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Radiation Polymerization of 4-(Acryloylamido)benzonitrile: Zinc and Copper Complexes

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Summary. The new polymer containing cyano groups was synthesized by γ-irradiation. The oximated polymer was prepared using hydroxylamine hydrochloride in basic medium. The characterization of monomer, polymer, and oximated ones was confirmed by infrared and nuclear magnetic resonance spectroscopy. The complex formation of the amidoxime salt towards Zn^{II}, Cu^{II}, and Zn^{II}/Cu^{II} mixture in aqueous solution was studied by atomic absorption spectroscopy, energy dispersive spectroscopy, and electron spin resonance spectrometry. The significant binding capacity of these metal ions revealed its selectivity to Zinc(II) ion. The thermal stability of polymers and complexed ones was investigated using thermogravimetry analysis. The change in their morphology was observed by scanning electron microscopy (SEM).

Keywords. Oximated polymer; Complex formation; Thermal stability; Morphology.

Introduction

There are numerous studies on extraction of toxic metal ions in industrial effluent, waste, and seawaters. Unconventional materials have been used as absorbants for this purpose [1–3]. Chelating polymers have been playing an important role in this field, in particular those containing amidoxime groups are 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 from aqueous solution has been reported recently [7, 8]. Divinylbenzene cross-linked poly(acrylamidoxime) resins were obtained and utilized successfully in the determination of trace metals in natural water [9]. The synthesis of new polymer ligands has great practical applications [10]. The reaction of acryloyl chloride or methylacryloyl chloride with the corresponding amines to prepare new functional monomers has been reported [11, 12]. Most of these polymers are prepared by employing the conventional method of chemical initiator [11, 13] or irradiation technique [14, 15].

The main objective of the present work is to prepare a new polymer containing amidoxime moiety and investigate the complexation capacity towards metal ions in solution. This was achieved by preparing the new monomer containing cyano group, 4-(acryloylamido)benzonitrile (*AMBN*), which was 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), and thermogravimetric analysis (TGA).

Results and Discussion

Characterization of Monomer and Polymer

The reaction between acryloyl chloride with 4-aminobenzonitrile was carried out in dry acetone, for about 1 h. Saturated ammonium carbonate solution

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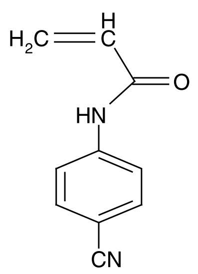
Table 1. Assignment of peaks in ^{13}C NMR spectra of *AMBN* monomer and *PAMBN*

Sample	C_1	C_2	C_3	C_4	$C_{5,10}$	$C_{6,9}$	C_7	C_8
AMBN	103.92	102.07	120.73	164.69	136.48	125.34	154.66	129.92
PAMBN	34.66	36.68	172.26	163.47	132.53	125.48	153.63	129.98

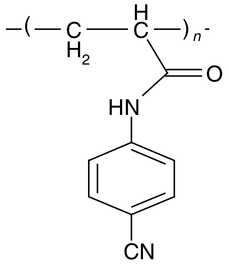
was added to neutralize the evolved hydrochloric acid. The solid monomer 4-(acryloylamido)benzonitrile (*AMBN*) was filtered off, washed thoroughly with water, and recrystallized from ethanol (m.p. 168°C). Polymerization experiments illustrate the variation of M_{50} values for unloaded and loaded bends (repeating unit) with the irradiation dose (kGy). It may be observed that the loaded blend sample has attained clearly the highest value of M_{50} over the whole irradiation range rather than unloaded blend infact may be due to rupture on irradiation with a gamma ray dose of 60, 100, 140, 180, 210, and 230 kGy, respectively. Although M_{50} values are reported only for this limited irradiation range, it may be seen that these values are almost similar to those of unloaded blend composition. In the later case the values of M_{50} attained may be attributed to induced cross-linking by irradiation, the relative increase in M_{50} in this case reinforced blends is attributed to the structure state and in agreement with manufacture of transferred matrix polymer [16]. The yield of polymer increases with increased gamma dose radiation, the best method to obtain the polymer without initiator.

^{13}C NMR

The structures of the monomer *AMBN* and the polymer *PAMBN* are displayed in A and B and the carbon-13 NMR data are given in Table 1.



