Synthesis, Optical Absorption, Fluorescence, Quantum Efficiency, and Electrical Conductivity Studies of Pyridine/Pyridinium Dialkynyl Organic and Pt(II)-σ-Acetylide Monomers and Polymers†

Kevin A. Bunten and Ashok K. Kakkar*

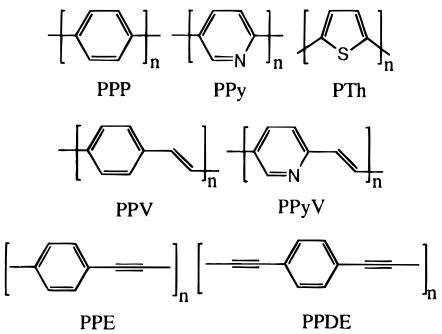
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada

Received October 19, 1995; Revised Manuscript Received January 22, 1996⊗

ABSTRACT: Synthesis of a variety of 2,5- and 2,6-diethynylpyridine based organic and Pt^{II}-σ-acetylide monomers and polymers is reported. Quaternization of pyridine nitrogen *via* solution nucleophilic substitution reactions with methyl iodide and methyl triflate yields stable pyridinium analogs and is accompanied by strong red shifts in the UV−vis absorption spectra. The latter is indicative of enhanced π-electron delocalization along the backbone upon quaternization. These compounds exhibit strong fluorescence with quantum yields of 0.015−0.058 for the monomers and 0.060−0.223 for the polymers. Quaternization leads to enhanced fluorescence intensities and quantum efficiencies. These polymers are insulators in the ground state, however, and, upon doping with iodine, they exhibit semiconducting behavior.

Introduction

The design of highly conjugated polymers containing diverse backbone structures has been a subject of great interest due to their potential applications as new materials for nonlinear optics, light emitting diodes, liquid crystals, and conductivity.[1−6] Much of the earlier efforts in this area have been directed at studying poly(arylenes) such as poly(*p*-phenylene) (PPP), poly(pyridine-2,5-diyl) (PPy), and poly(thiophene-2,5-diyl) (PTh). Extension of π-conjugation by incorporation of vinylene group in PPP or PPy to give poly(phenylenevinylene) (PPV) and poly(pyridylvinylene) (PPyV) has been demonstrated to lead to enhanced physical properties of these polymers.[7] Similar polymers containing acetylene linkages in the backbone, poly(*p*-phenylethynyl) (PPE) or poly(*p*-phenyldiethynyl) (PPDE), have also been prepared.



The analogous rigid-rod diethynylpyridine based polymers constitute an intriguing class of electronically tunable compounds in which pyridinyl nitrogen can be quaternized *via* nucleophilic substitution reactions, which allows manipulation of electron rich (pyridine) to electron poor (pyridinium) backbone structures. The introduction of positive charge into the backbone upon quaternization influences electron delocalization and, thus, provides opportunities in tailoring molecule based properties such as absorbance, fluorescence, optical nonlinearity, and conductivity. The knowledge of the electronic structure of these polymers will be very useful in building polymeric materials for device applications. We report herein details on the synthesis and physical properties of monomeric and polymeric, organic and Pt(II)-σ-acetylide compounds based on pyridine/pyridinium dialkynes.

Experimental Section

All chemicals were purchased reagent grade and used as received. *trans*-$Pt(P^nBu_3)_2Cl_2$ was prepared by published procedures.[8] Solvents were purified according to standard procedures.[9] All reactions were carried out in standard chemical glassware under an atmosphere of nitrogen unless noted otherwise. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ solution NMR were recorded on either a Gemini-200 or Joel-270 spectrometer and referenced to solvents or internal references. Solid state $^{13}C\{^1H\}$ NMR were obtained on a Chemagnetics (CMX-300) instrument. The proton and carbon chemical shifts are reported relative to tetramethylsilane, and phosphorus signals are relative to phosphoric acid (85%). Mass spectra were obtained by CI or FAB on a KRATOS-MS25RFA instrument. The molecular weights of the polymers were determined by gel permeation chromatography,[10] matrix assisted laser desorption ionization−time of flight−mass spectroscopy, and infrared spectra.[11] UV−vis absorption spectra were recorded on a Hewlett Packard 8452A didode array spectrophotometer. The IR spectra were recorded on a Bruker IFS-48 spectrometer using a Bruker A-590 microscope. Emission spectra were measured by placing the sample at 90° to a Xe lamp (450 W) excitation source on a Spex Fluorolog instrument, and the corresponding absorbance spectra were measured on a Phillips PV-8800 UV−vis spectrophotometer. The quantum yields were calculated in comparison to anthracence using the standard procedure.[12] TGA analysis were performed on a Seiko 220 instrument. Conductivity measurements were carried out by the four point method.[1]

2,5-Bis[(trimethylsilyl)ethynyl]pyridine (1). To a 100 mL Schlenk type flask charged with 50 mL of freshly distilled diethylamine were added 2,5-dibromopyridine (3.60 g, 15.2 mmol), (trimethylsilyl)acetylene (3.03 g, 30.8 mmol), bis(triphenylphosphine)palladium(II) chloride (140 mg), and a catalytic amount of copper(I) iodide (∼5 mg), in that order. The solution was stirred for 12 h at room temperature under an atmosphere of nitrogen. Diethylamine was then removed *in vacuo*, and the precipitate was extracted into diethyl ether.

† Dedicated to Prof. The Lord Lewis (Cambridge, U.K.) on the occasion of his 65th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.

0024-9297/96/2229-2885$12.00/0

The compound was separated by chromatography on silica gel using petroleum ether and diethyl ether mixture in a 3:1 ratio as eluent. The product was further purified by sublimation and recrystallization from hexanes, affording a white crystalline solid. Yield: 3.41 g, 83%. MS (CI): 271. IR $\nu_{C\equiv C}$: 2156 cm^{-1}. UV λ_{max} (CH_2Cl_2): 272 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 8.60 (1H), 7.66 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 7.36 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 0.20, 0.24 (s, 18H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 152.6, 141.7, 138.8, 126.4, 119.5, 103.3, 101.2, 100.2, 97.04, −0.3. Anal. Calcd for $C_{15}H_{21}Si_2N$: C, 66.36; H, 7.80; N, 5.16. Found: C, 66.39; H, 7.94; N, 5.24.

2,5-Diethynylpyridine (2). Compound **1** (1.00 g, 3.7 mmol) was dissolved in 10 mL of methanol in a 100 mL Schlenk type flask. To this solution was added 4 mL of 1 M potassium hydroxide, and the solution was allowed to stir for 1 h. After removing the solvent *in vacuo*, the product was extracted into diethyl ether and washed several times with water and brine solution. The product was separated by column chromatography on silica using petroleum ether/diethyl ether in a 3:1 ratio and further purified by recrystallization in hexanes affording white needles. Yield: 0.4 g, 85%. MS (CI): 127. IR $\nu_{C\equiv C}$: 2106, 2022 cm^{-1}. UV λ_{max} (CH_2Cl_2): 260 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 8.64 (s, 1H), 7.70 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 7.41 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 3.28 (s, 1H), 3.23 (s, 1H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 152.9, 141.5, 139.1, 126.6, 119.0, 82.4, 82.3, 79.9, 79.0. Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.51; H, 4.02; N, 10.63.

2,6-Bis[(trimethylsilyl)ethynyl]pyridine (3). To a 100 mL Schlenk type flask, charged with 20 mL of freshly distilled diethylamine, were added 2,6 dibromopyridine (1.58 g, 6.68 mmol), (trimethylsilyl)acetylene (1.35 g, 13.74 mmol), bis-(triphenylphosphine)palladium(II) chloride (100 mg), and a catalytic amount of copper(I) iodide (∼4 mg), in that order under an atmosphere of nitrogen. The mixture was allowed to stir for 12 h, after which the diethylamine was removed *in vacuo*. The residue left behind was extracted into diethyl ether and filtered. The filtrate was collected and separated by chromatography on silica using petroleum ether and diethyl ether in a 3:1 ratio as eluent. The product was further purified by recrystallization from hexanes, yielding long white needles. Yield: 1.5 g, 82%. MS (CI): 271. IR $\nu_{C\equiv C}$: 2153 cm^{-1}. UV λ_{max} (CH_2Cl_2): 236 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 7.57 (dd, 1H, $J_{H\text{-}H}$ = 7 Hz), 7.36 (d, 2H, $J_{H\text{-}H}$ = 8 Hz), 0.23 (s, 18H). Anal. Calcd for $C_{15}H_{21}Si_2N$: C, 66.36; H, 7.80; N, 5.16. Found: C, 66.49; H, 7.68, N, 4.92.

