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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** El-Sawy, Naeem M. , Ismail, Sahar A. and Ali, Amr El-Hag(2009) 'Polymerization of Prepared 3-N-Acryloylamidobenzonitrile by Gamma Irradiation and Its Use in Adsorption of Chromium Ions', Journal of Macromolecular Science, Part A, 46: 1, 25 – 31

**To link to this Article:** DOI: 10.1080/10601320802511729

**URL:** <http://dx.doi.org/10.1080/10601320802511729>

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# Polymerization of Prepared 3-N-Acryloylamidobenzonitrile by Gamma Irradiation and Its Use in Adsorption of Chromium Ions

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Received May 2008, Accepted June 2008

3-N-acryloylamidobenzonitrile (AMBN) monomer was first prepared and then polymerized in dimethylformamide (DMF) using  $\gamma$ -irradiation to form a new polymer (PAMBN) containing nitrile groups. The characterization of the monomer and its polymer was carried out by Fourier Transform Infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The prepared polymer was modified into amidoximated form using hydroxylamine hydrochloride in basic medium. The complex formation of the amidoxime towards Cr (III) was investigated by X-ray fluorescence (XRF) and inductive coupled plasma (ICP). The thermal stability of the prepared polymer was examined using thermogravimetric analysis (TGA). The change in surface morphology of the prepared polymer and its complexed ones was observed by scanning electron microscope (SEM). The reusability of the chelating polymer with Cr (III), adsorption-desorption was studied. The results obtained from the chelated polymeric material showed promising application in extraction of heavy metal ions from industrial effluents.

**Keywords:**  $\gamma$ -irradiation, complex formation, thermal stability, morphology, heavy metal ions

## 1 Introduction

Many studies have been reported on the preparation of polymers by conventional chemical initiators (1–6) or irradiation techniques (7, 8). Recently, radiation polymerization or radiation-induced graft polymerization of vinyl monomers are widely used to modify chemical and physical properties of polymers or copolymers. Ionizing radiation has many advantages such as uniform creation of radical sites and consequently, effective to form polymeric materials under the reaction condition (9). In the conventional treatment methods, heavy metal ions can be removed by chemical precipitation (10), ion exchange resins (11–13) and adsorption (14, 15).

Chelating polymers are important in the field of metal recovery due to the presence of ligands, which contain atoms able to form donor-acceptor bonds with transition metals. The amidoximation of cyano groups in polymeric chains into amidoxime groups was widely exploited to recover some transition metals such as chromium (16–19), gold (20, 21) and uranium (22, 23) from aqueous solutions.

Therefore, in this study, a new polymeric material was prepared by  $\gamma$ -irradiation of AMBN monomer containing nitrile groups. The characterization of monomer and its polymer (PAMBN) was confirmed using FTIR and NMR. The amidoximation process was carried out by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in basic medium. The chelating ability of the amidoximated polymer towards Cr (III) was investigated by XRF and ICP. The reusability of chelating polymer with Cr (III), adsorption and desorption was studied. The surface morphology of polymer and its complexes with Cr (III) was examined by SEM.

## 2 Experimental

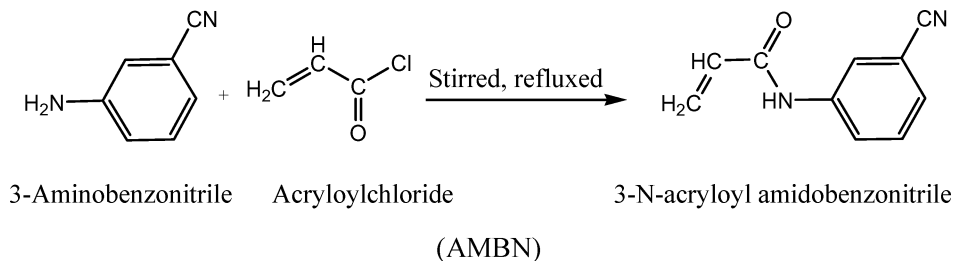
### 2.1 Materials

A reagent grade of 3-aminobenzonitrile and acryloyl chloride (Aldrich, Germany) were of purity 99%. Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) and  $\text{Cr}(\text{NO}_3)_3\cdot 3\text{H}_2\text{O}$  (Hopkin and Williams Ltd, England) were used as received. Other chemicals were reagent grade and used without further purification.

