# Synthesis of Poly[$N'$-(2-cyanoacetyl)acrylohydrazide] and Its Copolymers with Styrene and $N$-Phenylacrylamide: Characterization, Complexation, Thermal Stability, Swelling, and Morphology

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**ABSTRACT:** $N'$-(2-cyanoacetyl)acrylohydrazide (CAH) was obtained with the treatment of 2-cyanoacetohydrazide with acryloyl chloride in acetonitrile. The obtained acrlyoyl derivative was transferred to the corresponding polymer, poly[$N'$-(2-cyanoacetyl)acrylohydrazide] (PCAH), through treatment with 2,2'-azobisisobutyronitrile at 75°C. Copolymers with styrene or $N$-phenyl acrylamide monomers were synthesized with different ratios. The structures of these polymers were characterized with elemental analysis and spectral data. The morphology, metal uptake, and ion selectivity of the polymers were studied. In addition, the swelling behavior of the polymer and metallopoymer complexes at different times of drying was also investigated. Thermogravimetric analysis of the polymer and polymer complexes under air reflected that PCAH–Pb was the most stable, followed by PCAH, PCAH–Hg, PCAH–Cu, PCAH–Ni, and PCAH–Co. A similar stability with little difference was reported under nitrogen. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 200–210, 2010

**Key words:** copolymerization; morphology; synthesis; thermogravimetric analysis (TGA)

## INTRODUCTION

A polymer containing a hydrazide part in the main chain of the polymer was first reported in 1942 and was synthesized by the condensation of hydrazine with dicarboxylic acid.[1,2] Polyhydrazides are generally synthesized by the low-temperature solution polycondensation of dihydrazide with diacid chloride in amide solvents in the presence of an inorganic salt.[3–23] Polyhydrazides are high-performance materials. The polymers can be spun to fibers with exceptionally high moduli of elasticity to what are known as high-modulus fibers, and these are used to reinforce plastics and as tire cords. Polyhydrazide can be used in protective and decorative coating-strengthening agents, binders for nonoven fabrics, and textile finishing agents.[23] The syntheses of polymers containing hydrazide groups hanging on aliphatic backbone chains have been reported.[24,25] In general, the polymer properties can be modified through the preparation of their copolymers. The copolymers are capable of having different properties as a mixture of the monomer properties or new characteristics may appear. In general, a change in the surface of the copolymer compared to the polymer has been observed. The presence of an aromatic ring incorporated into the aliphatic polymer may provide a good and useful modification. This article reports the following: (1) the synthesis of $N'$-(2-cyanoacetyl)acrylohydrazide (CAH or **2**) and the corresponding polymer poly[$N'$-(2-cyanoacetyl)acrylohydrazide] (PCAH), (2) the investigation of the use of PCAH in waste treatment through the study of metal uptake and ion selectivity, and (3) the copolymer synthesis of CAH with styrene or $N$-phenylacrylamide (NPA or **3**) with the presence of an aromatic ring in the polymeric chain as one of our goals. The monomer, polymer, and copolymers were characterized with elemental analysis and spectral data.

## EXPERIMENTAL

### Materials

2-Cyanoacetohydrazide, acryloyl chloride, styrene, and aniline (Aldrich, Milwaukee, WI) were used as received. All metal salts and other chemicals were reagent grade and were used without further purification.

## Elemental analysis and physical measurements

Elemental analysis was performed on a LECO CHNS-932 elemental analyzer (USA). IR spectra were recorded as KBr discs of the monomers, polymers, copolymers, and metallopolymer complexes on a PerkinElmer system 2000 Fourier transform infrared spectrophotometer (Kyoto, Japan). ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker DPX 400 400-MHZ superconducting NMR spectrometer (Coventry, UK) in hexadeuterated dimethyl sulfoxide as the solvent and tetramethylsilane as an internal standard; chemical shifts were reported as δ (ppm). Scanning electron microscopy (SEM) for the polymers and copolymers was examined at room temperature with a JSM 6300 JEOL scanning electron microscope (Akishima, Japan) at 20 kV. Energy-dispersive spectroscopy (EDS) was performed with a LINK's ex1 Π energy-dispersive spectrometer (Oxford Instruments, Analytical, Hywycombe, Buks, United Kingdom) attached to the scanning electron microscope to measure the absorbed ion solution. Mass spectra were recorded on an Incos XL Finnegan MAT gas chromatograph/mass spectrometer (USA).

## Synthesis of the monomers, polymers, and copolymers

### Synthesis of CAH

An ice-cold solution of acryloyl chloride (0.01 mol) in acetonitrile (30 mL) was added dropwise to a cold solution of 2-cyanoacetohydrazide (0.01 mol) in acetonitrile (50 mL). The reaction was stirred for 2 h in the temperature range from 0 to −5°C. The solid product, so formed, gave the salt N′-(2-cyanoacetyl)acrylohydrazide hydrochloride (**1**). The reaction mixture was neutralized with a saturated solution of ammonium hydrogen carbonate to give CAH. The solid product was collected by filtration and then washed with cold water (2 × 100 mL) and crystallized from EtOH. The CAH melting point was 194°C (mp from refs. [24] and [25] = 195°C) with a yield of 90%.

ANAL. Calcd: C, 47.05%; H, 4.57%; N, 27.45%. Found: C, 47.06%; H, 4.41%; N, 27.26%.

### Synthesis of NPA

An ice-cold solution of acryloyl chloride (0.01 mol) in acetone (30 mL) was added dropwise to a cold solution of aniline (0.01 mol) in acetone (50 mL). The reaction temperature was kept in the range from 0 to −5°C for 2 h. The solid product (NPA) was neutralized with a saturated solution of ammonium hydrogen carbonate to give NPA. The solid product was collected by filtration and then washed with cold water (2 × 100 mL) and crystallized from EtOH. The melting point was 105°C (mp from refs. 26 and 27 = 104–105.5°C) with a 92% yield.

## Polymerization

*Synthesis of PCAH.* The polymerization of CAH (0.01 mol) was carried out in dimethylformamide (DMF; 50 mL) and 0.02 mol % 2,2′-azobisisobutyronitrile (AIBN) at 75°C for 3 h (water bath). PCAH was obtained after the cooling and treatment of the reaction mixture with an ethanol/water mixture (1 : 1 v/v) by filtration, and then, it was washed with ethanol (3 × 10 mL). The isolated polymer was refluxed in ethanol for 3 h for purification, filtered off while hot, and dried at 50°C under reduced pressure for 48 h. The same reaction product with very little difference in the yield was obtained without the bubbling of nitrogen gas during the polymerization process.

