

## Chapter 7

# Synthesis and Characterization of Polymers with Oligoaniline Side Chains

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Polymers containing oligomeric aniline side chains were synthesized via free radical polymerization. All monomers with dimer aniline units and acrylates with trimer aniline unit were polymerized under standard conditions with AIBN as initiator. For acrylamides with trimer aniline unit, blocking of the diphenyl amine group was necessary for the successful polymerization. The UV-vis spectroscopy of the polymer with a trimer side chain was similar to that of polyaniline. Low electrical conductivity was observed for some of the polymers when doped with iodine.

Polyaniline (PANI) has been one of the most intensively studied conducting polymers in the last decade. It can be easily made by chemical or electrochemical oxidative polymerization. PANI has high electrical conductivity and good environmental stability. Many potential applications have been proposed and investigated, such as rechargeable batteries, electromagnetic shielding, antistatic fibers, separation membranes, sensors, and corrosion resistant coatings (*1*). In the past decade, PANI has been widely studied as a unique replacement for barrier coatings in corrosion protection of metal surfaces. Our early work showed that PANI was able to provide protection against corrosion to mild steel substrates, even when the coating was scratched and the bare metal exposed to aqueous salt and dilute HCl solutions. Subsequent outdoor testing verified the usefulness of these coatings in a severe

marine environment (2, 3). One of the challenges in the application of PANI is its processability. PANI is difficult to dissolve in common, environmentally benign solvents. In good solvents such as NMP, gelation occurs and is dependent on both the concentration of polymer and polymer molecular weight. Stabilization of these solutions can be achieved through additives (3). PANI is not melt processable, and crosslinks at elevated temperatures which leads to a decrease in the conductivity (4). Thus, it is necessary to develop new methods to improve the melt and solution processability of polyaniline.

Monodisperse  $\pi$ -conjugated oligomers have been the target of much research due to their well-defined structure, high solubility, and special properties (5). Oligomers serve initially as the model compounds to obtain information such as electronic, photonic and morphologic properties of corresponding intractable polymers. Additionally, research on conjugated oligomers has advanced because of their promising applications in molecular scale electronics and nanotechnology. Oligoanilines were one of the earliest studied  $\pi$ -conjugated oligomer systems. In the 1960s, Honzl and co-workers synthesized a series of aniline oligomers and found that high conductivity was obtained even in short chain oligomers upon doping with iodine (6). Wudl et al. showed that octaaniline has nearly identical spectroscopy and electrical conductivity as polyaniline (7). Other studies showed that the aniline oligomers can also protect metal from corrosion (8).

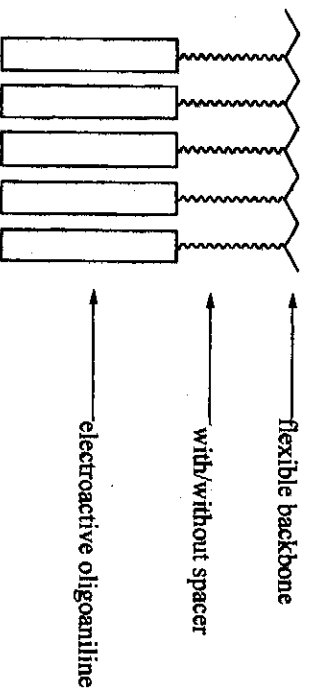


Figure 1 Schematic of polymer structure

In this paper, we report the synthesis of polymers with aniline side chains. The generalized structure is shown in Figure 1. The corresponding monomers are shown in Figure 2. Incorporation of aniline groups through covalent bonds prevents the loss of active species through migration. The polymer structure can be controlled precisely to obtain appropriate physical properties, such as glass transition temperature, and film forming properties through copolymerization with comonomers such as butyl acrylate and ethylhexyl acrylate, which are common in the coatings industry. The electroactivity of the coating can then be

readily controlled by the length of aniline oligomer and the content of oligomer in the final polymers. These monomers are anticipated to be incorporated in emulsion polymerization, which is widely used in water-based coatings.

The homopolymers of the oligomeric monomers were prepared by free radical polymerization in organic solvents. The thermal properties were characterized with TGA and DSC. Initial results of UV-vis spectroscopy and electrical conductivity are discussed for some of the polymers. The results were compared to that of polyaniline.