### 2.2 Monomer Synthesis

The reaction between acryloyl chloride with 3-aminobenzonitrile was carried out in dry acetone for about

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**Sch. 1.** Schematic representation for the preparation of 3-N-acryloylamidobenzonitrile.

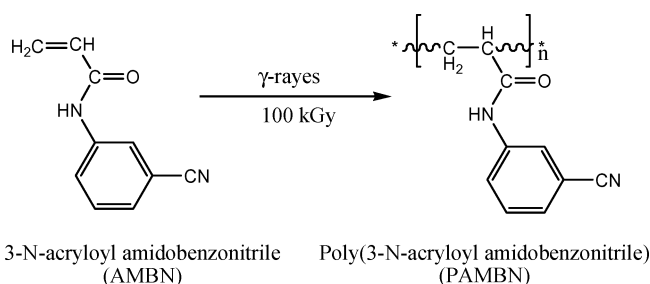
one hour. Saturated ammonium carbonate solution was added to neutralize the evolved hydrochloric acid. The solid monomer 3-N-acryloylamidobenzonitrile (AMBN) was filtered off; washed thoroughly with water and recrystallized from ethanol (m.p. 165°C). Elemental analysis: found C = 68.78%, H = 4.66% and N = 16.25%. The reaction can be represented as shown in Scheme 1.

### 2.3 Radiation Polymerization

Polymer was obtained by radiation polymerization of monomer using  $\gamma$ -rays, in which the monomer powder was dissolved in DMF in glass ampoule. The glass ampoule content was deaerated by nitrogen gas for 5 min, sealed and then subjected to  $\gamma$ -radiation from  $^{60}\text{Co}$  source at a dose of 100 kGy at dose rate of 7.96 kGy/h. The ampoule content was poured into an excess of ethanol and the polymeric substance of poly(3-N-acryloylamidobenzonitrile) (PAMBN) was filtered off and re-precipitated from DMF solution into ethanol. Finally, it was dried in a vacuum oven till a constant weight and analyzed. Elemental analysis: found C = 66.1%, H = 5.46% and N = 15.74%. The polymerization reaction can be represented as shown in Scheme 2.

### 2.4 Amidoximation of PAMBN Polymer

The prepared polymer (PAMBN) was allowed to react with 0.25M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in ethanol/NaOH at 60°C for 12 h.



**Sch. 2.** Schematic representation for the gamma-radiation polymerization of 3-N-acryloylamidobenzonitrile.

### 2.5 Nuclear Magnetic Resonance Spectroscopy

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) were recorded using Bruker advanced DPX 400 MHz spectrometer.

### 2.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was done using Mattson 1000 Unicam (Cambridge, England). The wavenumber range used in this study was 400–4000  $\text{cm}^{-1}$  in order to detect the functional groups of monomer, polymer and polymer complexed with Cr (III). The powder samples were pressed in KBr discs before measurements.

### 2.7 X-Ray Fluorescence (XRF)

The XRF was recorded using ORTEC 6110 TEFA (Tube Excited Fluorescence Analyzer) system, USA to detect the adsorbed metal ions in the solid polymer matrix.

### 2.8 Metal Uptake Measurement

The amidoximated polymer was immersed in aqueous solution of Cr (III) of initial concentration of ( $C_1$ ) and adjusted to the pH = 5. The mixture was stirred throughout the experiment at room temperature for 2 h and then removed from the solution. The residual concentration of Cr (III) ions in the feed solution ( $C_2$ ) was determined by ICP (Plasma JY Ultima threme elemental, France). The metal uptake (Q) was calculated as follows:

$$Q = (C_1 - C_2)V/W$$

Where Q is the metal uptake (mmol/g), W is the weight of the amidoximated dry polymer in (g). V is the volume of solution in (L),  $C_1$  and  $C_2$  are the concentration (mmol/L) of the metal ion solution before and after adsorption, respectively.

### 2.9 Thermogravimetric Analysis (TGA)

A Shimadzu TGA system of type TGA-50 (Japan) was used in nitrogen gas to examine the thermal stability of the samples at heating rate 20°C/min.