2,6-Diethynylpyridine (4). 2,6-Bis[(trimethylsilyl)ethynyl]pyridine (0.71 g, 2.6 mmol) was dissolved in 10 mL of methanol, and 3 mL of a 1 M aqueous solution of potassium hydroxide was added. The solution mixture was allowed to stir for 2 h. Then, the solvent was removed *in vacuo*, and the precipitate was extracted into diethyl ether. The product was washed several times with water and a brine solution. It was then purified by chromatography on silica using a 1:1 mixture of petroleum ether and diethyl ether, and by recrystallization from hexanes affording off-white needles. Yield: 0.20 g, 61%. MS (CI): 127. IR $\nu_{C\equiv C}$: 2098, 2022 cm^{-1}. UV λ_{max} (CH_2Cl_2): 240 nm. ^1H NMR (200 MHz, $CDCl_3$) δ ppm 7.63 (dd, 1H, $J_{H\text{-}H}$ = 7 Hz), 7.43 (d, 2H, $J_{H\text{-}H}$ = 8 Hz), 3.15 (s, 2H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 142.8, 136.6, 127.1, 82.1, 77.8. Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96; N, 11.02. Found: C, 83.37; H, 3.92; N, 10.70.

2,5-Bis[(trimethylstannyl)ethynyl]pyridine (5). Method A. To a stirred solution of **2** (0.38 g, 2.99 mmol) in tetrahydrofuran at −78 °C was added dropwide 0.6 mL of 10 M *n*-butyllithium and the temperature was gradually increased to room temperature. The solution was cooled again to −78 °C, trimethyltin chloride (1.19 g, 5.96 mmol) in 2 mL of tetrahydrofuran was added dropwise, and the solution was slowly brought to room temperature. The solvent was removed *in vacuo*, and the product was extracted into hexanes. Purification was carried out by repeat recrystallization from hexanes affording a white solid. Yield: 0.91 g, 67%.

Method B. To a solution of **2** (0.35 g, 2.75 mmol) in 10 mL of dry diethyl ether was added trimethyltin dimethylamine (1.72 g, 8.26 mmol) under an inert atmosphere of nitrogen. The solution was allowed to stir for 4 h, and the solvent was then removed *in vacuo*. The solid was collected and further purified by recrystallization from hexane, yielding large white crystals. Yield: 0.50 g, 40%. MS (CI): 453. IR $\nu_{C\equiv C}$: 2136 cm^{-1}. UV λ_{max} (CH_2Cl_2): 276 nm. ^1H NMR (270 MHz, C_6D_6) δ ppm 8.81 (s, 1H), 7.22 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 7.03 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 0.16 (s, 9H), 0.13 (s, 9H). Anal. Calcd for $C_{15}H_{21}NSn_2$: C, 39.79; H, 4.67; N, 3.10. Found: C, 39.19; H, 4.52; N, 2.80.

2,5-Bis[(phenylethynyl)ethynyl]pyridine (6). Oxygen was passed through a rigorously stirred solution of copper(I) chloride (0.023 g, 0.22 mmol) in 20 mL of freshly distilled pyridine until no further color change was noted (∼7 min). To this was slowly added a solution of **2** (0.09 g, 0.71 mmol) in 7 mL of phenylacetylene, and the mixture was continuously stirred under oxygen for 15 min. The pyridine was evaporated to about 5 mL, and a red precipitate was collected from solution. The remaining pyridine fraction was evaporated to dryness, and the residue was extracted into dichloromethane. The soluble portion was purified by chromatography on silica using dichloromethane as an eluent. The product was collected and purified by recrystallization from chloroform and dichloromethane, affording white needles. Yield: 0.023 g, 10%. MS (CI): 327. IR $\nu_{C\equiv C}$: 2219 cm^{-1}. UV λ_{max} (CH_2Cl_2): 340 nm. ^1H NMR (200 MHz, $CDCl_3$) δ ppm 8.72 (s, 1H), 7.76 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 7.57−7.49 (b, 6H), 7.47−7.28 (b, 5H).

***N*-Methyl-2,5-bis[(trimethylsilyl)ethynyl]pyridinium Iodide (7).** The monomer **1** (0.40 g, 1.48 mmol) was dissolved in 6 mL of dichloromethane, and to the solution thus obtained was added 0.5 mL of methyl iodide. The solution mixture was left to stir for 24 h. The dichloromethane was removed *in vacuo*, and the yellow solid was washed with hexanes. The product was dissolved in dichloromethane and purified by repeat precipitations with hexanes, affording a bright yellow solid. Yield: 0.51 g, 84%. MS (FAB): 415. IR $\nu_{C\equiv C}$: 2165 cm^{-1}. UV λ_{max} (CH_2Cl_2): 340 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 9.43 (s, 1H), 8.32 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 8.01 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 4.62 (s, 3H), 0.30 (s, 9H), 0.24 (s, 9H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 149.23, 146.41, 135.51, 131.51, 123.71, 119.98, 109.32, 95.94, 93.10, 48.91, −0.96. Anal. Calcd for $C_{16}H_{24}NI$: C, 46.48; H, 5.85; N, 3.39. Found: C, 46.78; H, 5.81; N, 3.24.

***N*-Methyl-2,5-bis[(trimethylsilyl)ethynyl]pyridinium Triflate (8).** To a solution of compound **1** (0.32 g, 1.17 mmol) in 5 mL of dichloromethane was added 1 mL of methyl triflate, and the solution was allowed to stir for 24 h. Then, the product was precipitated by the addition of hexanes, filtered, and washed repeatedly with hexanes, affording a white crystalline solid. Yield: 0.44 g, 85%. MS (FAB): 434. IR $\nu_{C\equiv C}$: 2174 cm^{-1}. UV λ_{max} (CH_2Cl_2): 340 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 9.10 (s, 1H), 8.20 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 7.87 (d, 1H, $J_{H\text{-}H}$ = 8 Hz), 4.52 (s, 3H), 0.34 (s, 9H), 0.27 (s, 9H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 149.51, 146.07, 135.88, 131.44, 123.97, 122.68, 119.99, 108.55, 95.95; 93.10, 48.06, −0.77, −1.02.

***N*-Methyl-2,6-bis[(trimethylsilyl)ethynyl]pyridinium Iodide (9).** A solution of **3** (100 mg, 0.368 mmol) in 5 mL of dichloromethane containing 1 mL of methyl iodide was stirred for 24 h under an atmosphere of nitrogen. The product was precipitated from solution with excess hexanes, filtered, and washed with 20 mL of hexanes. The solid was collected and dried on a Schlenk line. The product, initially yellow, slowly turns red over a period of days even under an inert atmosphere of N_2. Yield: 0.13 g, 88%. MS (FAB): 414. IR $\nu_{C\equiv C}$: 2168 cm^{-1}. UV λ_{max} (CH_2Cl_2): 344 nm. ^1H NMR (270 MHz, $CDCl_3$) δ ppm 8.92 (1H, $J_{H\text{-}H}$ = 8 Hz), 8.14 (2H, $J_{H\text{-}H}$ = 8 Hz), 4.52 (s, 3H), 0.32 (s, 18H). $^{13}C\{^1H\}$ NMR (67.94 MHz, $CDCl_3$) δ ppm 146.23, 138.43, 132.21, 118.81, 94.44, 46.95, 0.97.

***N*-Methyl-2,5-bis[(phenylethynyl)ethynyl]pyridinium Iodide (10).** To a solution of **6** (0.010 g, 0.03 mmol) in 3 mL of dichloromethane was added 3 mL of methyl iodide, and the solution was stirred at room temperature for 24 h. The product was precipitated from solution with excess hexanes, filtered, washed with 20 mL of hexanes, and dried on the vacuum line for several hours. Yield: 0.07 mg, 50%. MS (MALDI-TOF-Cation): 342. IR $\nu_{C\equiv C}$: 2210 cm^{-1}. UV λ_{max}

(CH_2Cl_2): 412 nm. ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 9.72 (s, 1H), 8.43 (d, 1H, J_{H-H} = 8 Hz), 8.01 (d, 1H, J_{H-H} = 8 Hz), 7.80−7.31 (b, 10H), 4.39 (s, 3H).

