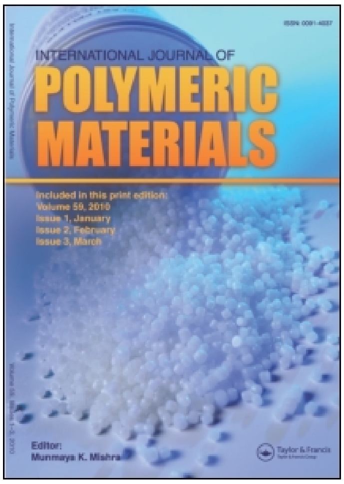

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Radiation Polymerization of 4-*N*-Acryloylamidobenzonitrile: Amidoximation, Complexation and Biological Activity

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A new polymer containing cyano groups was synthesized by γ-irradiation. The amidoximated polymer was prepared using hydroxylamine hydrochloride in basic medium. The characterization of monomer, polymer and amidoximation was confirmed by IR and NMR spectroscopy. The complex formation of the amidoxime salt towards Ag^I, Cu^{II} *and* Ag^I/Cu^{II} *mixture in aqueous solution was studied by AAS, EDS, and ESR spectrometry. The binding capacity of these metal ions is selective in favor of silver(I) ion. The thermal stability of polymers and their complexes was investigated using TG analysis. The change in their morphology was observed by SEM. Potential biological activity of the polymer and its complexes towards some types of bacteria and fungi was tested under the same conditions. Silver (I) complexed polymer had a strong biocidal activity for all tested bacteria and fungi.*

Keywords: amidoximated polymer, complex formation, ion selectivity, thermal stability and morphology

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INTRODUCTION

There are numerous studies on extraction of toxic metal ions in industrial effluent, waste and seawater. Unconventional materials have been used as absorbents for this purpose [1–3]. Chelating polymers have been playing an important role in this field, those containing amidoxime groups being most promising candidates. Amidoximated polymers have been widely exploited to recover uranium[4] from seawater. Recovery of gold[5], chromium[6], mercury[3], copper[6] and a series of other metal ions have been reported recently [7–11]. Divinylbenzene cross-linked poly(acrylamidoxime) resins were obtained and utilized successfully in the determination of trace metals in natural water [7–12]. The synthesis of new polymer ligands has great practical applications [13]. In previous work we reported the reaction of acryloyl chloride or methacryloyl chloride with the corresponding amines to prepare new functional monomers [14–15]. Most of these polymers are prepared by employing conventional methods of chemical initiator [14–16] or irradiation technique [17,18].

The main objective of the present work was to prepare a new polymer containing amidoxime moiety and to investigated its complexation capacity towards metal ions in solution. This was achieved by preparing a new monomer containing cyano group, 4-*N*-acryloyl amidobenzonitrile (AMBN), which then polymerized by γ-irradiation. The reaction of this polymer with hydroxylamine hydrochloride gave the required amidoximated polymer. Physicochemical characterization was accomplished using infrared (IR), nuclear magnetic resonance (NMR), electron spin resonance (ESR), atomic absorption spectroscopy (AAS), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA). The biological activity towards certain types of bacteria and fungi has been tested.

EXPERIMENTAL

Materials

Reagent grade 4-aminobenzonitrile and acryloyl chloride (Aldrich, Germany) were of 99% purity. Hydroxylamine hydrochloride and transition metal nitrates such as $Cu(NO_3)_2{\cdot}3H_2O$ and $AgNO_3$ (Hopkin and Williams Ltd., England) were used as received. Other chemicals were reagent grade and used without further purification.

Monomer Synthesis

The reaction between acryloyl chloride with 4-aminobenzonitrile was carried out in dry acetone, for about 1h. Saturated ammonium carbonate solution was added to neutralize the evolved hydrochloric acid. The solid monomer 4-*N*-acryloylamidobenzonitrile (AMBN) was filtered off, washed thoroughly with water, and recrystallized from ethanol (m.p. 168°C). Elemental analysis: found, $C = 67.76\%$, $H = 4.65\%$, and $N = 16.27\%$.

Polymerization

Polymer was prepared by a simultaneous radiation technique. The monomer powder was dissolved in dimethylformamide (DMF) in glass ampoules. The reactant mixture in the glass ampoule was sealed and then subjected to γ-radiation from ^{60}Co for 25 Mrad at a dose rate 75 min/h. The ampoules contents were poured into a large excess of ethanol and the polymer Poly(4-*N*-acryloylamidobenzonitrile) (PAMBN) was filtered off and reprecipitated from DMF solution into ethanol. Finally, it was dried in a vacuum oven till constant weight and analyzed. Elemental analysis: found, $C = 65.07\%$, $H = 5.25\%$ and $N = 15.61\%$.