## 2.10 Scanning Electron Microscopy (SEM)

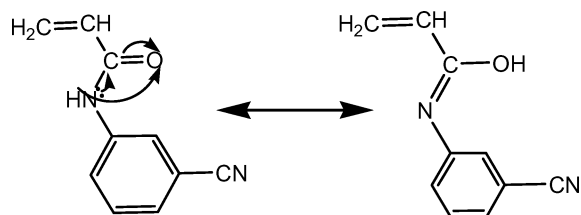
The surface morphology of the prepared polymer and its chelated polymer with Cr(III) ions at room temperature was observed by a scanning electron microscope (model JSM-5400 JEOL, Japan) at 20 kV.

## 3 Results and Discussion

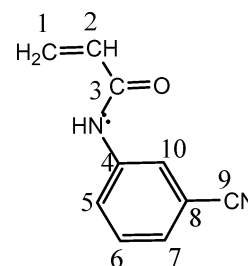
### 3.1 Characterization of the Prepared Monomer and its Polymer

#### 3.1.1. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$

$^1\text{H-NMR}$  spectrum of AMBN in  $\text{DMSO-d}_6$  showed signals at 5.8 ppm (d, 2H,  $\text{CH}_2$ ), 6.3 ppm (m, 1H, CH), 7.52, 7.87 and 8.18 ppm (3s, 4H, Ar-H) and 10.48 ppm (s, 1H, NH) as shown in Figure 1. Meanwhile, the signals appeared at 6.3 ppm (m, 1H, CH) may be due to the presence of resonance structure of monomer (keto-enol form) which are represented as follows:



Also, Figure 2 shows the  $^{13}\text{C-NMR}$  of monomer (AMBN) which exhibited number of carbons contained in the structure. The data can be represented as follows:



$\text{C}_1 = 119.53$ ,  $\text{C}_2 = 122.86$ ,  $\text{C}_3 = 164.39$ ,  $\text{C}_4 = 140.53$ ,  $\text{C}_5 = 128.75$ ,  $\text{C}_6 = 124.72$ ,  $\text{C}_7 = 127.85$ ,  $\text{C}_8 = 132.17$ ,  $\text{C}_9 = 112.49$  and  $\text{C}_{10} = 131.10$ .

However, the  $^1\text{H-NMR}$  of the prepared polymer (PAMBN) in ( $\text{DMSO-d}_6$ ) exhibited signals at 1.8 ppm (s, 2H,  $\text{CH}_2$ ), 2.3–2.9 ppm (m, 1H, CH), 7.1–8.0 ppm (m, 4H, Ar-H) and 9.9 ppm (s, 1H, NH) as shown in Figure 3. Therefore, the broad signals appeared at 1.8 ppm and 9.9 ppm confirmed the macromolecules of polymer can be formed.

### 3.2 FTIR Spectroscopy

Figure 4 (a and b) shows the FTIR spectra of (AMBN) monomer and its PAMBN polymer. The IR spectra of the monomer and its polymer showed characteristic bands at  $2231\text{ cm}^{-1}$  due to  $-\text{C}\equiv\text{N}$  groups, and  $1665\text{--}1658\text{ cm}^{-1}$  absorption band characteristic for  $-\text{CONH}-$ . The absorption

