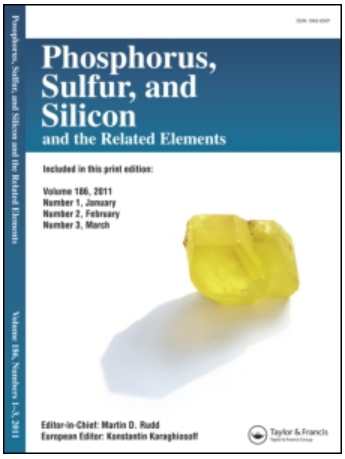

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Green Synthesis of Poly(aminomethylenephosphonic) Acids

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GREEN SYNTHESIS OF POLY(AMINOMETHYLENEPHOSPHONIC) ACIDS

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The reaction of polyamines with phosphorous acid and formaldehyde in water under focused microwave irradiation provides a facile and rapid synthesis of poly(aminomethylenephosphonic) acids.

Keywords Metal extractant; microwave irradiation; polyphosphonic acid; water solvent

INTRODUCTION

Aminophosphonic acids constitute an important class of biologically active compounds, and their synthesis has been a focus of considerable attention in synthetic organic chemistry as well as in medicinal chemistry.[1] These acids are considered to be structural analogues of the corresponding amino acids. Thus, acting as competitive inhibitors, they can act as false substrates during the course of amino acid metabolism. Aminophosphonic acids are also very good ligands for the coordination of metal ions so they can be used for the extraction of metals such as iron, copper, nickel, and uranium in hydrometallurgy.[2] These acids also form complexes on the surface of metals such as iron[3] and consequently are very suitable as anticorrosion agents.[4] These acids are also precursors of organic materials[5] or hybrid materials for metal organic frameworks (MOF).[6] The phosphonic acids can be also

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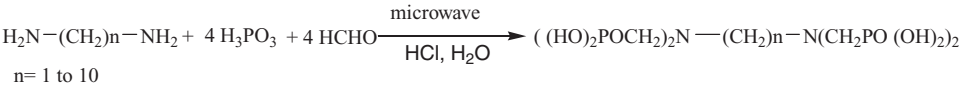
useful for the modification of inorganic surfaces or for grafting organic compounds on inorganic surfaces.[7] They can be used for making supported catalysts[8] or modified inorganic nanoparticles,[9] and they can also be used as enzyme inhibitors.[10]

RESULTS AND DISCUSSION

The aminophosphonic acids are generally obtained by hydrolysis of esters obtained via the Kabachnik–Fields reaction[11] of a carbonyl compound, a dialkylphosphite, and an amine. The Kabachnik–Fields reaction can be efficiently activated by microwave irradiation;[12] nevertheless there are often secondary reactions during the subsequent hydrolysis of the phosphonate. The Irani–Moedritzer[13] synthesis is less general than the Kabachnik–Fields reaction, but it has the advantage of giving the aminophosphonic acid directly without a hydrolysis step. The Irani–Moedritzer reaction times are in general long, so the use of microwave irradiation for assisting the reaction is of interest. We describe this reaction in aqueous medium without organic solvent under focused microwave irradiation. Water is an inexpensive, nonflammable, nontoxic solvent, and it has the advantage of warming up quickly under microwave irradiation. Carrying out reactions using microwave heating, as opposed to conventional heating, has the major advantage of shorter reaction times because of the rapid heating.[14]

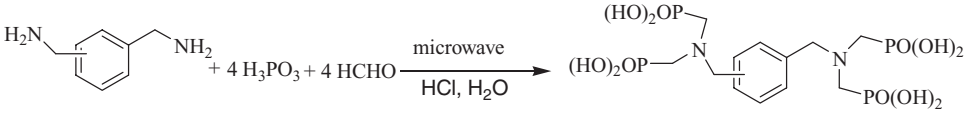
The Irani–Moedritzer reaction can be compared with a Mannich reaction and takes place by the addition of phosphorous acid to the iminium salt formed by reaction of an aqueous solution of formaldehyde with the amine in acidic medium.

We obtained various polyaminopolymethylenephosphonic acids by refluxing polyaminoalkanes with phosphorous acid and formaldehyde in hydrochloric media (Schemes 1 and 2) under microwave irradiation in a resonance mono-mode cavity.



Scheme 1 Synthesis of diaminoalkane-*N,N,N',N'*-tetrakis(methanephosphonic acids) from diaminoalkanes.

