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Preparation and Properties of Poly(methacrylamide)s Containing Oligoaniline Side Chains

Ru Chen and Brian C. Benicewicz*

Department of Chemistry, New York State Center for Polymer Synthesis, Rensselaer Polytechnic Institute, Troy, New York 12180

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ABSTRACT: New poly(methacrylamide)s containing oligoaniline side chains were synthesized and characterized. Oligoanilines were prepared by palladium-catalyzed amination, followed by reaction with methacryloyl chloride to give methacrylamide monomers. Polymers were prepared by free radical polymerization. The polymers were prepared in the leucoemeraldine state and were oxidized to the emeraldine state by exposure to oxygen gas. The electrochemical characterization of these polymers by cyclic voltammetry indicated that the redox behaviors were similar to the corresponding oligoanilines.

Introduction

Conducting polymers have been extensively studied since the important discovery of Shirakawa et al.[1] that an organic polymer could display high conductivity at room temperature when exposed to an appropriate dopant. Because of their unique electrical and optical properties, conducting polymers have a wide variety of potential applications from electronic and optoelectronic devices such as field effect transistors, electroluminescent, electrochromic, and photovoltaic devices to sensors, gas separation membranes, electromagnetic shielding layers, and corrosion protective coatings.[2−4]

Early studies on conjugated polymers were plagued by difficulties in processing the intractable materials and imperfections in the conjugated polymer structures. Conjugated oligomers were initially introduced as model compounds to rationalize and predict the properties of the intractable polymeric analogues. Because of the monodisperse composition, well-defined structure, and special physical, electronic, and optical properties, conjugated oligomers also have potential applications in molecular electronics and nanotechnology. Incorporation of conjugated oligomers into polymer structures combines the properties of the specific oligomer and desirable polymer properties such as mechanical strength and film-forming properties. Shirota et al.[5−7] showed that oligothiophenes can be attached to vinyl and methacrylate polymers as side chains. These polymers showed an electrical conductivity in the range of semiconductors and have potential applications in electrochromic devices. Dufour et al.[8] copolymerized 3-octylthiophene with a thiophene monomer containing an oligoaniline side chain which displayed spectroelectrochemical properties of both polyaniline and poly(thiophene). Polymers with conjugated aniline oligomers in the main chains have also been prepared by an acid-induced polycondensation.[9] This polymer displayed good solubility in common organic solvents and electrical conductivities up to 1 S/cm upon doping. Electroactive polyimides derived from the bis-amino-terminated aniline trimer were also reported by Wei et al.[10] Yu et al.[11,12] reported on the synthesis of rod−coil diblock copolymers containing an oligo(*p*-phenylenevinylene) block and polyisoprene or poly(ethylene glycol) block. These copolymers self-assembled into different nanoscale morphologies such as lamellae and cylindrical micelles which may lead to electrical and optical properties absent in conjugated homopolymers.

Polymers containing pendant conjugated oligomers are of interest because of the variety of possible oligomers, processability, and potential applications in electronic devices.[7] The electrical and electrochemical properties can be tailored by adjusting the oligomer length, incorporation of ring substituents, and alteration of the basic chemical structure of the oligomer. Polymer properties can be easily modified and improved through copolymerization. The covalent bond attachment of the oligomers to the polymer backbone also prevents the loss of active species from the bulk polymer through migration and extraction. In this paper, we report the synthesis of poly(methacrylamide)s with oligoaniline side chains, polymers **1** and **2** (Figure 1). The effect of oligoaniline side chain length on the redox behavior of the polymer will be reported and discussed.

Experimental Section

All chemicals were purchased from ACROS Organics unless otherwise specified. *p*-Aminodiphenylamine (98%), benzophenone (99%), tetra-*n*-butylammonium tribromide (98+%), di-*tert*-butyl bicarbonate (97%), 4-(dimethylamino)pyridine (DMAP, 99%), ammonium formate (99%), palladium acetate ($Pd(OAc)_2$, 47.5% Pd), sodium *tert*-butoxide (98%), methacryloyl chloride (Aldrich, 98+%), and triethylamine (99%) were all used as received without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from ethanol. Bis[(2-diphenylphosphino)phenyl] ether (DPEphos)[13] and *N*-(diphenylmethylene)-4-bromoaniline **(3)**[14] were synthesized according to literature methods. Toluene and tetrahydrofuran (THF, HPLC grade) were refluxed over sodium metal for 24 h followed by distillation under argon. *N*,*N*-Dimethylformamide (DMF) was treated with 5 Å molecular sieves and distilled under reduced pressure. Deuterated chloroform ($CDCl_3$, 99.9 at. % D) and deuterated methyl sulfoxide (DMSO-d_6, 99.9 at. % D) were used as received. Elemental analysis was performed by Midwest Microlabs. NMR spectra were recorded on a Varian 500 spectrometer using solvent residues as references. A Shimadzu GCMS-QP-5000 spectrometer was used to confirm the chemical structure and purity of all compounds prepared in this work. Fourier transform infrared (FTIR) spectrometry was performed using a Bio-Rad FTS3000 spectrometer. UV−vis spectra were recorded on Perkin-Elmer Lamda 4C UV/vis spectrophotometer. Thermal analysis was carried out in a nitrogen atmosphere with a heating rate of 20 °C/min on a

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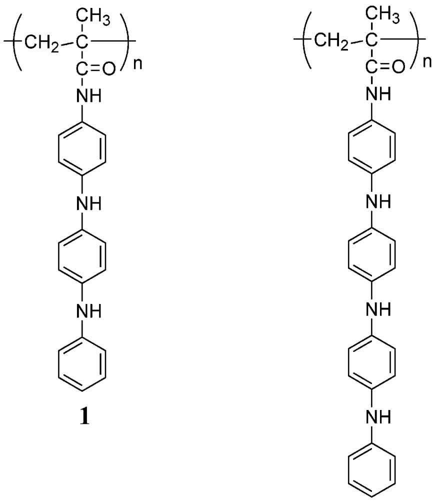


