Chelating Polymer Granules Prepared by Radiation-Induced Homopolymerization. II. Characterizations

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ABSTRACT: Characterizations of chelating polymer adsorbent granules, incorporating amidoxime groups based on polyacrylonitrile (PAN), prepared for selective adsorption of uranium and likely other transition metals were studied. PAN was prepared by radiation-induced polymerization technique and followed by amidoximation reaction. Conversion of PAN into polyacrylamidoxime (PAO) was studied by fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Morphology and thermal properties were also investigated. PAO was investigated in the separation of uranium from iron-rich silicate rock samples and subjected to x-ray fluorescence analysis (XRF). Selective adsorption for uranium and low affinity for alkali and alkaline earth metals were observed. The order of selectivity was found to be U $\gg$ Cu > Fe > Ni > Cr > V $\gg$ Ca > K. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1180–1187, 2006

Key words: chelating; polymer; amidoxime; radiation; uranium

INTRODUCTION

Most analytical procedures for the determination of uranium and thorium show difficulties with Egyptian iron-rich silicate rocks (hematitized granites) because of the interference with the rock forming elements.[1–4] This requires a selective separation technique for accurate procedures of evaluation.

The lack of selectivity of the conventional ion exchange resins has led to the discovery and development of a new class of polymers.[5] Chelating ion exchange resins incorporating a variety of chelating groups on different types of polymeric matrices have been synthesized for the separation of metal ions owing to their greater selectivity over simple ion-exchange resins. The selectivity of most chelating groups for metals resides predominantly in their ability to form chelates with cations depending on the coordination number and the geometry of the ions.[6] A number of chelating resins containing such groups as iminodiacetic acid, amidoxime, aminophosphonic acid, oxine, thiols, pyridine etc., are now commercially available. Chelating resins containing ligands of amidoxime groups have attracted much attention in the separation of uranium.[7–18]

Synthesis of chelating polymers containing amidoxime groups by radiation-induced polymerization was studied in our previous works.[16–18] The use of high energy radiation in the synthesis of polymer has a dual effect; the crosslinking process usually accompanies radiation-induced polymerization of crosslinkable polymers at high doses.[19] The crosslinked structure of polymer is essentially required for the packed column application. Moreover, the crosslinked polymer might form a more stable complex with metal ions due to its rigid network structures.[20] The advantages of using radiation polymerization technique are as follows: (1) ionizing radiation initiates radical polymerization at ambient temperature in the absence of chemical initiators,[21] (2) the initiation step of radiation polymerization is temperature independent and the overall activation energies are much smaller than in the chemically initiated process,[17,22–24] (3) the resulting polymer is homogenous and free from any impurities and the molecular weight can be controlled by varying doses and dose rate,[25] and (4) the degree of crosslinking and solubility of the resulting polymer can be controlled by adjusting the radiation conditions.[26,27] Kinetic of radiation-induced polymerization of acrylonitrile was studied in detail in Part I.[17] The aim of the present work is to study the characterizations of chelating polymer adsorbent and its application in the separation of uranium from iron-rich silicate rock samples.

EXPERIMENTAL

Synthesis of chelating polymer

Radiation-induced polymerization

Radiation-induced homopolymerization was carried out in a Pyrex tube containing acrylonitrile monomer

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solution in DMF (45%) and exposed to cobalt-60-rays at a dose rate of 8.5 kGy/h, located at the National Center for Radiation Research and Technology (NCRRT), Cairo, under air atmosphere. The polymer yield was separated and washed several times by distilled water, then filtered, and dried at 70°C for 6 h.

Amidoximation

Amidoxime groups were introduced to the prepared polyacrylonitrile (PAN) by treatment with 3% hydroxylamine–alcohol solution at 70°C for 2 h under reflux. The resulted polyacrylamidoxime (PAO) was washed with distilled water to remove excess hydroxylamine, and then dried at 70°C for 6 h. The conversion of PAN into PAO was confirmed by FTIR analysis. The IR spectra showed the disappearance of the band associated with nitrile groups —C≡N and the appearance of a band at 3000–3500 cm^{-1} (broad, N—H and O—H stretching vibration), a band at 1650 cm^{-1} (C=N stretch vibration), and a third band at 920 cm^{-1} (N—O, stretch vibration).