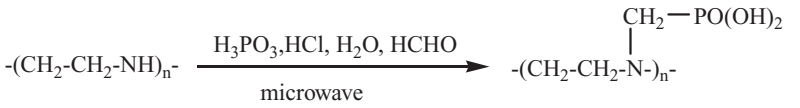
Although the reaction also takes place under multimode irradiation by the use of a commercial furnace, the yields obtained are worse. After cooling and evaporation of half the volume of water, the aminophosphosphonic acid crystallized as a white solid. It was then recrystallized in a water–isopropanol mixture.



Scheme 2 Synthesis of diaminoalkane-*N,N,N',N'*-tetrakis(methanephosphonic acids) from diaminoalkanes.

The yields reported in the literature correspond to the crude products, and it is necessary to recrystallize the acids in order to obtain pure products according to their ^{31}P NMR spectra. That can pose problems when the acids are very soluble in water, e.g., compound **2** is obtained as a crude product with 95% yield, but after recrystallization, only 63% of pure product is obtained due to its high solubility in water.

With the dendritic polyethylenimine of different molecular mass range ($M_w = 20000$ to 750000), we have obtained polymeric aminophosphonic acids useful as resins for extraction of metal ions and anticorrosion agent (Scheme 3).



Scheme 3 Synthesis of diaminoalkane-*N,N,N',N'*-tetrakis(methanephosphonic acids) from diaminoalkanes.

The reactions were carried out in a tubular reactor fitted with an effective cooling mechanism, which permits refluxing of the solution without the formaldehyde escaping from the reaction media. This reactor was irradiated in a resonance mono-mode cavity. Although the reactions also took place under multimode irradiation of a commercial furnace, the yields obtained were worse.

After cooling and evaporation of half the volume of water, the aminomethanephosphosphonic acid crystallized as a white solid. It was then recrystallized in a water–isopropanol mixture. The activation by microwaves allows better yields than conventional heating.

Many of these polyphosphonic acids were prepared previously under classical reflux conditions,[15] but since their spectra were generally not reported in the literature, we systematically describe their NMR spectroscopic properties here.

CONCLUSION

The one-pot synthesis of polyaminophosphonic acids under microwave irradiation is general, simple, fast, and efficient, and it allows interesting aminophosphonic acids to be obtained which are useful as biologically active molecules, coordinating agents of metals, or precursors of materials (organic or MOF).

EXPERIMENTAL

Instrumentation

The infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer equipped with accessories ATR. Samples were analyzed NMR spectroscopically by use of a multinuclear Bruker B 400 FT-spectrometer. Samples of the products were diluted in D_2O in the presence of Na_2CO_3. Microwave irradiation reactions were performed in a mono-mode resonance microwave oven (Synthewave 402, Prolabo) working with the frequency of 2450 MHz, controlled with an IR thermometer and monitoring by a computer. Microanalyses were performed on the automatic C,H,N analyzer Thermoquest. The membrane Nadir® was utilized for the dialyses.

Chemicals

All chemicals used except for polyethylenimines were from Aldrich or Fluka. Polyethylenimines (Lupasol®) were gifted by BASF.

Diaminomethane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (1)

A mixture of diaminomethane dihydrochloride (2.38 g, 20 mmol), phosphorous acid (6.56 g, 80 mmol), water (5mL), hydrochloric acid (36%, 4 mL), and formaldehyde (37%, 7.5 mL, 100 mmol) was irradiated in a glass cylinder reactor fitted with a cooler filled under microwave irradiation at 240 W for 10 min. After cooling and evaporation, a white solid was obtained after filtration. The product (**1**) is very soluble in water, and only a small part was crystallized (yield: 15%) although the phosphonation was quantitative (^{31}P NMR). ^{1}H NMR: 2.96–2.99 (m, 2H, N-CH2), 3.66 (d, $^{2}J_{HP} = 12.50$ Hz, 8H, N-CH2-P); ^{13}C NMR: 44.61 (CH2-N), 52.89 (d, $^{1}J_{CP} = 137.70$ Hz, N-CH2-P); 54.61 $^{1}J_{CP} = 135.20$ Hz, N-CH2-P); ^{31}P NMR: 7.89.

