

Detection of Arsenic Agents by Polyhydroxamic Acid

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ABSTRACT: Arsenic agents are among the most destructive and fatal factors that exist in the environment, chemical agents, medicines, toxics, pesticides, etc., and working with these compounds is too limited and difficult due to their high toxicity. These deadly, dangerous, and weakening toxins are consumed for a large variety of purposes in the military industries. So measurement and identification of them are of great necessity. In this research work, acryl carboxyhydroxamic acid monomer was first prepared from acrylamide and then polymerized under radical conditions in the presence of azobisisobutyronitrile as an initiator. The produced polyhydroxamic acid (PHA) has antibacterial and anticancer properties as

well as high complex-forming properties with transition elements. By using the chelating properties of PHA, we took steps to identify arsenic agents such as trichloroarsine, dichloroethylarsine, and lewisites (I, II, III). This polymer, possessing unique properties, measures well the arsenic of low concentrations, lower than 10 ppm, existing in the samples within a very short time (a few seconds). We will also be able to perform qualitative assessments on it through instrumental methods or titration, if required. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2338–2343, 2011

Key words: detection; arsenic agents; polyhydroxamic acid

INTRODUCTION

Hydroxamic acids show remarkable chemical properties. The first reports concerning these compounds were provided by Lossen and Leibigs in 1869.¹ Sheradsky² presented modern methods for arylation of benzene and heterocycles. Hydroxamic acids and derivatives substituted on their nitrogen can react as bidentate ligands with metal ions such as Cu(II), Cr(III), Fe(III), etc. and create colored complexes.³ These compounds play an important role in taking the iron ion in the body metabolism.⁴ Hydroxamic acids are prepared through a reaction between halide acids and sodium aci-nitroalkanes. When the reaction is fulfilled in pyridine, the product will be benzoyl hydroxamic chloride. From the reaction of one monohydroxamic acid and one ketene results in a good product of dihydroxamic acid.

Reports of the use of hydroxamic polymers as ion exchangers have appeared sporadically over the past 50 years.⁵ Polymers are synthesized by either polymerization of vinyl monomers bearing hydroxamic acid groups^{6,7} or by converting functional groups in a polymer into hydroxamic acids.^{8,9} As in this case, chemical and physical properties of these polymers are improved.¹⁰ One of these chemical properties is the ability to complex with certain metal ions. A

large number of compounds have been produced from heteroaromatics containing hydroxamic acid groups that, in addition to high properties of complex-forming, show a good conductivity and suitable electrochemical behavior in electrode surface.^{11,12}

Arsenic (As) is an important environmental concern because of its high toxicity to a broad spectrum of living organisms at the level of parts per billion. The contamination of drinking water and groundwater with As has been reported in many parts of the world.¹³ As can exist in natural environment in three oxidation states: As⁵⁺, As³⁺ [or As(III)], and As⁰ [or As(0)]. The mobility and chemical form of As determine its toxicity.¹⁴ The trivalent inorganic forms, such as arsenic trichloride and arsenic trioxide, are highly toxic and are 60 times more poisonous than the metal, its pentavalent salts, or organo-As compounds.¹⁵ The behavior of As species will change, depending on the biotic and abiotic conditions of the water. The detection of trace amounts of As appears to be a pressing need as the scale of the As problem for nature and the human life has become clear. Indeed, a number of detection methods have been developed.¹⁶ Most of them possess limits of detection below the World Health Organization guideline values of 10 ppb. However, some methods for the determination of As at the level of the World Health Organization guidelines have also been developed, reported, and reviewed elsewhere.^{17,18} The reliable techniques are suitable for laboratory conditions only. In addition, they are time-consuming and not suitable for the routine

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analysis of a large number of samples. Therefore, a rapid, portable sensor needs to be developed to overcome these problems. The use of electrochemical methodologies^{16,19} for detecting As has recently come to the forefront of research as a possible means of fulfilling these requirements. In the last work, we investigated of sensing effects polystyrene graft polyaniline for cyanide compounds.²⁰ Cyanide agents are very dangerous compounds that are called "blood agents" and used as chemical warfare agents. So, we would like detect these compounds in low concentrations human for safety.