4-(acryloylamido)
benzonitrile (*AMBN*)
A



poly 4-(acryloylamido)
benzonitrile (*PAMBN*)
B

IR Spectroscopy

The IR spectra of *AMBN* monomer and *PAMBN* had characteristic sharp absorption bands at 2222 cm^{-1} due to C≡N groups and at 1685–1668 cm^{-1} due to –CONH–. The absorption band at 1602–1599 cm^{-1} represents the phenyl ring and the absorption band at 3242–3100 cm^{-1} represents the $-CH_2$ gray. After amidoximation, C≡N groups were replaced by $H_2N-C=N-OH$ (amidoxime groups). The absorption band appearing at 3400–3000 cm^{-1} characterizes the hydroxyl and amino groups in amidoxime groups and the C=N group gives a sign at 1602 cm^{-1}. During the amidoximation process the hydrophobic cyano groups (C≡N) are completely converted to hydrophilic amidoxime groups which are good ligands for complexation [8, 16].

Complex Formation

Ion Selectivity

From the mixture containing Zn^{II} and Cu^{II} ions, it can be seen that Zn^{II} is more absorbed by the polymer than Cu^{II} under the same conditions. Therefore, *PAMBN* is promising in the field of metal recovery from aqueous solution. Table 2 exhibits the capacity of amidoximated polymer towards Zn^{II}, Cu^{II}, and mixture of Zn^{II}/Cu^{II} ions. The capacity of *PAMBN-AO*-Zn (*pH* = 6.8) is more than that of *PAMBN-AO*-Cu (*pH* = 4.80) whereas the ratio between them is 2:1. Furthermore, the capacity of amidoximated polymer towards Zn^{II} ions is much higher than the one towards Cu^{II} ions in the mixture containing both of them. The *pH* before and after reaction is 6.12 and

Table 2. The capacity of amidoximated polymer towards Zn^{II}, Cu^{II}, and mixture of Zn^{II}/Cu^{II} solutions (mol/g) at room temperature

Zn^{II}	Cu^{II}	Mixture of Zn^{II}/Cu^{II} (1/1)	
		Zn^{II}	Cu^{II}
2.689×10^{-3}	1.400×10^{-3}	1.280×10^{-3}	0.48×10^{-3}

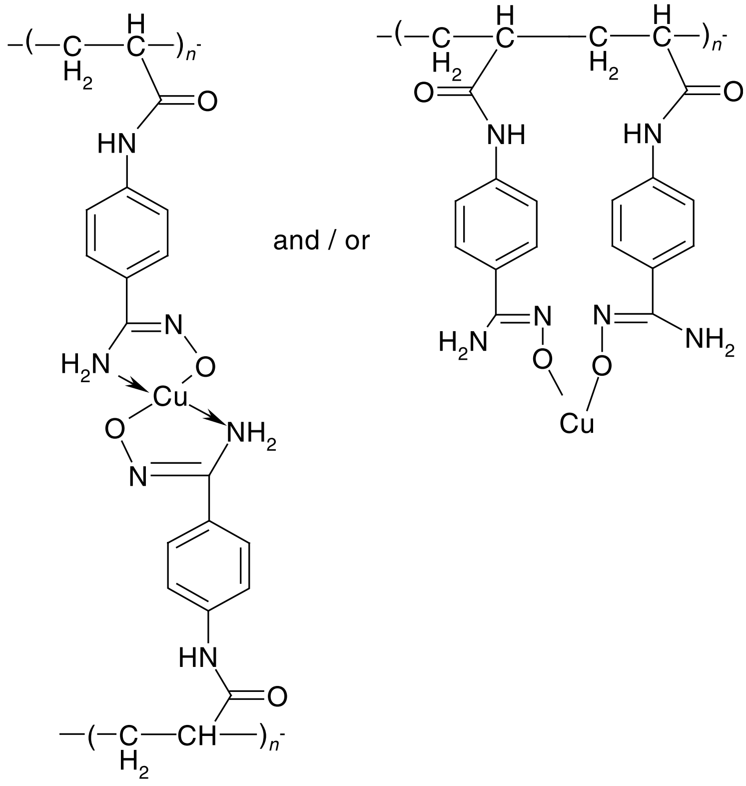


Fig. 1. Intermolecular cross-linking

4.9. This indicates release of hydrogen ion on the expense of metal ions.

ESR Investigation

The amidoxime group can coordinate certain metal ions selectively, therefore, structural data can be infered 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 that is characteristic of the hyperfine structure of Cu(II)