Preparation of Amidoxime Polymer

The PAMBN was reacted with 0.25 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in ethanol/NaOH at 60°C for 12 h. The amidoxime polymer (PAMBN-AO) was dried and the conversion to amidoxime structure was determined by the disappearance of the cyano groups band from its FTIR spectra.

Synthesis of Amidoxime Polymer-metal Complexes

The PAMBN—AO was immersed in 3M NAOH in a water bath at 60°C overnight. The sodium salt of amidoxime polymer was washed with distilled water and then dried in vacuum oven at 50°C. The sodium salt of amidoxime polymer was reacted with 1.0wt.% $Cu(NO_3)_2{\cdot}3H_2O$, O, $AgNO_3$ and a mixture of Ag^{I}/Cu^{II} (1:1 mole). The complex was formed immediately at room temperature. The complexed-metal powder was characterized using several techniques.

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C nuclear magnetic resonance (NMR) were recorded using a Bruker AVANCE DPX400 MHz spectrometer.

IR Spectra

IR spectra were measured for the monomer, polymer and amidoximated polymer using a Shimadzu 5000 FTIR spectrometer. The test samples were used without diluents or supports.

Electron Spin Resonance (ESR)

ESR measurements were carried out at room temperature with a Bruker spectrometer, model ECS 106 in the x-band range (9.4 GHz). The *g*-values were estimated using a varian-standard "strong-pitch" with $g = 2.0028$. The polymer powder was placed in the sample tubes. The orientation direction of the polymer was either parallel or perpendicular to the axis of the magnetic field.

Atomic Absorption Spectroscopy (AAS)

AAS measurements were carried out with a Perkin-Elmer 5000 pc (USA).

Energy Despersive Spectroscopy (EDS)

EDS chemical area mapping for the test materials was done with LINK's exl II energy dipersive spectrometer (Oxford Instruments UK) attached to the scanning electron microscope vide infra to measure the ion selectivity of the polymer.

Scanning Electron Microscopy (SEM)

The polymer-complex with Ag^{I}, Cu^{II} and Ag^{I}/Cu^{II} ions at room temperature was examined in a model JSM-6300 JEOL scanning electron microscope (Japan) at 20 kV.

Thermogravimetry Analysis (TG)

TG was carried out in a dynamic atmosphere of pure nitrogen gas using a Shimadzu DSC 50 analyzer (Japan) set at a heating rate of 20°C/min.

Biological Activity

400 μg/mL (W/V) of complexed polymer with Ag^{I}, Cu^{II} and Ag^{I}/Cu^{II} in sterile DMSO was transferred in a well of 12 mm diameter, made by a borer in agar medium. Plates were incubated after 37°C for 24 h (for bacteria) and 25°C for 48 h (for fungi). The activities were expressed as inhibition zones (mm diameter, clear areas) as antibacterial and

antifungal effect. The least concentration which showed inhibitory effect on any specific microorganism was considered as the minimum inhibitory concentration (MIC), which was determined using streptomycin and mycostatin as references.

RESULTS AND DISCUSSION

A. Characterization of Monomer and Polymer

i) ^{1}H NMR and ^{13}C NMR

The proton spectra of the monomer AMBN and the polymer PAMBN are displayed in Figure 1A and B respectively and the carbon-13 NMR data are given in Table 1.

ii) IR Spectroscopy

Figure 2 shows the IR spectra of AMBN monomer (curve a), PAMBN (curve b) and amidoximated PAMBN (curve c). The monomer and its polymer had a characteristic sharp absorption band at 2222 cm^{-1} due to C≡N groups, and 1685–1668 cm^{-1} absorption band characteristic of –CONH–. The absorption band at 1602–1599 cm^{-1} represents aromatic ring (phenyl) and the absorption band at 3242–3100 cm^{-1}