1,2-Diaminoethane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (2)

A mixture of 1,2-diaminoethane (0.6 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was microwave irradiated 240 W for 2 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 10 min at 240 W. After cooling and evaporation, a white solid was obtained after filtration. Yield 63%; mp: 247°C; ^{1}H NMR: 2.94 (d, $^{2}J_{HP} = 11.20$ Hz, 8H, N-CH2-P), 3.35–3.39 (m, 4H, N-CH2); ^{13}C NMR: 52.28 (CH2-N), 53.0 (d, $^{1}J_{CP} = 135.20$ Hz, N-CH2-P); ^{31}P NMR: 7.41; IR (cm^{-1}): 2286 ($\nu_{P\text{-}OH}$), 1105 ($\nu_{P=O}$), 1010, and 944($\nu_{P\text{-}O}$).

1,3-Diaminopropane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (3)

A mixture of 1,3-diaminopropane (0.85 mL, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was microwave irradiated at 240 W for 2 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 12 min at 240 W. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with acetone and water. Yield 64%; mp: 130°C; ^{1}H NMR: 1.93–1.97 (m, 2H), 3.21 (d, $^{2}J_{HP} = 11.30$ Hz, 8H, N-CH2-P), 3.33–3.37 (m, 4H); ^{13}C NMR: 19.11, 42.0, 50.91 (d, $^{1}J_{CP} = 138.0$ Hz, N-CH2-P); ^{31}P NMR: 8.45; IR (cm^{-1}): 3000 (ν_{OH}), 1471 ($\nu_{P=O}$), 917($\nu_{P\text{-}O}$).

1,4-Diaminobutane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (4)

A mixture of 1,4-diaminobutane (0.88 g, 10 mmol.), phosphorous acid (3.28 g, 40 mmol), water (3 mL), hydrochloric acid (36%, 3 mL), and formaldehyde (6 mL, 80 mmol) was irradiated at 240 W for 15 min. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with a mixture of 2-propanol and water. Yield 68%; mp: 240°C; ^{1}H NMR: 1.74–1.78 (m, 4H), 3.16 (d, $^{2}J_{HP} = 11.40$ Hz, 8H, N-CH2-P), 3.43–3.48 (m, 4H); ^{13}C NMR: 20.41, 51.89 (d, $^{1}J_{CP} = 136.0$ Hz, N-CH2-P), 55.80; ^{31}P NMR: 6.51.

1,6-Diaminohexane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (5)

A mixture of 1,6-diaminohexane (1.16 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated at 240 W for 2 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was

irradiated for 20 min at 240 W. After cooling and evaporation, the precipitated was filtered and the white solid was washed with water. Yield 91%; mp: 242°C; ^{1}H NMR: 1.26–1.30 (m, 4H), 1.63–1.67 (m, 4H), 3.32–3.36 (m, 4H), 3.65 (d, $^{2}J_{HP}$ = 13.20 Hz, 8H, N-CH2-P); ^{13}C NMR: 21.11; 23.20; 34.89; 49.52 (d, $^{1}J_{CP}$ = 136.70 Hz, CH2-P). ^{31}P NMR: 7.79; IR (cm^{-1}): 2750 (ν_{OH}), 2362 ($\nu_{P\text{-}OH}$), 1178 ($\nu_{P=O}$), 1020 and 944 ($\nu_{P\text{-}O}$).

1,7-Diaminoheptane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (6)

A mixture of 1,7-diaminohexane (2.6 g, 20 mmol), phosphorous acid (6.56 g, 80 mmol), water (15 mL), and hydrochloric acid (36%, 6 mL) was irradiated in a glass cylinder reactor fitted by a cooler filled at 240 W for 2 min. After this, formaldehyde (12 mL, 160 mmol) was added rapidly, and the mixture was irradiated for 15 min at 240 W. After cooling, water and acetone were added. Two immiscible phases were obtained; the upper phase was the product. After evaporation of solvent, **6** was obtained as a white solid. Yield 62%; ^{1}H NMR: 1.23–1.27 (m, 6H), 1.61–1.65 (m, 4H), 3.35 (t, J = 8.0 Hz, 4H), 3.43 (d, $^{2}J_{HP}$ = 12.80 Hz, 8H, N-CH2-P); ^{13}C NMR: 22.50; 24.69; 27.11; 50.62 (d, $^{1}J_{CP}$ = 138.20 Hz, CH2-P); 56.71; ^{31}P NMR: 8.10; IR(cm^{-1}): 2758 (ν_{OH}), 2165 (ν_{POH}), 1135 ($\nu_{P=O}$), 1002 and 928 (ν_{PO}).