*Synthesis of the copolymers.* To a mixture of CAH and styrene or CAH and N-phenyl acrylamide (NPA) at different molar ratios (50 : 50, 30 : 70, or 20 : 80) in DMF (50 mL), AIBN (0.02 mol %) was added. The reaction mixture was heated to 75°C for 3 h. Then, the mixture was treated with an ethanol/water mixture (1 : 1); the solid product so formed was collected and then washed with ethanol (3 × 10 mL). The isolated copolymers were refluxed in ethanol for 3 h for purification, filtered off while hot, and dried at 50°C under reduced pressure for 48 h.

### Synthesis of the metallopolymer complexes

A solution of PCAH (0.01 mol) in DMF (20 mL) was added to 0.01 mol of $M(NO_3)_2 \cdot nH_2O$ (M = $Pb^{2+}$, $Hg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, or $Co^{2+}$) solution in DMF (20 mL). The reaction mixture was heated under reflux at 150°C for 3 h, left overnight, and filtered. The collected solid was washed several times with deionized water (4 × 10 mL), ethanol (3 × 10 mL), and diethyl ether (3 × 5 mL) and dried *in vacuo* at 60°C for 24 h.

## Ion selectivity measurements

A mixture of an aqueous solution containing 0.01 mol of $M(NO_3)_2 \cdot nH_2O$ (M = $Pb^{2+}$, $Hg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$) was added to 0.5 g of PCAH. The mixture was left for 24 h with shaking or without shaking and then filtered off. The concentration of the remaining metals in the aqueous solution was measured by inductively coupled plasma (ICP).

## Swelling measurements

A packet of dried polymer (PCAH) and its metallopolymer complexes were immersed in deionized water for 24 h. They were then removed from the water and hanged for 15 min; we then determined
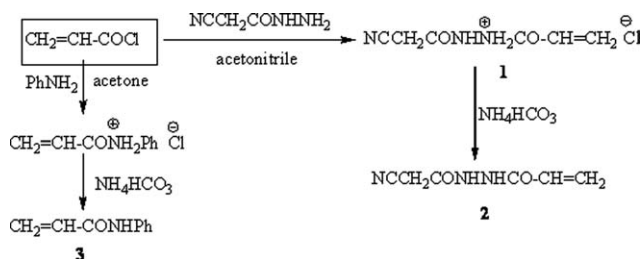
Scheme 1
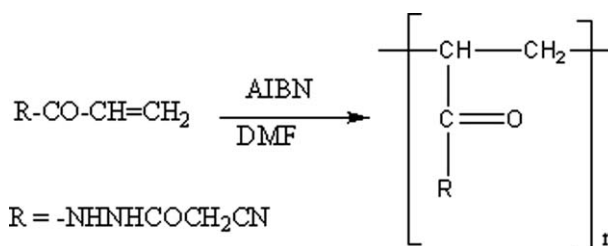


Scheme 2

the weight and reweighed the samples after 30 min. The swelling was calculated as follows:

$$\text{Swelling } \% = (W_s - W_p) \times 100/W_p$$

where $W_s$ and $W_p$ represent the weight of the swollen polymer or swollen polymer complexes and the initial weight of the polymer or polymer complexes, respectively.

## RESULTS AND DISCUSSION

### Synthesis of the monomer and polymer

The synthesis of CAH in aqueous media was described elsewhere.[25,26] In this study, synthesis in acetonitrile gave CAH in an excellent yield compared to that in aqueous media. This may have been due to the prevention of the expected side reaction of acryloyl chloride with water to form acrylic acid as a byproduct that consumed the amount of acryloyl chloride, which, of course, affected on the yield percentage. 1 was obtained when the solution of 2-cyanoacetohydrazide was treated in acetonitrile with the acryloyl chloride solution. This salt was neutralized with an ammonium hydrogen carbonate solution to afford the targeted monomer 2 (cf. Scheme 1). Compound 3 was prepared earlier,[27,28] whereas in this article, a modified method for preparation is described.

The radical solution polymerization of CAH was carried out in DMF solvent in the presence of AIBN at 75°C with a continuous stream of nitrogen gas bubbled through the reaction medium. The precipitation of the polymer was obtained via the addition of an ethanol/water mixture (1 : 1). The polymers

were collected by filtration and purified by refluxing in ethanol for 3 h. Scheme 2 shows the equation representing the formation of PCAH.

### Characterization of the monomer and polymer

The monomer CAH was characterized by elemental analysis and spectral data (cf. Table I). The elemental analysis data showed close agreement of the calculated and found values, which confirmed the formation of the suggested monomer CAH (cf. experimental). The spectral analysis of CAH is discussed in the following text.
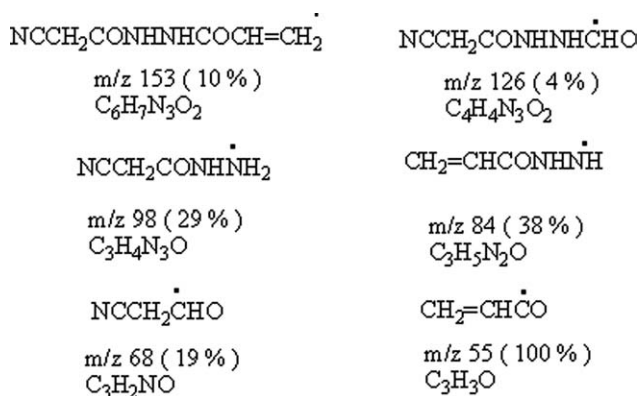
### Mass spectrum of the monomer

The mass spectrum of CAH showed $m/z$ at 153, which agreed with its molecular formula, $C_6H_7N_3O_2$. From the fragment pattern, it was clear that the base peak appeared at $m/z$ 55, which may have been rationalized to the stability of such an allylic radical. Other fragment structures at $m/z$ values of 126, 98, 84, and 68 are indicated in Scheme 3.