1

2

Figure 1. Chemical structures of the poly(methacrylamide)s containing oligoaniline side chains.

thermal gravimetric analysis (TGA) Perkin-Elmer 7 series instrument with Pyris software or a Mettler-Toledo DSC 822e and TGA/SDTA 851e. The molecular weight of the polymers was measured on a Waters GPC system equipped with a refractive index detector (Waters 2410) and three Styragel columns packed with 5 μm particles (HR1: effective molecular weight 100−5000; HR3: effective molecular weight 500−30 000; HR4: effective molecular weight 5000−500 000) using THF as the eluent at a flow rate of 0.3 mL/min. The column temperature was set at 30 °C. Molecular weights were reported relative to polystyrene standards. Cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with a three-electrode electrochemical cell using SCE and Pt wire as the reference and counter electrodes, respectively. The working electrode was prepared by casting the polymer as a film on the surface of Pt electrode. Sulfuric acid aqueous solution (1.0 M) was used as the supporting electrolyte. The scan rate was 100 mV/s.

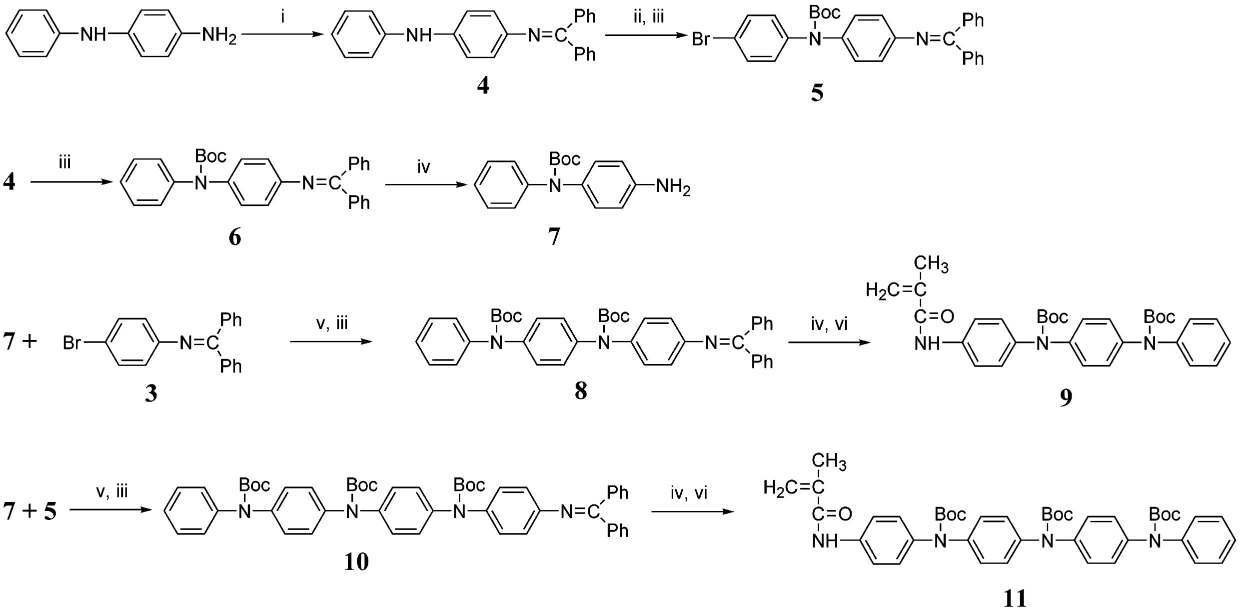
***N*-(Diphenylmethylene)-*N*′-(*tert*-butoxycarbonyl)-*N*′-(4-bromophenyl)-*p*-phenylenediamine (5).** *p*-Aminodiphenylamine (22.32 g, 121.1 mmol) and benzophenone (20.00 g, 109.8 mmol) were dissolved in toluene (125 mL). Molecular sieves, 5 Å (30.0 g), were added to the solution. The mixture was refluxed for 48 h under a nitrogen atmosphere. The solution was decanted, and the molecular sieves were washed with ethyl ether until the filtrate was colorless. The organic solutions were combined and concentrated. The solid residue was dissolved in ethyl acetate and washed with NaOH solution (2 M) and finally brine. The organic solution was dried with anhydrous sodium sulfate and concentrated. The crude solid was recrystallized in methanol/ethyl acetate. The yellow crystals were dried in vacuo at 50 °C for 24 h. The yield of product **4** was 35.69 g (93%). Compound **4** (10.00 g, 28.72 mmol) was dissolved in dichloromethane (80 mL), and tetra-*n*-butylammonium tribromide (15.24 g, 31.61 mmol) was added in one portion. The solution was stirred at room temperature for 1 h, and then sodium sulfite solution (22%, 50 mL) was added with stirring for 30 min, followed by the addition of sodium hydroxide solution (2 M, 25 mL). The organic phase was washed with distilled water, dried over anhydrous sodium sulfate, and concentrated. The residue was dissolved in THF (80 mL), to which di-*tert*-butyl bicarbonate (7.52 g, 34.5 mmol) and 4-(dimethylamino)pyridine (0.58 g, 4.7 mmol) were added. The solution was refluxed for 24 h and concentrated. The residue was recrystallized in methanol/ethyl acetate and dried in vacuo at 50 °C for 24 h. The yield of the slightly yellow crystals was 13.28 g (88%); mp 163−165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.3 Hz, 2H, Ar), 7.50−7.33 (m, 5H, Ar), 7.31−7.20 (m, 3H, Ar), 7.11 (dd, J = 7.9, 1.3 Hz, 2H, Ar), 7.02 (d, J = 8.8 Hz, 2H, Ar), 6.94 (d, J = 8.5 Hz, 2H, Ar), 6.68 (d, J = 8.5 Hz, 2H, Ar), 1.39 (s, 9H, $-OC(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 153.7, 149.7, 142.5, 139.6, 137.9, 136.2, 131.7, 131.1, 129.7, 129.5, 128.9, 128.4, 128.1, 127.8, 127.6, 121.7, 118.3, 81.6, 28.3. IR (KBr, cm^{-1}): 3059, 3028, 2977, 2926, 1709, 1490, 1324, 1161, 701. Anal. Calcd for $C_{30}H_{27}BrN_2O_2$: C, 68.31; H, 5.16; Br, 15.15; N, 5.31. Found: C, 68.24; H, 5.07; Br, 15.14; N, 5.27.