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. There are the axial type with $g_{\|} = 2.066$ and $A_{\|}$ (splitting factor) $= 163.96\,\mathrm{G}$ and the axial type with $g_{\perp} = 2.298$ and $A_{\|}$ (splitting factor) $= 163.96\,\mathrm{G}$. This splitting value indicates that the structure of the $\mathrm{Cu^{II}}$ complex is square planar or distorted octahedral which agrees with previous studies [7, 8, 10]. This verifies that $\mathrm{Cu^{II}}$ ions were bonded with amidoxime groups after *PAMBN-AO* was treated with $\mathrm{Cu^{II}}$ ions. Therefore, we infer that the structure of the amidoximated polymer, which coordinates with $\mathrm{Cu^{II}}$ ions, may exists in two forms. ESR allows to discriminate between the two proposed types of linking, the probable coordination modes are shown in Fig. 1.

The IR spectrum of *PAMBN-AO* complexed with $\mathrm{Zn^{II}}$ exhibits a smaller band at 3400–3000 $\mathrm{cm^{-1}}$ which characterizes the hydroxyl and amino groups. This may be due to coordination of $\mathrm{Zn^{II}}$ ions with the amidoxime groups. The proposed structure may be as shown in Fig. 2.

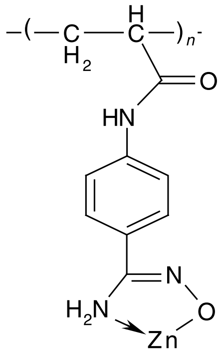


Fig. 2. Intramolecular coordination only

Table 3. Thermogravimetric analysis of *PAMBN* and its amidoximated derivative complexed with Zn^{II}, Cu^{II}, and Zn^{II}/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*	6.585	4.499	1.890	53.988	13.141	77.543
(b) *PAMBN-AO*	6.386	4.688	10.815	3.788	16.162	68.128
(c) *PAMBN-AO*-Cu	9.488	6.267	4.422	32.01	41.168	93.223
(d) *PAMBN-AO*-Zn	7.099	3.887	8.624	28.476	38.043	86.518
(e) *PAMBN-AO*-Zn/Cu	8.018	6.097	10.629	27.716	46.053	92.698

Thermal Stability Measurements

The TG curves for the original *PAMBN*, amidoximated *PAMBN*, *PAMBN-AO*-Cu, *PAMBN-AO*-Zn, and *PAMBN-AO*-Cu mixture complexes were measured. Table 3 shows 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. Afterwards, the weight loss increased for the polymer and its amidoximated derivative while the presence of metal ions in the structure decreased the weight loss at the range between 200 and 40°C. Moreover, the stability of complexed polymer vanished due to the complete decomposition of geometrical structures. Therefore, the sequence of stability of various polymeric materials is as follows: *PAMBN-AO* > *PAMBN* > $-Zn^{II} > -Zn^{II}/Cu^{II} > -Cu^{II}$.