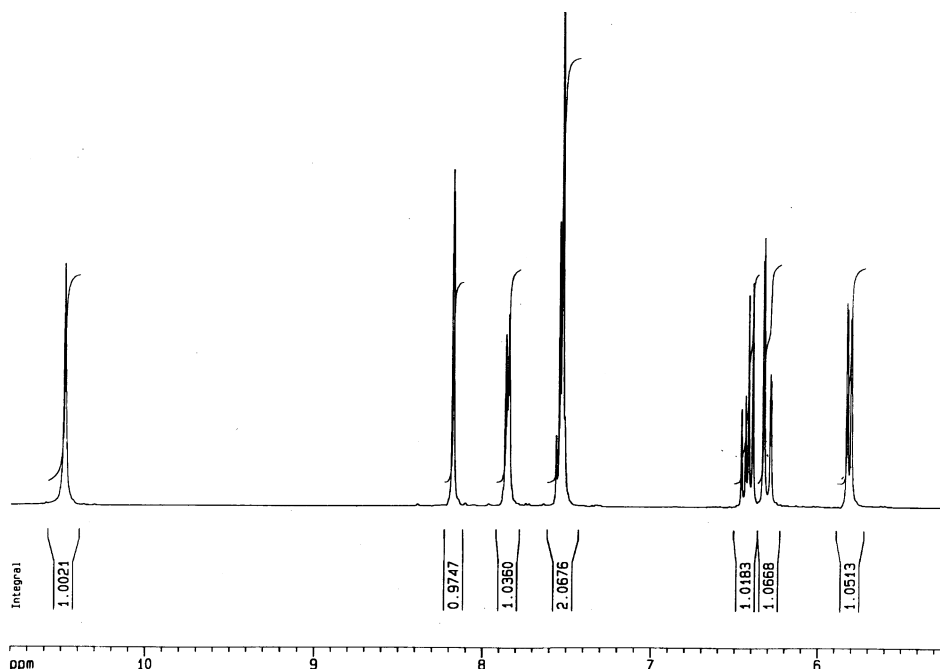
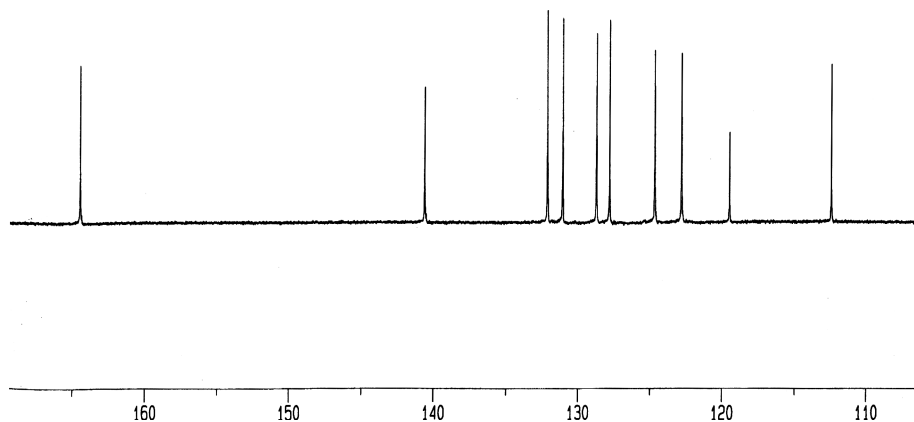


Fig. 1.  $^1\text{H-NMR}$  spectrum of AMBN monomer.



**Fig. 2.**  $^{13}\text{C}$ -NMR spectrum of AMBN monomer.

band at  $1606\text{--}1587\text{ cm}^{-1}$  characteristic for the aromatic ring (phenyl) and the absorption band at  $3434\text{--}3134\text{ cm}^{-1}$  represents  $-\text{CH}_2-$  and  $-\text{CONH}-$ . After amidoximation, Figure 5 shows the spectrum of the amidoximated polymer. The characteristic bands were observed, whereas  $-\text{C}\equiv\text{N}$  groups were expected to replace with amidoxime groups  $\text{H}_2\text{NC}=\text{N}-\text{OH}$  at the end of the reaction. The absorption band appearing at  $3433\text{--}3200\text{ cm}^{-1}$  characterizes the hydroxyl and amino groups in the amidoxime groups,  $\text{C}=\text{N}$  at  $1600\text{ cm}^{-1}$  and  $1654\text{ cm}^{-1}$  which of carbonyl group of  $-\text{CONH}-$  (c.f. Fig. 5). During the amidoximation process, the nitrile groups ( $\text{C}\equiv\text{N}$ ) are completely converted to amidoxime groups, meaning that the replacement of the hydrophobic nitrile groups to hydrophilic amidoxime groups as a good ligand for chelation (17, 24, 25).