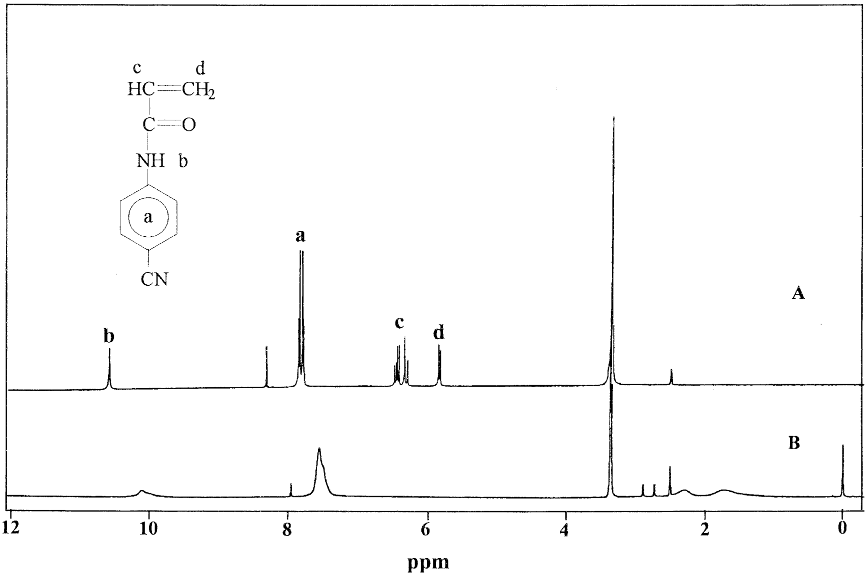
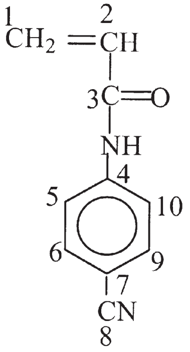


FIGURE 1 ^{1}H-NMR spectrum of AMBN monomer (A) and PAMBN (B).

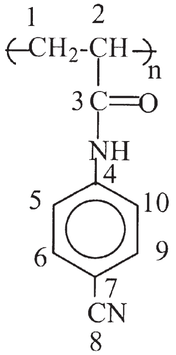
TABLE 1 Assignment of Peaks in ^{13}C-NMR Spectra of AMBN Monomer and PAMBN

Sample	C_1	C_2	C_3	C_4	$C_{5,10}$	$C_{6,9}$	C_7	C_8
AMBN	105.92	106.07	169.73	164.49	134.18	120.14	144.06	119.89
PAMBN	31.63	36.65	174.26	163.17	133.52	120.45	143.03	119.92



4-*N*-acryloyl amidobenzonitrile

(AMBN)



poly(4-*N*-acryloyl amidobenzonitrile

(PAMBN)

represents $-CH_2$ (*cf.* curves a and b). After amidoximation, the characteristic bands were observed, whereas $C{\equiv}N$ groups were expected to be replaced with $H_2N{-}C{=}N{-}OH$ (amidoxime groups) at the end of the reaction. The absorption band appearing at 3400–3000 cm^{-1} characterizes the hydroxyl and amino groups in amidoxime groups and $C{=}N$ at 1602 cm^{-1} (curve c). During the amidoximation process the cyano groups ($C{\equiv}N$) are completely converted to amidoxime groups, meaning the replacement of hydrophobic nitrile groups by hydrophilic amidoxime groups as good ligands for complexation [8,19].

B. Complex Formation

i) Ion Selectivity

Figure 3 shows the energy dispersive spectroscopy (EDS) of a mixture consisting of Ag^{I} and Cu^{II} solutions. It can be seen that the Ag^{I} is more absorbed by the polymer than Cu^{II} ion, under the same