1,8-Diaminooctan-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (7)

A mixture of 1,8-diaminooctane (1.44 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (4 mL), hydrochloric acid (36%, 4 mL), and formaldehyde (6 mL, 80 mmol) was irradiated for 15 min at 240 W. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with acetone and water. Yield 64%; mp: 248°C; ^{1}H NMR: 1.24–1.28 (m, 8H), 1.62–1.66 (m, 4H), 3.14 (d, $^{2}J_{HP}$ = 11.40 Hz, 8H, N-CH2-P), 3.37 (t, J = 7.40 Hz, 4H). ^{13}C NMR: 23.30, 25.55, 28.21, 52.0, 53.29 (d, $^{1}J_{CP}$ = 136.20 Hz, CH2-P); ^{31}P NMR: 6.71.

1,9-Diaminononane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (8)

A mixture of 1,9-diaminononane (1.58 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), hydrochloric acid (36%, 4 mL), and formaldehyde (6 mL, 80 mmol) was irradiated for 15 min at 240 W. After cooling and evaporation, the precipitate was crystallized in water, 2-propanol, and acetone. Yield (80%); ^{1}H NMR: 1.24–1.28 (m, 10H), 1.66–1.69 (m, 4H), 3.46 (d, $^{2}J_{HP}$ = 12.80 Hz, 8H, N-CH2-P), 3.41 (t, J = 8.0 Hz, 4H); ^{13}C NMR: 23.01, 25.30, 27.78, 27.91, 51.14 (d, $^{1}J_{CP}$ = 132.90 Hz, CH2-P), 57.0; ^{31}P NMR: 7.71.

1,10-Diaminodecane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (9)

A mixture of 1,10-diaminodecane (1.72 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), hydrochloric acid (36%, 4 mL), and formaldehyde (6 mL, 80 mmol) was irradiated for 15 min at 240 W. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with acetone and water. Yield 80%; ^{1}H NMR: 1.24–1.28 (m, 12H), 1.66–1.69 (m, 4H), 3.17 (d, $^{2}J_{HP}$ = 11.20 Hz, 8H, N-CH2-P), 3.41

(t, $J = 8.0$ Hz, 4H); ^{13}C NMR: 23.40, 25.75, 28.51, 28.59, 53.86 (d, ^{1}JCP = 125.50 Hz, CH2-P), 56.80; ^{31}P NMR: 6.59.

1,12-Diaminododecane-*N,N,N′,N′*-tetrakis(methanenephosphonic acid) (10)

A mixture of 1,12-diaminododecane (2 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated at 240 W for 2 min. After this, formaldehyde (3.3 mL, 44 mmol) was added rapidly, and the mixture was irradiated for 30 min at 240 W. After cooling and evaporation, the precipitated was filtered, and the white solid was washed with acetone and water. Yield 93%; mp: 230°C; ^{1}H NMR: 1.13–1.18 (m, 16H), 1.56–1.61 (m, 4H), 3.10 (d, $^{2}J_{HP} = 11.20$ Hz, 8H, N-CH2-P), 3.32 (t, $J = 7.70$ Hz, 4H); ^{13}C NMR: 22.79, 25.11, 27.79, 28.02, 28.12, 52.81 (d, $^{1}J_{CP} = 126.50$ Hz, CH2-P); ^{31}P NMR: 7.83; IR (cm^{-1}): 2919 (ν_{OH}), 2275 ($\nu_{P=O}$), 1151 ($\nu_{P=O}$), 936 ($\nu_{P\text{-}O}$), 585 (ν_{CH}).

Piperazine-*N,N′*-bis(methanephosphonic Acid) (11)

Piperazine (0.86 g, 10 mmol) in a quartz tube with a cooler was added to a mixture of phosphorous acid (1.64 g, 20 mmol), water (3 mL), and hydrochloric acid (3 mL). Then formaldehyde (3 mL, 40 mmol) was added, and the unit was irradiated at 240 W for 15 min. The product precipitated directly in the tube; it was filtered and washed with water. Yield 82%; white solid; mp: 260°C; ^{1}H NMR: 3.14 (d, 4H, $^{2}J_{HP} = 11.87$ Hz, N-CH2-P), 3.46–3.49 (m, 8H, N-CH2); ^{13}C NMR: 53.11, 56.12 (d, $^{1}J_{CP} = 133.99$ Hz, CH2-P); ^{31}P NMR: 9.41; IR (cm^{-1}): 2930 (ν_{OH}), 1260 and 1240 ($\nu_{P=O}$), 943 ($\nu_{P\text{-}O}$).