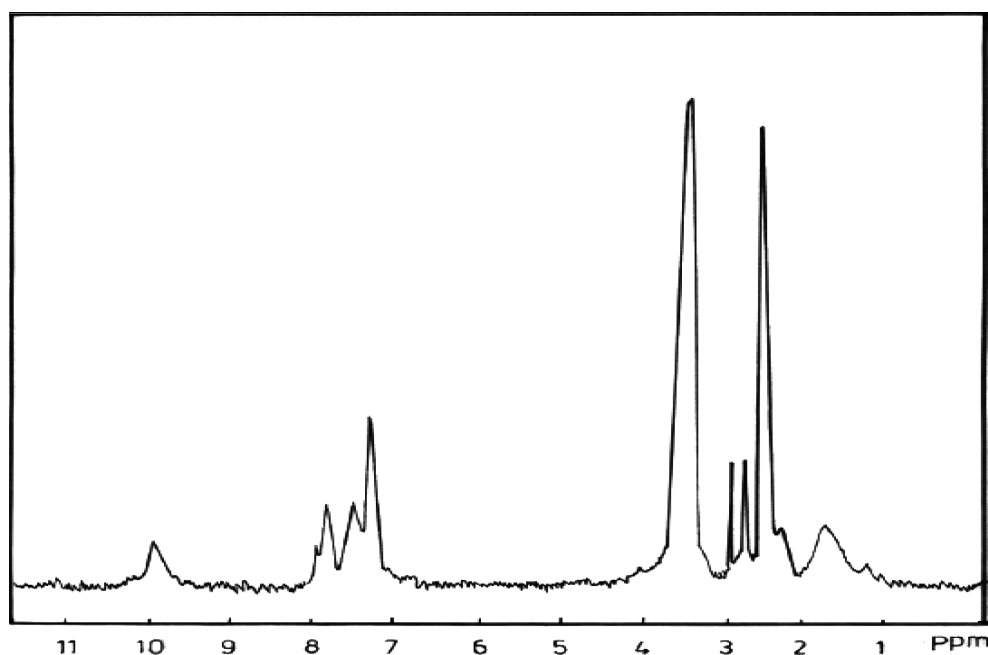
### 3.3 Complex Formation

#### 3.3.1. X-ray Fluorescence (XRF)

Figure 6 shows the adsorption capacity of the chelated polymer with Cr (III) was measured after immersing in 100 ppm of feed solution of Cr(III) at pH 5 for 12 h at room temperature. The Cr (III) appears at 5.5–6.0 keV. Therefore, the proposed structure of the reaction between Cr (III) and amidoximated polymer was illustrated as shown in Scheme 3.

#### 3.4 Reusability of Chelated Polymer

The reusability of the prepared polymer (PAMBN) towards the chelation of Cr (III) was determined by ICP measurements. The amount of the chelated Cr (III) and that



**Fig. 3.**  $^1\text{H}$  NMR spectrum of PAMBN polymer.

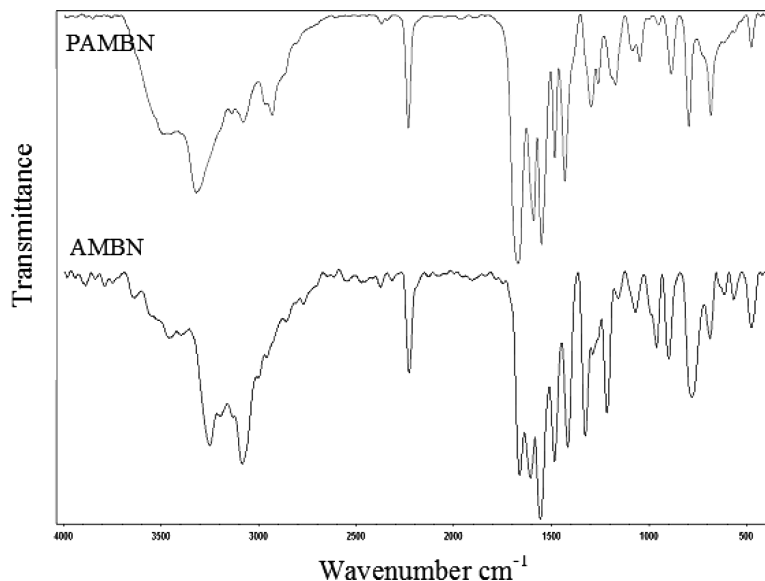


Fig. 4. FTIR spectra of (a) AMBN monomer and (b) PAMBN polymer.

desorbed by 0.2 M HCl at room temperature was found to be 2.92, 2.85 and 2.75 for the three cycles, respectively. The results of adsorption-desorption cycles revealed that a slight decrease in the adsorption capacity of Cr(III) obtained after three cycles. The obtained results are in good agreement with other studies (15).