Adsorption of metals

1.0 g granite (Gattar V, North Eastern Desert, Egypt) was digested in 30 mL of $4M$ HNO_3 and adjusted at pH of 2–3. Uranium and likely other heavy metals were separated from granite solution by PAO granules, using batch procedure. 0.5 g of PAO granules were added to the digested granite solution with stirrer. After 2 h, the PAO-metal complex was isolated on a small filter paper, washed with distilled water, and then dried. The qualitative and quantitative analysis of granite sample and PAO-complex were performed by X-ray fluorescence.
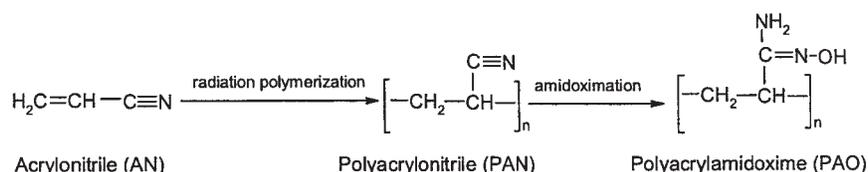
Measurements

FTIR spectra were measured for the samples in the form of KBr disk using Shimadzu-8201 FTIR Spectrometer. X-ray diffraction of the samples were recorded within the angle range $2\theta = 5$–50° on Shimadzu XRD-610 diffractometer using Cu K$_\alpha$ radiation. The data were collected at scan speed of 8 deg/min and 1.0 s at each step. The operating voltage and current were 30 kV and 20 mA, respectively. The prepared polymers were photographed by using Scanning Electron Micrograph (SEM) (JEOL 5400). The polymer sample was mounted with adhesive on specimen holder and then coated under vacuum with a thin layer of gold, scanned by oscilloscope viewing and TV monitoring before being photographically recorded in JOEL 5400-SEM. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed on DSC-50 (Shimadzu) and TGA-50 (Shimadzu) respectively, with a scan rate of 10°C/min in N_2 atmosphere. X-ray fluorescence (XRF) analysis was performed with a wavelength dispersive spectrometer-Philips (X' Unique II), equipped with flow and scintillation (fs) detectors. The X-ray tube equipped with Sc-Mo target was operated at 60 kV and 30 mA.

RESULTS AND DISCUSSION

Chelating polymer adsorbent containing amidoxime groups was synthesized by radiation-induced polymerization of acrylonitrile monomer and followed by hydroxylamine treatment of the resulting PAN granules as shown in Scheme 1:

H$_2$C=CH —C≡N $\xrightarrow{\text{radiation polymerization}}$ [—CH$_2$—CH—]$_n$ (C≡N) $\xrightarrow{\text{amidoximation}}$ [—CH$_2$—CH—]$_n$ (C=N-OH, NH$_2$)

Acrylonitrile (AN)   Polyacrylonitrile (PAN)   Polyacrylamidoxime (PAO)

Amidoximation reaction converts the active intermediate nitrile groups into the chelating amidoxime groups. The polymerization of PAN proceeds in a heterogeneous medium resulting in polymer precipitate in the reacting medium, and separate as a fine powder. The kinetic of radiation-induced polymerization of acrylonitrile in precipitating media was investigated in Part I.[17] The crosslinking process usually accompanies radiation-induced polymerization of crosslinkable polymers at high doses.[19] The crosslinked polymer ligand might form a more stable complex with metal ions than with a noncrosslinked polymer, and it might show some selectivities for metal ions because of its rigid network structure.[20]

Morphology properties

X-ray diffraction (XRD)