As agents are among the destructive and fatal factors that exist in the environment, chemical agents, medicines, toxics, pesticides, etc. On the other hand, working with these compounds is too limited and difficult due to their high toxicity. These compounds are consumed as deadly, dangerous, and weakening toxics for a large variety of purposes in military industries. Therefore, concentration, tracing, and identification of them are a great necessity. Identification and detection of the previous agents, however, have little been studied. Perhaps this is the reason for no reports being presented about consumption and application of them for military and nonmilitary purposes. In the present article, we will take an important step for fast identification of trichloroarsine (TCA), dichloroethylarsine (DCEA), and lewisiteI (LI), lewisiteII (LII) and lewisiteIII (LIII) through creation of coloring complexes.

MATERIALS AND METHODS

Instrumentals and materials

Melting points were measured with an electrothermal 9100 melting point apparatus. GC mass spectrometer (QP100 Shimadzu) was used for mass spectroscopy. Fourier-transform infrared spectrometer (FTIR; 8101 M-Shimadzu) was used in spectral measurements of the film and reported (sh = sharp, w = weak, m = medium, s = short, b = broad). Proton nuclear magnetic resonance (¹H-NMR, FT-¹H-NMR) spectra were recorded at 250 MHz on a Bruker WP 200 SY spectrometer. ¹H-NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and integration. FTIR spectra were recorded on a 8101 M-Shimadzu. UV-Visible spectra were obtained from films of tin oxide glass electrodes by Perkin-Elmer Lambda 15 spectrophotometer and mass spectra with a Kratos MS80.

Acrylamide (Fluka AG, Buchs SG) was recrystallized twice from methanol (analytical reagent grade) and dried in vacuum over silica gel for a week. The arsenic agents such as trichloroarsine (TCA) was purchased from Aldrich and dichloroethylarsine (DCEA), trade names: ethyldichloroarsine; ethylarsine dichloride. $M_w = 175$, liquid, colorless, m.p. =

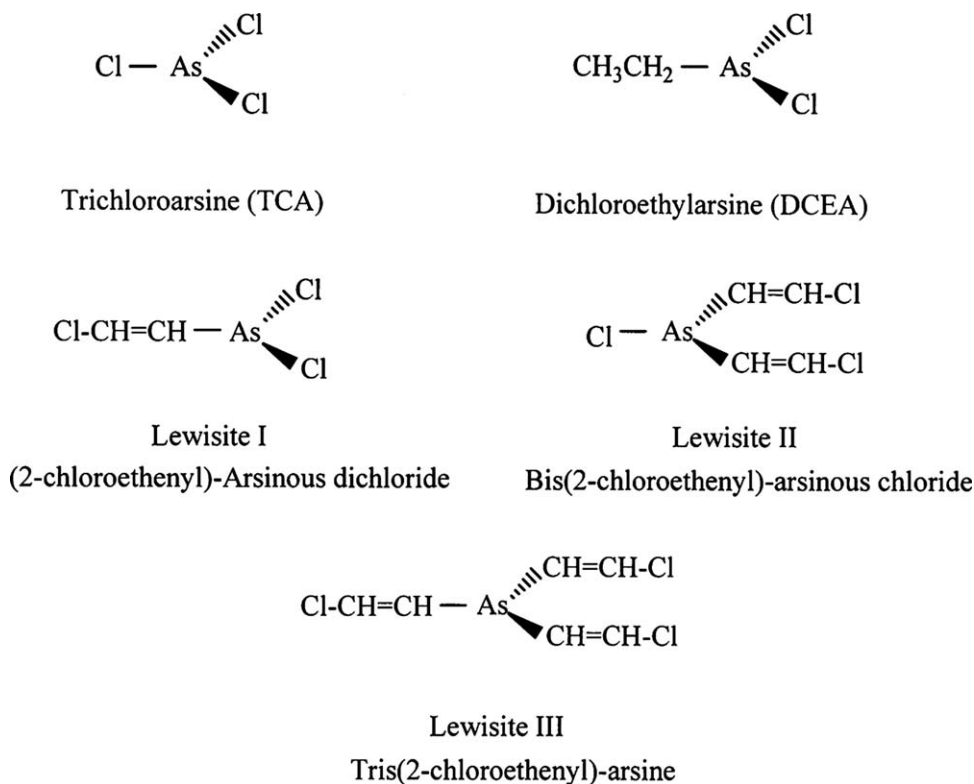
-65°C , b.p. (760 mmHg) = 156°C , $d_{14} = 1.742$ g/mL was prepared from Shanghai Chemical Company. Lewisite I (LI), index name: 2-chloroethenyl arsinous dichloride, trade names: dichloro(2-chlorovinyl)arsine; (2-chloroethyl)arsinoudichloride; 2-chlorovinyl-dichloroarsine. $M_w = 207.32$, liquid, brown, m.p. = 0.1°C , f.p. = -13°C , b.p. (760 mmHg) = 196°C , $d = 1.888$ g/mL, LCt50 = 1400 mg/min/m³, Lewisite II (LII), index name: bis(2-chloroethenyl)arsinous chloride, trade names: dichlorodivinyl-chloroarsine; arsinous chloride bis(2-chloroethenyl). $M_w = 233.32$ and Lewisite III (LIII), index name: tris(2-chloroethenyl)arsine, trade names: β,β,β' -trichlorovinylarsine, $M_w = 259.32$ (Scheme 1) were purchased from Shanghai Chemical Company via cell tube test (under control of Meysami national company security) and technical materials with 94–96% purities. Hydroxylamine hydrochloride (Fluka AG, CH-9470, Buchs) was used as purchased. Acetonitrile (Merck) was dried on silica gel, distilled on phosphorous pentoxide, and then on calcium hydride in the presence of a nitrogen stream. All the other materials used in this work were purified commercial products or were prepared by literature methods.

