown that the metal/ligand ratio in all the polychelates is 1:2.

When the polyligand is reacted with Cd(II), Cu(II), and Ni(II) acetates, it yielded complexes corresponding to the general formula ML_2 . The analytical data of these complexes are presented in Table I. The metal/ ligand ratio of all the synthesized complexes was found to be 1:2. In general, when investigations of the IR spectra of the complexes are carried out, some IR bands of the polyligand shift to different frequencies, disappear, or lose their intensities after complexation.

These facts confirm the formation of the expected compounds, which is also in agreement with their elementel analyses. From the above observations, the structure of the complexes are proposed as shown in the above structure.

The most important IR spectral bands of the polyligand and its complexes are provided in Table II.

Thermal methods of analysis

The TG curves of poly(TCMMA) and poly(TCMMA)-Cu(II), -Ni(II), and -Cd(II) complexes are shown in Figure 3. The polymer complexes are obviously more stable than the TCMMA homopolymer. The stabilities are in the order poly(TCMMA)-Cu(II) > poly (TCMMA)-Ni(II) > poly(TCMMA)Cd(II) > poly (TCMMA). The greater stabilities of the polymer complexes than the homopolymer may be attributable to the formation of stable four-membered ring structures in all the polymer complexes.

The homopolymer and the complexes degrade in three stages. The thermoanalytical results are shown in Table V. We found from the TGA results that the thermal stabilities of the acetate complexes are higher than the homopolymer. It is possible that the different groups in the polyligand lead to a decrease in the stability of the complexes. Further, it is known that the electronegativity and atomic radius of the central metal atom also affect the thermal stability. All the complexes completely decompose to the corresponding metal oxides (CuO, NiO, or CdO).

Magnetic properties and electronic spectral studies

The magnetic moments of the complexes (Table I) were measured at room temperature. The Ni(II) and

 TABLE V

 Thermoanalytical Results of Poly(TCMMA) and Its Corresponding Metal Complexes

		W	Weight Loss (%) at Temperatures					
Compound	IDT	275°C	350°C	400°C	475°C			
Poly(TCMMA)	208	19.0	30.8	36.0	49.1			
Poly(TCMMA)-Cu(II)	275	_	17.4	34.8	67.5			
Poly(TCMMA)-Ni(II)	270	2.4	45.2	61.4	73.2			
Poly(TCMMA)-Cd(II)	210	7.4	17.6	24.4	55.2			

IDT, initial decomposition temperature.

Antimicrobial Effects of Monomer, Polyligand, and Its Complexes								
	E.c.			E.a.			C.a.	S.c.
	S.a.	ATCC	L.m.	B.s.	CCM	K.p.	CCM	UGA
Compound	COWAN	25922	SCOTTA	LMG	2531	FMCS	314	102
TCMMA	_	10	_	_	11	_	_	
Poly(TCMMA)	_	_	_	_	_	9	_	_
Poly(TCMMA)-Cu(II)	14	15	20	12	19	13	14	15
Poly(TCMMA)-Ni(II)	14	13	13	_	13	15	8	_
Poly(TCMMA)-Cd(II)	8	8	9	8	11	9	10	_

 TABLE VI

 Antimicrobial Effects of Monomer, Polyligand, and Its Complexes

Compound concentration = $100 \ \mu g/disk$; (—) the compounds have any activity against the microorganism.

Cu(II) complexes are paramagnetic and their magnetic susceptibility values are 2.81 and 1.89 Bohr magneton (B.M.), respectively. The Cu(II) complex shows a normal μ_{eff} value of 1.89 B.M., indicating the presence of one unpaired electron. The magnetic moment of the Ni(II) complex was found to be 2.81 B.M. (Table I), which is indicative of its four-coordinated tetrahedral geometry.^{36,37} These values suggest a tetrahedral complex geometry for Ni(II) and a square-planar structure geometry for Cu(II) complexes for polyligands.^{38,39} The Cd(II) complex is diamagnetic. The diamagnetic nature of the complex is consistent with the tetrahedral ligand around the cadmium ion. The tendency for Cd(II) centers to avoid planar four-coordinate stereo-chemistries has been reported.^{40,41}

The electronic spectral bands of all complexes, as well as the spectra of the polyligand, are given in Table III. In the complexes, the low intensity bands in the 700–500 nm range are consistent with $d \rightarrow d$ transitions of the metal ions and intraligand $n \rightarrow \pi^*$ transitions.⁴² The more intense bands at 450–300 nm in the complexes may be due to the coincidence of charge transfer, $d \rightarrow \pi^*$, and $L \rightarrow M$ transitions.⁴³ In the electronic spectra of the Cd(II) complex there are $M \rightarrow L$ charge-transfer bands at 630 nm, which are assigned to the tetrahedral geometry.

Antimicrobial effects

The fungicidal and bacteriological activities of the polyligands and their metal complexes were determined against six bacterias and two yeasts as described in the Experimental section. The filter paper disk method^{44,45} was employed for the bacteria and yeasts. The results of the tests (Tables III, VI) showed some compounds to be very effective on some of the microorganisms.

It has been suggested that the ligands with the N and O donor system might have inhibited enzyme production, because enzymes that require a free hydroxy group for their activity appear to be especially susceptible to deactivation by the ions of the complexes. Chelation reduces the polarity of the central ion mainly because of the partial sharing of its positive charge with the donor groups and possible π -electron delocalization within the whole chelate ring.⁴³ This chelation increases the lipophilic nature of the central atom, which favors its permeation through the lipid layer of the membrane.

CONCLUSION

In this study, the results show that the monomer and polyligand exhibit no inhibition toward some microorganisms under the test conditions. However, complexes of the polyligand exhibit an inhibition zone that was significantly increased with antibiotic disks of polychelates in culture, depending on the disk concentration. The detailed biological activity data are given in Tables III and VI.

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