1-(2-Aminoethyl)piperazine-*N,N′,N′*-tris(methanenephosphonic Acid) (12)

1-(2-Aminoethyl)piperazine (1.29 g, 10 mmol), placed in a quartz tube with refrigerant, was added to a mixture of phosphorous acid (2.46 g, 30 mmol), water (3 mL), and hydrochloric acid (3 mL). Then formaldehyde (4.5 mL, 60 mmol) was added, and the unit was irradiated at 240 W for 15 min. The product precipitated directly in the tube; it was filtered and washed with water. Yield 80%; white solid; mp: 171°C; ^{1}H NMR: 3.04 (m, 8H, CH2-N), 3.19 (d, 2H, $^{2}J_{HP} = 11.50$ Hz, CH2-P), 3.28 (d, 4H, $^{2}J_{HP} = 11.25$ Hz, 2 CH2-P), 3.58 (s, 4H, CH2); ^{13}C NMR: 49.80 (2 CH2-N), 51.25 (CH2-N), 53.69 (d, $^{1}J_{CP} = 130$ Hz, 2 **C**H2-P), 53.81 (2 CH2-N), 53.90 (CH2-N), 55.20 (d, $^{1}J_{CP} = 129$ Hz, **C**H2-P); ^{31}P NMR: 7.69, 8.0.

1,10-Diazacyclooctadecane-*N,N′*-bis(methanephosphonic Acid) (13)

A mixture of 1,10-diazacyclooctadecane (0.26 mL, 1 mmol), phosphorous acid (0.16 g, 2 mmol), water (0.3 mL), and hydrochloric acid (36%, 0.3 mL) was irradiated at 200 W for 5 min. Formaldehyde (3 mL, 40 mmol) was added rapidly, and the mixture was irradiated at 240 W for 16 min. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with water and acetone. Yield 70%; mp: 261–263°C; ^{1}H NMR: 3.59 (d, $^{2}J_{PH} = 11.95$ Hz; 4H, N-CH_2-P), 3.95 (t, $^{3}J_{HH} = 5.47$ Hz, 8H), 4.04

(s, 8H), 4.20 (t, $^3J_{HH} = 5.39$ Hz, 8H); ^{13}C NMR: 48.33 (d, $^1J_{CP} = 137.60$ Hz, N-CH_2-P), 53.19, 62.20, 68.35; ^{31}P NMR: 7.52; IR (cm^{-1}): 3151 (ν_{OH}), 2342 ($\nu_{P=O}$), 1132 ($\nu_{P=O}$), 1052 ($\nu_{C\text{-}O}$), 964 ($\nu_{P\text{-}O}$).

1,2-Diaminocyclohexane-*N,N,N′,N′*-tetrakis(methanenephosphonic) Acid (14)

A mixture of 1,2-diaminocyclohexane (1.14 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated in a glass cylinder reactor fitted with a cooler at 200 W for 5 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 12 min at 240 W. After cooling and evaporation, the precipitate was crystallized with acetonitrile, and the white solid washed with water. Yield 71%; mp: 260°C; ^{1}H NMR: 2.12 (qt, $^3J_{HH} = 7.20$ Hz, 4H), 2.55 (q, $^3J_{HH} = 7.12$ Hz, 4H), 3.56 (d, $^2J_{HP} = 11.30$ Hz, 8H, N-CH2-P), 3.44 (t, $^3J_{HH} = 6.9$ Hz, 2H); ^{13}C NMR: 22.37, 48.80, 49.25 (d, $^1J_{CP} = 150$ Hz, N-CH_2P), 51.60 (d, $^1J_{CP} = 145$ Hz, N-CH_2-P), 60.39; ^{31}P NMR: 13.59 and 15.0; IR (cm^{-1}): 2980 (ν_{OH}), 2352 ($\nu_{P=O}$), 1092 ($\nu_{P=O}$), 1018 and 942 ($\nu_{P\text{-}O}$).