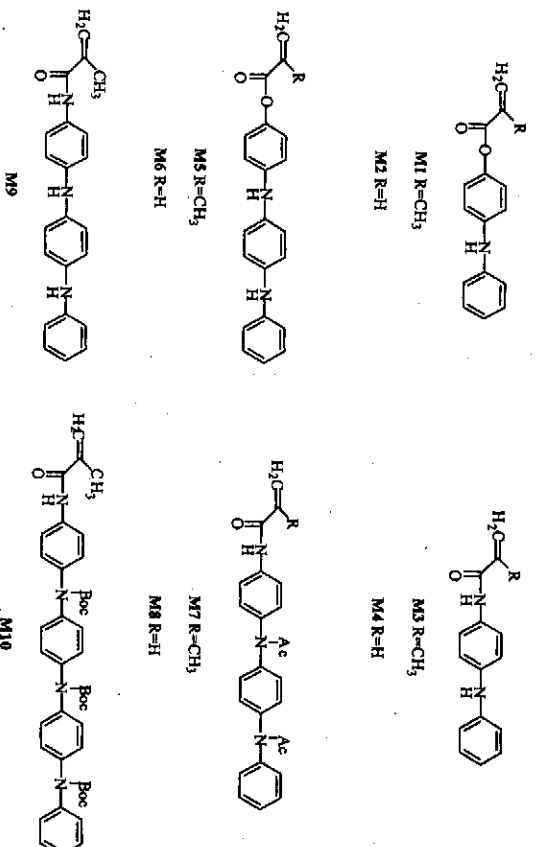


Figure 2 Chemical structures of monomers

## Experimental

### Materials and Instruments

All chemicals were purchased from ACROS. Bis[(2-diphenylphosphino) phenyl] ether (DPEphos) was prepared according to a literature method (9). Solvents were purified according to standard literature methods (10). <sup>1</sup>H NMR spectra were recorded on a Varian 500 spectrometer. Solvent residues were

used as reference. A Shimadzu GCMS-QP5000 spectrometer was used to confirm the chemical structures and determine monomer purity. UV-vis spectra were recorded on Perkin Elmer Lambda 4C UV/vis spectrophotometer. The electrical conductivity was measured on resistivity testing unit and hand applied four-point probe manufactured by Jandel Engineering Limited. Thermal analysis was carried out on differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) Perkin Elmer 7 series instrument with Pyris™ software. Inherent viscosity was measured with an Ubbelohde viscometer at 30.00° on 5.0mg/mL DMF solutions. Molecular weights of the polymers were measured on a Waters GPC system equipped with refractive index detector Waters 2410 and 3 Styragel® columns (HR 1, HR 3, and HR 4) using THF as the eluent at a flow rate of 0.3mL/min. The instrument was calibrated with polystyrene standards.

### Oligoaniline Synthesis

**4-(4'-Aminophenylamino) diphenylamine (3)** was synthesized according to a method in the literature, Scheme 1 (11,12).

**4-[1-(phenylamino)phenylamino]-phenol (4)** was prepared according to Scheme 2. N-phenyl 1,4-phenylenediamine (5.00 g, 27.2 mmol), hydroquinone (5.68 g, 51.6 mmol) and zinc chloride (0.72 g, 5.3 mmol) were charged into a three-necked flask. The mixture was heated to 180°C with stirring in nitrogen atmosphere. The reaction was continued for 4h. The reaction mixture was cooled to room temperature and 0.1M HCl aq. solution (50mL) was added. The mixture was heated to 100 °C with stirring for 1h and filtered. The product was recrystallized from toluene in the presence of small amount of phenylhydrazine. Slightly pink crystals, 3.92 g, 52% yield; mp 140-141°C. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 8.87(s, 1H), 7.70 (s, 1H), 7.44 (s, 1H), 7.13 (t, J= 7.3 Hz, 2H), 6.98-6.93 (m, 2H), 6.90-6.82 (m, 6H), 6.69-6.62 (m, 3H). MS (EI) m/z 276 (M<sup>+</sup>). Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O: C, 78.24; H, 5.84; N, 10.14. Found C, 78.10; H, 5.89; N, 9.90.