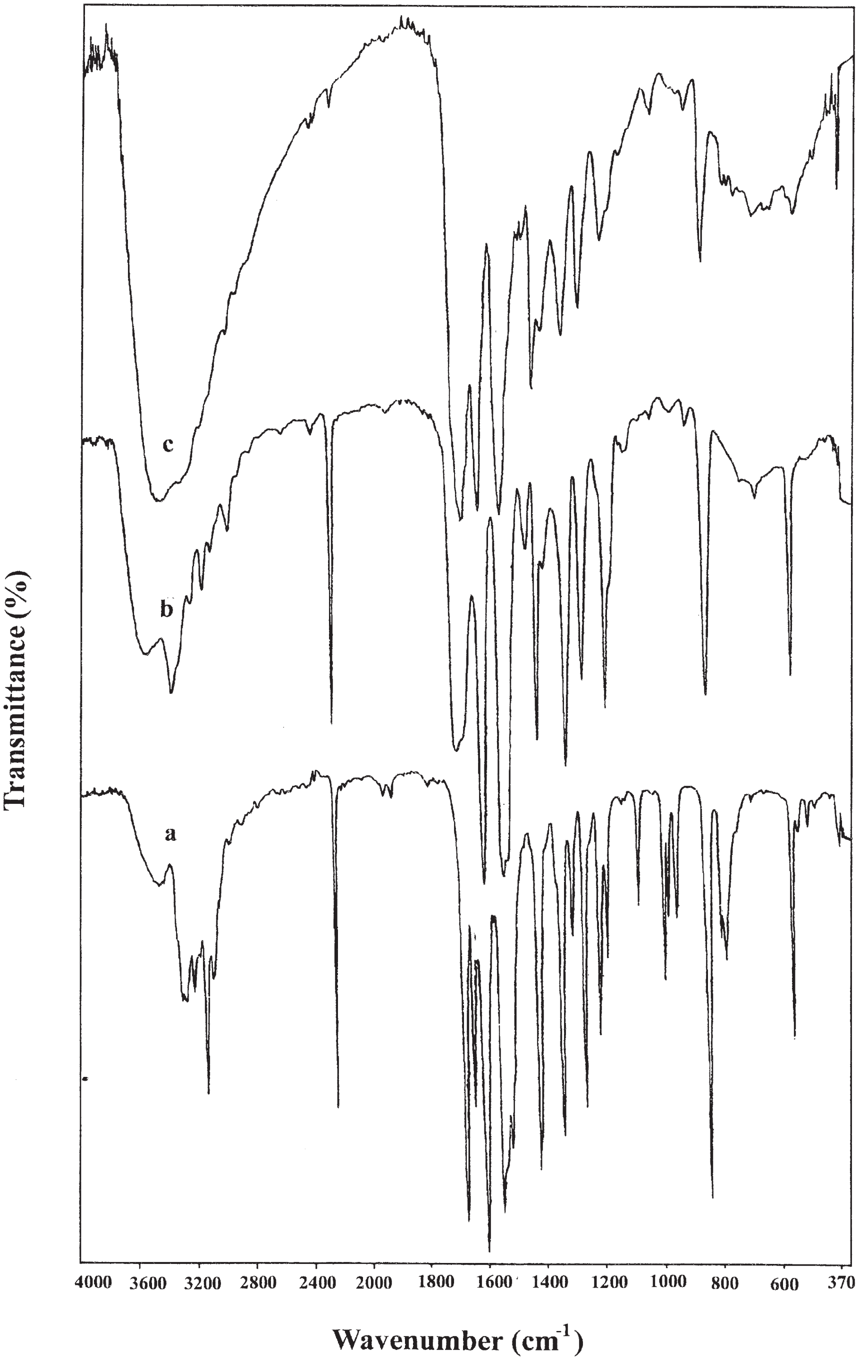


FIGURE 2 IR spectra of AMBN monomer (curve a), PAMBN (curve b), and PAMBN-AO (curve c).

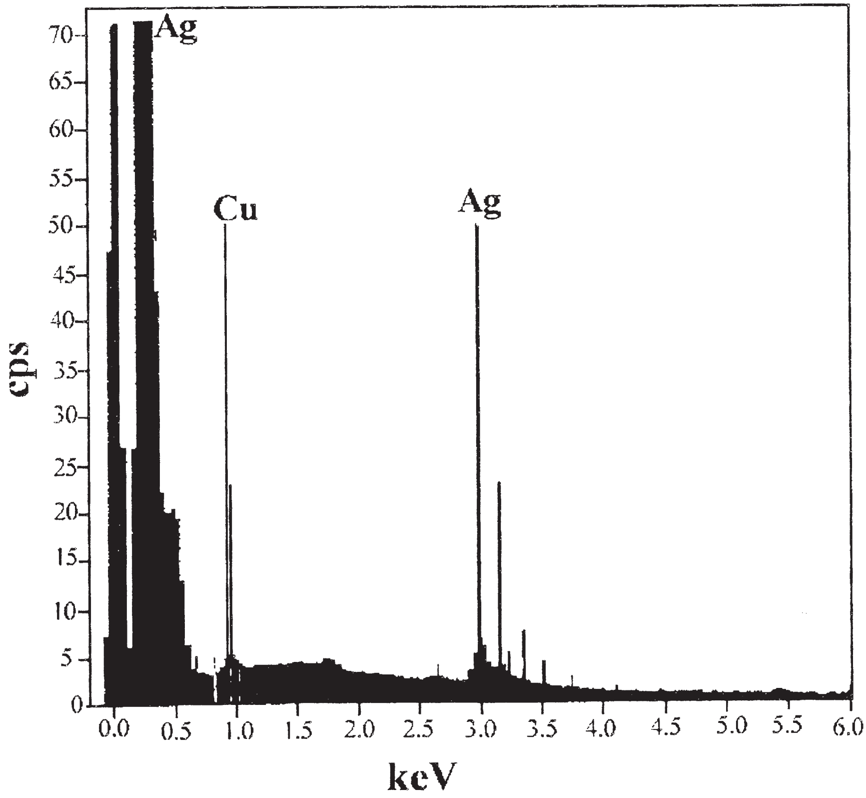


FIGURE 3 EDS of mixture of Ag^{I}/Cu^{II} solution reacted with sodium salt of PAMBN-AO at room temperature.