2,2-Diaminopropane-*N,N,N′,N′*-tetrakis(methanenephosphonic Acid) (15)

A mixture of 2,2-diaminopropane (0.85 mL, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated in a glass cylinder reactor fitted with a cooler at 240 W for 2 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 28 min at 240 W. After cooling and evaporation, the precipitate was crystallized from acetonitrile/methanol (1:1). Yield 43%; mp: 138°C; ^{1}H NMR: 1.35 (s, 3H), 1.73–1.77 (m, 3H), 3.12 (d, $^2J_{HP} = 11.0$ Hz, 8H, N-CH2-P); ^{13}C NMR: 13.51, 17.09, 30.0, 50.10 (d, $^1J_{CP} = 138.70$ Hz, CH2-P); ^{31}P NMR: 8.79; IR (cm^{-1}): 2750 (ν_{OH}), 1324 ($\nu_{P\text{-}OH}$), 1120 ($\nu_{P=O}$), 1015 and 966 ($\nu_{P\text{-}O}$).

1,4-Bis(aminomethyl)benzene-*N,N′*-bis(methanephosphonic Acid) (16)

A mixture of 1,4-bis(aminomethyl)benzene (1.36g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated in a glass cylinder reactor fitted with a cooler at 240 W for 1 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 12 min at 240 W. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with water. Yield 93%; mp: 260°C; ^{1}H NMR: 3.50 (d, $^2J_{HP} = 11.37$ Hz, 8H, N-CH2-P), 4.98 (s, 4H, N-CH2-Ar), 7.90 (s, 4H, H_{ar}); ^{13}C NMR: 51.57 (d, $^1J_{CP} = 131.20$ Hz, N-CH2-P), 57.44 (CH2-N), 129.87 and 159.20 (C_{ar}); ^{31}P NMR: 6.64; IR (cm^{-1}): 3023 (ν_{OH}), 2343 ($\nu_{P=O}$), 1484 ($\nu_{C=C}$), 1167 ($\nu_{P=O}$), 952 ($\nu_{P\text{-}O}$), 684 and 774 (ν_{CH}).

1,3-Bis(aminomethyl)benzene-*N,N′*-bis(methanephosphonic Acid) (17)

A mixture of 1,3-bis(aminomethyl)benzene (1.36 g, 10 mmol), phosphorous acid (3.28 g, 40 mmol), water (3 mL), and hydrochloric acid (36%, 3 mL) was irradiated in a glass cylinder reactor at 240 W for 2 min. After this, formaldehyde (6 mL, 80 mmol) was added rapidly, and the mixture was irradiated for 12 min at 240 W. After cooling

and evaporation, the precipitate was filtered, and the white solid was washed with acetone and water. Yield 46%; ^{1}H NMR: 3.17 (d, $^{2}J_{HP}$ = 11.30 Hz, 8H, N-CH2-P), 4.6 (s, 4H, N-CH2-Ar), 7.52–7.57 (m, 4H, H_{ar}); ^{31}C NMR: 51.50 (d, $^{1}J_{CP}$ = 131.0 Hz, N-CH2-P), 59.39 (CH2-N), 130.31 and 133.79 (Car); ^{31}P NMR: 6.79.

1,2-Bis(aminomethyl)benzene-*N,N′*-bis(methanephosphonic Acid) (18)

A mixture of 1,2-bis(aminomethyl)benzene (0.395 g, 1.86 mmol), phosphorous acid (0.62 g, 7.44 mmol), water (2 mL), and hydrochloric acid (36%, 2 mL) was irradiated at 210 W for 2 min. After this, formaldehyde (1.2 mL, 15 mmol) was added rapidly, and the mixture was irradiated at 210 W for 8 min. After cooling and evaporation, the precipitate was filtered, and the yellow solid was washed with water and 2-propanol. Yield 68%; mp: 240°C; ^{1}H NMR: 2.20 (s, 4H, N-CH2-Ar), 3.21 (d, 8H, $^{2}J_{HP}$ = 11.25 Hz, N-CH2-P), 7.34–7.62 (m, 8H, H_{ar}); ^{13}C NMR: 52.21 (d, $^{1}J_{CP}$ = 125.0 Hz, N-CH2-P), 59.79 (CH2-N), 127.33; 127.70; 129.21; 130.09; 132.31; 137.20; 138.81 and 142.22 (C_{ar}); ^{31}P NMR: 6.69; IR (cm^{-1}): 3000–2850 ($\nu_{P\text{-}OH}$), 1455 (ν_{CH2}), 1143 ($\nu_{P=O}$), 1010 and 930 ($\nu_{P\text{-}O}$).