### 3.5 Thermal Stability Measurements

Figure 7 shows the TG curves for the monomer (curve a), unirradiated polymer (curve b) and irradiated polymer exposed to 100 kGy (curve c). It can be seen from Figure 7 that the prepared monomer is stable up to about 200°C. Afterwards, the remaining weight (%) was decreased with elevating the temperature. However, the thermal stability of unirradiated polymer (curve b) and irradiated one (curve c) are higher than that of the monomer, which are reached up

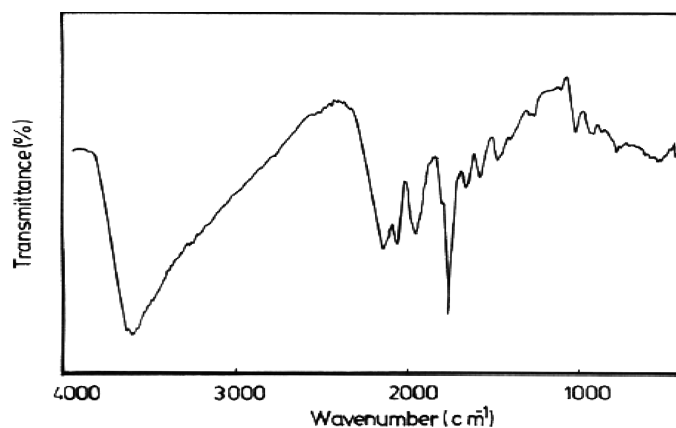


Fig. 5. FTIR spectrum of amidoximated PAMBN.

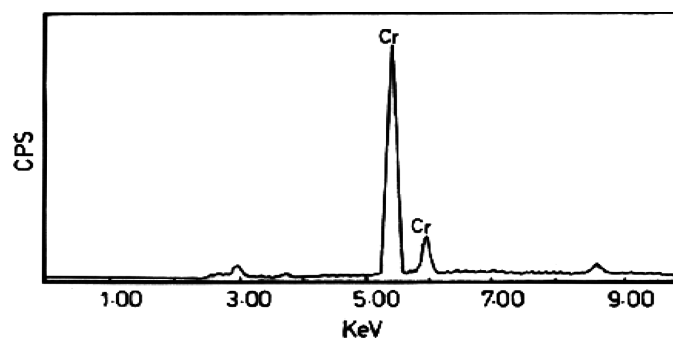
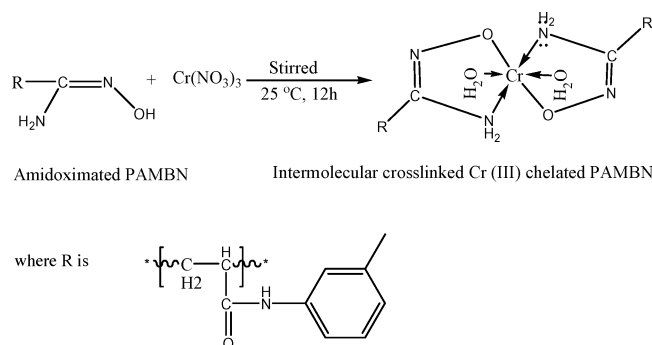
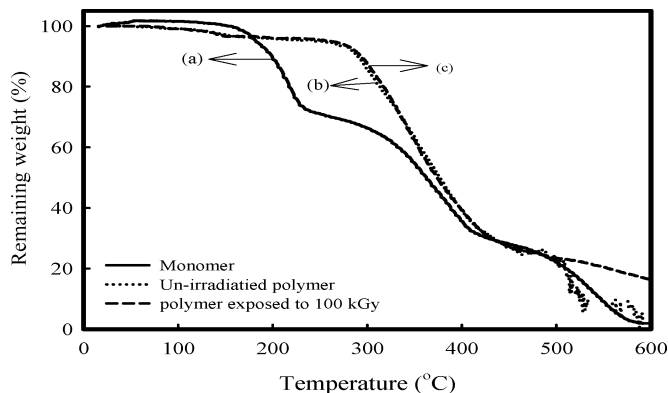


Fig. 6. X-ray fluorescence of chelated Cr(III) ion with amidoximated PAMBN at room temperature.

to 300°C and then degraded from 300 to 500°C. Moreover, there is no significant change in the thermal stability due to the exposure to gamma irradiation until 100 kGy compared with the unirradiated one.