conditions. Therefore, PAMBN is promising in the field of metal recovery from aqueous solution. Table 2 exhibits the capacity of amidoximated polymer towards Ag^{I}, Cu^{II} and mixture of Ag^{I}/Cu^{II} ions. The capacity of PAMBN-AO-Ag ($pH = 6.7$) is more than that of PAMBN-AO-Cu ($pH = 4.60$) whereas the ratio between them is 2:1,

TABLE 2 The Capacity of Amidoximated Polymer Towards Ag^{I}, Cu^{II} and Mixture of Ag^{I}/Cu^{II} Solutions (mol/g) at Room Temperature

Ag^{I}	Cu^{II}	Mixture of Ag^{I}/Cu^{II}	
2.659×10^{-3}	1.402×10^{-3}	Ag^{I} 1.286×10^{-3}	Cu^{II} 0.43×10^{-3}

respectively. Furthermore, the capacity of amidoximated polymer towards Ag^I ions much more than that Cu^{II} ions in the mixture formed from both of them. The pH before and after reaction is 6.12 and 4.8, respectively.

ii) ESR investigation

The amidoxime group can coordinate some metal ions selectively. Therefore, the polymer-metal complex can be determined from the ESR spectrum in which an interaction occurs between the spin of the central metal ion and a coordinated ligand, the strength of which is given by its g value. The ESR spectrum of the polymer-Cu complex exhibits a signal characteristic of the hyperfine structure of Cu^{II} as shown in Figure 4. The peak is well resolved into four peaks because of hyperfine coupling. The values of the g factor and constants for hyperfine structure A can be measured directly. These are $g_{\|} = 2.298$, $g_{\perp} = 2.066$ and $A_{\|}$ (average) splitting factor = 163.96 G. The results for Cu^{II} are the axial type with $g_{\perp} = 2.066$ and $g_{\|} = 2.298$. The spectrum shows a hyperfine structure on $g_{\perp}$ with $A_{\|}$ (splitting factor) = 163.96 G and it may represent a square planar or distorted octahedral environment. This is in good agreement with the results obtained in previous studies [7,8,20]. This verified that Cu^{II} ions were

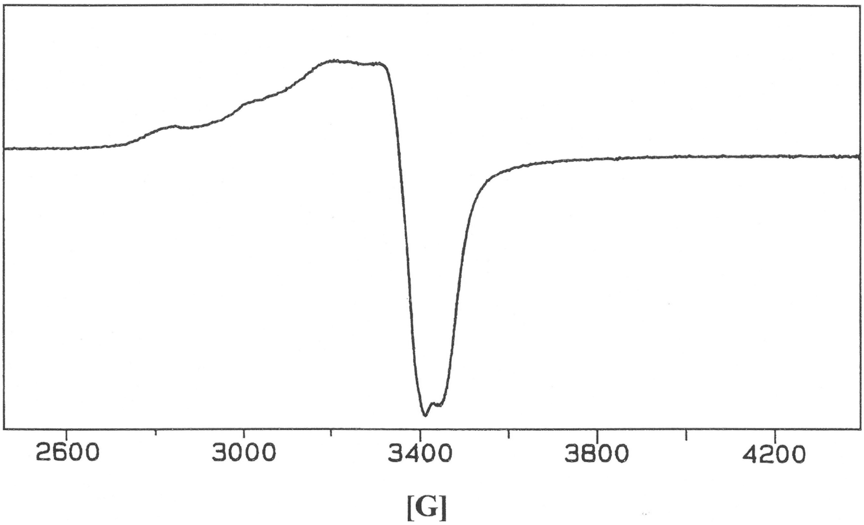
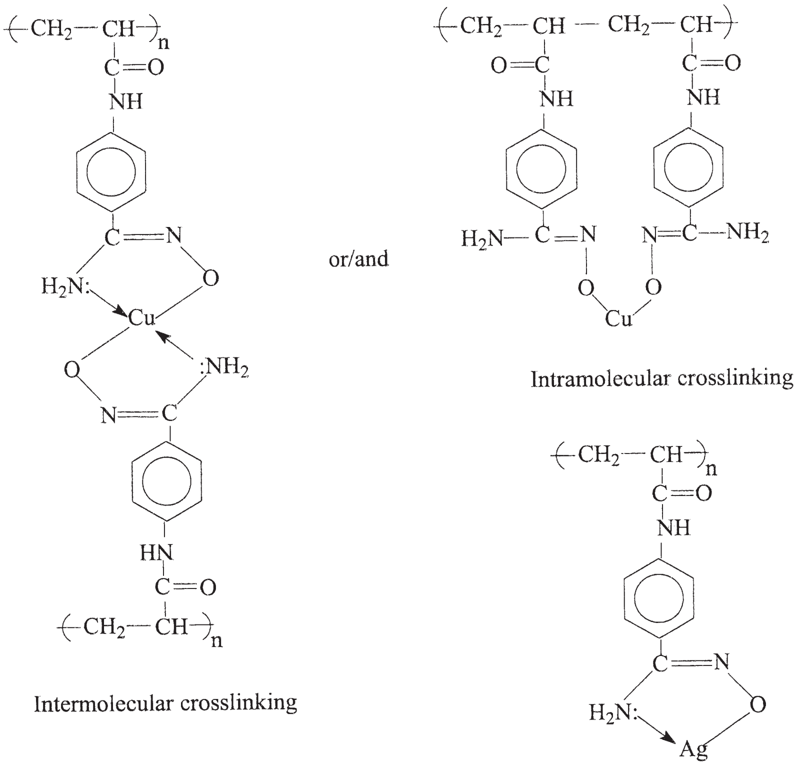