1-Amino-3-ethylaminopropane-*N,N,N′*-tris(methanephosphonic Acid) (19)

1-Amino-3-ethylaminopropane (2.04 g, 20 mmol), placed in a quartz tube with refrigerant, was added to a mixture of phosphorous acid 4.92g (60 mmol), water (2 mL), and hydrochloric acid (6 mL). Formaldehyde (9 mL, 120 mmol) was then added, and the unit was irradiated at 240 W for 15 min. After cooling and evaporation, the precipitate was filtered, and the white solid was washed with 2-propanol. Yield 80%; ^{1}H NMR: 0.83 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.77–1.81 (m, 2H, CH2), 2.88–2.91 (m, 6H, CH2-N) 3.12 (d, $^{2}J_{HP}$ = 12.75 Hz, 6H, N-CH2-P); ^{13}C NMR: 7.70 (CH_3), 18.01 (CH2), 41.89 (CH2-N), 48.10 (d, $^{1}J_{CP}$ = 138.30 Hz, CH_2-P), 50.70 (d, $^{1}J_{CP}$ = 136.50 Hz, CH_2-P), 52.59 (CH2-N); ^{31}P NMR: 8.31 and 8.78.

1-Amino-3-methylaminopropane-*N,N′,N′*-tris(methanephosphonic Acid) (20)

1-Amino-3-methylaminopropane (0.88 g, 10 mmol), placed in a quartz tube with refrigerant, was added to a mixture of phosphorous acid (2.46 g, 30 mmol), water (3 mL), and hydrochloric acid (3 mL). Formaldehyde (4.5 mL, 60 mmol) was then added, and the unit was irradiated for 12 min at 240 W. After cooling and evaporation, a white solid was obtained after crystallization with 2-propanol and filtration. Yield 74%; mp: 220°C; ^{1}H NMR: 1.93–1.97 (m, 3H, CH_3-N), 2.75 (s, 4H, CH_2-N), 2.90 (d, $^{2}J_{HP}$ = 12.70 Hz, 2H, N-CH2-P), 3.05 (d, $^{2}J_{HP}$ = 12.70 Hz, 4H, N-CH2-P), 3.23–3.27 (m, 2H). ^{13}C NMR: 18.78 (CH_3-N), 42.51 (CH_2), 51.35 (d, $^{1}J_{CP}$ = 138.30 Hz, CH_2-P), 52.20 (d, $^{1}J_{CP}$ = 138.30 Hz, CH_2-P), 54.19 (CH_2-N). ^{31}P NMR: 6.11 and 6.70; IR (cm^{-1}): 3000–2850 ($\nu_{P\text{-}OH}$), 1466 (ν_{CH2}), 1160 ($\nu_{P=O}$), 920 ($\nu_{P\text{-}O}$).

Ethyleneimine-N-methanephosphonic Acid Polymer (21)

Different polyethyleneimines were used such as Lupasol® (BASF) G2O (1.3kDa), WF (25 kDa), P (750 kDa), SK (2000 kDa). For example Lupasol (BASF) WF: average

molecular weight 25000; average motives (C_2H_6N) = 581; structure dendritic NH_2/NH/N = 1/1.20/0.76. To polyethyleneimine (1.72 g, 50% in water, 20 mequ) placed in a quartz tube with cooler, a mixture of phosphorous acid (1.64 g, 20 mmol), water (2 mL), and hydrochloric acid (2 mL) was added. The mixture was irradiated for 8 min at 175 W. Then formaldehyde (3.3 mL, 40 mmol) was added. The solution was dialyzed with water. After evaporation, the polymer was obtained. Yield 90%; Tg: 122°C; ^{1}H NMR: 2.80–3.40 (m, CH2-N); ^{13}C NMR: 43.0–45.60 (m, N-CH2-P), 47.60–51.60 and 50.60–54.60 (m, CH2-P); ^{31}P NMR: 7.80; IR (cm^{-1}): 2340 ($\nu_{P\text{-}OH}$), 1110 ($\nu_{P=O}$), 1030 ($\nu_{P\text{-}O}$). Anal. for the ideal linear polymer $(C_3H_8NO_3P)_x$ calcd.: C 26.29; H 5.88; N 10.22%, found: C 27.08; H 7.25; N 11.16%.