Poly(2,5-diethynylpyridine) (11). Oxygen was bubbled through a rigorously stirred solution of copper(I) chloride (0.025 g, 0.26 mmol) in 15 mL of freshly distilled pyridine for 10 min. Then a solution of **2** (0.114 g, 0.89 mmol) in 5 mL of pyridine was added dropwise and stirred for 20 min, and a brown red precipitate had formed in the flask. The mixture was then diluted with 30 mL of methanol, and the precipitate was filtered and washed with methanol followed by dichloromethane and diethyl ether. The reddish brown polymer was collected and dried on the vacuum line for several hours. Yield: 0.11 g, 98%. M_w = 1300 (IR determination of end groups) n = 9. IR $\nu_{C\equiv C}$: 2208, 2164, 2106 cm^{-1}. UV λ_{max} (HCOOH): 388 nm. ^{13}C{^{1}H} NMR (solid state, 75.34 MHz) δ ppm 152.84, 140.11, 128.21, 118.40, 82.40, 80.94, 75.72.

Poly(2,6-diethynylpyridine) (12). Oxygen was bubbled through a rigorously stirred solution of copper(I) chloride (0.075 g, 0.78 mmol) in 40 mL of freshly distilled pyridine for 10 min, and a solution of **4** (0.314 g, 2.47 mmol) in pyridine was added. The mixture was stirred for 20 min, and then diluted with methanol, filtered, and washed with excess methanol, dichloromethane, and diethyl ether. The light brown percipitate was dried under vacuum for several hours. Yield: 0.282 g, 90%. M_w (IR approximation) 1300. IR $\nu_{C\equiv C}$: 2224, 2153, 2111, 2013 cm^{-1}. UV λ_{max} (HCOOH): 262 nm. ^{13}C-{^{1}H} NMR (solid state, 75.34 MHz) δ ppm 140.48, 128.21, 82.67, 72.71.

Copolymer: 2,6- and 2,5-Diethynylpyridine 75/25 (13). Oxygen was bubbled through a rigorously stirred solution of copper(I) chloride (0.075 g, 0.78 mmol) in 40 mL of freshly distilled pyridine for 10 min. To the latter was added a solution of **4** (0.225 g, 1.77 mmol) and **2** (0.075 g, 0.59 mmol) in 5 mL of pyridine, and the solution was allowed to stir for 20 min. The solution was diluted with methanol, and the polymer precipitate was filtered and washed repeatedly with methanol, dichloromethane, and diethyl ether, in that order. The reddish brown powder thus obtained was then dried *in vacuo* for several hours. Yield: 0.298 g, 99%. M_w (IR approximation) 1200. IR $\nu_{C\equiv C}$: 2218, 2153, 2113, 2013 cm^{-1}. UV λ_{max} (HCOOH): 372 nm. ^{13}C{^{1}H} NMR (solid state, 75.34 MHz) δ ppm 150.00, 140.69, 128.42, 118.25, 82.01, 73.15.

Copolymer: 2,6- and 2,5-Diethynylpyridine 50/50 (14). Oxygen was bubbled through a rigorously stirred solution of copper(I) chloride (0.075 g, 0.78 mmol) in 40 mL of freshly distilled pyridine for 10 min , and then a solution of **4** (0.15 g, 1.18 mmol) and **2** (0.15 g, 1.18 mmol) in 5 mL of pyridine was added. After stirring for 20 min, the solution was diluted with methanol, and a reddish brown solid was filtered, washed with methanol, dichloromethane, and diethyl ether, and then dried under vacuum. Yield: 0.27 g, 90%. M_w (IR approximation) 1200. IR $\nu_{C\equiv C}$: 2215, 2152, 2112 cm^{-1}. UV λ_{max} (HCOOH): 372 nm. ^{13}C{^{1}H} NMR (solid state, 75.34 MHz) δ ppm 153.24, 140.69, 128.42, 118.88, 81.88, 73.12.

Poly(*trans*-bis(tri-*n*-butylphosphine)platinum 2,5-diethynylpyridine) (15). Method A. To a flask charged with 20 mL of freshly distilled diethylamine were added **2** (0.02 g, 0.16 mmol), *trans*-bis(tri-*n*-butylphosphine)platinum dichloride (0.105 g, 0.16 mmol), and a catalytic amount of copper(I) iodide (∼3 mg). The mixture was allowed to stir under reflux at 70 °C for 24 h. The solvent was then removed *in vacuo*, and the residue was extracted into dichloromethane and passed through a short alumina column. The product, an orange yellow solid, was collected and purified by precipitation from toluene with excess hexanes. Yield: 0.099 g, 85%.

Method B. Compound **5** (0.06 g, 0.13 mmol), *trans*-bis-(tributylphosphine)platinum dichloride (0.089 g, 0.13 mmol), and copper(I) iodide (4 mg) were dissolved in that order in 10 mL of dry toluene. The solution was allowed to stir for 48 h. Toluene was then removed *in vacuo* and the residue was extracted into dichloromethane. The solution was passed through a short alumina column, and the product was purified by precipitation with hexanes followed by washing with diethyl ether. The yellow solid was collected and dried on the vacuum linefor 5 h. Yield: 0.07 g, 74%. IR $\nu_{C\equiv C}$: 2106 cm^{-1}. UV λ_{max} (CH_2Cl_2): 382 nm. M_n = 47 000 (M_w/M_n = 2.9). ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 0.89 (m, 18H), 1.41 (m, 24H), 2.08 (m, 12H), 7.01 (br m, 1H), 7.92 (br m, 1H), 8.35 (br s, 1H). ^{31}P-{^{1}H} NMR (109 MHz, $CDCl_3$) δ ppm 5.48 (J_{Pt-P} = 2340 Hz). Anal. Calcd for $C_{33}H_{57}P_2NPt$: C, 54.72; H, 7.86; N, 1.93. Found: C, 51.98; H, 7.22; N, 2.68.

Poly(*N*-methyl-2,5-diethynylpyridinium triflate) (16). In a dry evacuated Schlenk flask, **11** (0.045 g, 0.36 mmol) and 2 mL of methyltriflate were allowed to stir under nitrogen for a week. Then, the methyl triflate was removed *in vacuo* and the solid polymer was collected and washed repeatedly with dichloromethane and hexanes. The residue was dried on the vacuum line for several hours. Yield: 0.08 g, 78%. IR $\nu_{C\equiv C}$: 2222, 2167, 2122 cm^{-1}. UV λ_{max} (HCOOH): 394 nm.

Poly(*N*-methyl-2,6-diethynylpyridinium triflate) (17). To a dry Schlenk flask containing 2 mL of methyl triflate was added compound **12** (0.030 g, 0.24 mmol), and the mixture was allowed to stir for 7 days under an atmosphere of nitrogen. The excess methyl triflate was removed *in vacuo*, and the product was collected and washed repeatedly with dichloromethane, followed by washing with hexanes. The dark polymer was collected and dried under vacuum for several hours. Yield: 0.055 g, 79%. IR $\nu_{C\equiv C}$: 2228, 2165, 2121 cm^{-1}. UV λ_{max} (HCOOH): 388 nm.

Poly(bis(tri-*n*-butylphosphine)platinum *N*-methyl-2,5-diethynylpyridinium iodide) (18). A Schlenk type flask was charged with 15 mL of dry THF, and 0.031 g (0.043 mmol) of **15** was added. The mixture was allowed to stir under an atmosphere of nitrogen. Methyl iodide (1 mL) was then added, and the solution was stirred for 48 h. The solvent was removed *in vacuo*, and the residue was extracted into dichloromethane. The polymer was purified by precipitation from dichloromethane with hexanes. Yield: 0.029 g, 79%. IR $\nu_{C\equiv C}$: 2088 cm^{-1}. UV$_{\lambda max}$ (CH_2Cl_2): 440 nm. M_n = 18 000 (M_w/M_n = 32). ^{31}P{^{1}H} NMR (109 MHz, $CDCl_3$) δ ppm 2.66 (J_{Pt-P} = 2260 Hz).