FIGURE 4 ESR spectra of Cu (II) complex of PAMBN-AO at room temperature.



Intermolecular crosslinking

Intramolecular crosslinking

Intramolecular structure

SCHEME 1

bonded with amidoxime groups after the PAMBN-AO complexed with Cu^{II} ions. Therefore, we infer that the structure of the amidoximated polymer, which coordinates with Cu^{II} ions, is perhaps in two forms. However, the coordinated form of Ag^{I} ions has one structural form. The probable mechanisms are shown in Scheme 1.

C. Biological Activity

The complexed polymer containing Ag^{I}, Cu^{II} and mixture of Ag^{I}/Cu^{II} show biological activities toward bacteria and fungi under the same conditions. Table 3 shows that PAMBN-AO-Cu^{II} has strong biological activity against *B. subititis* while moderate effect on *S. aureus* and *A. niger*. However, it has no effect on *E. coli*. Meanwhile,

TABLE 3 In Vitro Bactericidal and Fungicidal Activity of PAMBN and its Amidoximated Polymer with Ag^{I}, Cu^{II} and Mixture of Ag^{I}/Cu^{II}

		Amidoximated polymer with		
Test organism	polymer	$-Ag^{I}$	$-Cu^{II}$	$-Ag/Cu^{II}$
E. coli	++	+++	–	+++
S. aureus	++	++++	+++	+++
B. subititis	+++	++++	++++	+++
A. niger	–	++++	+++	–

+ : slight effect = 15 mm; ++ : moderate effect = 20 mm; +++ : severe effect = 25 mm; ++++ : very severe effect = 30 mm.

PAMBN-AO-Ag^{I}/Cu^{II} exhibited biological activity against *E. coli, S. aueus* and strong effect on *B.subitis*, while it has no effect on the *A. niger*. Furthermore, PAMBN-AO-Ag^{I} has strong biological activity on all these kinds of bacteria and fungi. It is noteworthy that the previous studies [21,22] found strong biocidal activity for Ag^{I} complex. On the other hand, PAMBN has only a slight antibacterial effect and is inactive on fungi.

In view of the characterization results of the present set of complexed polymer, the varied biological activity observed may be related to the different structures of some metal ions assumed in Scheme 1. The Ag^{I}-complex may give linear geometrical structure while Cu^{II}-complex has square planar geometrical structure. From the above results the linear shape may be more effective on the various types of microorganisms.