Figure 1(a,b) shows the XRD of PAN and PAO, respectively. The XRD of PAN shows an intense peak (100) reflection located at $2\theta = 17°$ and a weak peak at $2\theta = 29°$ superimposed on an amorphous halo. Conversion of PAN into PAO leads to the disappearance of the crystalline phase of PAN and
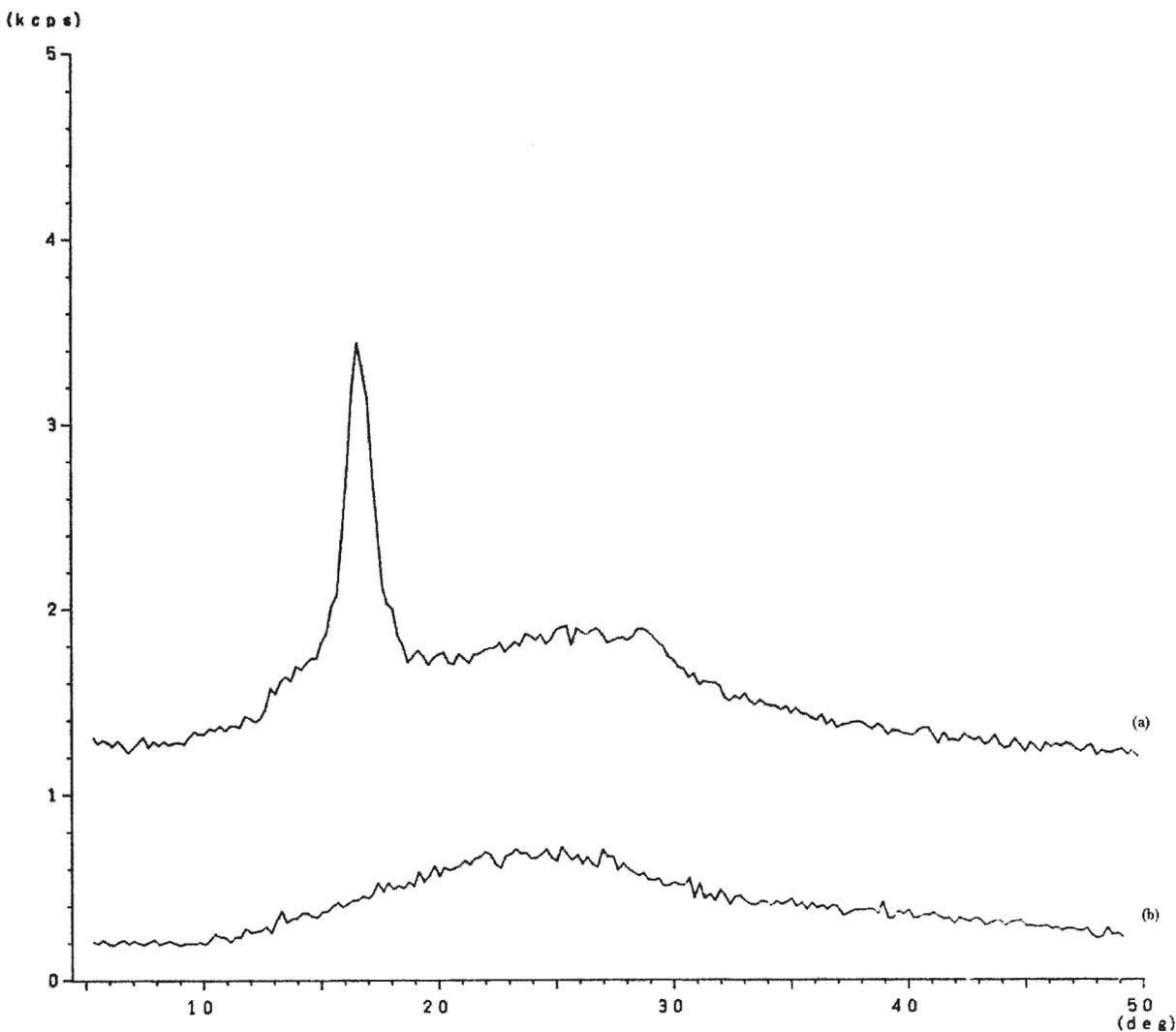
Figure 1 XRD of (a) PAN and (b) PAO.

the appearance of amorphous phase of PAO. The crystal lattice and the oriented structure of PAN are completely distorted because of the disappearance of stifflike conformation of PAN, resulting from the intermolecular repulsion of the nitrile dipoles. In addition, the hydrophilic nature of PAO reduces the degree of crystallinity; the adsorbed water disrupts the crytallinity by increasing the interchain distances.