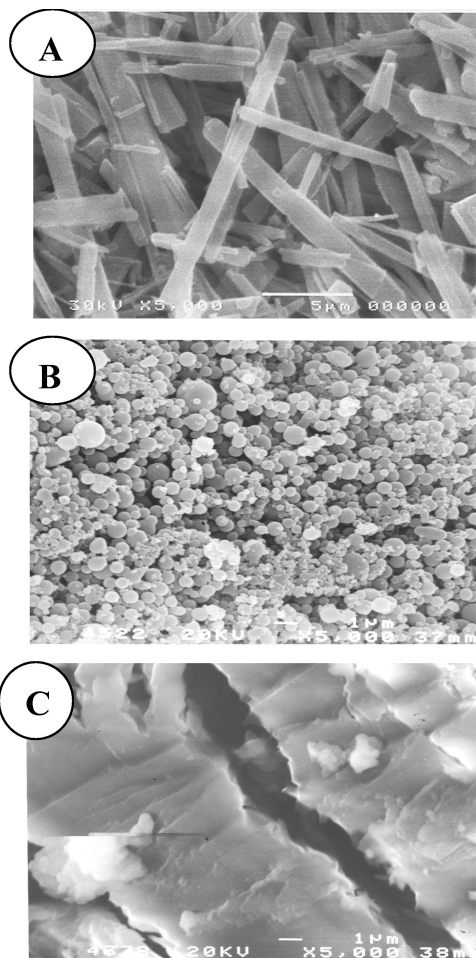
Sch. 3. Schematic representation for the complexation of  $\text{Cr}^{3+}$  with poly(3-N-acryloylamidobenzonitrile).



**Fig. 7.** TG curves for (a) AMBN monomer, (b) unirradiated PAMBN polymer and (c) irradiated PAMBN polymer.

### 3.6 Surface Morphology

Figure 8 shows SEM micrographs of the surface morphology of AMBN, PAMBN and amidoximated complexed polymer with Cr (III). Figure 8A shows the shape as similar to short fibers unhomogenously distributed, while



**Fig. 8.** Scanning electron micrographs of the prepared (A) AMBN monomer, (B) PAMBN polymer and (C) its amidoximated polymer complexed with Cr(III) ions at room temperature.

Figure 8B shows distinct spheres in a regular gathering structure. However, the scanning electron micrograph of the complexed modified polymer with Cr (III), Figure 8C, shows a non-smooth surface with a clear crack.

The results suggested that the embedding of amidoxime group via the polymeric matrix increased the hydrophilicity and reactivity with metal ions by complexation, which cause the change in the surface morphology. Therefore, the reusability of the chelate polymer for recovering metal ions and then give amidoximated polymer time to allow to react the metal ions with amidoximated polymer several times in aqueous system may give the same morphologies as in Figure 8A and B.

## 4 Conclusions

Poly (3-N-acryloylamidobenzonitrile) was obtained by  $\gamma$ -irradiation of synthesized 3-N-acryloylamidobenzonitrile. From the discussion of the experimental results, the following may be concluded:

The synthesized monomer and its polymer were characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C NMR}$ , elemental analysis and FTIR spectrophotometry.

The prepared polymer was modified to form amidoximated polymeric materials by reacting with hydroxylamine hydrochloride in basic medium, then complexed with Cr(III). The complexation was confirmed by XRD and ICP.

The adsorption-desorption of the chelated modified polymeric powder towards Cr(III) was designed to take advantage of the evident complexing tendency of a new polymer in the field of metal recovery.

The thermal stability of the prepared polymer and irradiated one is higher than that of the synthesized monomer.

The chelation of Cr(III) with amidoximated polymer provides a significant change in surface morphology due to complexation of metal ions.

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