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Synthesis and Initial Characterization of Poly[2-(*N,N*-dimethylamino)-1,4-phenylenevinylene]

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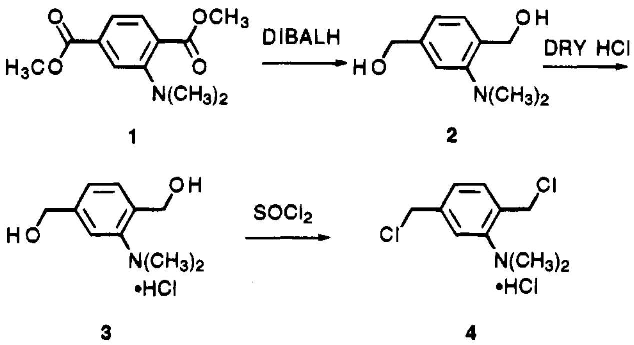
Introduction

Conducting polymers have been the subject of intense research efforts over the past 20 years. The ability to change the electromagnetic properties of the polymer (e.g., optical and/or infrared absorption or conductivity) by oxidation or reduction of the electroactive polymer make them suitable for many applications, including batteries, antistatic coatings, actuators, light emitting diodes, and electrochromic devices. Poly(1,4-phenylenevinylene) (PPV) and its mono- and disubstituted derivatives have been studied extensively in recent years.[1] Of particular interest are the dialkoxy-substituted derivatives which lower the oxidation potential of the polymer, rendering the conducting form stable under ambient atmosphere.[2] When dissimilar dialkoxy units are used (for example, 2-(2-ethylhexoxy)-5-methoxy), the neutral conjugated form of the polymer can be soluble in organic solvents.[2b] Work has been reported on poly(2-nitro-1,4-phenylenevinylene) (PNOPPV)[3] and more recently copolymers of PNOPPV and PPV.[4] At the printing of this paper there are no reports, to our knowledge, of amino-substituted phenylenevinylenes, which may have even lower oxidation potentials than their corresponding alkoxy counterparts.

Key precursors to amino-substituted phenylenevinylenes are the bis(chloromethyl) aniline compounds. However, there is considerable difficulty in synthesizing amino-substituted chloromethyl derivatives of benzene. It is difficult to chloromethylate amino-substituted benzenes; the highly acidic conditions necessary for such transformations protonate the amine and deactivate the ring to substitution. Amino-substituted xylenes have been found to be unsuitable and extremely dangerous for halogenation by *N*-chloro- and *N*-bromosuccinimide because of side reactions.[5] The synthetic route must therefore be modified.

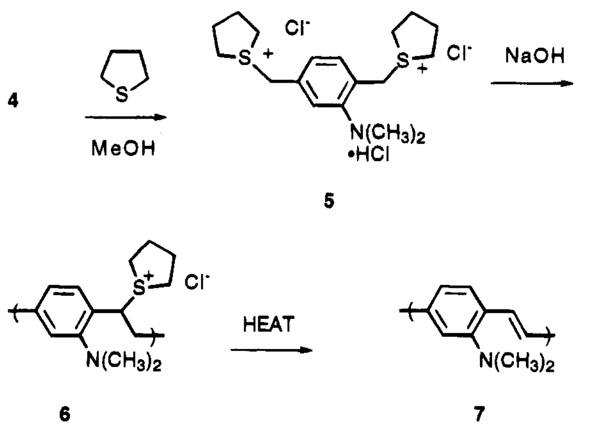
This paper describes the synthesis and characterization of 1,4-bis(chloromethyl)-2-*N,N*-dimethylaniline hydrochloride (**4**) and its conversion to poly[2-(*N,N*-dimethylamino)-1,4-phenylenevinylene] (AMPPV, **7**) via both the Wessling[6] precursor route and directly by its treatment with potassium *tert*-butoxide (t-BuOK) in tetrahydrofuran (THF). The polymer products from each of these routes are compared and discussed.

Scheme 1

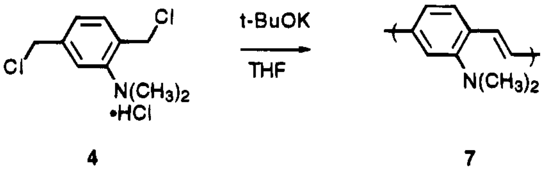


Experimental Section

Monomers and polymers were synthesized via Scheme 1 and the following reactions (Scheme 1). The sulfonium salt precursor polymer was made by polymerizing the bis sulfonium salt of compound **4** and then heating the resulting precursor polymer at elevated temperature *in vacuo*.



AMPPV (**7**) was also prepared by treating compound **4** with excess t-BuOK in dry THF under nitrogen. In this case the polymer **7** is formed directly.