***N*-(Diphenylmethylene)-*N*′-(*tert*-butoxycarbonyl)-*N*′-(phenyl)-*p*-phenylenediamine (6).** Compound **4** (24.00 g, 68.93 mmol) was dissolved in THF (200 mL). Di-*tert*-butyl bicarbonate (18.00 g, 82.47 mmol) and 4-(dimethylamino)pyridine (1.26 g, 10.3 mmol) were added. The solution was refluxed for 24 h. The solvent was removed by rotary evaporation. The crude solid was recrystallized in ethyl acetate/hexanes and dried in vacuo at 50 °C for 24 h. Product: slightly yellow needles, 29.52 g (95%); mp 154−155 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.1 Hz, 2H, Ar), 7.46 (t, J = 7.0 Hz, 1H, Ar), 7.40 (t, J = 7.6 Hz, 2H, Ar), 7.32−7.20 (m, 5H, Ar), 7.18−7.06 (m, 5H, Ar), 6.97 (d, J = 8.5 Hz, 2H, Ar), 6.67 (d, J = 8.3 Hz, 2H, Ar), 1.40 (s, 9H, $-OC(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 154.0, 149.3, 143.3, 139.7, 138.5, 136.3, 131.0, 129.7, 129.5, 128.9, 128.7, 128.4, 128.1, 127.6, 126.4, 125.3, 121.6, 81.0, 28.4. IR (KBr, cm^{-1}): 3059, 3027, 2982, 2924, 1707, 1497, 1319, 1163, 695. Anal. Calcd for $C_{30}H_{28}N_2O_2$: C, 80.33; H, 6.29; N, 6.25. Found: C, 80.31; H, 6.32; N, 6.26.

***N*-(Diphenylmethylene)-*N*′-(*tert*-butoxycarbonyl)-*N*′-[4-(*N*−*tert*-butoxycarbonylanilino)]phenyl-*p*-phenylenediamine (8).** Compound **6** (24.00 g, 53.50 mmol), ammonium formate (40.61 g, 644.0 mmol), and palladium on carbon (5%, 2.83 g, 1.33 mmol Pd) were charged into a round-bottomed flask and purged with argon. THF (100 mL) and methanol (250 mL) were added, and the reaction mixture was refluxed for 24 h. The solution was concentrated, and the residue was dissolved in dichloromethane, filtered through Celite, and then concentrated. The solid was ground and washed with hexanes and then filtered. The white powder was dried in vacuo at 50 °C for 24 h. Yield of product **7** was 15.00 g (98%). Compound **7** (5.00 g, 17.6 mmol), palladium acetate (69.8 mg, 0.311 mmol), and DPEphos (246.0 mg, 0.457 mmol) were charged into a flask and purged with argon. Compound **3** (4.92 g, 14.6 mmol) was added, followed by toluene (30 mL). The solution was warmed to 50 °C to aid the dissolution. Sodium *tert*-butoxide (3.00 g, 31.2 mmol) was added in one portion. Additional toluene (20 mL) was added to wash the flask wall. The reaction mixture was heated to 110 °C with stirring for 24 h. The solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane, washed with distilled water, and dried over anhydrous sodium sulfate and concentrated. The residue was dissolved in THF (100 mL), and di-*tert*-butyl bicarbonate (4.12 g, 18.9 mmol) and 4-(dimethylamino)pyridine (0.38 g, 3.1 mmol) were added. The reaction mixture was refluxed for 24 h. The solvent was removed, and the solid was recrystallized in methanol. Product **8** was obtained as a pink solid 6.92 g (74%); mp 149−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.3 Hz, 2H, Ar), 7.47 (t, J = 7.1 Hz, 1H, Ar), 7.40 (t, J = 7.4 Hz, 2H, Ar), 7.33−7.22 (m, 5H, Ar), 7.21−7.06 (m, 9H, Ar), 6.96 (d, J = 8.5 Hz, 2H, Ar), 6.67 (d, J = 8.3 Hz, 2H, Ar), 1.44 (s, 9H, $-OC(CH_3)_3$), 1.38 (s, 9H, $-OC(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 154.0, 149.4, 143.0, 140.6, 140.0, 139.7, 138.2, 136.3, 131.0, 129.7, 129.5, 128.9, 128.4, 128.1, 127.7, 127.2, 127.0, 126.3, 125.9, 121.6, 81.4, 81.1, 28.4, 28.3. IR (KBr, cm^{-1}): 3059, 3027, 2976, 2925, 1711, 1494, 1325, 1162, 697. Anal. Calcd for $C_{41}H_{41}N_3O_4$: C, 76.97; H, 6.46; N, 6.57. Found: C, 76.70; H, 6.65; N, 6.54.