### $^1$H-NMR and $^{13}$C-NMR spectra of the monomer

The $^1$H-NMR spectra of CAH were recorded from a hexadeuterated dimethyl sulfoxide solution in the absence and in the presence of $D_2O$. The $^1$H-NMR spectrum of CAH exhibited a broad band at $\delta$ 10.37 ppm, which disappeared in the presence of $D_2O$. Therefore, this signal was assigned to NH protons. Its low field position and shape referred to the participation of the NH protons in hydrogen bonding. The signals due to ethylenic protons ($CH_2=$) appeared as a doublet at $\delta = 5.75$ and 5.73 ppm, and

TABLE I
IR, $^1$H-NMR, and $^{13}$C-NMR Data for the Monomer and Polymer

| Compound | IR | $^1$H-NMR | $^{13}$C-NMR |
|---|---|---|---|
| CAH | 3188 (NH), 3046 (ethylenic H), 2812 (aliphatic H), 2261 (CN), 1679 (CO), and 1598 (C=C) | 10.37 (br, 2H, 2NH), 6.32 and 6.29 (1H, CH=), 5.75 and 5.73 (2H, CH₂=), and 3.78 (2H, CH₂) | 164.04 and 162.01 (2CO), 130.15 (CH=), 128.35 (CH₂=), 116.68 (CN), and 24.78 (CH₂) |
| PCAH | 3498 (OH), 3247 (br, NH), 2929 (aliphatic H), 2263 (CN), and 1713 and 1664 (CO) | 10.25 and 9.80 (br, NH), 7.95 (br, OH), 3.83 (br, CH₂), 3.76 (br, CH), and 1.54 (br, —CH₂—) | 173.76 and 163.41 (CO), 116.66 (CN), 35.41 (CH₂), 31.81 (CH), and 24.77 (—CH₂—) |

$NCCH_2CONHNHCOCH=\overset{\cdot}{CH_2}$

m/z 153 ( 10 % )
$C_6H_7N_3O_2$

$NCCH_2CONH\overset{\cdot}{N}H_2$

m/z 98 ( 29 % )
$C_3H_4N_3O$

$NCCH_2\overset{\cdot}{C}HO$

m/z 68 ( 19 % )
$C_3H_2NO$

$NCCH_2CONHN\overset{\cdot}{H}CHO$

m/z 126 ( 4 % )
$C_4H_4N_3O_2$

$CH_2=CHCONH\overset{\cdot}{N}H$

m/z 84 ( 38 % )
$C_3H_5N_2O$

$CH_2=CH\overset{\cdot}{C}O$

m/z 55 ( 100 % )
$C_3H_3O$

**Scheme 3**



**Scheme 4**

CH= protons were represented at δ = 6.32 and 6.29 ppm. The upfield signal at δ = 3.78 ppm was characteristic for cyanomethylene protons (cf. Table I).

Table I shows the ^{13}C-NMR spectrum of CAH, which reveals the presence of signals at δ = 164.04 and 162.01 ppm for two carbonyl carbons, whereas ethylenic carbons appeared at δ = 130.15 and 128.35 ppm. The nitrile group carbon and methylene carbon appeared at δ = 116.68 and 24.78 ppm, respectively. Thus, the ^{1}H-NMR and ^{13}C-NMR data were in agreement and confirmed the structure of the monomer.

### Infrared spectra of the monomer and polymer

The IR spectra of CAH and PCAH were recorded as KBr discs. Table I shows the main bands with their tentative assignments.

The investigation of the spectral data showed the following points:

1. The spectrum of CAH displayed bands at 1598 $cm^{-1}$ due to —CH=CH$_2$. This band was not observed in the IR spectrum of the corresponding polymer. In addition to the sharp and strong band for NH of the monomer at 3188 $cm^{-1}$, a broad band in the polymer at 3498 and 3247 $cm^{-1}$ due to enolic OH and more NH bands, respectively, in the polymeric chain confirmed the polymerization via —CH=CH$_2$ groups.
2. The presence of cyano groups at 2261 and 2263 $cm^{-1}$ with respect to the CAH and its corresponding polymer, respectively, confirmed the polymerization without cyclization, as described by El-Mossalamy and Al-Thabaiti.[25]
3. The carbonyl group band traced at 1679 $cm^{-1}$ for CAH, whereas it appeared as a broad band split into two bands at 1713 and 1664 $cm^{-1}$ in the case of its polymer. This may have been due to the difference between the two carbonyl groups. The appearance of one of these bands
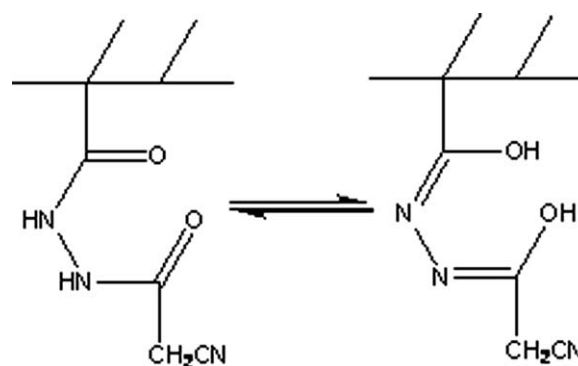
at a lower wave number compared with the monomer may have been due to the formation of H bonding, whereas the second one appearing at a high wave number referred to the free carbonyl group.

### ^{1}H-NMR and ^{13}C-NMR spectra of the polymer

The ^{1}H-NMR of PCAH showed a broad two bands at δ = 10.25 and δ 9.80 ppm due to the presence of NH protons. The bands at δ = 6.32, 6.29, 5.75, and 5.73 ppm in the monomer due to —CH=CH$_2$ disappeared; this confirmed the polymerization. In addition, a new band δ = 7.95 ppm as a singlet appeared, and this may have been due to the formation of OH groups in enolic form, as indicated in Scheme 4. A broad band at δ = 3.83 ppm referred to the presence of methylene groups, which shifted downfield because of the presence of α-cyano and α-carbonyl groups. Furthermore, methine protons and methylene protons appeared at δ = 3.76 and 1.54 ppm, respectively, as broad bands. All these data confirmed the polymerization of the monomer.