Preparation of 2,5-Bis(hydroxymethyl)-*N,N*-dimethylaniline Hydrochloride (3). Into a 500 mL round bottom flask were placed 10 g (0.0421 mol) of dimethyl 2-(*N,N*-dimethylamino)terephthalate (**1**) made by a method similar to Kauffmann[7] and 100 mL of toluene. To this solution was added 120 mL of 1.5 M DIBALH with cooling and stirring; the reaction temperature was kept below 40 °C. Completion of the reaction is evidenced by the disappearance of the yellow color of the original solution. After addition of sufficient DIBALH, the reaction temperature was kept at 40 °C for about 5 min. The flask was cooled to 0 °C, and 400 mL of methanol was added carefully. The addition of the first few mL of methanol was accompanied by vigorous gas evolution due to unreacted DIBALH. The stirred mixture was then heated to reflux for 15 min, cooled, and filtered. The filter cake was washed with 200 mL of methanol. The filtrate was then concentrated on the rotary evaporator. The oily residue (compound **2**) was dissolved in 150 mL of ether and was treated with hydrogen chloride gas. The solid was filtered, washed with ether, and dried. The yield was 9.1 g (92.1%). For analysis, the compound was recrystallized from acetonitrile to give 2,5-bis(hydroxymethyl)-*N,N*-dimethylaniline hydrochloride

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(**3**); mp 121–122 °C. Anal. Calcd for $C_{10}H_{16}ClNO_2$: C, 55.18; H, 7.41; Cl, 16.29; N, 6.43. Found: C, 55.52; H, 7.52; Cl, 16.36; N, 6.67.

Preparation of 2,5-Bis(chloromethyl)-*N,N*-dimethylaniline Hydrochloride (4). Thionyl chloride (35 mL) was added to 2 g (0.00919 mol) of 2,5-bis(hydroxymethyl)-*N,N*-dimethylaniline hydrochloride (**3**). The solids went into solution immediately, accompanied by evolution of heat and gas. The reaction was stirred for several minutes. The volatiles were removed under reduced pressure to yield 2.38 g of a crystalline residue. The solid was dissolved in a minimum amount of hot acetonitrile and filtered. An equivalent amount of ethyl acetate was added. After the solution cooled crystals were deposited. After filtration and drying the yield of **4** was 1.8 g (77%); mp 149 °C dec; ^{1}H NMR (400 Mz) ($CDCl_3$) δ 3.34 (s, 6H), 4.65 (s, 2H), 5.37 (s, 2H), 7.52 (d of d, $J = 1.6, 8$ Hz, 1 H, 7.59 (d, $J = 8$ Hz, 1H), 7.64 (d, $J = 1.6$ Hz, 1H), 11.0 (br, 1H); ^{13}C NMR (400 Mz) ($CDCl_3$) δ 41.51, 44.33, 47.40, 120.60, 130.56, 131.92, 134.11, 140.79, 140.95; MS (m/z) (HCl comes off under probe conditions) 217, 182, 167, 147, 130, 117, 103, 91, 77, 51. Anal. Calcd for $C_{10}H_{14}Cl_3N$: C, 47.18; H, 5.54; Cl, 41.78; N, 5.50. Found: C, 47.04; H, 5.54; N, 5.34.

Preparation of Sulfonium Salt (5). Into a 50 mL flask equipped with a magnetic stirrer were placed 1.75 g (0.007 mol) of 2,5-bis(chloromethyl)-*N,N*-dimethylaniline hydrochloride (**4**), 3.0 g (0.032 mol) of tetrahydrothiophene, and 15 mL of methanol. The mixture was heated to 40 °C and stirred for about 5 h. The resulting solution was cooled and poured into 500 mL of acetone at 0 °C, yielding a very hygroscopic resinous material. This material (**5**) (approximately 3 g) was dissolved in 8 mL of water and used directly in the next step.

Preparation of Polymer (6). Both solutions used in the following polymerization step were deoxygenated with N_2 at room temperature for 2 h. To 8 mL of a 0.87 M (approximately) aqueous solution of the sulfonium salt monomer **5** was added all at once under nitrogen 10 mL of a 1.44 M aqueous solution of NaOH (0.014 mol). The contents of the flask turned orange-yellow and slightly cloudy after about 5 min. After 35 min the pH was about 12, indicating that the amine hydrochloride groups were converted to free base. The water was neutralized to pH 5 with dilute hydrochloric acid, and the mixture turned pale yellow and became less cloudy. This mixture was dialyzed (molecular weight cut off 3500 Da) for about 4 days against deionized water to remove salt and low molecular weight material. The resulting solution was filtered, giving a clear solution of **6** that fluoresced green upon excitation with UV light.