***N*-(Methacryloyl)-*N*′-(*tert*-butoxycarbonyl)-*N*′-[4-(*N*-*tert*-butoxycarbonylanilino)]-*p*-phenylenediamine (9).** Compound **8** (5.00 g, 7.82 mmol), ammonium formate (7.39 g, 117 mmol), and palladium on carbon (5%, 0.86 g, 0.40 mmol Pd) were charged into a round-bottomed flask and purged with argon. THF (100 mL) and methanol (250 mL) were added, and the reaction mixture was refluxed for 24 h. The solution was concentrated, and the residue was dissolved in dichloromethane, filtered through Celite, and concentrated. The solid was ground and washed with hexanes and then filtered. The

Scheme 1[a]



[a] (i) Ph_2CO, toluene, reflux, 48 h; (ii) n-Bu_4NBr_3, CH_2Cl_2, rt, 1 h; (iii) $(Boc)_2O$, DMAP, THF, reflux, 24 h; (iv) NH_4HCO_2, Pd/C, THF/MeOH, reflux, 24 h; (v) $Pd(OAc)_2$, DPEphos, NaOt-Bu, toluene, 110 °C, 24 h; (vi) methacryloyl chloride, THF, Et_3N, 0 °C, 24 h.

white powder was dried in vacuo at 50 °C for 24 h; yield 3.48 g (94%). This amine (3.00 g, 6.31 mmol) was dissolved in THF (25 mL) under a nitrogen atmosphere. Triethylamine (1.70 g, 16.8 mmol) was added, and the reaction mixture was cooled with a ice bath. Methacryloyl chloride (0.79 g, 7.6 mmol) in THF (25 mL) was added slowly into the solution. After completion, the reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off and washed with THF. The solutions were combined, and the solvent was removed with rotary evaporation. The residue was dissolved in dichloromethane, washed with HCl solution (1 M), Na_2CO_3 solution (1 M), and distilled water. The solution was dried with anhydrous sodium sulfate. The solvent was removed, and the residue was separated by column chromatography (silica gel, ethyl acetate/hexanes, 1:1). The product was obtained as a white powder: 2.34 g, (68%); mp 178−180 °C (decomposition). ^1H NMR (500 MHz, DMSO-d_6): δ 9.84 (s, 1H, −NH), 7.66 (d, J = 8.8 Hz, 2H, Ar), 7.34 (t, J = 7.8 Hz, 2H, Ar), 7.25−7.10 (m, 9H, Ar), 5.79 (s, 1H, cis =CH), 5.51 (s, 1H, trans =CH), 1.94 (s, 3H, =C−CH_3), 1.37 (s, 18H, −$OC(CH_3)_3$). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.8, 153.0, 152.9, 142.7, 140.4, 140.0, 137.8, 137.0, 128.9, 127.4, 127.1, 127.1, 126.8, 125.9, 120.5, 120.0, 80.4, 80.4, 27.8, 27.8, 18.7. IR (KBr, cm^{-1}): 3331, 3043, 2977, 2930, 1711, 1511, 1327, 1162, 1057. Anal. Calcd for $C_{32}H_{37}N_3O_5$: C, 70.70; H, 6.86; N, 7.73. Found: C, 70.90; H, 6.88; N, 7.72.

Compounds **10** and **11** were obtained by the same procedures.

Compound 10. Obtained as pink solid in 63% yield; mp 184−185 °C (decomposition). ^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.3 Hz, 2H, Ar), 7.46 (t, J = 7.1 Hz, 1H, Ar), 7.40 (t, J = 7.4 Hz, 2H, Ar), 7.33−7.22 (m, 5H, Ar), 7.21−7.06 (m, 13H, Ar), 6.95 (d, J = 8.5 Hz, 2H, Ar), 6.67 (d, J = 8.4 Hz, 2H, Ar), 1.44 (s, 9H, −$OC(CH_3)_3$); 1.43 (s, 9H, −$OC(CH_3)_3$); 1.39 (s, 9H, −$OC(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 154.0, 143.0, 140.8, 140.6, 140.3, 139.7, 138.2, 136.3, 131.1, 129.8, 129.6, 129.0, 128.9, 128.4, 128.1, 127.7, 127.2, 126.4, 126.0, 121.6, 81.5, 81.5, 81.2, 28.4, 28.4. IR (KBr, cm^{-1}): 3059, 3027, 2977, 2928, 1711, 1506, 1325, 1162, 698. Anal. Calcd for $C_{52}H_{54}N_4O_6$: C, 75.16; H, 6.55; N, 6.74. Found: C, 74.94; H, 6.63; N, 6.75.

Compound 11. Obtained as white solid in 78% yield; mp 141−143 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 9.84 (s, 1H, −NH), 7.66 (d, J = 8.8 Hz, 2H, Ar), 7.34 (t, J = 7.8 Hz, 2H, Ar), 7.25−7.10 (m, 13H, Ar), 5.81 (s, 1H, cis =CH), 5.51 (s, 1H, trans =CH), 1.95 (s, 3H, =CCH_3), 1.38 (s, 27H, −$OC(CH_3)_3$). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.8, 153.0, 152.9, 152.9, 142.6, 140.5, 140.4, 140.3, 140.0, 139.7, 137.8, 137.0, 128.9, 127.4, 127.2, 127.1, 127.1, 126.9, 125.9, 120.5, 120.0, 80.5, 80.5, 80.4, 27.8, 27.8, 27.7, 18.7. IR (KBr, cm^{-1}): 3335, 3043, 2977, 2930, 1712, 1511, 1327, 1162, 1057. Anal. Calcd for $C_{43}H_{50}N_4O_7$: C, 70.28; H, 6.86; N, 7.62. Found: C, 70.32; H, 6.95; N, 7.60.