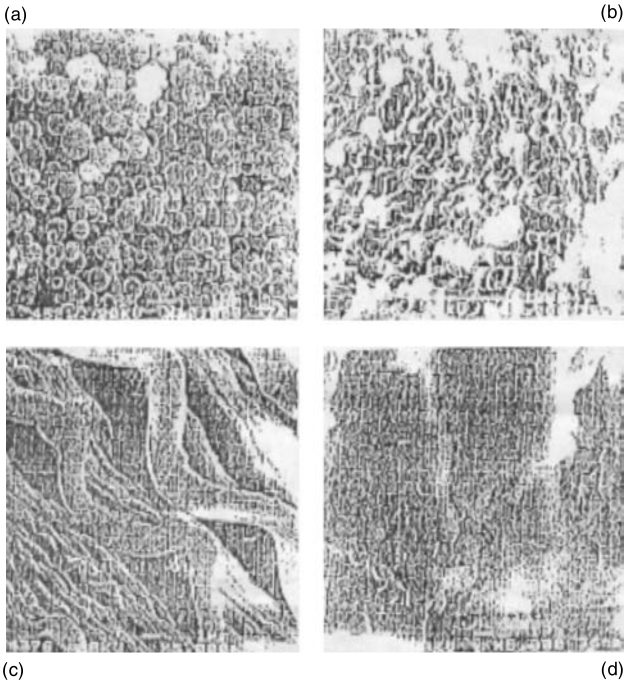


Fig. 3. Scanning electron micrographs of the trunk *PAMBN* (a), *PAMBN-AO* (b), polymer complex with Zn^{II}(c), and polymer complex with Cu^{II}(d) at room temperature

Morphology

Figure 3 shows the morphologies of *PAMBN* (Fig. 3a), amidoximated *PAMBN* (Fig. 3b), and modified polymer complexed with Zn^{II} (Fig. 3c) and Cu^{II} (Fig. 3d) observed by SEM at room temperature. Figure 3d shows distinct spheres in a regular gathering structure. The scanning electron micrograph depicted in Fig. 3b shows that the polymer modified by amidoxime groups, which appear mostly as spheres, was congregated to form a contagious structure. However, the scanning electron macrograph of modified polymer complexed with Zn^{II}, prepared *via* the sodium salt of amidoxime groups, shows a contexture similar to "string shape". Whereas the modified polymer complexed with Cu^{II} indicates by its rough surface that the formation of Cu^{II} complex has occurred.

The results suggest that the embedding of amidoxime groups in the matrix of the polymer by converting cyano groups to amidoxime groups increased the hydrophilicity and reactivity present. Consequently, the change of surface morphology was observed. Moreover, the introduction of metal ions *via* 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 complexed polymers. Whereas the one complexed with Zn^{II} may have a linear structure, the one with Cu^{II} may consist of a sequence of planar or distorted octahedral structures.

Experimental

Materials

Reagent grade 4-aminobenzonitrile and acryloyl chloride (Aldrich, Germany) were of purity 99%. Hydroxylamine hydrochloride and transition metal nitrates such as $Cu(NO_3)_2 \cdot 3H_2O$ and $ZnNO_3$ (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 1 h. Saturated ammonium carbonate solution was added to neutralize the evolved hydrochloric acid. The solid monomer 4-(acryloylamido)benzonitrile (*AMBN*) was filtered off, washed thoroughly with water, and recrystallized from ethanol (m.p. 168°C). Elemental analysis: found C 67.7, H 4.7, N 16.3%, calcd. C 70.2, H 4.1, N 16.4%.

Polymerization

The polymer was prepared by radiation-induced polymerization of the monomer. The monomer powder was immersed in dimetylformamide (*DMF*) in glass ampoules. The mixture in the glass ampoules was sealed and then subjected to γ-radiation from ^{60}Co with 0.0–2.5 Gy at a dose rate of 0.3 kGy/h with modulus stress at 50% elongation (M_{50}) as a function of irradiation dose in atmosphere using a gamma type 4000 from energy authourity of Egypt. The ampoules contents were poured into a large excess of ethanol and the polymer poly(4-(acryloylamido)benzonitrile) (*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 68.4, H 3.8, N 15.6%, calcd. C 70.0, H 4.4, N 16.3%.

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 3 *M* NaOH in a water bath at 60°C for overnight. The sodium salt of amidoxime polymer was washed with distilled water and then dried in a vacuum oven at 50°C. The sodium salt of amidoxime polymer was reacted with 1.0 wt% $Cu(NO_3)_2 \cdot 3H_2O$, $ZnNO_3$, and a mixture of Zn^{II}/Cu^{II} (1:1 mole). The complex was formed immediately at room temperature. The complexed-metal powder was characterized using different techniques.

Nuclear Magnetic Resonance Spectrocopy (NMR)

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Brucker 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 the Varian-standard "strong-pitch" with $g = 2.0028$. The polymer powder was placed in the sample tubes. The stretching 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 5000pc (USA).

Scanning Electron Microscopy (SEM)

The polymer complexed with Zn^{II}, Cu^{II}, and Zn^{II}/Cu^{II} ions at room temperature were 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.

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