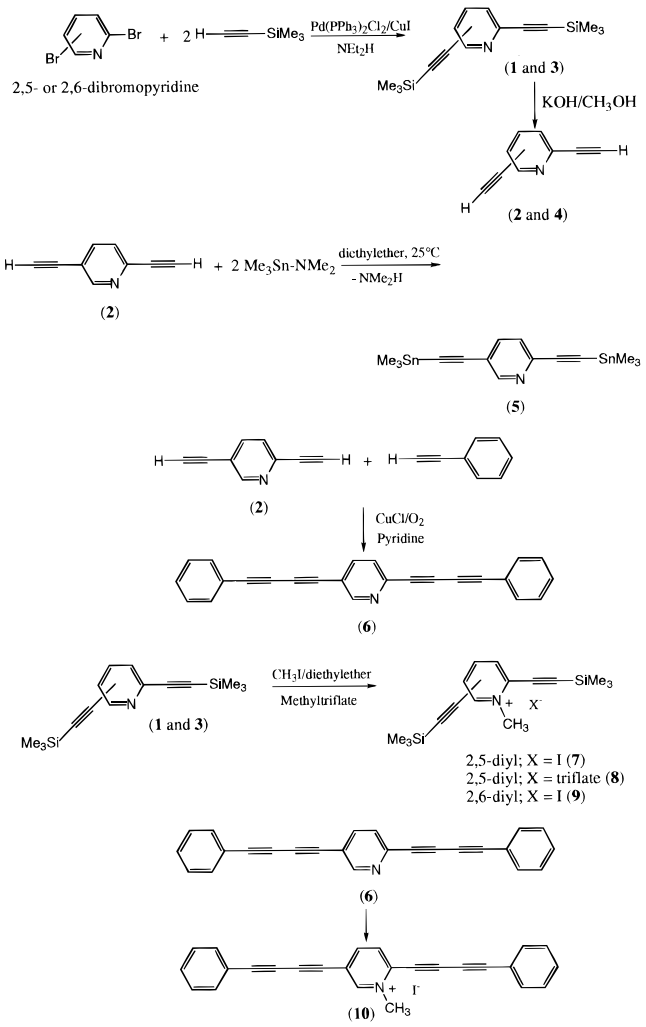
Poly((pyridin-2-yl-ethynyl)-*N*-methyl-5-ethynylpyridinium iodide) (19). **7** (50 mg, 0.12 mmol), 2.5-dibromopyridine (28 mg, 0.12 mmol), $Pd(PPh_3)_4$ (11 mg), and CuI (∼5 mg) were dissolved, in that order in 25 mL of distilled THF, and allowed to stir under nitrogen for 48 h. The solvent was then removed *in vacuo*, and the residue was extracted into dichloromethane. The product was purified by repeat precipitation from dichloromethane with hexanes. Yield: 25 mg, 60%. M_w = 1100 (MALDI-TOF-Cation). IR $\nu_{C\equiv C}$: 2112 cm^{-1}. UV λ_{max} (CH_2Cl_2): 526 nm.

Poly(*trans*-bis(tri-*n*-butylphosphine)platinum *N*-methyl-2,5-diethynylpyridinium iodide) (20). **7** (95 mg, 0.23 mmol), *trans*-$Pt(P^nBu_3)_2Cl_2$, and CuI (∼4 mg) were dissolved, in that order in 50 mL of THF and allowed to stir under nitrogen at reflux temperature for 40 h. The solvent was removed *in vacuo*, and the residue was purified by repeat precipitations from dichloromethane with hexanes. The product was washed with hexanes and dried under vacuum. Yield: 0.029 g, 79%. M_w = 1700 (MALDI-TOF-Cation). IR $\nu_{C\equiv C}$: 2092 cm^{-1}. UV λ_{max} (CH_2Cl_2): 534 nm. ^{31}P{^{1}H} NMR (109 MHz, $CDCl_3$) δ 1.61 ppm (J_{Pt-P} = 2310 Hz).

Results and Discussion

Synthesis. Monomers. The monomeric compounds 2,5-bis[(trimethylsilyl)ethynyl]pyridine (**1**) and 2,6-bis-[(trimethylsilyl)ethynyl]pyridine (**3**) were prepared by a Heck type[13] palladium-catalyzed dehydrohalogenation reaction by condensing 2,5- or 2,6-dibromopyridine with 2 equiv of (trimethylsilyl)acetylene in the presence of $Pd(PPh_3)_2Cl_2$/CuI catalyst mixture (Scheme 1). The hydrolysis of **1** and **3** was easily achieved by treatment with methanolic KOH to give 2,5- (**2**) or 2,6-diethynylpyridine (**4**). The 2,5-bis[(trimethylstannyl)ethynyl]-pyridine derivative (**5**) was conveniently prepared by reacting the corresponding dialkynyl compound, **2**, with a slight excess of trimethyltin dimethylamine, in which the only byproduct is the volatile dimethylamine. This is a preferred route[14] to the synthesis of **5** to the traditional method of first reacting the dialkyne **2** with

Scheme 1. Synthesis of Monomeric and Oligomeric Compounds

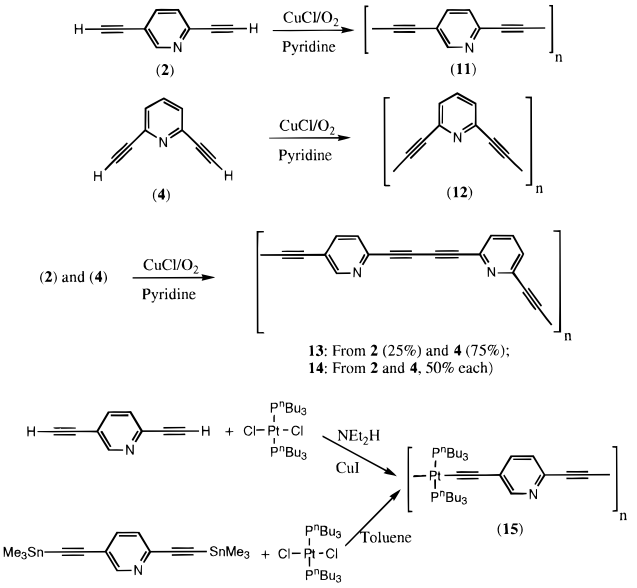


^{n}BuLi at −78 °C, followed by the addition of toxic trimethyltin chloride. The synthesis of 2,5-bis[(phenylethynyl)ethynyl]pyridine (**6**) was achieved by a slight modification of Hay's reaction[11] in which oxygen was bubbled through a solution mixture of **2**, a large excess of phenylacetylene, and a catalytic amount of CuI.

The bis[(trimethylsilyl)ethynyl]pyridine compounds **1** and **3** and compound **6** are readily quaternized by reacting them (i) with methyl iodide to give compounds **7**, **8**, and **9**; and (ii) with methyl triflate to give compound **10**. Attempts to quaternize the terminal alkynes **2** and **4** were unsuccessful, as the reactions yielded a large distribution of products. It is possible that quaternization leads to the activation of the ethynyl C−H bond, which facilitates the formation of oligomers.

Polymers. Pyridine alkynyl polymers were prepared by Hay's oxidative coupling reaction.[11] The rigid-rod poly(2,5-diethynylpyridine) (**11**) and kinked poly(2,6-diethynylpyridine) (**12**) were prepared by oxidative coupling of **2** or **4** in the presence of CuCl and O_2 in pyridine (Scheme 2). The copolymers **13** and **14** were similarly prepared by reacting varying amounts of **2** and **4** in pyridine with a catalytic mixture of CuCl and O_2. The dark red colored rigid-rod polymer **11** was found to be insoluble in common organic solvents and slightly soluble in nitro- or chlorobenzene. As expected, the kinked polymer **12** and copolymers **13** and **14** were slightly more soluble than **11**. All the above-mentioned

Scheme 2. Synthesis of Polymers



polymers (**11**−**14**) dissolved in concentrated formic and sulfuric acids.