Polymerization of Compound 9. AIBN (10.0 mg, 6.09 × 10^{-2} mmol) was dissolved in DMF (10 mL). Compound **9** (1.00 g, 1.84 mmol) was then dissolved in 2 mL of AIBN/DMF solution. The reaction mixture was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated to 70 °C for 24 h with stirring. The polymer was precipitated from methanol/water (2:1) three times, filtered, and dried in a vacuum oven at 60 °C for 24 h. The yield was 0.65 g (65%). The GPC analysis gave $M_n = 2.8 \times 10^4$, $M_w = 5.2 \times 10^4$, and PDI = 1.9. ^1H NMR (500 MHz, DMSO-d_6): δ 9.02 (s, 1H, −NH−), 7.41 (b, 2H, Ar), 7.25 (b, 2H, Ar), 7.12 (b, 9H, Ar), 1.96 (b, 2H, −CH_2−), 1.32 (b, 21H, −CH_3). IR (KBr, cm^{-1}): 2977, 1711, 1510, 1327, 1161, 1056, 847. Anal. Calcd for $C_{32}H_{37}N_3O_5$: C, 70.70; H, 6.86; N, 7.73. Found: C, 70.95; H, 6.80; N, 7.33.

Polymerization of Compound 11. AIBN (10.0 mg, 6.09 × 10^{-2}mmol) was dissolved in DMF (20 mL). Compound **11** (0.504 g, 0.686 mmol) was then dissolved in 2 mL of AIBN/DMF solution. The reaction mixture was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated to 70 °C for 24 h with stirring. The polymer was precipitated from methanol/water (2:1) three times, filtered, and dried in a vacuum oven at 60 °C for 24 h. The yield was 0.38 g (76%). The GPC analysis gave $M_n = 5.8 \times 10^3$, $M_w = 1.1 \times 10^4$, and PDI = 1.9. ^1H NMR (500 MHz, DMSO-d_6): δ 9.09 (s, 1H, −NH−), 7.45 (b, 2H, Ar), 7.24 (b, 2H, Ar), 7.10 (b, 13H, Ar), 1.97 (b, 2H, −CH_2−), 1.31 (b, 30H, −CH_3). IR (KBr, cm^{-1}): 2977, 1712, 1510, 1326, 1161, 1055, 847. Anal. Calcd for $C_{43}H_{50}N_4O_7$: C, 70.28; H, 6.86; N, 7.62. Found: C, 69.91; H, 6.94; N, 7.60.

Results and Discussion

Oligomer and Monomer Synthesis. Several methods have been used for the preparation of oligoanilines. Honzl et al.[15] prepared aniline oligomers by the reaction of diethyl succinoylsuccinate and aromatic amines,

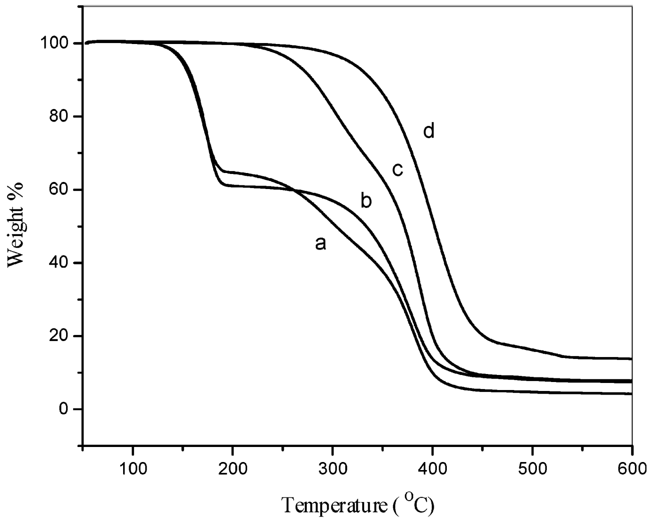


Figure 2. TGA thermograms of (a) *t*-Boc-protected polymer **1**, (b) *t*-Boc-protected polymer **2**, (c) polymer **1**, and (d) polymer **2**, carried out in a nitrogen atmosphere.

followed by hydrolysis, decarboxylation, and aromatization. This procedure was modified by Wudl et al.[16] for the preparation of octaaniline. Condensation between arylamines and phenol using a condensing reagent was applied in the oligomer synthesis by Ochi et al.[17] Rebourt et al.[18] prepared aniline trimers and tetramers by a modified Ullmann reaction without base. A method similar to the oxidative polymerization of polyaniline was developed by Wei et al.[19] However, the product contained oligomers with different chain lengths, and intensive purification steps were necessary to obtain well-defined products. Also, oligomers containing substituent groups are difficult to prepare using this method. Recently, palladium-catalyzed amination has emerged as a powerful method for the formation of aromatic C—N bonds. The versatility of the methodology has been demonstrated by the synthesis of aniline oligomers with different functional end groups.[14] Numerous catalyst/ligand systems have been studied for this reaction. The most common system is tri(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP). In this work the catalyst system palladium acetate ($Pd(OAc)_2$) and DPEphos was used for the coupling reaction of an aromatic amine with an aryl bromide. Compared with other catalysts, palladium acetate is stable in air and not very expensive. DPEphos can be prepared by a two-step, one-pot reaction in medium scale with low cost. This ligand is also stable in air. Buchwald et al.[20] reported that this catalyst was highly efficient for the C—N coupling reaction. Its application in the synthesis of aniline oligomers has not been reported. In our experiments, the catalyst system $Pd(OAc)_2$/DPEphos was highly efficient for the synthesis of aniline oligomers.

Table 1. Properties of Poly(methacrylamide)s with Oligoaniline Side Chains

	M_n[a]	M_w[a]	PDI[a]	$T_{5\%}$[b] (°C)
t-Boc-protected polymer **1**	2.8×10^4	5.2×10^4	1.9	150
t-Boc-protected polymer **2**	5.8×10^3	1.1×10^4	1.9	151
polymer **1**	2.0×10^4	3.3×10^4	1.6	261
polymer **2**	3.4×10^3	4.6×10^3	1.4	317

[a] Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (PDI) of polymers according to gel permeation chromatography relative to polystyrene standards with tetrahydrofuran as eluent. [b] $T_{5\%}$ is the temperature at 5% weight loss.