REFERENCES

1. V. P. Kukhar and H. R. Hudson, *Aminophosphonic and Aminophosphinic Acids, Chemistry and Biological Activity* (J. Wiley & Sons, New York, 2000).
2. (a) O. Abderrahim, M. A. Didi, B. Moreau, and D. Villemin, *Solv. Extract. Ion Exchange*, **24,** 943 (2006); (b) N. E. Belkhouche, M. A. Didi, R. Romero, J. Å. Jönsson, and D. Villemin, *J. Membr. Sci.*, **284,** 398 (2006) and references cited therein.
3. C. J. Morin, M. Carli, R. Al. Rifaï, P. A. Jaffrès, D. Villemin, and P. L. Desbène, *Chromatographia*, **62,** 139 (2005).
4. (a) K. D. Demadis, S. D. Katarachia, and M. K. Koutmos, *Inorg. Chem. Comm.*, **8,** 254 (2005); (b) K. D. Demadis, M. Papadaki, R. G. Raptis, and H. Zhao, *J. Solid State Chem.*, **181,** 679 (2008); (c) H. Amar, J. Benzakour, A. Derja, D. Villemin, and B. Moreau, *J. Electroanal. Chem.*, **558,** 131 (2003); (d) H. Amar, T. Braisaz, D. Villemin, and B. Moreau, *Mater. Chem. Phys.*, **110,** 1 (2008).
5. J. Sopkova de Oliveria Santos, V. Montouillot, F. Fayon, C. Fernandez, L. Delain-Bioton, D. Villemin, and P. A. Jaffrès, *New J. Chem.*, **28,** 1244 (2004).
6. (a) A. Turner, P. A. Jaffrés, E. J. MacLean, D. Villemin, V. McKee, and G. B. Hix, *J. Chem. Soc., Dalton Trans.*, 1314 (2003); (b) D. Kong, J. Zon, and J. McBee Clearfield, *Inorg. Chem.*, **45,** 977 (2006) and references cited.
7. D. Villemin, B. Moreau, F. Siméon, G. Maheut, C. Fernandez, V. Montouillout, V. Caignaert, and P. A. Jaffrès, *J. Chem. Soc., Chem. Commun.*, 2060 (2001).
8. P. H. Mutin, G. Guerrero, and A. C. R. Vioux, *C. R. Chim.*, **6,** 1153 (2003).
9. T. Georgelin, B. Moreau, N. Bar, D. Villemin, V. Cabuil, and O. Horner, *Sensors Actuators B*, **134,** 451 (2008).
10. J. Beck, S. Gharbi, A. Herteg-Fernea, L. Vercheval, C. Bebrone, P. Lassaux, A. Zervosen, and J. Marchand-Brynaert, *Eur. J. Org. Chem.*, 85 (2009) and references cited therein.
11. (a) M. I. Kabachnik and T. Ya. Medved, *Dokl. Akad. Nauk SSSR*, **83,** 689 (1952); *Chem. Abstr.* **47**, 2724 (1953); (b) E. K. Fields, *J. Am. Chem. Soc.*, **74,** 1528 (1952); (c) D. Redmore, In *Topics in Phosphorus Chemistry*, E. J. Grifith, M. Grayson, eds. (John Wiley & Sons, New York, 1976); (d) R. A. Cherkasov and V. I. Galkin, *Russ. Chem. Rev.*, **67,** 857 (1998); (e) S. C. Fields, *Tetrahedron*, **55,** 12237 (1999); (f) K. Moonen, I. Laureyn, and C. V. Stevens, *Chem. Rev.*, **104,** 6177 (2004); (g) N. S. Zefirov and E. D. Matveeva, *Arkivoc*, 1 (2008).
12. F. Siméon, J. F. Saint-Clair, and D. Villemin, Alkylmethyleneaminophosphonics acids synthesis under microwave irradiation. *Proceedings of the First International Conference on Microwave Chemistry*, Prague, Czech Republic, Sept. 7–11, 1998, p. 186.
13. K. Moedritzer and R. Irani, *J. Org. Chem.*, **31,** 1603 (1966).
14. (a) P. Lidström and J. P. Tierney, eds., *Microwave-Assisted Organic Synthesis* (Blackwell, Oxford, UK, 2005); (b) A. Loupy, ed., *Microwaves in Organic Synthesis* (Wiley-VCH, Weinheim, Germany, 2006).
15. F. Nguyen and F. Hui, *Eur. J. Water Quality*, **37,** 189 (2006).