Preparation of acrylhydroxamic acid

To the appropriate acrylamide (0.05 mol) and hydroxylamine hydrochloride (13.9 g, 0.2 mol) dissolved in 80 mL methanol, 50 mL KOH (5M) are added dropwise with stirring. After stirring for 36 h at room temperature, methanol is evaporated and the solid residue is acidified with acetic acid/water (50 : 50; 50 mL) and extracted with ethyl acetate (3 × 50 mL). The concentration of organic phases affords an oil, which after azeotropic coevaporation with toluene (2 × 20 mL) and then with ethanol (2 × 20 mL) afforded a solid. Washing with ether (10 mL) gave acrylcarbohydroxamic (yield, 87%), mp = 87°C , UV: $\lambda_{\text{max}} = 207$ nm (intensity = 2.54) in acetonitrile, FTIR: 3450(w), 3080(s), 1690(w), 1600(sh), 1420(s), 1020(m), 990(sh), 885(sh) cm⁻¹, mass spectrum: (20 eV) $m/e = 87$.

Preparation of poly(hydroxamic acid)

Poly(hydroxamic acid) (PHA) was prepared by polymerizing a solution of acrylhydroxamic acid (95 : 5 v/v), water/DMF with azobisisobutyronitrile in N₂ atmosphere at 60°C and after 30 min the polymer thus produced precipitated in ice methanol. PHA prepared has the highest percentage of hydroxamic acid (100%) functional group, which was to be prepared for the first time. FTIR: 3435(w), 2983(sh), 1690(w), 1550(sh), 1426(m), 1230(m), 1030(m), 925(m), 870(s), 720(s) cm⁻¹. Elemental analysis: calculated: %C = 41.49, %H = 5.75, %N = 16.09, %O = 36.78; found: %C = 42.22, %H = 5.76, %N = 15.68, %O = 36.3.