^{13}C-NMR of PCAH agreed with all of the data, which supported the polymerization of the monomer to its corresponding polymer. The carbonyl groups appeared downfield at δ = 173.76 and 163.41 ppm. The presence of cyano groups at δ = 116.66 ppm confirmed that the polymerization took place without cyclization. Other sp$^3$ carbons appeared at δ = 35.41, 31.81, and 24.77 ppm for the —CH$_2$CN, CH—, and CH$_2$ carbons, respectively. The disappearance of the ethylenic carbons confirmed the formation of the polymer.
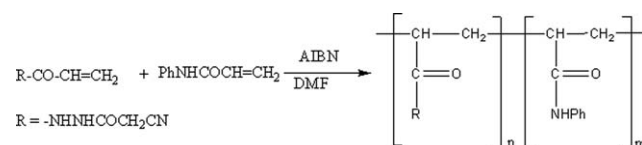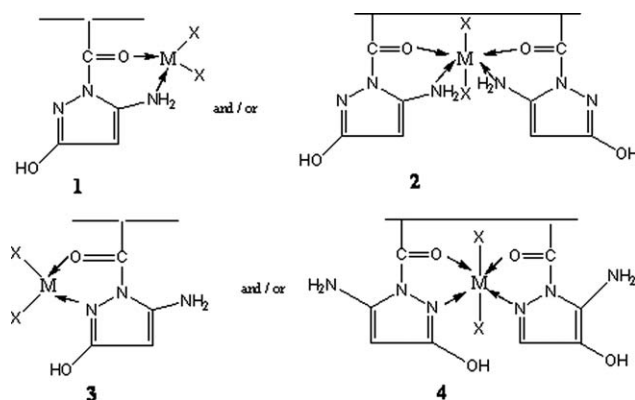


**Scheme 5**
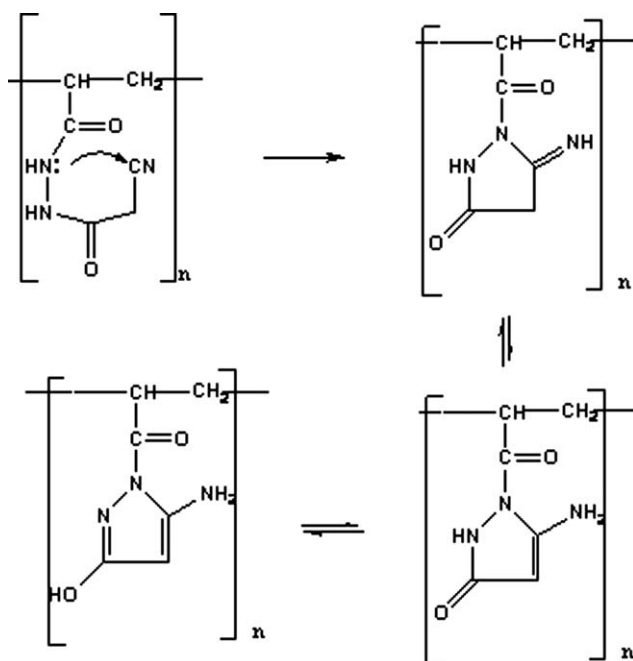
**Scheme 6**



**Scheme 7**

### Synthesis of the copolymers

A mixture of CAH and styrene or NPA with different ratios was heated at 75°C in the presence of AIBN to give the corresponding copolymers, PCAH-co-polystyrene (PS) and PCAH-co-poly(N-phenylacrylamide) (PNPA; cf. Scheme 5). Infrared spectra of the copolymers' skeletal vibration involving carbon–carbon stretching within the benzene ring at 1606 and 1600 cm$^{-1}$ for PCAH-co-PS and PCAH-co-PNPA, respectively, were observed. Moreover, other characteristic bands in the IR spectra of PCAH-co-PS at 1638, 1638, 1516, and 1222 cm$^{-1}$ were observed. The two copolymers exhibited bands of the monosubstituted aromatic bands at 900–675 cm$^{-1}$ because of the out-of-plane bending of the ring C—H bands. In-plane bending bands appeared in the range 1300–1000 cm$^{-1}$ in both copolymers.

### Formation of the metallopolymer complexes

The formation of the complex was obtained when a suspension of polymer and metal salt was heated under refluxing at 150°C for 3 h in DMF. Such reaction conditions helped in the intramolecular cyclization of hanging chains of the polymer to give the aminopyrazole derivatives.[24,25] This was observed and confirmed from the IR spectra, which revealed the disappearance of the cyano group and the appearance of amino function. The cyclization was assumed to proceed via the addition of a lone pair of nitrogen atoms to the cyano group followed by tautomerization to give the aminopyrazole derivatives, as indicated in Scheme 6.

### Infrared spectra of the metallopolymer complexes

The IR spectrum of the polymer revealed the presence of OH bands in the range from 3399 to 3448 cm$^{-1}$. The NH band appeared in case of the monomer at 3188 cm$^{-1}$, whereas in case of the polymer, NH appeared at 3247 cm$^{-1}$. This band disappeared in case of the polymer complexes with Hg, Pb, Cu, and Co, whereas in the case of Ni, a band at 3261 cm$^{-1}$ appeared. This explained the formation of the complex at NH$_2$ in all cases (cf. Scheme 7, structures 1 and 2) except in the Ni complex, where the pyrazole nitrogen lone pair was shared in complexation (cf. Scheme 7, structures **3** and **4**). Furthermore, the carbonyl group shifted ($\Delta\upsilon = 2$–16 cm$^{-1}$), which supported the conclusion that the carbonyl group shared in the complex formation.

**TABLE II**
**Ion Selectivity of PCAH from a Mixture Containing Pb, Co, Ni, Hg, and Cu Ions Without Shaking for 24 h at Room Temperature**

| Metal ion | Blank (mg/L) | ICP (mg/L) | pH value | Metal uptake (mg/L) | Metal uptake (%) |
|---|---|---|---|---|---|
| Pb | 2202 | 2190 | 5.5 | 12 | 0.5 |
| Co | 662 | 633 | 5.5 | 29 | 4.4 |
| Ni | 626 | 625 | 5.5 | 1 | 0.2 |
| Hg | 2774 | 375 | 5.5 | 2399 | 86.5 |
| Cu | 642 | 615 | 5.5 | 27 | 4.2 |

| Metal ion | Blank (mg/L) | ICP (mg/L) | pH value | Metal uptake (mg/L) | Metal uptake (%) |
|-----------|--------------|------------|----------|---------------------|------------------|
| Pb | 2007.57 | 61.76 | 3.5 | 1945.81 | 96.9 |
|    |         | 57.65 | 4.5 | 1949.92 | 97.1 |
|    |         | 76.74 | 5.5 | 1930.83 | 96.2 |
| Co | 573.53  | 17.01 | 3.5 | 556.52  | 97.0 |
|    |         | 16.35 | 4.5 | 557.18  | 97.2 |
|    |         | 22.42 | 5.5 | 551.11  | 96.1 |
| Ni | 558.01  | 16.75 | 3.5 | 541.26  | 97.0 |
|    |         | 15.74 | 4.5 | 542.27  | 97.2 |
|    |         | 21.44 | 5.5 | 536.57  | 96.2 |
| Hg | 8625.60 | 248.03 | 3.5 | 8377.57 | 97.1 |
|    |         | 184.83 | 4.5 | 8440.77 | 97.9 |
|    |         | 79.26 | 5.5 | 8546.34 | 99.1 |
| Cu | 658.51  | 10.79 | 3.5 | 647.72  | 98.4 |
|    |         | 3.52  | 4.5 | 654.99  | 99.5 |
|    |         | 5.58  | 5.5 | 652.93  | 99.2 |