Scanning electron microscopy (SEM)

Figure 2(a,b) shows the SEM of PAN and PAO, respectively. SEM of PAN shows microsphere particles. The monodispersity is obtained because of the initiation is rapid compared with the overall reaction time, and the period of repetitive nucleation is so short that monodispersity results from subsequent uniform growth on the existing nuclei.[28,29] The γ-ray produces

free radicals at a faster rate to initiate polymerization, and then insoluble polymer powder is formed as soon as the chain length has reached its solubility limit.[21,28] The subsequent amidoximation of PAN and its conversion into PAO lead to aggregate and stick the growing spheres together forming amorphous phase as shown in Figure 2.

Thermal properties

Figure (3) shows the TGA and DSC of PAN. The degradation of PAN starts at 315°C, which appeared as a single peak between 315 and 341°C in DTG thermogram. DSC shows a sharp exotherm in the temperature range 240–290°C. Figure (4) shows the TGA and DSC of PAO. The first step of the weight loss at low temperature indicates the hydrophilicity of PAO. The ratio of water content reaches to 10%. The degradation of PAO starts at 180°C and distrib-
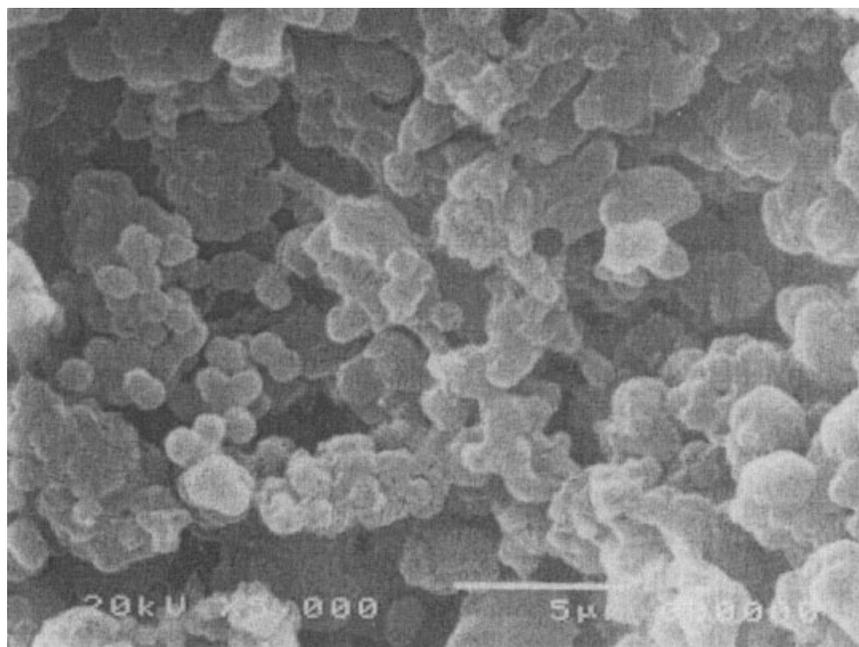
(b)
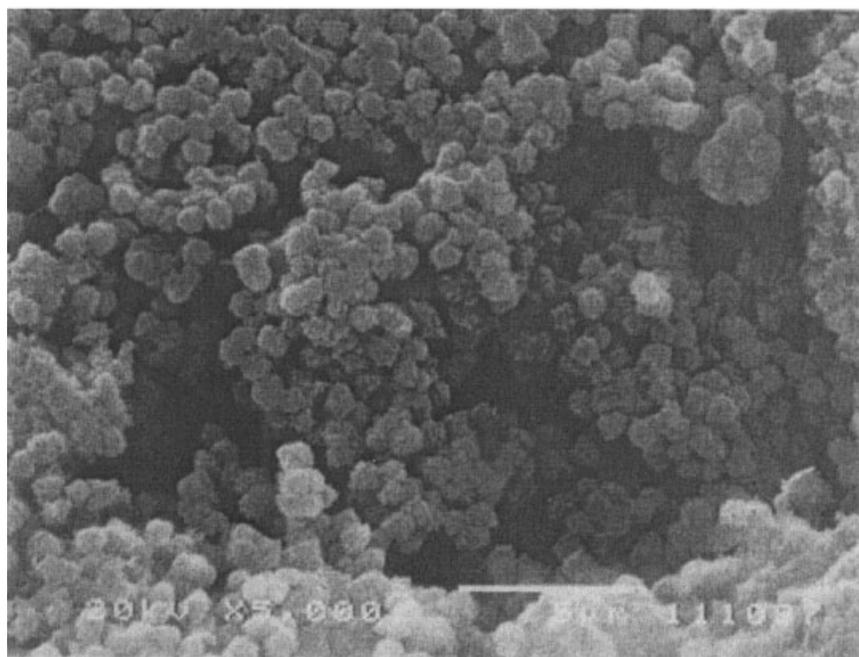
(a)