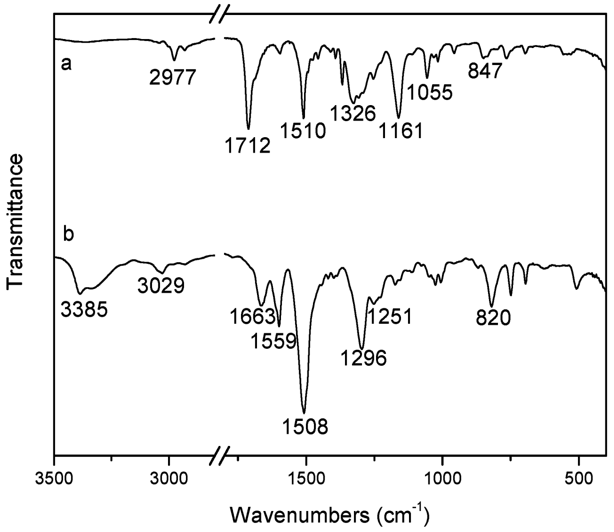


Figure 3. FTIR spectra of (a) *t*-Boc-protected polymer **2** and (b) polymer **2**.

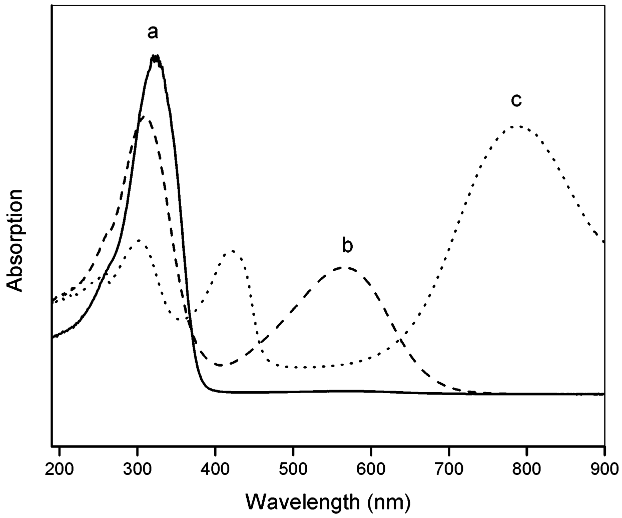


Figure 4. UV—vis spectra of polymer **2** in DMF solution: (a) reduced, (b) oxidized, and (c) doped with sulfuric acid.

The synthesis of the monomers explored in this work is shown in Scheme 1. Compound **7** was prepared from 4-aminodiphenylamine, in which the primary amine group was first converted to an imine and the secondary amine was subsequently protected by a *tert*-butoxycarbonyl group, followed by recovery of the primary amine by catalyzed hydrogenation. *N*-Diphenylmethylene-4-bromoaniline (**3**) was prepared by protection of 4-bromoaniline by diphenylmethylene.[14] Compound **5** was prepared from 4-aminodiphenylamine by initial protection of the primary amine group, bromination, and then protection of the secondary amine as a *tert*-butyl carbamate. Compound **7** was coupled with bromides **3** and **5** using palladium-catalyzed aromatic amination, followed by protection with a *t*-Boc group, affording the protected aniline oligomers **8** and **10**, respectively. The free amines of these oligomers were recovered by palladium-catalyzed hydrogenation. The resultant compounds were reacted with methacryloyl chloride to form the methacrylamide monomers.

In the synthetic procedures, the NH group was protected as a *tert*-butyl carbamate, which is a widely

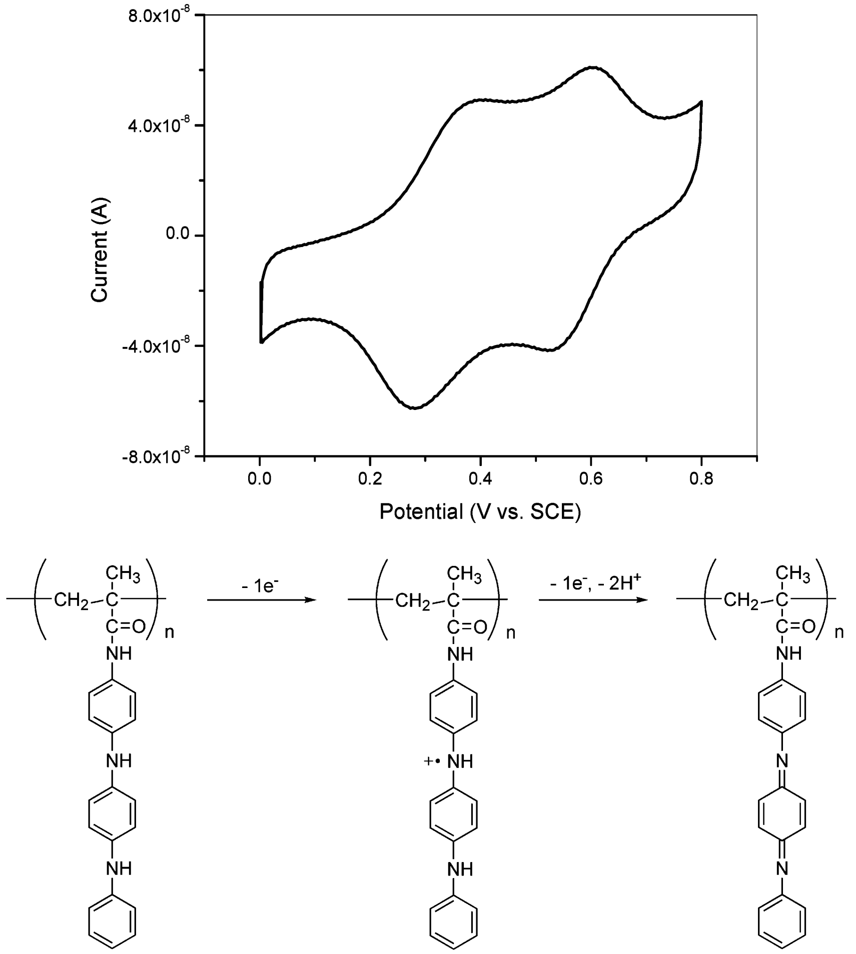


Figure 5. Cyclic voltammogram of polymer **1**, measured in aqueous H_2SO_4 (1.0 M) with scan rate of 100 mV/s. The proposed oxidation mechanism is shown below.