## Ion selectivity

### Metal capacity of the chelating polymer as a function of pH

The metal capacities of the chelating polymer, PCAH, as a function of pH are reported in Tables II and III. As shown in Table II, only Hg ion uptake was very high, more than 86%, whereas all of the other metal ions were in the range 0.2–4.4%. This may have been because the size of Hg ions fitted better with the polymer cavities, which increased the embedding of Hg ions in the polymeric chain. Table II shows the data obtained without shaking, whereas Table III shows the data obtained with shaking. The observed extraction of metal ions was attributed to the complex formation with the hydrazide part of the polymer. This study was carried out at different pH values. The data were determined at pH = 3.5, 4.5, and 5.5. This study was also carried in a mixture of all metals (Pb, Co, Cu, Hg, and Ni) with shaking and without shaking with the same time of treatment. In general, the metal uptake was very low without shaking compared to that with shaking. The metal uptake of $Hg^{2+}$ without shaking

was greater than that of the other metals, which may have been because the $Hg^{2+}$ size fit the polymer cavities better than that of the other metal ions. The metal uptake percentage with shaking, as indicated in Table III, could be arranged in the following order: at pH = 3.5, $Cu^{2+} > Hg^{2+} > Co^{2+} > Ni^{2+} > Pb^{2+}$; at pH = 4.5, $Cu^{2+} > Hg^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+}$; and at pH = 5.5, $Cu^{2+} > Hg^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+}$. The adsorptions of $Cu^{2+}$ and $Hg^{2+}$ at all pH values were higher than those of $Co^{2+}$, $Ni^{2+}$, and $Pb^{2+}$. The higher metal uptake was observed at pH 4.5. These higher metal chelating capacities were attributed to the presence of the hydrazide group, which acted as a good chelating group. With respect to $Co^{2+}$, $Ni^{2+}$, and $Pb^{2+}$, it seemed that pH 3.5 was more selective for $Co^{2+}$, whereas 4.5 was selective for $Ni^{2+}$. In addition, pH 5.5 was more selective for $Pb^{2+}$.

## Thermogravimetry

Many studies on the thermal cyclization of polyhydrazide including hydrazide linkages in polymeric chains have been reported.[19] The thermogravimetric analysis (TGA) of PCAH and their metallopolymer
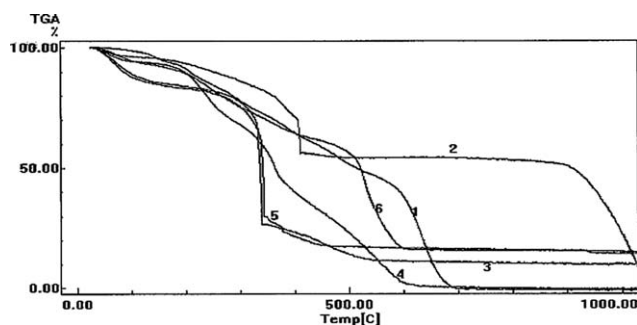


**Figure 1** TGA for PCAH and its complexes in air: (1) PCAH, (2) PCAH–Pb, (3) PCAH–Ni, (4) PCAH–Hg, (5) PCAH–Co, and (6) PCAH–Cu.
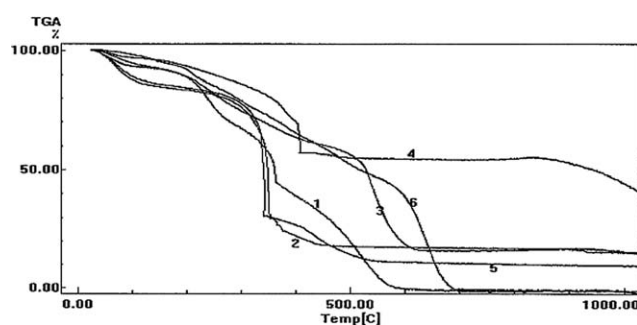


**Figure 2** TGA for PCAH and its complexes in nitrogen: (1) PCAH–Hg, (2) PCAH–Co, (3) PCAH–Cu, (4) PCAH–Pb, (5) PCAH–Ni, and (6) PCAH.
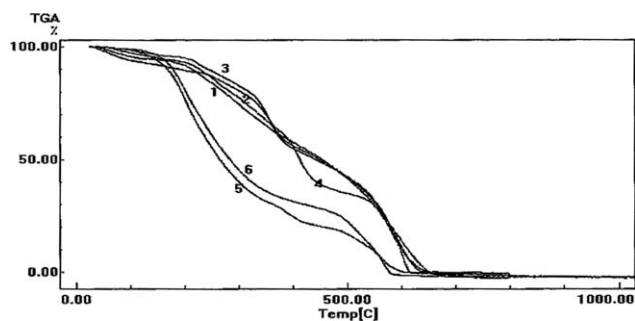
**Figure 3** TGA for the copolymers in nitrogen: (1) PCAH-*co*-PS (50 : 50), (2) PCAH-*co*-PS (20 : 80), (3) PCAH-*co*-PS (30 : 70), (4) PCAH-*co*-PNPA (50 : 50), (5) PCAH-*co*-PNPA (20 : 80), and (6) PCAH-*co*-PNPA (30 : 70).



**Scheme 8**

complexes data are given in Figures 1 and 2. The weight loss percentage (8–13%) for the polymer and its complexes in the temperature range 25–200°C was due to the loss of water absorbed or adsorbed within the compound in addition to H bonding in the polymeric material. The total weight loss was obtained in air and under nitrogen. From the TGA data, we observed that the PCAH had some little difference on behavior upon heating in air (Fig. 1), compared to heating under nitrogen (Fig. 2). Total weight loss was observed at about 694.54°C. All of the metal complexes were less stable than PCAH, except the $Pb^{2+}$ complex. The order of stability in air was as follows: $Pb^{2+} >$ PACAH $> Hg^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+}$, whereas under nitrogen, it was ordered according to the following: $Pb^{2+} >$ PACAH $> Cu^{2+} > Hg^{2+} > Ni^{2+} > Co^{2+}$. This order was similar to that under heating in air except in case of the $Hg^{2+}$ and $Cu^{2+}$ order.