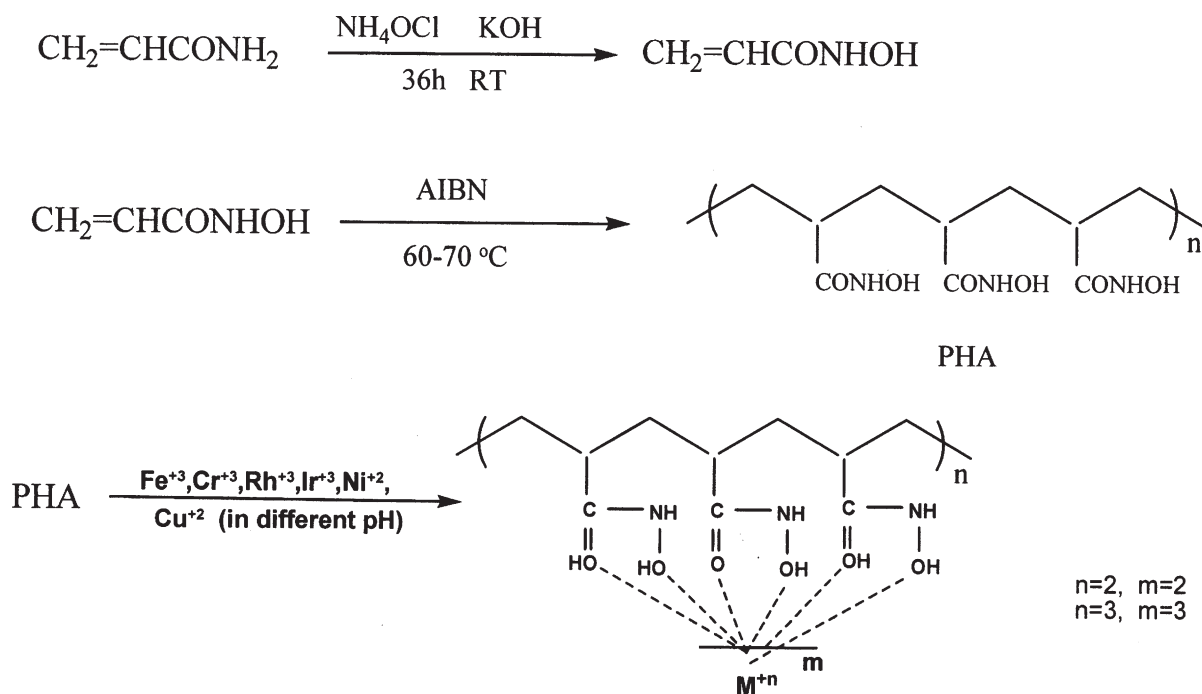


Scheme 1 Index and trade names of arsenic agents.

General preparation of metal complexes with PHA

The preparation of metal complexes with PHA is depicted in Scheme 2 and carried out the same as in our works.^{3,12}

M = Fe, PHA (0.05 g) was added under N₂ atmosphere to a solution of anhydrous FeCl₃ (0.191 g, 1.17 mM) in 50 mL tetrahydrofuran (THF) containing 4 mL pyridine. The mixture was stirred for 5 h



Scheme 2 PHA and its metal complexes.

TABLE I
Number-Average Molecular Mass of the Components
Resulted from Fractional Decantation of
PHA Through GPC Method

Fraction	M_n	M_w	I
1	105,700	179,690	1.7
2	96,600	144,900	1.5
3	75,400	105,560	1.4
4	36,000	50,400	1.4

at room temperature and evaporated under reduced pressure to give a solid residue. The remains were washed several times with ether and then dissolved in 100 mL dichloromethane and washed with water; the organic layer was separated and finally after evaporating the solvent gave the red color complex.

FTIR (PHA-Fe^{III}): 3430(w), 2989(sh), 1582(m), 1429(m), 1045(sh), 980(sh), 870(m), 770(m) cm⁻¹. UV-Visible (PHA-Fe^{III}): λ_{\max} = 260 nm (intensity = 1.41), 340 nm (intensity = 1.14), 470 nm (intensity = 7.81) in acetonitrile.

M = Al, PHA (0.05 g) was dissolved in 10 mL water and then was added to a solution (gel form) of 30 mL ethanol dissolved freshly Al(OH)₃ (0.780 g, 0.01M). The mixture was heated 20 min until boiling and then cooled. The precipitate was separated. It was an violet color complex.

FTIR (PHA-Al^{III}): 3450(w), 3005(sh), 2980(sh), 1590(m), 1440(m), 1049(sh), 985(sh), 876(m), 780(m) cm⁻¹.

M = Rh, PHA (0.05 g) was dissolved in 10 mL ethanol. Then the solution was added to a solution of 45 mL water dissolved RhCl₃ (2.094 g, 0.01M) and sodium acetate (2 g). The mixture was heated 10 min until boiling and then cooled. The precipitate was separated. It was an orange color complex and it was recrystallized with ethanol.

FTIR (PHA-Rh^{III}): 3460(w), 2990(sh), 1610(m), 1530(m), 1440(m), 1070(sh), 890(sh) cm⁻¹. UV-Visible (PHA-Rh^{III}): λ_{\max} = 360 nm (intensity = 0.85), 430 nm (intensity = 0.50) in acetonitrile.