D. Thermal Stability Measurements

Figure 5 illustrates the TG curves for the original PAMBN (curve a), amidoximated PAMBN (curve b), PAMBN-AO-Cu (curve c), PAMBN-AO-Ag (curve d) and PAMBN-AO-Ag/Cu mixture (curve e) complexes. Table 4 and Figure 5 show that the weight loss of the initial decomposition temperature (IDT) at the range 25–200°C for polymeric substrate, amidoximated material and complexed ones is due to the removal of water in polymeric material during the initial heating. Afterwards, the weight loss (%) increased for the polymer and its amidoximated form while the presence of metal ions in the structure decreased the weight loss (%) at the range between 200–400C. Moreover, the stability of complexed polymer vanished due to the complete decomposition of its geometrical structure. Therefore, the sequence of

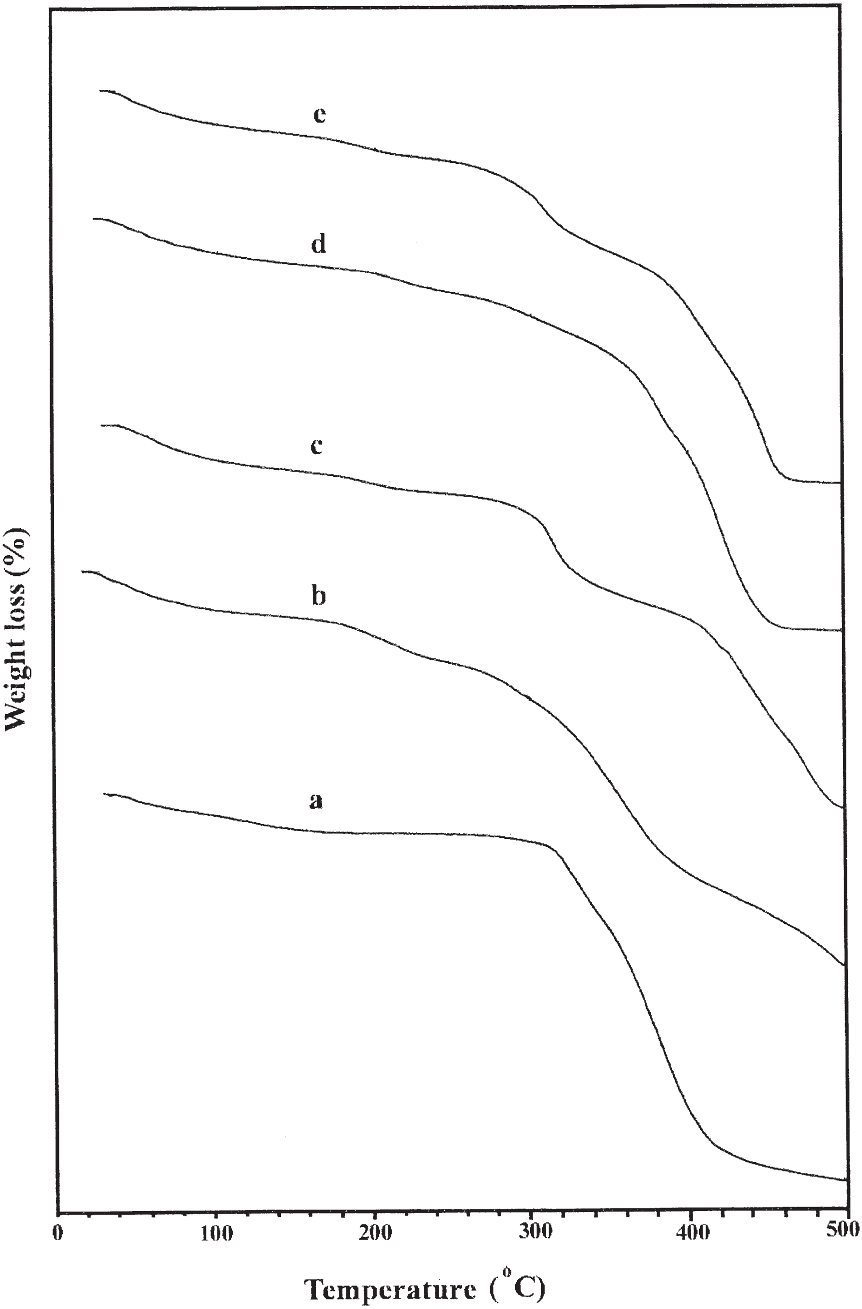


FIGURE 5 TG curves for the initial PAMBN (curve a), PAMBN-AO (curve b), complexed-Cu^{II} (curve c), complexed-Ag^{I} (curve d) and\ complexed-Ag^{I}/Cu^{II} (curve e), respectively.