**Compound 6:** p-Aminodiphenylamine (22.32g, 121.3mmol) and benzophenone (20.00g, 109.9mmol) were added to toluene (125mL). 5A molecular sieves (30.0g) were added to the solution under nitrogen atmosphere. The mixture was refluxed for 48h. The solution was decanted, and the molecular sieves were washed with ethyl ether until the filtrate was colorless. The organic solutions were combined and solvent was removed. The solid residue was taken up in ethyl acetate and washed with NaOH solution and brine. The organic solution was dried with anhydrous sodium sulfate and concentrated. The yellow solid was dried in vacuo at 50°C for 24h. Product **5**: 37.80g. Compound **5** (25.00g, 71.84mmol) was dissolved in THF (180mL). Di-tert-butyl dicarbonate (18.79g, 86.19mmol) and 4-(dimethylamino)pyridine (1.31g, 10.74mmol) were added. The solution was refluxed for 6h. The solvent was removed by rotary evaporation. The solid was recrystallized in ethyl

acetate/hexane and dried in vacuo at 50°C for 24h. Pale yellow needles, 25.73g, 80% yield: mp 154-155°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.74(d, J=8.3Hz, 2H), 7.49-7.44(m, 1H), 7.43-7.33 (m, 2H), 7.32-7.20 (m, 5H), 7.18-7.06(m, 5H), 6.97(d, J=8.5Hz, 2H), 6.67(d, J=8.3Hz, 2H), 1.40(s, 9H). Anal. Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 80.33; H, 6.29; N, 6.25. Found C, 79.78; H, 6.31; N, 6.32.

**Compound 7:** Compound 5 (8.53g, 24.5mmol) was dissolved in dichloromethane (50 mL) and tetra-n-butylammonium tribromide (13.03g, 27.03mmol) was added in one portion. The solution was stirred at room temperature for 1h, then saturated sodium sulfite solution (50mL) was added with stirring for 30min, followed by sodium hydroxide solution(2.0M, 25mL). The layers were separated, and the organic phase was washed with distilled water, dried over anhydrous sodium sulfate, and concentrated. The residue was dissolved in THF (60mL), then di-tert-butyl bicarbonate (6.41g, 29.40mmol) and 4-(dimethylamino)pyridine (0.45g, 3.7mmol) were added. The solution was refluxed for 6h, and concentrated. The residue was recrystallized in methanol and dried in vacuo at 50 °C for 24h. Slightly pink crystals, 8.86g, 69% yield: mp 163-165°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.74(d, J=7.3Hz, 2H), 7.50-7.33(m, 5H), 7.31-7.20(m, 3H), 7.11(dd, J=7.9, 1.3Hz, 2H), 7.02(d, J=8.8Hz, 2H), 6.94(d, J=8.5Hz, 2H), 6.68(d, J=8.5Hz, 2H), 1.39(s, 9H). Anal. Calcd. for C<sub>30</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 68.31; H, 5.16; N, 5.31. Found C, 68.27; H, 5.20; N, 5.30.

**Compound 9:** Compound 6 (24.00g, 53.57mmol), ammonium formate (40.61g, 644.6mmol) and palladium on carbon (5%, 2.83g, 1.33mmol Pd) were charged into a round-bottomed flask, and purged with argon. THF (100mL) and methanol (250mL) were added. The reaction mixture was heated to 55°C for 12h. The solution was concentrated and taken up with dichloromethane, filtered through Celite and concentrated. The solid was triturated with hexanes, and filtered. The white powder was dried in vacuo at 50 °C for 24h. Product 8: 14.92g. Compound 8 (0.50g, 1.76mol), palladium acetate (6.6mg, 2.9×10<sup>-2</sup>mmol) and DPPEphos (21.0mg, 3.9×10<sup>-2</sup>mmol) were charged into a flask and purged with argon. Compound 7 (0.77g, 1.46mmol) was added, followed by toluene(6mL). The solution was warmed to 50°C to help the dissolution. Sodium tert-butoxide (0.21g, 2.19mmol) was added in one portion. Additional toluene (4mL) was added to wash the flask wall. The reaction mixture was heated to 100°C with stirring for 24h. 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 (10mL) and di-tert-butyl bicarbonate (0.47g, 2.2mmol) and 4-(dimethylamino)pyridine (43.3mg, 0.355mmol) were added. The reaction mixture was heated to 60°C for 12h. The solvent was removed, and the solid was recrystallized in methanol. Pink powder, 0.59g, 49% yield: mp 184-185°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.74(d, J=8.3Hz, 2H), 7.50-7.44(m, 1H), 7.43-7.38(m, 2H), 7.33-7.22 (m, 5H), 7.21-7.06(m, 13H), 6.95(d, J=8.5Hz, 2H), 6.67(d, J=8.4Hz, 2H), 1.44(s, 9H); 1.43(s, 9H); 1.39(s, 9H). Anal. Calcd. for C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>: C, 75.16; H, 6.55; N, 6.74. Found C, 74.94; H, 6.63; N, 6.75.