The insoluble nature of the polymers limits their characterization by standard solution techniques. However, solid state ^{13}C NMR of these polymers provided invaluable information regarding their backbone structure. For example, solid state ^{13}C{^{1}H} NMR of the rigid-rod polymer, poly(2,5-diethynylpyridine) (**11**) (Figure 1), showed five aromatic carbon and two acetylenic carbon resonances (A). Upon dipolar dephasing of the spectra which eliminates resonances due to carbon atoms with any hydrogen atoms directly bonded to them, alkynyl

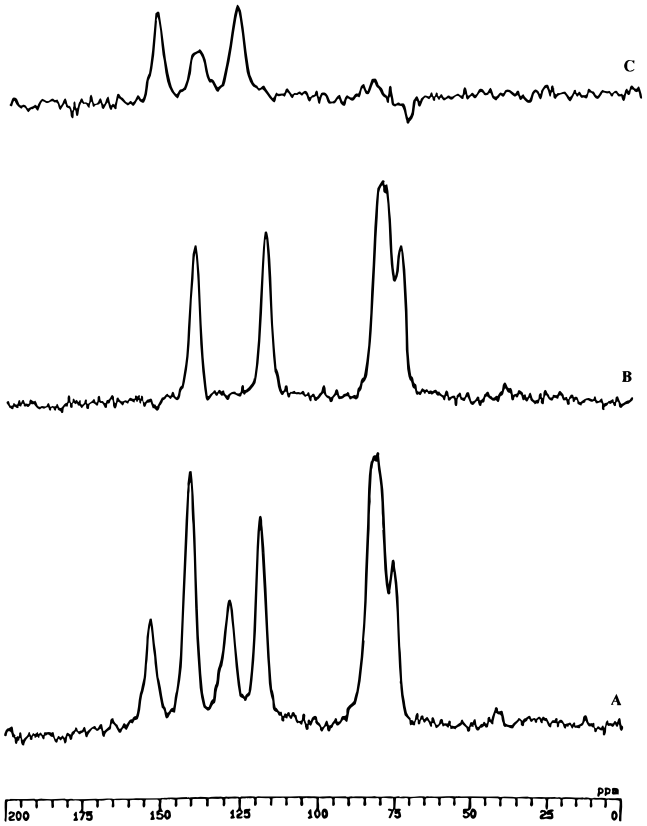


Figure 1. Solid state ^{13}C NMR of the polymer **11**. (A) Complete spectrum; (B) after dipolar phasing; (C) after subtraction of B from A.

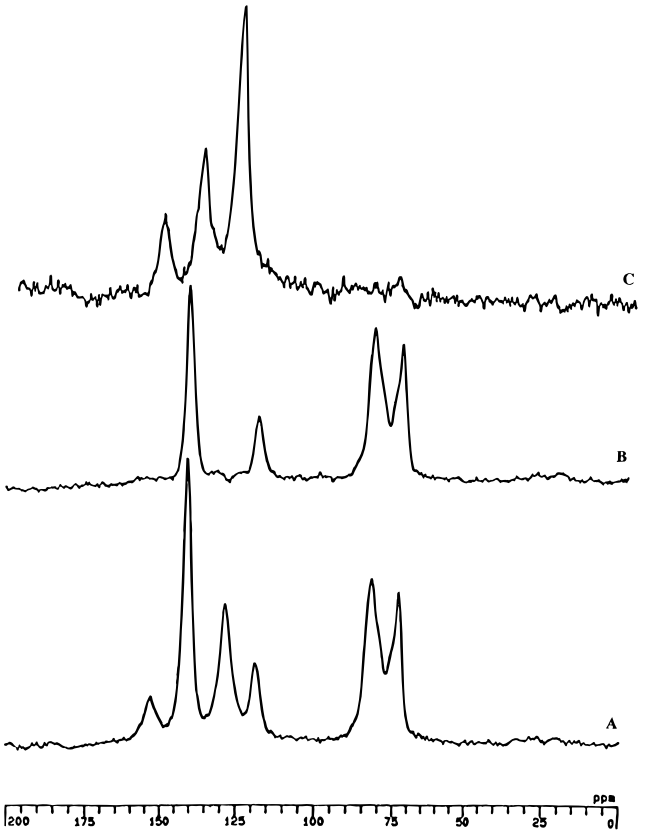


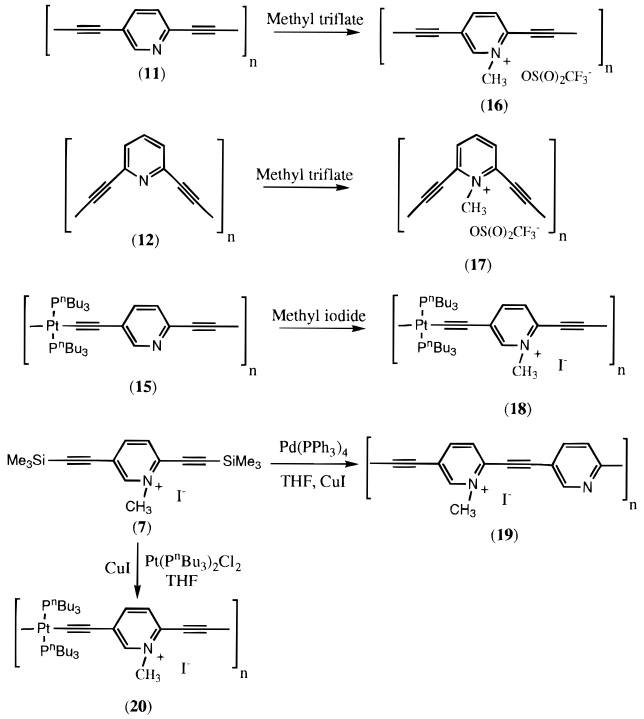
Figure 2. Solid state ^{13}C NMR of the polymer **14**. (A) Complete spectrum; (B) after dipolar phasing; (C) after subtraction of B from A.

and two aromatic carbon peaks were observed (B). Subtraction of the above two spectra gives resonances for the carbon atoms containing hydrogen atoms directly bonded to them (C). Similar observations can be made from the spectra of polymer **14** (Figure 2). The resonances for any terminal acetylenic (C≡C−H) resonances were found to be absent in these spectra, indicating the polymeric nature of these compounds.

It has been demonstrated[10,15] that the organometallic polymers containing Group 8−10 metals in the backbone are highly soluble in common organic solvents and that the π-conjugation is maintained through the metal centers linking acetylene units in such polymers. The rigid-rod Pt(II)-σ-acetylide polymer **15** was prepared by two synthetic routes: (i) by a dehydrohalogenation reaction[10] of **2** with $Pt(P^nBu_3)_2Cl_2$ in diethylamine using CuI as a catalyst; and (ii) by reacting bis[(trimethylstannyl)ethynyl]pyridine (**5**) with $Pt(P^nBu_3)_2Cl_2$ in toluene containing a catalytic amount of CuI.[15] Both reactions yielded a yellow solid which was highly soluble in common organic solvents; however, the molecular weight of the polymer (determined by the gel permeation chromatography method) prepared by the (bis(trimethylstannyl)alkynyl route was found to be higher (M_n = 48 000) than the one prepared by using Hagihara's route (M_n = 28 000).

The organic polymers **11** and **12** were randomly quaternized by a reaction of the solid with neat methyl iodide or methyl triflate to give polymers **16** and **17** (Scheme 3). The quaternization, in general, led to increased solubility of these polymers. The random quaternization of the Pt(II)-acetylide polymer was achieved by reacting it in solution with methyl iodide to give polymer **18**. A dehalogenation reaction[16,17] of **7** with 2,5-dibromopyridine in the presence of a catalytic

Scheme 3. Quaternization of Polymers



amount of $Pd(PPh_3)_4$ and CuI in THF yielded polymer **19** which is 50% quaternized. The fully quaternized Pt(II) polymer (**20**) was similarly prepared by the reaction of **7** with $Pt(P^nBu_3)_2Cl_2$ in the presence of a catalytic amount of CuI. The synthesis of polymers **19** and **20** by the above process suggests that the electropositive character at Si in **7** is increased upon quaternization which facilitates the dehalogenation reaction with the elimination of Me_3Si-Br/or Cl.

Physical Properties. Thermal Stability. The thermal stability of organic and organometallic polymers was determined by thermogravometric analysis (TGA). The unquaternized organic polymers (**11**) and (**12**) were found to decompose explosively in nitrogen at 150 and 160 °C, respectively (Figures 3 and 4). Polymer **12** with a kinked backbone was more stable to temperature than the rigid-rod analog. Quaternization of these polymers with methyl triflate (**16** and **17**) yielded materials which decomposed gradually as the temperature was increased. These polymers began to degrade (5% TGA loss) with elevation of temperature at 60 °C for **16** and 110 °C for **17** (Figures 3B and 4B). The organometallic polymer **15** had higher thermal stability than the organic analogs (Figure 5) with a 5% TGA loss at 320 °C. After quaternization of the polymer **15** with methyl iodide (polymer **18**), the decomposition was observed at 250 °C. It appears that quaternization on the polymer backbone reduces the thermal stability of these polymeric materials.