The TGA data in air generally was more compatible with the metal uptake data, whereas as the metal uptake increased, the stability increased and was closer to that of the polymer. In addition, the stability increased and was closer to that of the polymer. The metal residue percentage in air was as follows: $Co^{2+} \approx Cu^{2+} > Ni^{2+} > Hg^{2+} > Pb^{2+}$, whereas that under nitrogen was $Pb^{2+} > Cu^{2+} \approx Co^{2+} > Ni^{2+} >$
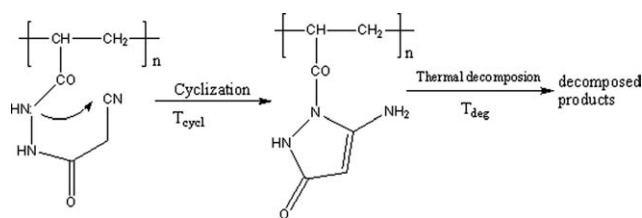
$Hg^{2+}$. The metal residue in the case of air may have been in the form of metal oxide or polyoxide, whereas in the case of nitrogen, a nitride may have formed. The polymer data reflected that the polymer was more stable than metal complexes; this may have been due to the energy required to cyclize the hung chain ($T_{cycl}$) to aminopyrazole and then the greater energy required for thermal decomposition ($T_{deg}$) of the new obtained polypyrazole.

## TGA of the prepared polymers and copolymers

In light of the TGA data for the copolymers (Fig. 3) versus the polymer, it was clear that the polymer was more resistant to heat than the copolymers; this may have been due to the fact that PCAH consumed some of the heat for cyclization (i.e., $T_{cycl}$) to the corresponding polypyrazole, which was followed by the additional heat needed for thermal degradation (i.e., $T_{deg}$; Scheme 8). Thus, the heat required for the thermal decomposition of the polymer seemed to be more than that needed for the copolymer. This was confirmed by study of the TGA of the copolymer, for example, the TGA of PCAH-*co*-PS, with different ratios. The copolymer was less stable than that of PCAH, where the side chain percentage, which cyclized, decreased. Thus, as the styrene percentage increased, the temperature of the complete weight loss percentage decreased. However, for the copolymers with 50, 70, and 80% styrene, the TGA showed complete weight loss at 670, 655, and 641°C, respectively. Similarly, TGA of PCAH-*co*-PNPA showed the same behavior. The TGA of the 50%

**TABLE IV**
**Swelling Data for the Polymer and Its Metallopolymer Complexes**

| Compound | Drying time (min) | $W_p$ | $W_s$ | Swelling (%) |
|---|---|---|---|---|
| PCAH | 15 | 0.2 | 0.362 | 81 |
| PCAH–Hg(II) | 15 | 0.2111 | 1.8557 | 779.1 |
| PCAH–Pb(II) | 15 | 0.1748 | 3.1045 | 1676.0 |
| PCAH–Co(II) | 15 | 0.106 | 1.4295 | 1248.6 |
| PCAH–Ni(II) | 15 | 0.2045 | 3.8112 | 1763.7 |
| PCAH–Cu(II) | 15 | 0.2027 | 2.044 | 908.4 |
| PCAH | 30 | 0.2 | 0.2973 | 48.7 |
| PCAH–Hg(II) | 30 | 0.2111 | 1.6266 | 670.5 |
| PCAH–Pb(II) | 30 | 0.1748 | 1.766 | 910.3 |
| PCAH–Co(II) | 30 | 0.106 | 1.2643 | 822.5 |
| PCAH–Ni(II) | 30 | 0.2045 | 1.8866 | 1092.5 |
| PCAH–Cu(II) | 30 | 0.2027 | 1.5818 | 680.4 |
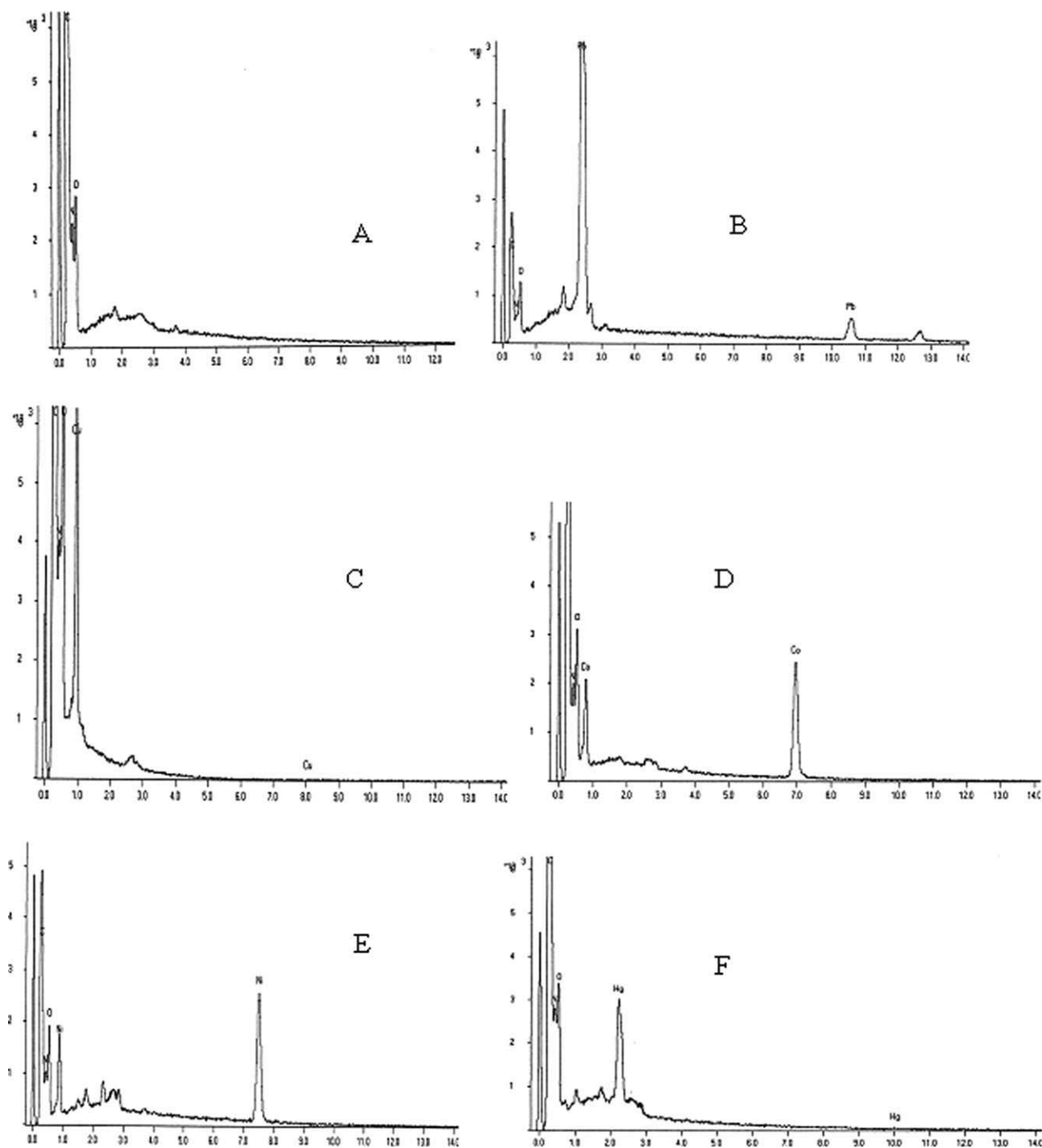
**Figure 4** EDS for (A) PCAH, (B) PCAH–Pb, (C) PCAH–Cu, (D) PCAH–Co, (E) PCAH–Ni, and (F) PCAH–Hg.