Film Casting and Pyrolysis of Polymer 6. A 5 mL aliquot of an aqueous solution of polymer **6** was placed on a treated glass substrate (the glass was treated with dichlorodimethylsilane to facilitate removal of the polymer film) and allowed to evaporate. The resulting pale green film could be easily removed from the substrate: IR 3358, 3002, 2936, 2862, 2829, 2785, 1604, 1504, 1470, 1453, 1207, 1095, 1045, 806 cm^{-1}. Anal. Calcd for $C_{14}H_{20}ClNS$ (polymer **6**): C, 62.32; H, 7.47; Cl, 13.14; N, 5.19; S, 11.88. Found: N, 5.54. The fresh film was then heated in vacuo at 250 °C for 12 h in order to obtain polymer **7**: IR 3020, 2937, 2854, 2828, 2784, 1610, 1494, 1466, 1414, 1273, 1188, 1145, 1116, 1094, 1050, 980, 958, 905, 853, 814, 742, 646 cm^{-1}. Anal. Calcd for $C_{10}H_{11}N$ (polymer **7**): C, 82.72; H, 7.64; N, 9.65. Anal. Calcd for $C_{10}H_{12}ClN$ (hydrochloride of polymer **7**): C, 66.12; H, 6.66; Cl, 19.52; N, 7.71. Found: N, 6.95.

Reaction of 4 with Potassium *tert*-Butoxide To Form Polymer 7. Compound **4** (0.25 g) was added to a solution of 0.66 g of t-BuOK in 35 mL of THF with cooling in a dry ice/2-propanol bath. A yellow-green solution formed which turned dark red after about 30 min. After 2 h the dry ice bath was removed and the solution stirred for an additional 2.5 h at around 25 °C. Fifty mL of methanol was added, and the mixture was filtered. The bright orange powder was washed with methanol and then several times with water. This material was insoluble in all organic solvents used. The yield was approximately 0.09 g (60%). ^{13}C NMR (solid state, NQS/MAS) δ 44.5, 121.5, 130.5, 137.2, 152.1; IR 3024, 2976, 2937, 2862, 2825, 2780, 1711, 1667, 1595, 1551, 1500, 1452, 1414, 1309, 1190, 1143, 1095, 1050, 978, 906, 877, 853, 821, 636 cm^{-1}. Anal. Calcd for $C_{10}H_{11}N$ (polymer **7**): C, 82.72; H, 7.64; N, 9.65. Found: C, 80.84; H, 7.66; N, 9.84.

It has been shown by Heeger and co-workers[8] that the emeraldine base of polyaniline can be treated with acids including camphorsulfonic acid to obtain a soluble form of polyaniline, the emeraldine salt. Since AMPPV has an amino group the polymer might be made soluble (but likely not conducting) by treatment of the free base with camphorsulfonic acid. To this end, 0.149 g of polymer **7** and 0.265 g of camphorsulfonic acid were added to 10 mL of cresol in a 25 mL flask. The flask and contents were placed in an ultrasonic bath for 24 h. After 24 h a pale green solution was obtained and was filtered. The hydrocamphor sulfonate of AMPPV was found to be soluble in hexafluoro-2-propanol and trifluoracetic acid. Films cast from these solvents were orange. Infrared analysis of a film cast on a KBr pellet confirmed the presence of camphorsulfonate, providing supporting evidence for quarternization of the amine.

2,5-Bis(chloromethyl)-4-nitro-*N,N*-dimethylaniline. A 0.5-mL portion of 70% aqueous nitric acid (7.8 equiv) was added carefully to 10 mL of 98% sulfuric acid, and the resulting solution was cooled to 5 °C (ice bath). 2,5-Bis(chloromethyl)-*N,N*-dimethylaniline hydrochloride salt (**4**) (0.255 g, 1 mmol) was added in one portion. The clear yellow solution was allowed to warm to rt and stirred for 5 h and then poured into 100 mL of ice–water. The solution was neutralized by the addition of 45 mL of 4 M NaOH followed by a small amount of saturated aqueous $NaHCO_3$. This solution was extracted with 3 × 50 mL of CH_2Cl_2. The combined extracts were then dried with $MgSO_4$ and concentrated in vacuum to give 0.23 g of an orange glass (87%). This material was a mixture of approximately 33% 2,5-bis(chloromethyl)-6-nitro-*N,N*-dimethylaniline and 67% 2,5-bis(chloromethyl)-4-nitro-*N,N*-dimethylaniline which was separated by column chromatography on silica gel eluting with 40% (by volume) ethyl acetate/hexanes to give 0.061 g of 2,5-bis(chloromethyl)-6-nitro-*N,N*-dimethylaniline ($R_f = 0.42$) as a yellow glass and 0.120 g of 2,5-bis(chloromethyl)-4-nitro-*N,N*-dimethylaniline ($R_f = 0.27$) as yellow crystals; ^{1}H NMR ($CHCl_3$) δ 2.93 (6H), 4.78 (2H), 5.02 (2H), 7.18 (1H), 8.23 (1H); ^{13}C NMR ($CHCl_3$) δ 43.65, 43.81, 61.89, 119.79, 127.36, 132.69, 133.33, 140.48, 155.86.