**Compound 10:**

Similar procedure to the synthesis of compound 8. Product: white powder, 96% yield. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.34-7.25(m, 2H); 7.22-7.07(m, 11H); 6.96(dd, J = 8.5, 1.2Hz, 2H); 6.61(dd, J = 8.7, 1.3Hz, 2H); 3.65(broad, 2H), 1.46-1.42(m, 27H).

**Monomer Synthesis**

Aniline oligomer was dissolved in THF with nitrogen protection. Triethylamine was added. The reaction mixture was cooled in an ice bath. Methacryloyl chloride (or acryloyl chloride) solution in THF was added slowly into the solution. After completion, the reaction mixture was stirred at room temperature for 24h. The precipitate was filtered off and washed with THF. The solutions were combined and the solvent was removed with rotary evaporation. The residue was taken up with dichloromethane, washed with HCl aqueous solution, Na<sub>2</sub>CO<sub>3</sub> solution and distilled water. The solution was dried with anhydrous sodium sulfate. The solvent was removed and the residue was crystallized from ethyl acetate/hexanes. The product was dried in vacuo at 50°C for 24h.

**4-Anilinothiophenyl methacrylate (M1):** white needle crystals from heptanes in 60% yield; mp 72-73°C. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 8.19 (s, 1H), 7.23 (t, J = 7.9Hz, 2H), 7.14-6.96 (m, 6H), 6.82 (t, J = 7.3Hz, 1H), 6.25 (s, 1H), 5.86 (s, 1H), 2.06-1.94 (m, 3H). GC/MS (EI) m/z 253 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.65; H, 6.00; N, 5.55.

**4-Anilinothiophenyl acrylate (M2):** pale yellow crystals from heptanes in 40% yield; mp 47-49°C. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 8.20 (s, 1H), 7.23 (t, J = 7.0Hz, 2H), 7.14-6.96 (m, 6H), 6.82 (t, J = 7.3Hz, 1H), 6.51 (dd, J = 17.3, 1.2Hz, 1H), 6.39 (dd, J = 17.3, 10.2Hz, 1H), 6.12 (dd, J = 10.3, 1.2Hz, 1H). GC/MS(EI) m/z 239(M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub>: C, 75.30; H, 5.48; N, 5.85. Found: C, 74.91; H, 5.49; N, 5.82.

**N-(4-Anilinothiophenyl)-methacrylamide (M3):** was prepared according to a literature method (13). Pale blue crystals, 80% yield; mp 109 - 110°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.49 (s, 1H), 7.44 (d, J = 8.8Hz, 2H), 7.28-7.20 (m, 2), 7.09-6.96 (m, 4H), 6.90(t, J = 7.3, 1.2Hz, 1H), 5.78 (s, 1H), 5.70 (s, 1H), 5.46-5.40 (m, 1H), 2.07-2.04 (m, 3H). GC/MS (EI) m/z 252(M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.11; H, 6.44; N, 11.04.

**N-(4-Anilinothiophenyl)-acrylamide (M4):** pale yellow solid, 50% yield; mp 150-152°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.54 (s, 1H), 7.46 (d, J = 8.5Hz, 2H), 7.32-7.12 (m, 2H), 7.10-6.94 (m, 4H), 6.90 (t, J = 7.3Hz, 1H), 6.41 (d, J = 16.8Hz, 1H), 6.25 (dd, J = 16.8, 10.3Hz, 1H), 5.80-5.60 (dd+broad peak, J = 10.1, 1.3Hz, 2H). GC/MS (EI) m/z 238 (M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.11; H, 5.97; N, 11.20.

**Monomer 5:** pale blue solid, 82% yield; mp 99-100°C. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 7.93(s, 1H), 7.89(s, 1H), 7.20-7.15(m, 2H), 7.06-6.88(m, 10H), 6.72(t, J = 7.3Hz, 1H), 6.24(s, 1H), 5.85(s, 1H), 1.99(s, 3H). GC/MS (EI) m/z

344(M<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.70; H, 5.85; N, 8.13. Found: C, 76.19; H, 5.70; N, 8.03.

**Monomer 6:** separated with liquid chromatography, pale blue solid, 26% yield: mp 107-110°C. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 7.94(s, 1H), 7.89(s, 1H), 7.20-7.15(m, 2H), 7.07-6.90(m, 10H), 6.72(t, J=7.3Hz, 1H), 6.50(dd, J=17.3Hz, 1.5Hz, 1H), 6.38(dd, J=10.4, 1.5Hz, 1H), 6.10(dd, J=10.3Hz, 1.5Hz, 1H). GC/MS (EI) m/z 330 (M<sup>+</sup>). Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34; H, 5.49; N, 8.48. Found: C 76.13; H, 5.61; N, 8.36.