Figure 2   SEM of (a) PAN and (b) PAO.

utes over a broader temperature range. DSC shows an endothermic peak at 74°C corresponding to the removal of water molecules, confirming the hydrophilicity of PAO. A broader exotherm between 180 and 340°C with maximum peak at 263°C is observed. The exotherm of PAO is accompanied by two steps of weight losses, which appeared in two peaks at 210 and 264°C in DTG thermogram. The entropy of melting ΔS_m of PAN is 2.0, whereas the entropy of melting ΔS_m of PAO reaches to 7.1. This is attributed to the strong intramolecular repulsive force of PAN, which stiffens the molecular chains, thereby reducing the conformational disordering.
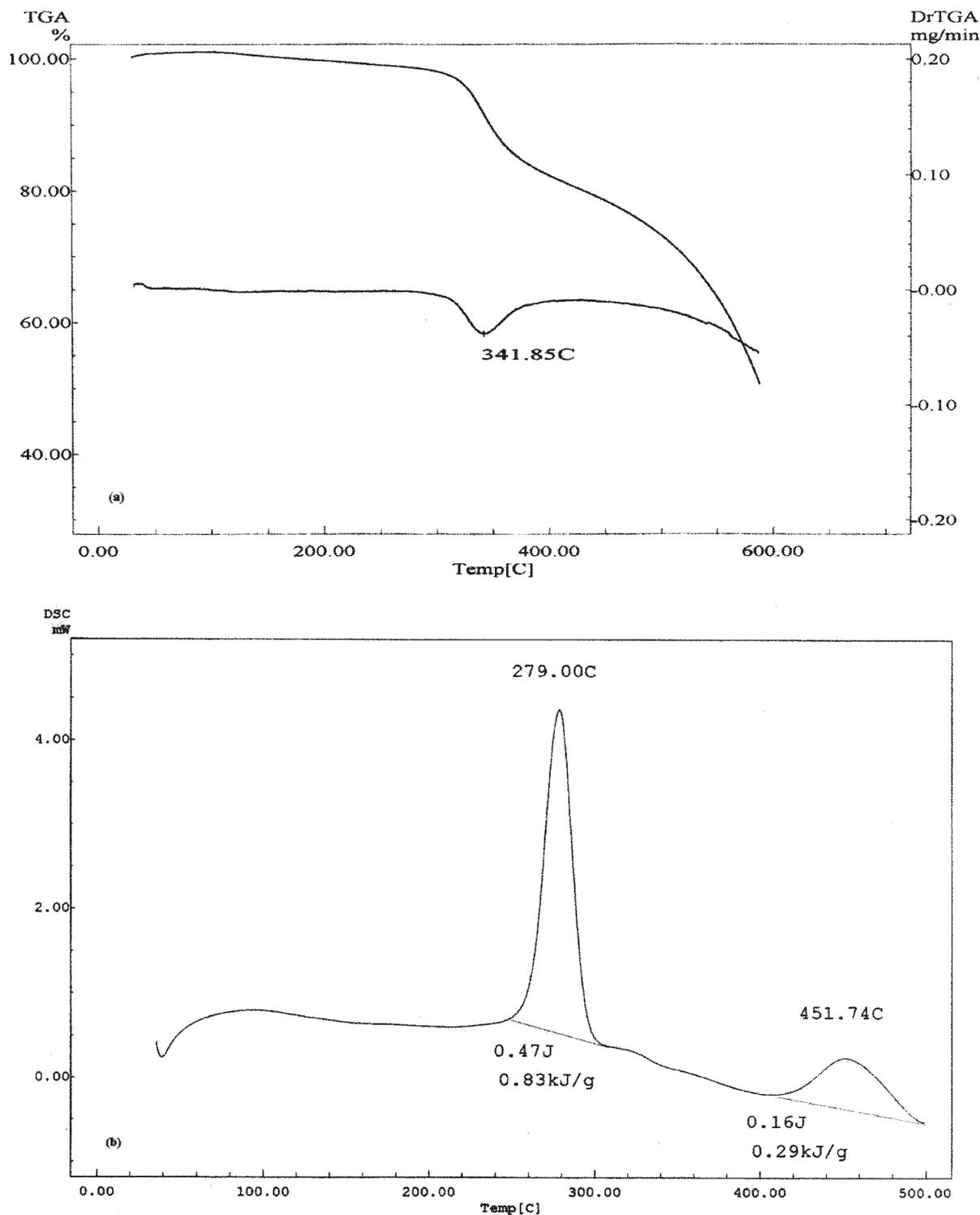
Figure 3 TGA and DSC of PAN.