PCAH-*co*-PNPA copolymer showed complete weight loss at 665°C, whereas that of 70 and 80% PCAH-*co*-PNPA showed complete weight loss at 602 and 601°C, respectively.

**Swelling behavior**

It is known that the presence of a cyanoacetohydrazide chain as a hydrophilic side chain, which is able to form

H bonding with water molecules, should increase the water uptake of PCAH compared to polyethylene as a backbone chain. The swelling process was done through the immersion of the polymer or metallopolymer in a packet in distilled water, which was left for up to 24 h. Then, it was removed from water and dried by hanging for 15 min; this was followed by determination of the weight. The weight was also determined after 30 min of drying. Table IV shows the swelling data after

15 min of drying and 30 min of drying for the polymer and metallopolymer complexes. The water uptake of the polymer complexes was higher compared to that of the polymer itself. This may have been due to the dramatic changes in the surfaces of the polymer complexes, as indicated in the structure and morphology. The swelling percentages were calculated with the following equation:

$$\text{Swelling } \% = (W_s - W_p) \times 100/W_p$$

where $W_s$ and $W_p$ represent the weights of the swollen polymer or metallopolymer complexes and the weight of the polymer or metallopolymer before swelling, respectively. According to the data tabulated in Table IV, the water uptake was arranged in the following order: Ni complex > Pb complex > Co complex > Cu complex > Hg complex > Polymer.

### EDS

Figure 4 shows the EDS of the PCAH and their metallopolymer complexes. The data obtained from Figure 4(A–F) shows the EDS spectra of PCAH, PCAH–Pb, PCAH–Cu, PCAH–Co, PCAH–Ni, and PCAH–Hg. The data reflected that the absorption of these

metal ions was approximately in the same range. All these data confirmed the presence of metal ions.

### Structure and morphology of the polymer and copolymers

The morphologies of PCAH, the copolymer, and its metallopolymer complexes of $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Co^{2+}$ are shown in Figures 5 and 6. In general, the morphologies of the metallopolymers seemed to be completely different than that of the polymer itself. This difference may have been due to the strong embedding of the metal ions in the polymer matrix. The polymerization of CAH with the corresponding polymer with microstructure is described in terms of tactic shape.

Random coils of such a microstructure may have been probable in the case of the polymer, whereas in the case of an isotactic complex, it was more probable. The metal ions inserted between the R groups to form the metallopolymer complex, whereas the atactic form could not be ruled out. Thus, in the case of the metallopolymer, we had a mixture of different structures, so a dramatic change in morphology was observed. Figure 5(A) shows SEM of the polymer PCAH with a magnification of 750×. From a microgram, the surface of the polymer was round with cracking on the surface. Figure 6(A) represents the