used protecting group and can be readily removed by pyrolysis or other mild chemical methods.[14] The introduction of the *t*-Boc group prevents oxidation of the anilino units and side reactions involving the secondary amines.[14] The *t*-Boc group also improves the solubility of intermediates and products. Most importantly, the protection is necessary for the free radical polymerization of the monomers. The diphenylamine moiety is an effective free radical inhibitor,[21] which prevents free radical polymerization of the corresponding monomers. Our preliminary experiments showed that the polymerization of methacrylamide monomers containing unprotected oligoaniline side chains was not successful.[22] When acyl groups were used as protective groups, the polymerization proceeded normally. However, the solubility of the resulting polymers was low, and the polymers precipitated early from the reaction mixture. Also, the removal of the acyl group required vigorous hydrolytic conditions which cleaved the amide bond that attached the oligoaniline moiety to the polymer backbone. In this work, the primary and secondary amines were protected with diphenylmethylene and *tert*-butoxycarbonyl groups, respectively, which allowed the selective protection and mild deprotection of the various oligomers, monomers, and polymers. The diphenylmethylene group was quantitatively removed by catalyzed hydrogenation in the presence of palladium on carbon.

Polymer Synthesis. Methacrylamide monomers containing the *t*-Boc-protected oligoaniline side chains were polymerized by free radical polymerization in DMF using AIBN as initiator. These polymers showed good solubility in common organic solvents, such as toluene, THF, DMSO, and DMF. In contrast, similar polymers with the acyl protecting group were not soluble in toluene or THF.[22] The number-average molecular weights of protected polymers **1** and **2** were 2.8×10^4 and 5.8×10^3, respectively. The molecular structures of the polymers were confirmed by proton NMR and FTIR. To obtain electroactive polymers, the protecting groups were removed after the polymerization. Thermolysis of protected oligoanilines in an inert atmosphere quantitatively removed the *t*-Boc group, affording oligoanilines in their reduced state. In the TGA study in nitrogen, *t*-Boc-protected polymers **1** and **2** started to lose weight at about 140 °C (Figure 2). The total weight loss in the first step of decomposition for polymers **1** and **2** was 36% (theoretical loss 37%, calculated from molecular weight of repeating unit) and 39% (theoretical loss 41%), respectively. This showed that the removal of the *t*-Boc group was essentially quantitative. The thermograms also indicated that the resulting polymers **1** and **2** were stable up to about 250 °C. Polymers **1** and **2** were prepared by heating the precursors in Schlenk tubes under argon at 180 °C for 10 h. Molecular weight characterization and thermal stability (temperature at 5% weight loss) of the polymers are summarized in Table 1.

Polymer Characterization. The resulting polymers, **1** and **2**, were soluble in THF, DMSO, and DMF. GPC analysis showed that the molecular weights were slightly lower than those of their precursors, 2.0×10^4

and 3.4 × 10^3, respectively. This was attributed to the loss of the bulky *t*-Boc groups, causing a decrease in the hydrodynamic volume of the macromolecules in solution. Proton NMR spectra of the polymers in DMSO-d_6 showed that the proton resonance of the *tert*-butyl group (1.31 ppm) disappeared completely. New resonances due to amine groups appeared after thermolysis (7.72 and 7.28 ppm for polymer **1**; 7.72, 7.60, and 7.30 ppm for polymer **2**). The FTIR spectrum was obtained by casting a film on a KBr pellet (Figure 3). The protected polymers exhibit peaks at 1712 and 1161 cm^{-1} which were assigned to the stretching vibration of carbonyl and the stretching of $O-C(CH_3)_3$ from the *tert*-butyl carbamate protective groups. These peaks disappeared after the thermolysis. A new peak appeared at 3385 cm^{-1} which was attributed to the N−H stretching of the diphenylamine moiety. The spectra of polymer **1** and the precursor are similar to those of polymer **2** and its precursor.

Polymers **1** and **2** in the reduced state were dissolved in DMF and then oxidized by bubbling oxygen into the solution. The reduced polymer **1** exhibits a single strong absorption at 317 nm of the UV−vis spectrum. Oxidation of the colorless solution resulted in an intense blue-purple solution, with a sharp peak at 308 nm and a broad peak at 481 nm. The first peak was ascribed to the $\pi-\pi^*$ transition in the benzenoid ring. The second peak is associated with a benzenoid to quinoid excitonic transition. The oxidized polymer was doped with sulfuric acid, and the solution turned green. Three peaks were displayed in the UV−vis spectrum at 270, 391, and 752 nm. The protonation of the oxidized polymer caused the low wavelength absorption to split. The high wavelength absorption red-shifted and extended toward the near-IR with an increase in intensity. The spectrum of polymer **2** was similar to that of polymer **1**, except that the absorption peaks shifted slightly to longer wavelengths (Figure 4). The chromophore (conjugated oligoaniline) in polymer **2** is one unit longer than that in polymer **1**. The absorption shift to longer wavelengths with the increase in conjugation length has been observed in many series of conjugated oligomers.[23] The reduced state of polymer **2** exhibited a single strong absorption at 320 nm, while the oxidized state showed a sharp peak at 311 nm and a broad peak at 565 nm. The acidified solution displayed three peaks at 302, 420, and 789 nm.