Separation of uranium from iron-rich silicate rocks

Spectrophotometric analysis for the determination of uranium shows difficulties with Egyptian iron-rich silicate rocks (e.g., hematitized granites) because of the interference with some of the rock forming elements.

Application of PAO granules in the separation of uranium and likely other heavy metals from this rock was studied by batch experiment. Figure 5(a,b) shows the XRF spectrum of rock sample and PAO-metals complex. Elements detected qualitatively were U, Fe, Cu, Ni, Cr, V, K, and Ca. A significant increase in the
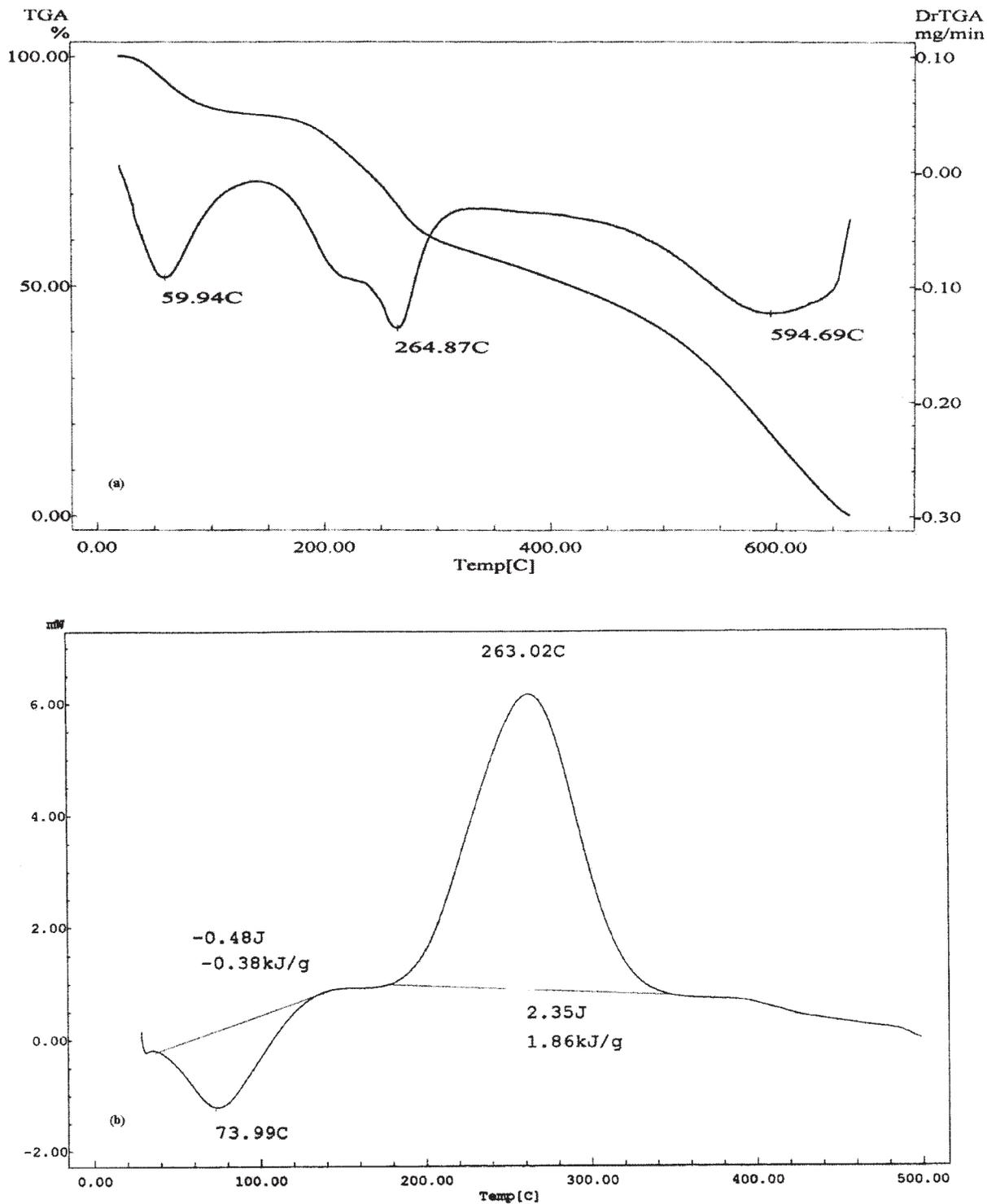
Figure 4 TGA and DSC of PAO.