M = Ir (NH₄)₃IrCl₆ (4.591 g, 0.01M) and sodium acetate (0.9 g) were dissolved in 10 mL water. The ethanol was added until a gel precipitate was obtained and then the solution of PHA (0.05 g) in 10 mL ethanol was added. The mixture was heated at 50°C for 2 h, cooled, and stirred 3 days in room temperature. The crude material was purified on a silica gel column chromatography with appropriate solvents (benzene/petroleum ether 50/50). This red color complex was recrystallized in dichloromethane/ethanol.

FTIR (PHA-Ir^{III}): 3430(w), 2995(sh), 1610(m), 1425(m), 1067(sh), 870(sh) cm⁻¹. UV-Visible (PHA-Ir^{III}): λ_{\max} = 350 nm (intensity = 0.76), 470 nm (intensity = 0.35), 530 nm (intensity = 0.15) in acetonitrile.

M = Cr, Cr(NO₃)₃·9H₂O (3.2 g, 8 mM) was dissolved in 30 mL water and stirred magnetically.

Then PHA (0.05 g) dissolved in 150 mL of water was added, followed by 0.1 normal of NaOAC-HOAC for attaining a fixed pH 4.7. The final mixture was stirred 12 h at room temperature. After filtering, a blue solid precipitate was obtained and recrystallized from THF.

FTIR (PHA-Cr^{III}): 3440(w), 2990(sh), 1600(m), 1430(m), 1040(sh), 980(sh), 850(m) cm⁻¹.

M = Cu, CuCl₂·2H₂O (0.042 g, 0.25 mM) was dissolved in 20 mL water and then PHA (0.05 g) was added into it, and the pH 4–5 with dilution with H₂SO₄ was reached. The green color complex was obtained by washing with water and ether and then dried.

FTIR (PHA-Cu^{II}): 3630(w), 2920(sh), 1605(m), 1430(m), 1040(sh), 1030(sh), 870(m) cm⁻¹. UV-Visible (PHA-Cu^{II}): λ_{\max} = 360 nm (intensity = 1.10), 460 nm (intensity = 0.80) 560 nm (intensity = 0.35) in acetonitrile.

M = Ni, NiCl₂·2H₂O (0.059 g, 0.25 mM) dissolved in 10 mL water was added to the solution of PHA (0.05 g) dissolved in 20 mL water. Diluted NaOH was added until fixed pH 8.3. The blue precipitate was obtained; after washing with water and ether, the pure blue color complex was obtained.

FTIR (PHA-Ni^{II}): 3420(w), 2960(sh), 1595(m), 1429(m), 1045(sh), 1040(sh), 880(m) cm⁻¹.

M = Co, To an aqueous mixture of freshly prepared Co(OH)₃ was added an excess of PHA (0.05 g) and stirred for 12 h at room temperature. A pink complex was obtained.

FTIR (PHA-Co^{II}): 3460(w), 2990(sh), 1610(m), 1435(m), 1050(sh), 1001(sh), 880(m) cm⁻¹.

M = Pt, A solution of K₂PtCl₄ (0.305 g, 0.735 mmol) in 10 mL water was added dropwise to a rapidly stirred solution of PHA (0.05 g) in 10 mL acetone. The reaction mixture was heated for 15 min at 55°C, stirred for 12 h at room temperature, and heated for 3 h at 55°C again. The mixture was cooled, and the produced yellow precipitate was filtered and washed with hot water.

FTIR (PHA-Pt^{II}): 3500(w), 2890(sh), 1605(m), 1429(m), 1050(sh), 890(sh), 870(m), 780(sh) cm⁻¹.

M = Pd, A solution of PdCl₂ (0.662 g, 0.373 mmol) in 100 mL phosphate buffer pH 6.0 (0.1M) was added slowly to a stirred solution of PHA (0.05 g) in 20 mL of the buffer. The brown solution was stirred for 2 days at room temperature and then precipitated was dried in vacuum.

FTIR (PHA-Pd^{II}): 3440(w), 2910(sh), 1590(m), 1433(m), 1045(sh), 1010(sh), 890(m), 790(sh) cm⁻¹.