Infrared Spectra. Monomers. Acetylenic compounds exhibit strong $\nu_{C\equiv C}$ stretching frequencies in their IR spectra in the region 2000−2300 cm^{-1} which are characteristic of such compounds, and which are often used to identify acetylenic linkages.[18] The infrared $\nu_{C\equiv C}$ stretching frequencies for the compounds **1**−**20** are presented in Table 1. The monomeric compounds, bis(trimethylsilyl)alkynes (**1** and **3**) and bis(trimethylstannyl)alkynes (**5**), show strong $\nu_{C\equiv C}$ stretching frequencies at 2156, 2153, and 2137 cm^{-1}, respectively, and the corresponding terminal alkynes **2** and **4** display such frequencies at 2106 and 2022 cm^{-1} for each compound.

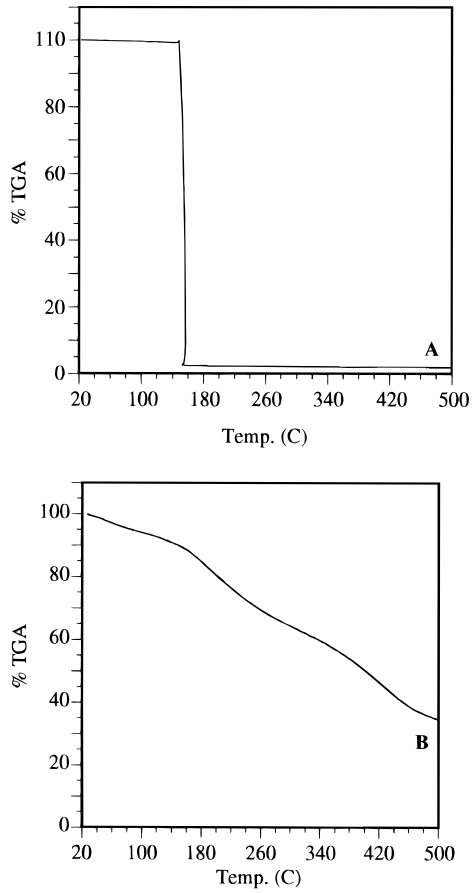


Figure 3. TGA % loss for polymers **11** (A) and **16** (B).

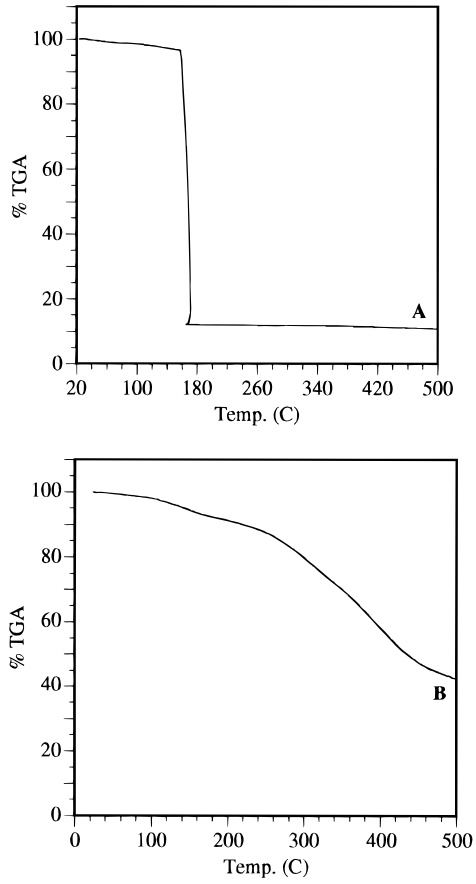


Figure 4. TGA % loss for polymers **12** (A) and **17** (B).

The compound with diacetylenic linkages (**6**) showed an intense $\nu_{C\equiv C}$ stretch at 2219 cm^{-1}.

The quaternization of the monomers with methyl iodide (Scheme 1) resulted in an overall increase of the $\nu_{C\equiv C}$ frequencies. The latter frequencies for the quaternized monomers **7**−**9** appear at 2165, 2174, and 2168 cm^{-1}, respectively. The intensities of these frequencies in the quaternized monomers were consistently lower. The quaternized long chain monomer **10** showed a $\nu_{C\equiv C}$ frequency at 2210 cm^{-1} which is shifted to lower wavenumbers by approximately 9 units as compared to the unquaternized monomer (**6**).

Polymers. As in the case of monomers, all the polymeric compounds exhibit strong $\nu_{C\equiv C}$ stretching frequencies in their IR spectra in the range of 2010−2220 cm^{-1} (Table 1). As expected, these $\nu_{C\equiv C}$ stretching frequencies appear at lower wavenumbers from their corresponding monomeric compounds, which is indicative of higher conjugation in the backbone. When the rigid-rod character of the compound is interrupted (as in polymer **12** and the corresponding copolymers **13** and **14**), the $\nu_{C\equiv C}$ stretching frequencies shift to higher wavenumbers, indicating a decrease in conjugation in the polymer backbone. The organometallic polymer (**15**) displayed a strong $\nu_{C\equiv C}$ stretching frequency at 2106 cm^{-1} which is characteistic of Pt(II)-σ-acetylide compounds.[10,15] The random quaternization of the kinked polymer **12** with methyl iodide (**17**) results in a lowering of the $\nu_{C\equiv C}$ stretching frequency, and such an effect of quaternization on the IR stretching frequencies is more evident in the soluble organometallic polymer which shows a significant shift to lower wavenumbers (2106 cm^{-1} before (**15**) and 2082 cm^{-1} after random quaternization (**18**)).

UV−Vis Spectra. Monomers. The solution UV−vis absorption spectra for these compounds were measured in dichloromethane, and the data are presented in Table 1. The monomeric compounds (**1**−**4**) exhibit intense absorption maxima at 250−280 nm. The long chain monomer **6** exhibits a λ_{max} at 340 nm which is indicative of higher π-conjugation in the latter compound compared to the other monomers. The quaternization of the monomers is accompanied by a shift in the λ_{max} values to lower energy; e.g., a maximum at 272 nm for monomer **1** shifts to 308 nm upon quaternization with methyl triflate (**5**); similarly, the absorption maximum for **6** at 320 nm is shifted to 412 nm upon quaternization (**10**) with methyl triflate.

Polymers. The position of the absorption maxima in UV−vis spectra is often used as a measure of the extent of π-electron delocalization along the backbone for the monomeric and polymeric compounds. The rigid-rod organic polymer (**11**) and the copolymers (**13**, **14**) show absorption maxima at 370−380 nm (Table 1, Figure 6) which are considerably shifted to lower energies in comparison to the monomers. As noted earlier for **6**, the latter indicates that the π-electrons are more delocalized along the backbone in these polymers. For the kinked polymer **12**, the λ_{max} is observed at 262 nm, which is significantly blue shifted as compared to the linear polymer. This is attributed to disruption of π-electron delocalization along the backbone in the former polymer. The organometallic polymer **15** showed a maximum at 382 nm, which is consistent with that of purely organic polymer **11** and indicates that the π-electron delocalization in this polymer is maintained through Pt(II) centers, and the metal participates in this process by contributing dπ(metal)-to-pπ(alkyne) metal to ligand charge transfer.