Cyclic voltammetry (CV) has been widely used to characterize the electrochemical properties of conducting polymers.[2] In this paper, the polymers were characterized by CV using a three-electrode electrochemical cell. A thin film of polymer was formed by evaporation of a THF−polymer solution on the surface of the Pt working electrode. The CV experiment was carried out in 1.0 M aqueous sulfuric acid solution with a scan rate of 100 mV/s. The CV spectrum showed two oxidation peaks at 0.385 and 0.597 V for polymer **1** (Figure 5). This result is similar to the results for *N*,*N*′-*p*-phenylenediamine, which displayed two reversible oxidation peaks corresponding to two one-electron-transfer processes.[24] The first oxidation involves the transfer of a single electron giving rise to a radical cation species. The second oxidation results in the transfer of another electron followed by the loss of two protons forming the uncharged imine.

In oligoanilines with longer conjugation lengths, e.g., *N*,*N*′-(4-anilinophenyl)-*p*-phenylenediamine, the electron transfer occurred in pairs, and two consecutive two-electron-transfer processes were observed.[24] The leucoemeraldine structure was converted first into the emeraldine and then the pernigraniline structure, as observed in polyaniline. In the repeat unit of polymer **1**, the oligoaniline was attached to the backbone through an amide group whose oxidation is not observed in the potential range of the experiment. Thus, the redox properties of this oligoaniline unit should resemble that of *N*,*N*′-diphenyl-*p*-phenylenediamine, which has been shown in this work.

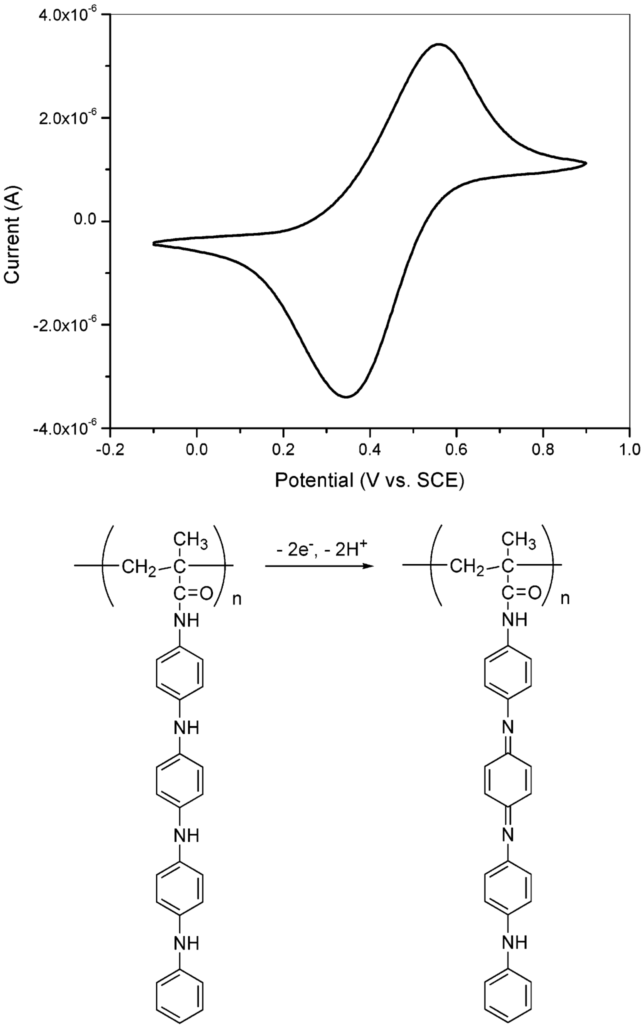


Figure 6. Cyclic voltammogram of polymer **2**, measured in aqueous H_2SO_4 (1.0 M) with scan rate of 100 mV/s. The proposed oxidation mechanism is shown below.

Similarly, the redox properties of polymer **2** should behave like *N*-phenyl-*N*′-(4-anilinophenyl)-*p*-phenylenediamine. Unfortunately, there are no reports on the electrochemistry of this oligoaniline. Only one peak was observed at 0.561 V for polymer **2** (Figure 6), which is similar to many longer oligomers that undergo two-electron transfer processes. Buchwald observed that oxidation of oligoanilines occurs through even-electron transitions when possible, while odd-numbered oligomers generate radical cations only transiently and at high potentials.[14]

For comparison, poly(*N*-(4-anilinophenyl)methacrylamide), a polymer similar to polymer **1** and **2** except that the side chain is dimeric rather than trimeric or tetrameric, was synthesized according to the literature.[25] The electrochemical properties of the polymer have not been reported previously. Oxidation did not occur when oxygen was bubbled through a polymer solution, and the UV−vis spectrum was unchanged by this treatment. Cyclic voltammetry showed that the polymer was not oxidized under the same experimental conditions as those for polymers **1** and **2**.

Conclusions

New methacrylamides containing oligoaniline side chains were synthesized using a palladium-catalyzed amination reaction, followed by reaction with methacryloyl chloride. Polymers were prepared by free radical solution polymerization. Blocking of the diphenylamine structures allowed facile polymerization to moderate molecular weights. The *tert*-butyl carbamate protective groups were removed quantitatively by thermolysis at 180 °C, providing a method to prepare polymers with well-defined oligoaniline side chains. The *t*-Boc protected polymers were more soluble in organic solvents than the analogous polymers with acyl protecting groups. These leucoemeraldine polymers were oxidized by simply bubbling oxygen gas through the polymer solutions. The electrochemical characterization by cyclic voltammetry demonstrated that the redox behavior of these side chain polymers was similar to the oligomeric anilines. Short side chain polymers underwent one-electron-transfer transitions whereas the longest side chain polymer underwent two-electron-transfer transitions.

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