Preparation of PHA with TCA and DCEA complexes

The PHA (0.1 g) was added under N₂ atmosphere to a suspension solution of anhydrous arsenic agents as arsenic, dichloroarsenic and trichloroarsenic (1.5

TABLE II
Time of Starting of Complex-Forming for PHA and Some of the Ions

Metal	Time (min)	Color	Metal	Color	Time (min)
Fe(III)	0.015	Red	Ni(II)	Blue	0.5
Al(III)	10	Violet	Cu(II)	Green	5
Rh(III)	10	Orange	Pd(II)	Brown	60
Cr(iii)	60	Blue	Pt(II)	Yellow	120
Ir(III)	120	Red	Co(II)	Pink	180

mmol) in 50 mL THF containing 1 mL pyridine. The mixture was stirred for 5 h at room temperature and evaporated under reduced pressure to give a solid residue that was washed several times with ether water. The organic layer was separated and evaporation of the solvent gave the brown-red color complex. FTIR(PHA-TCA): 3435(m), 2983(m), 1680(s), 1550(m), 1426(m), 1220(m), 1095(sh), 940(m), 880(m), 710(s) cm^{-1} . FTIR(PHA-DCEA): 3398(w), 3005(s), 2993(sh), 1675(m), 1589(m), 1420(m), 1085(sh), 985(sh), 880(m) cm^{-1} . UV-Visible (PHA-TCA): $\lambda_{\text{max}} = 215$ nm (intensity = 2.14), 270 nm (intensity = 2.11), 650 nm (intensity = 1.3) in acetonitrile. UV-Visible (PHA-DCEA): $\lambda_{\text{max}} = 210$ nm (intensity = 1.20), 260 nm (intensity = 1.35), 550 nm (intensity = 0.53) in acetonitrile.

Preparation of PHA with LI, LII, and LIII complexes

The PHA (0.1 g) was added under N_2 atmosphere to a solution of anhydrous arsenic agents as lewisite (I, II, III) (1.5 mmol) in 50 mL THF containing 1 mL pyridine. The mixture was stirred for 5 h at room temperature and evaporated under reduced pressure to give a solid residue which was washed several times with ether and then dissolved in 100 mL dichloromethane-washed water. The organic layer was separated and evaporation of the solvent gave the brown-red color complexes. FTIR: 3300–3400(m), 2950–3010(sh), 1670–1690(m), 1580–1630(m-sh), 1425–1450(m), 1050–1100(sh), 950–980(sh), 850–880(s) cm^{-1} . UV-Visible: $\lambda_{\text{max}} = 210$ –220 nm (intensity = 2–2.5), 240–260 nm (intensity = 2–2.7), 500–650 nm (intensity = 0.5–1) in acetonitrile.

RESULTS AND DISCUSSION

Polyacrylhydroxamic acid has been purified through reprecipitation in methanol and the molecular weight of fractions has been measured by GPC method. The results reached through this review have been summarized in Table I. Molecular weight of fractions and dispersion index are well. We used No. 1 fraction for all measurements.

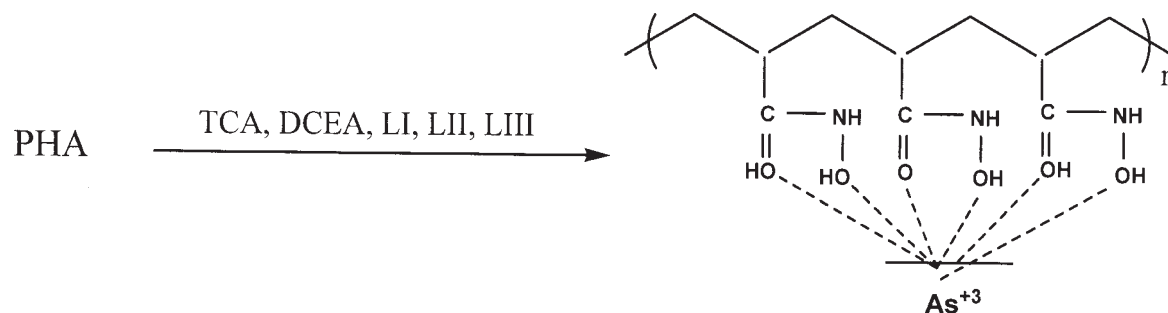
In continuation of previous work,^{3,12} we prepared a large number of complexes from PHA and transition metals such as Fe, Al, Rh, Cr, Ir, Cu, Ni, Co, Pt, and Pd under different pHs. Table II shows the starting times of complex formation for PHA-metals and the change of color for each of these complexes. Scheme 2 shows PHA and its metal complexes. Formation of PHA-Fe_{III} complex is very fast, so its K_f is highest.