TABLE 4 Thermogravimetric Analysis of PAMBN and its Amidoximated Complexed with Ag^{I}, Cu^{II} and Ag^{I}/Cu^{II}

Sample	Weight loss (%)					Total weight loss (%)
	25–100°C	100–200°C	200–300°C	300–400°C	400–500°C	
(a) PAMBN	6.525	3.499	1.390	52.988	13.141	77.543
(b) PAMBN-AO	6.380	3.887	10.913	30.786	16.162	68.128
(c) PAMBN-AO-Cu	9.487	6.167	4.422	31.010	42.167	93.223
(d) PAMBN-AO-Ag	7.094	3.787	8.624	29.470	37.543	86.518
(e) PAMBN-AO-Ag/Cu	8.103	5.897	10.529	27.716	40.453	92.698

stability of various polymeric materials is as follows: PAMBN-AO > PAMBN > $-Ag^{I}$ > $-Ag^{I}/Cu^{II}$ > $-Cu^{II}$.

The results suggest that the higher the ionic and coval radii, the higher the adsorption of metal ions obtained during the complex

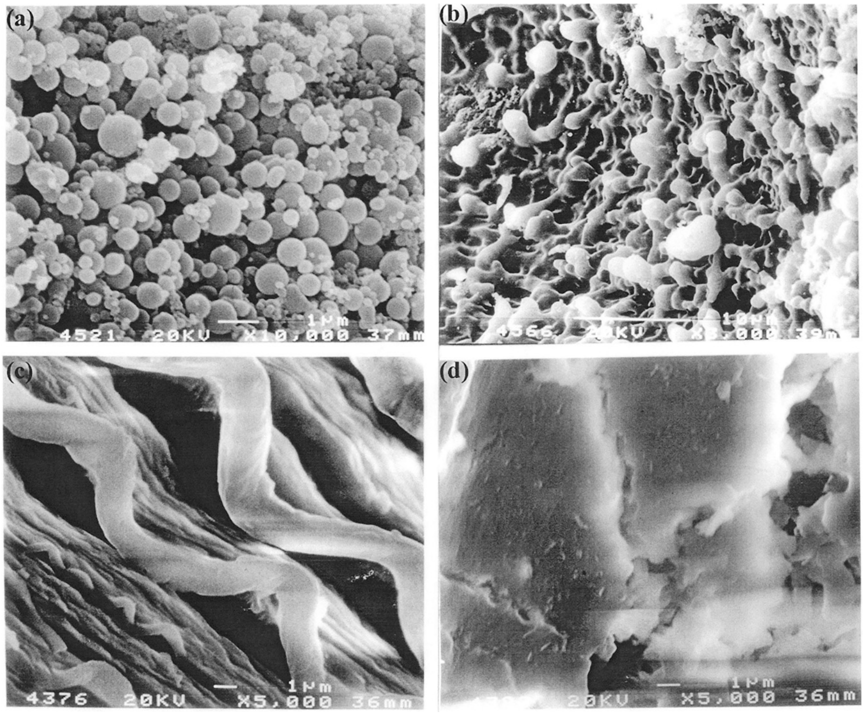


FIGURE 6 Scanning electron micrographs of the initial PAMBN (a), PAMBN-AO (b), polymer complex with Ag^{I} (c), and polymer complex with Cu^{II} (d) at room temperature.

formation. Consequently, the $-Ag^{I}$ is more adsorbed and stable in the amidoximated polymer than Cu^{II}.

E. Morphology

Figure 6 shows the morphologies of PAMBN (Figure 6a), amidoximated PAMBN (Figure 6b) and complexed modified polymer with Ag^{I} (Figure 6c) and Cu^{II} (Figure 6d) observed by SEM at room temperature, respectively. Figure 6(a) shows the distinct individual spheres of the polymer. The scanning electron micrograph depicted in Figure 6(b) shows that the modified polymer by amidoxime groups, which appears mostly as spheres, was aggregated to form a contiguous structure. However, the scanning electron macrograph of complexed modified polymer with Ag^{I} via sodium salt of amidoxime groups show the texture as stringy. While, the polymer modified with Cu^{II} indicates that a rough surface morphology was created due to the formation of copper(II) complex.

The results suggest that the embedding of amidoxime group in the matrix of polymer by converting cyano group to amidoxime group increased the hydrophilicity and reactivity. Consequently, the change of surface morphology was observed. Moreover, the introduction of metal ions into the modified polymeric material by complexation causes a change in the surface morphology. This is according to the nature of metal ions and also may be due to the geometrical structure of the complexed polymers: The silver(I) complexes may be linear while copper(II) complexes may be due to form a square planar or distorted octahedral environment.

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