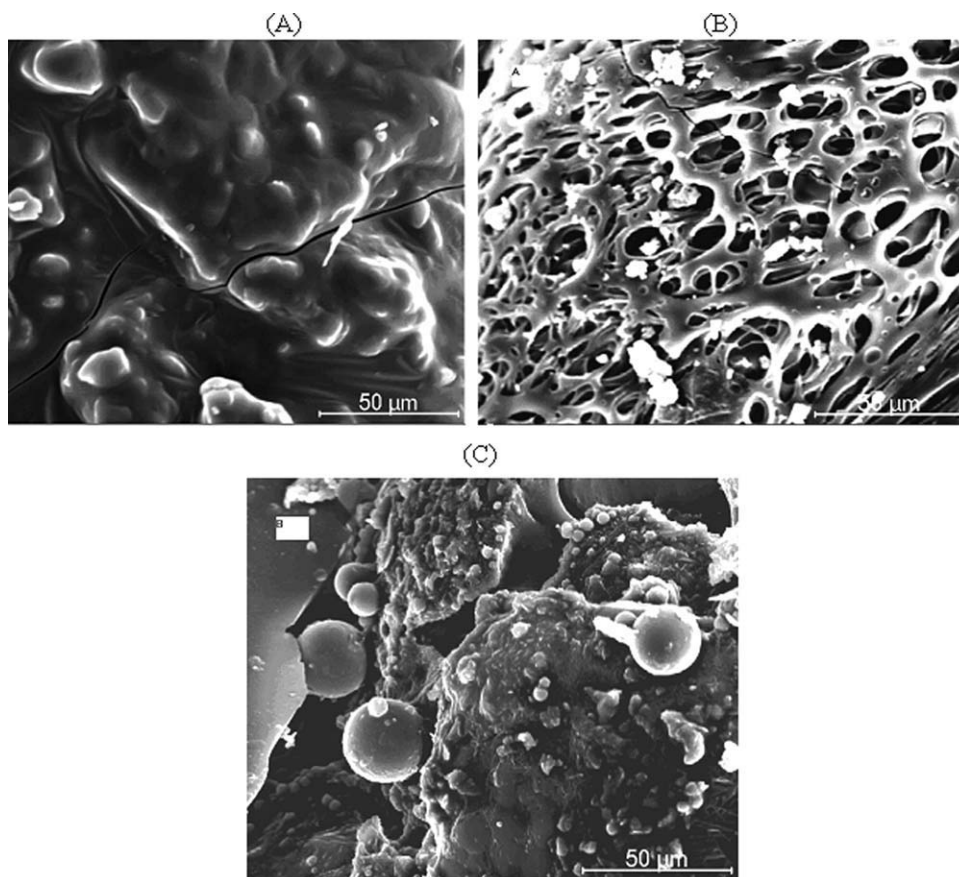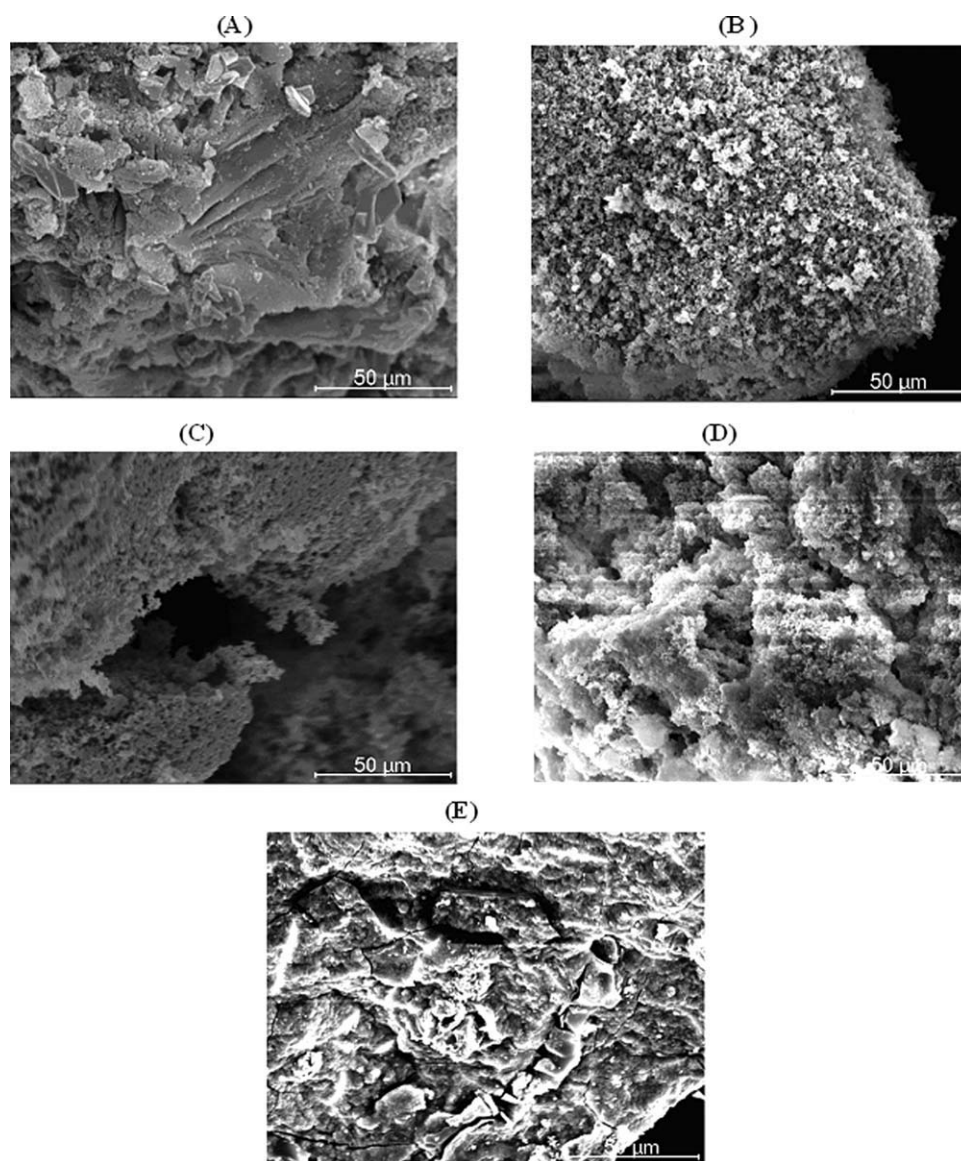**Figure 5**   SEM images of (A) PCAH, (B) PCAH-*co*-PS, and (C) PCAH-*co*-PNP.

**Figure 6** SEM images of (A) PCAH–Hg, (B) PCAH–Co, (C) PCAH–Pb, (D) PCAH–Ni, and (E) PCAH–Cu.

microgram of the PCAH–Hg complex, with its shape like a fine big platelet, whereas Figure 6(B) shows the microgram of the PCAH–Co complex, which shows a fine shape. Figure 6(C) represents the microgram of the PCAH–Pb complex, which seemed to be a big cavity. In addition, Figure 6(D) represents SEM of the PCAH–Ni complex, which had a stone shape. Figure 6(E) shows the microgram of the PCAH–Cu complex, which is like broad plates. The SEM of PCAH-*co*-PS [Fig. 5(B)] shows a different round shape nanoparticle with a size of 7.40 μm, whereas that of PCAH-*co*-PNPA [Fig. 5(C)] showed a small round nanoparticle with a size of 5.52 μm.

## CONCLUSIONS

The synthesis of CAH from the reaction of acryloyl chloride and cyanoacetahydrazide was performed in high yields, and then, CAH transferred to the corresponding polymer, PCAH, in the presence of AIBN and to various metallopolymer complexes. Copolymers of CAH with styrene and *N*-phenyl acrylamide with different molar percentages were also synthesized. CAH, PCAH, and the metallopolymer complexes were characterized by spectral data (i.e., IR, ^{1}H-NMR, and ^{13}C-NMR) and elemental analysis to assign structures. The ability of PCAH in waste treatment was investigated at different pH values to investigate the ion selectivity and metal uptake for mercury, lead, copper, cobalt, and nickel. All metal uptakes were in the range 96–99%. The swelling behavior reflected that the water uptake of PCAH–M was greater than that of PCAH. The thermal stability of PCAH and the PCAH–M complexes reflected the order of stability as PCAH–Pb followed by PCAH and then the other metal complexes. EDS

was used to confirm the structure of PCAH–M, and SEM reflected the change in the surface of PCAH due to complexation with different metals.

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