Using the chelating power of PHA, we have taken steps to identify and measure the arsenic agents such as TCA, DCEA, LI, LII, and LIII. Table III indicates color changing times as well as complex-forming of arsenic agents in different concentrations. As indicated by the results, minimum concentration for identification with suitable change in color is 5–10 ppm. Scheme 3 shows typical PHA-As agent complexes.

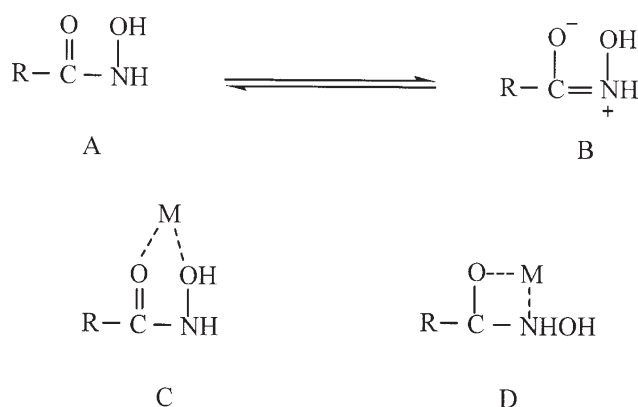
From the FTIR spectra of these complexes, we could evaluate the type of hydroxamic acid coordination. The electronic structure of hydroxamic acids may be shown by hybrid resonances of A-D that have been shown in Scheme 4. If the coordination of hydroxamic acids occurs via a nitrogen atom (D), then the structural contribution of (B) will decrease. If this coordination occurs via an oxygen atom (C), the structural contribution of (A) will decrease. If in

TABLE III
Color Changing Time of Complex-Forming with PHA and Different Arsenic Agents

Concentration (ppm)	Time of color changing (s)				
	PHA-TCA	PHA-EDCA	PHA-LI	PHA-LII	PHA-LIII
5	30	40	55	60	95
10	25	25	30	35	85
20	18	20	25	28	75
40	15	20	20	20	70
60	10	15	18	20	65
80	6	15	15	17	60



Scheme 3 Typical PHA-As agent complexes.



Scheme 4 Hybrid resonances of PHA (A-D).

the spectra of complexes in comparison with free ligand (PHA), $\nu(\text{C}=\text{O})$ shifts to a higher frequency and $\nu(\text{C}-\text{N})$ shifts to a lower frequency, this will indicate ligand coordination via a nitrogen atom [(A)

TABLE IV
FTIR Data (cm^{-1}) of PHA and Its Complexes

Sample	Vibration ($\text{C}=\text{O}$)	Vibration ($\text{C}-\text{N}$)
PHA	1690	1420
PHA-Fe	1582	1429
PHA-Al	1590	1440
PHA-Rh	1610	1440
PHA-Ir	1610	1425
PHA-Cr	1600	1430
PHA-Cu	1605	1430
PHA-Ni	1595	1429
PHA-Co	1610	1435
PHA-Pt	1605	1429
PHA-Pd	1590	1432
PHA-TCA	1680	1426
PHA-DCEA	1675	1420
PHA-LI	1580	1425
PHA-LII	1630	1450
PHA-LIII	1625	1430

and (D)]. On the other hand, if $\nu(\text{C}=\text{O})$ shifts to lower frequency and $\nu(\text{C}-\text{N})$ to a higher frequency, then it will indicate the ligand coordination via an oxygen atom [(B) and (C)], and so the $\nu(\text{O}-\text{H})$ should be eliminated. Considering the FTIR data in Table IV, the (B) and (C) forms are confirmed.

CONCLUSIONS

PHA has unique properties and well measures the arsenic agents of low concentrations, lower than 10 ppm. This polymer detects the arsenics in a very short time, near a few seconds. PHA is a sufficient candidate for detection of arsenic agents.

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