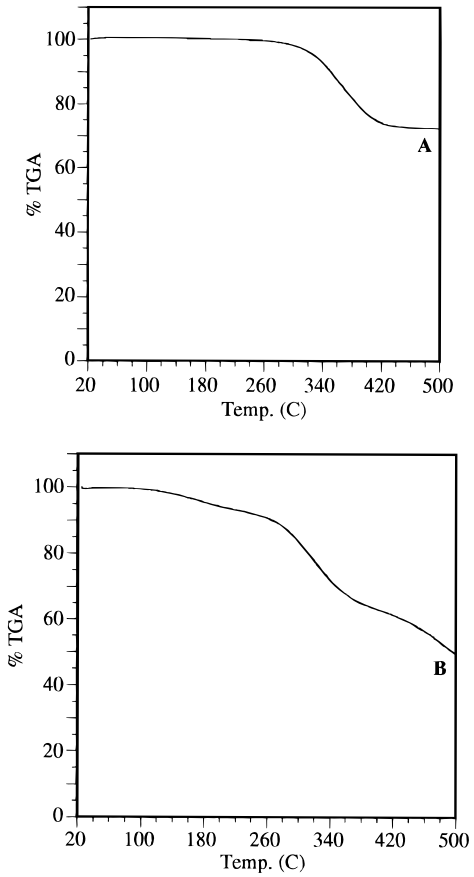


Figure 5. TGA % loss for the organometallic polymers **15** (A) and **18** (B).

Table 1

compound	IR (solid state) $\nu_{C\equiv C}$ (cm^{-1})	λ_{max} (nm)	quantum yield	conductivity (S cm^{-1})
1	2156	272[a]	0.015[a]	
2	2106, 2022	260[a]		
3	2153	236[a]	0.008[a]	
4	2106, 2022	240[a]		
5	2136	276[a]		
6	2219	340[a]		
7	2165	340[a]	0.019[a]	
8	2157	308[a]		
9	2168	344[a]	0.058[a]	
10	2210	412[a]		
11	2208, 2164, 2106	378[b]	0.094[b]	1.4×10^{-3}
12	2224, 2153, 2111, 2013	262[b]	0.059[b]	
13 (75% **4**, 25% **1**)	2218, 2153, 2113, 2013	372[b]	0.053[b]	
14 (50% **4**, 50% **1**)	2215, 2152, 2112	372[b]	0.071[b]	
15	2106	382[a]	0.003[a]	2.5×10^{-3}
16	2222, 2167, 2122	394[b]	0.183[b]	1.8×10^{-3}
17	2228, 2165, 2121	388[b]	0.223[b]	
18	2082	440[a]		3.4×10^{-3}
19	2112	399, 532[b]		
20	2090	534[a]		

[a] In CH_2Cl_2. [b] HCOOH.

Random quaternization of pyridine nitrogen in the above-mentioned polymers is accompanied by significant red shifts of the λ_{max} values. For example, the absorption maximum for the rigid-rod pyridine−dialkynyl polymer **11** at 378 nm shifts to 394 nm upon quaternization with methyltriflate (compound **16**). Similarly,

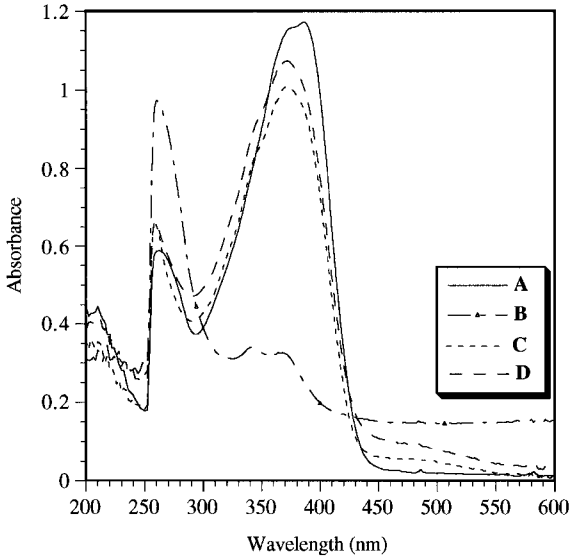


Figure 6. UV−vis absorption spectra of the organic polymers: **11** (A), **12** (B), **13** (C), **14** (D).

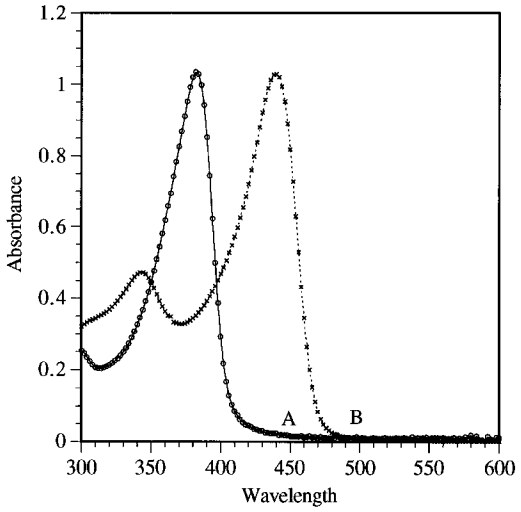


Figure 7. UV−vis absorption spectra of the Pt(II)-σ-acetylide polymers before (**15**) (A) and after quaternization (**18**) (B).

quaternization of the kinked polymer **12** (λ_{max} at 262 nm) shifts the absorption maximum to 388 nm. The large shift in the latter polymer compared to the highly conjugated rigid-rod polymer may be due to the higher degree of quaternization in the kinked polymer **12** due to its higher solubility. In general, the absorption maxima for the diethynylpyridine monomers and polymers shift to lower energies upon quaternization. The "red shift" effect upon quaternization is also evident in the organometallic polymer. For example, Figure 7 shows the UV−vis absorption spectrum of polymer **15** before (A) and after (B) quaternization with methyl iodide. The latter is red shifted by ∼40 nm. For the organic polymer which contains 50% of the quaternized nitrogen atoms in the backbone, two peaks at 399 and 532 nm are observed (Figure 8) which are also significantly red shifted. Similarly, the absorption maximum for the fully quaternized organometallic polymer appears at 534 nm which is approximately 150 nm red shifted as compared to the unquaternized analog **15**. In the case of pyridine−vinylene based polymers, it has been shown[19] that quaternization with methyl triflate leads to a blue shift, while protonation is accompanied by a red shift.

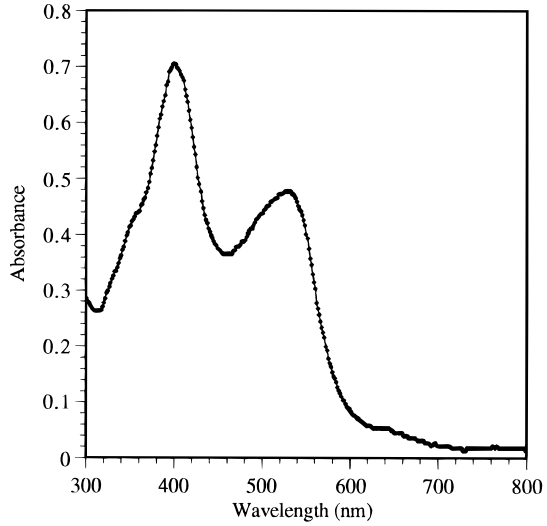


Figure 8. UV−vis absorption spectra of the organic polymer **19** (50% quaternized).

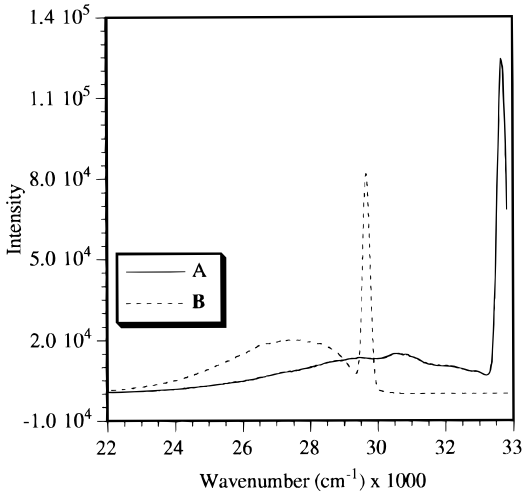


Figure 9. Fluorescence spectra of the monomers **1** (A) and **7** (B) in dichloromethane.

Fluorescence Properties. Emissive materials are of great current interest due to their suggested applications in building devices for light emitting diodes. Conjugated polymers with low lying charge excitation states hold considerable potential for such applications.[20] High quantum efficiencies in the absorbance fluorescence process is one of the essential features in the design of conjugated polymers for electroluminescent properties. The solution fluorescence spectra of the organic and organometallic monomers and polymers are shown in Figures 9−12. The unquaternized monomers **1** and **3** exhibit weak fluorescence intensities compared to their quaternized analogs **5** and **7**.