Synthesis Attempt of Poly[2-(*N,N*-dimethylamino)-5-nitro-1,4-phenylenevinylene] (AMNPPV). A THF solution of t-BuOK (0.65 g, 0.25 mmol in 10 mL THF) was added dropwise to a solution of 0.25 g of 2,5-bis(chloromethyl)-4-nitro-*N,N*-dimethylaniline in 10 mL of THF under nitrogen. The solution turned deep red instantly and turned greenish-black after a few hours. After 20 h the reaction was quenched with ethanol. The mixture turned brown immediately and a solid precipitated. The solution was neutralized to pH 7 with dilute HCl, filtered, washed with water, and dried. The resulting brown solid was, surprisingly, soluble in chloroform, but NMR analysis of this material is very difficult to interpret. Anal. Calcd for $C_{10}H_{11}N_2O_2$ (AMNPPV): C, 62.82; H, 5.80; N, 14.65; O, 16.73. Anal. Calcd for $C_{10}H_{12}Cl_2N_2O_2$ (2,5-bis(chloromethyl)-4-nitro-*N,N*-dimethylaniline): C, 45.65; H, 4.60; Cl, 26.95; N, 10.65; O, 12.16. Found: N, 7.26; Cl, 22.78. The high chlorine content in the brown solid suggests side reactions and/or Meisenheimer complex formation.[9]

Discussion

Comparison of Techniques. When heated, cyclic sulfonium salt precursor polymers give off primarily tetrahydrothiophene and hydrochloric acid. The thermal elimination of polymer **6** to polymer **7** is therefore complicated by the probable formation of the amine hydrochloride.

While the precursor method allows one to cast films, a consequence of this method is the possible quarterniza-

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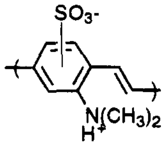
(9) Better results may be obtained with the Wessling route, and these experiments are in progress. Future plans also include more detailed conductivity and cyclic voltametry studies of polymer **7** and/or its camphorsulfonate (depending on whether polymer **7** can be made soluble by varying the alkyl groups on the amine), nitrating compound **3** followed by reduction, N-alkylation, and chlorination to make precursors for poly[2,5-bis(*N,N*-dimethylamino)-1,4-phenylenevinylene].

tion of the free amine by the elimination products, most likely HCl. This is evidenced by the difference in color between the heat-treated polymer **6** (brownish yellow, band gap 500 nm) and the polymer from the treatment of **4** with base (orange, estimated band gap 560 nm). Furthermore, the elemental analysis of the polymer from the treatment of **4** with base agrees much better with the calculated values for polymer **7** than the analysis of the heat-treated polymer **6**.

Sulfonation of AMPPV. It was also possible to sulfonate AMPPV using fuming sulfuric acid. Since fuming sulfuric acid is a strong oxidizing agent also, it should be possible to obtain the conducting form of sulfonated AMPPV, **8**. About 0.1 g of AMPPV was treated with 20% fuming sulfuric acid. After treatment with fuming sulfuric acid, a black rubbery solid was obtained. Conductivity of this solid was found to be 10^{-2} S/cm.



Summary and Conclusion

Poly[2-*N*,*N*-dimethylamino)-1,4-phenylenevinylene] (AMPPV) has been synthesized and characterized. The direct method, 1,4-bis(chloromethyl)-2-*N*,*N*-dimethylaniline hydrochloride treated with potassium *tert*-butoxide in THF, appears to provide cleaner final polymer than the polymer prepared using the Wessling route. The insoluble form of AMPPV can be made soluble by treatment with an equimolar amount of camphorsulfonic acid. Conductivity of the sulfonated/oxidized form of AMPPV was found to be 10^{-2} S/cm. 2,5-Bis(chloromethyl)-4-nitro-*N*,*N*-dimethylaniline and 2,5-bis(chloromethyl)-6-nitro-*N*,*N*-dimethylaniline were synthesized and characterized.

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Supplementary Material Available: Experimental procedures and compound characterization spectra (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.