intensity of U (L_α and M_α) spectra and a decrease in the intensity of K and Ca (K_α and K_β) spectra were observed for XRF of PAO-metals complex. The results of XRF quantitative analysis are shown in Table I. The selectivity of PAO against metals was determined by calculating the preconcentration ratio using the formula:

Preconcentration ratio

$$= \frac{\text{Concentration of metal adsorped on the PAO}}{\text{Initial concentration of metal in the granite sample}}$$

It is found that PAO possesses high selectivity for uranyl ion and low affinity for alkali and alkaline
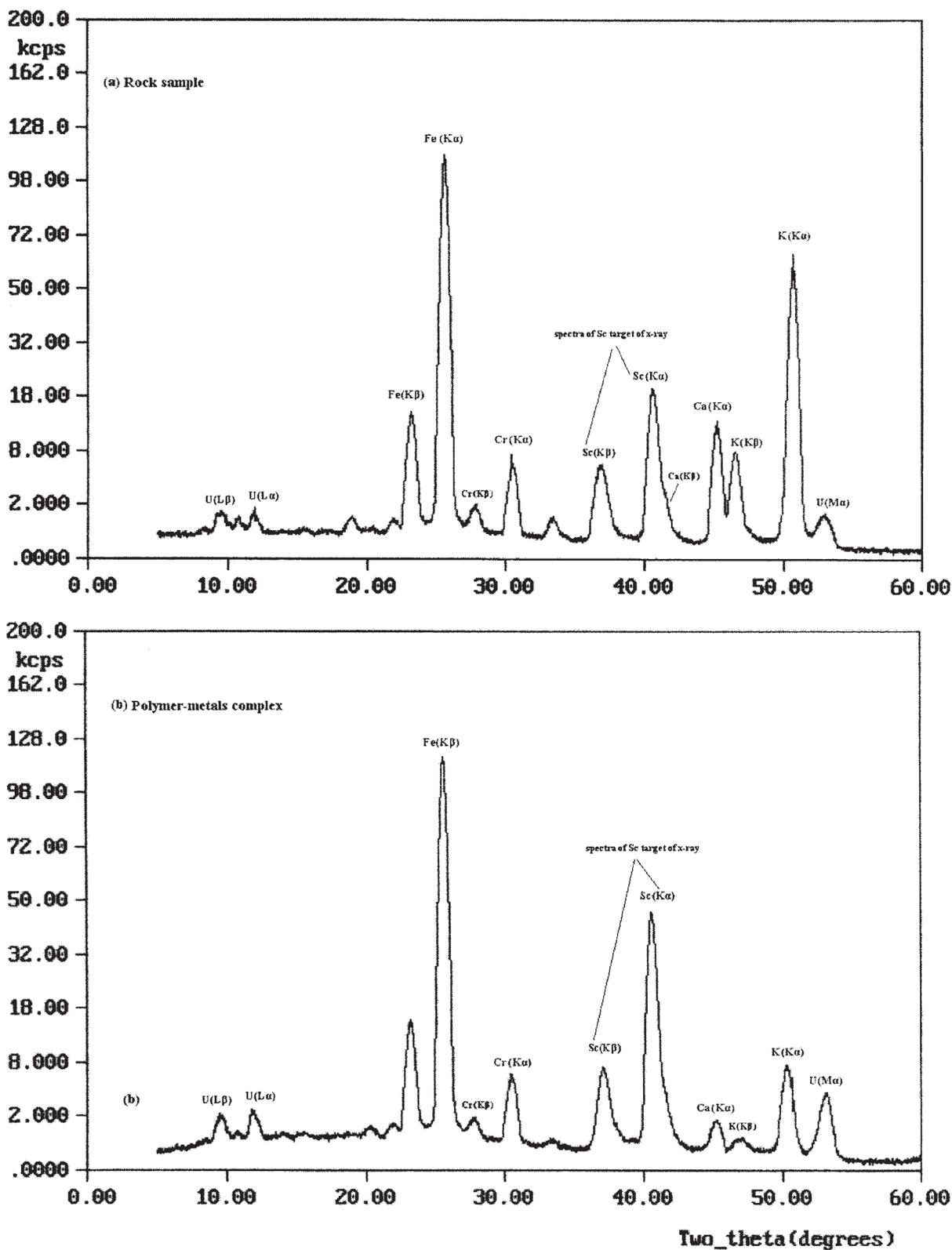
Figure 5 XRF spectrum of (a) rock sample and (b) PAO-metals complex.