The unquaternized organic polymers fluoresce strongly in solution, emitting a light blue to purple color. The rigid-rod polymer **11** and the copolymers **13** and **14** fluoresce in the region 20 000−25 000 cm^{-1}. As in the case of monomers, random quaternization of the polymers with neat methyl triflate leads to a significant increase in fluorescence intensity (Figures 10 and 11). Polymer **16** emits a blue-white light whereas polymer **17** emits a blue-purple one. The organometallic polymer **15** exhibited weak fluorescence in comparison to the organic polymers, and upon quaternization (compound **18**), no solution phase fluorescence was observed.

The quantum yields for the above monomers and polymers are reported in Table 1. As the π-conjugation length was increased, i.e., in going from the monomer to polymer, an increase in quantum yields was observed. For example, monomer **1** gives a quantum yield of 0.015 which for the related rigid-rod polymer is calculated to be 0.094. Similarly, for the 2,6-substituted monomer

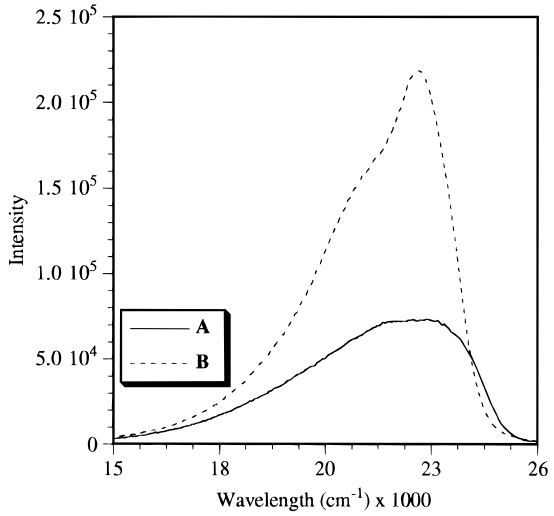


Figure 10. Fluorescence spectra of the organic polymers **11** (A) and **16** (B) in formic acid.

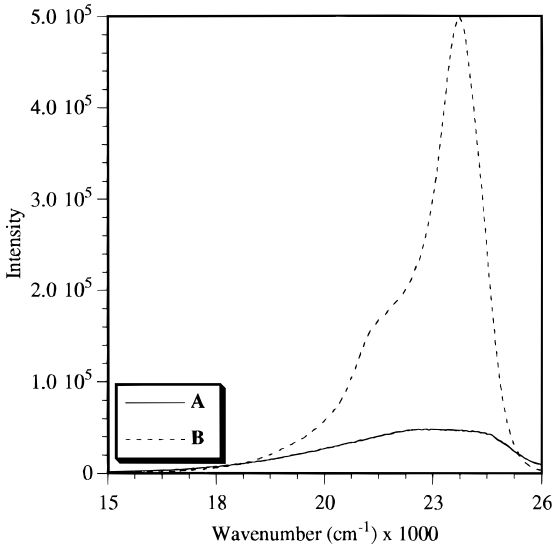


Figure 11. Fluorescence spectra of the organic polymers **12** (A) and **17** (B) in formic acid.

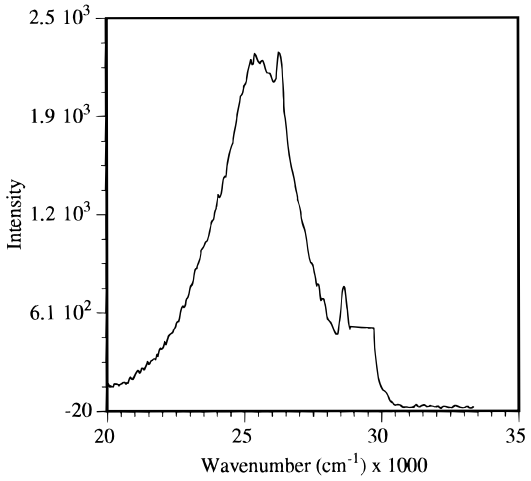


Figure 12. Fluorescence spectrum of the organometallic polymer **15** in dichloromethane.

3, the quantum yield is 0.008, and for the related polymer **12**, it is equal to 0.059. The quaternization also leads to an increase in quantum efficiency. For example, the unquaternized polymer **11** gives a quantum yield of 0.094 which increases to 0.183 upon quaternization with methyl triflate. Similarly, for the kinked polymer **12**, the quantum efficiency increases by a factor of 4 upon quaternization: before quaternization 0.059 and after quaternization 0.223.

Conductivity. Thin films of the unquaternized (**11** and **15**) and quaternized (**16** and **18**) rigid-rod polymers were cast onto glass by evaporation from solution. The average conductivity was measured using the four point method. It was found that the above polymers are insulators in the undoped state. The thin films were then exposed to iodine vapor, and the latter were found to be semiconducting. Quarternization on the pyridine nitrogen affords films with slightly higher conductivity than the unquaternized analogs (Table 1). For example, the rigid-rod organic (**11**) and organometallic (**15**) polymers upon doping show conductivities of 1.4×10^{-3} and 2.5×10^{-3} S cm^{-1}, respectively, which in the case of their quaternized doped analogs (**16** and **18**) increase to 1.8×10^{-3} and 3.4×10^{-3} S cm^{-1}.

Conclusion

We have synthesized a variety of diethynylpyridine based organic and Pt(II)-σ-acetylide monomers and oligomers which undergo facile nucleophilic substitution at pyridinyl nitrogen yielding stable pyridinium salts. A study of the linear optical properties of these compounds indicates that the entry of the positive charge into the backbone through pyridinyl nitrogen improves π-electron delocalization along the organic or organometallic backbone and has a significant effect on the physical properties which are dependent on the extent of π-conjugation. For example, the quaternization process influences their absorption and emission behavior, and (i) large red shifts in the λ_{max} values and (ii) significant enhancement of their fluorescent intensities and quantum efficiencies are observed. The quaternized polymers also show an approximately 40% increase in conductivity in the doped state compared to their doped unquaternized analogs. These results demonstrate that solution quaternization chemistry provides an alternative route to introduce positive charge into the backbone, induce enhanced conjugation, improve molecular properties, and thus allow electronic property control in onjugated polymers. Such materials offer promise for a variety of new materials based applications. Further investigations in the latter direction are currently being pursued.

Acknowledgment. We thank the NSERC of Canada and FCAR (Quebec, Canada) for financial support. We also thank Prof. Christien Reber and Prof. Michel Belletette of Universite de Montreal (Canada) for their help in measuring fluorescence spectra, and Mr. Fred Morin for his help in obtaining solid state NMR spectra.

References and Notes

(1) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.
(2) Kuzmany, H., Mehring, M., Roth, S., Eds. *Electronic Properties of Conjugated Polymers*; Springer: Berlin, 1987.
(3) Bredas, J. L., Chance, R. R., Eds. *Conjugated Polymeric Materials, Opportunities in Electronic and Molecular Electronics*; NATO ASI Series C; Kluwer: Dordrecht, 1990; p 182.
(4) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(5) Rutherford, D.; Stille, J. K.; Elliot, C. K.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294.
(6) Bunten, K. A.; Kakkar, A. K. *J. Mater. Chem.* **1995**, *5* (11), 2041.
(7) Tian, J.; Wu, C.-C.; Thompson, M. E.; Sturm, J. C.; Register, R. A.; Marsella, M. J.; Swager, T. M. *Polym. Prepr.* **1994**, *35* (1), 275.
(8) Kaufman, G.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 245.
(9) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.
(10) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 565.
(11) Hay, A. S. *J. Polym. Sci., PartA-1*, **1969**, *7*, 1625.
(12) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Compounds*; Academic Press: New York, 1965. See also: Eaton, D. *Pure Appl. Chem.* **1988**, *60*, 1107.
(13) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259.
(14) (a) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295. (b) Yam, C. M.; Kakkar, A. K. *J. Chem. Soc., Chem. Commun.* **1995**, 907.
(15) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4* (8), 1227.
(16) Wright, M. E. *Macromolecules* **1989**, *22*, 3256.
(17) Sonechika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1989**, *57*, 752.
(18) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1975.
(19) Tian, J.; Thompson, M. E.; Wu, C. C.; Sturm, J. C.; Register, R. A.; Marsella, M. J.; Swager, T. M. *Polym. Prepr.* **1994**, *35* (2), 761.
(20) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

MA951557F