earth metal ions. The order of selectivity was found to be $U \gg Cu > Fe > Ni > Cr > V \gg Ca > K$.

The high selectivity of PAO for uranium was attributed to the complexation of amidoxime groups with uranyl ion.[30] Amidoxime groups form ring structure during complexation with UO_2^{2+} ion, which prefer complexation by 6 coplanar donor atoms in equatorial plane of the ion.[31] Three of the amidoxime groups are

TABLE I
The Concentrations of Metals in the Rock Sample and PAO-Metals Complex Measured by XRF

Metals	Concentrations in granite (ppm)	Concentrations in PAO (ppm)	Preconcentration ratio
Fe	65.0×10^3 (6.5%)	86.0×10^3 (8.6%)	1.32
Ca	12.2×10^3 (1.22%)	2.1×10^3 (0.21%)	0.172
K	36.5×10^3 (3.65%)	2.9×10^3 (0.29%)	0.079
U	3027 (0.3%)	7154 (0.7%)	2.36
Cr	12.22	11.26	0.921
Cu	12.04	16.23	1.34
Ni	15.2	14.65	0.96
V	3.5	3.02	0.86

available to form a chelate with UO_2^{2+}, and the coordination number $n = 6$ gives the optimal distances for this chelation. The selective adsorption of uranyl ion by PAO is attributed to the difference of the stability constant of the complex between polymer ligand and metal ion (Scheme 2).
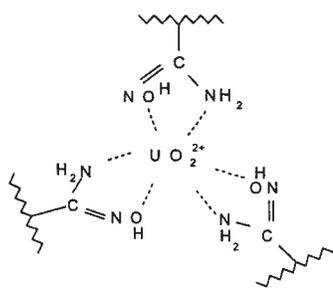
CONCLUSIONS

Chelating polymer adsorbent containing amidoxime groups based on PAN was prepared by γ-rays and followed by amidoximation reaction. Conversion of PAN into chelating polymer adsorbent was studied by FT-IR, XRD, SEM, TGA, and DSC. XRD and SEM showed the disappearance of the semicrystalline phase of PAN after conversion into polyacrylamidoxime. Thermal analysis studies showed that the degradation of PAN starts at 315°C, whereas the degradation of polyacrylamidoxime starts at 180°C and distributes over a broader temperature range. The chelating polymer adsorbent was investigated in the preconcentration of uranium from iron-rich silicate rock samples and subjected to XRF analysis. Selective adsorption for uranium and low affinity for alkali and alkaline earth metals were observed. The order of selectivity was found to be U ≫ Cu > Fe > Ni > Cr > V ≫ Ca > K.

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