**Monomer 7:** white powder from acetone, 51% yield: mp 194-195°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.88(s, 1H), 7.70-6.92(m, 13H), 5.78(s, 1H), 5.46(s, 1H), 2.04(s, 9H). GC/MS (EI) m/z 427 (M<sup>+</sup>). Anal. Calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>: C, 73.05; H, 5.89; N, 9.83. Found: C, 72.64; H, 5.97; N, 9.38.

**Monomer 8:** pale yellow powder from ethyl acetate, 72% yield: mp 203-204°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.30(s, 1H), 7.75-6.90(m, 13H), 6.40(d, J=16.8Hz, 1H), 6.23(dd, J=16.8Hz, 10.3Hz, 1H), 5.69(d, J=10.3Hz, 1H), 2.06(d, 6H). Anal. Calcd for C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: C, 72.62; H, 5.61; N, 10.16. Found: C, 71.24; H, 5.60; N, 9.64.

**Monomer 9:** pink powder from ethanol, 80% yield: mp 163-164°C. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.39-7.30(m, 3H), 7.20-7.13(m, 2H), 7.01-6.86(m, 8H), 6.78(t, J=7.3Hz, 1H), 5.70(s, 1H), 5.49(s, 2H), 5.36(s, 1H), 1.99(s, 3H). GC/MS (EI) m/z 343(M<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O: C, 76.94; H, 6.16; N, 12.24. Found: C, 74.38; H, 6.30; N, 11.58.

**Monomer 10:** separated by liquid chromatography, white powder, 93% yield. <sup>1</sup>H NMR (500MHz, DMSO-*d*<sub>6</sub>) δ 9.84(s, 1H), 7.68(d, J=8.8Hz, 2H), 7.37-7.31(m, 2H), 7.23-7.14(m, 13H), 5.81(s, 1H), 5.51(s, 1H), 1.95(s, 3H), 1.38(s, 27H). Anal. Calcd for C<sub>45</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub>: C, 70.28; H, 6.86; N, 7.62. Found: C, 69.58; H, 6.83; N, 7.38.

### Polymer Synthesis

Monomer (0.50g) and AIBN (5mg) were dissolved in DMF (5mL). 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 into methanol, filtered and dried in a vacuum oven at 60°C for 24 h.

## Results and Discussion

### Oligomer Synthesis

Several methods have been used for the preparation of oligoanilines. Ullmann condensation is the traditional method for the preparation of arylamines. However, vigorous conditions such as strong base, high

temperature, and elongated reaction times are required (14). Honzl prepared aniline oligomers by the reaction of diethyl succinoylsuccinate and aromatic amines, followed by hydrolysis, decarboxylation and aromatization (6). This procedure was modified by Wudl et al. for the preparation of octaniline (7). Condensation between aryl amines and phenol using a condensing reagent was applied in the oligomer synthesis by Furusho et al (15). Monkman et al. prepared aniline trimer and tetramer compounds by a modified Ullmann reaction (12). In the last five years, palladium catalyzed amination has emerged as a powerful method for the synthesis of arylamines. The versatility of the methodology has been demonstrated by the synthesis of aniline oligomers with different functional endgroups (16).

In this paper, the aniline trimer was synthesized by Ullmann condensation using copper as catalyst and reagent (Scheme 1). The excess amount of copper eliminates the need for the inorganic base and reduces side reactions. In the first step, the commercially available dimer was protected by acyl groups, which serves two functions in the reaction. The NH is blocked, preventing the further arylation of diphenylamine and activates the amide group toward condensation. When the iodonitrobenzene is used in excess, the dimer derivative was converted completely to the desired intermediate. The nitro group can be reduced to an amine group with sodium borohydride. The acyl protective groups were removed by hydrolysis in a potassium hydroxide-methanol solution.

Anilino-phenol was reported to be prepared by coupling of aniline with hydroquinone at 180°C in the presence of zinc chloride as catalyst (17). In this work, we attempted to prepare hydroxyl trimer 4 from aniline dimer in a similar way (Scheme 2). GC/MS analysis showed that the dimer was converted quantitatively after 4h. A small amount of N,N'-diphenyl-1,4-phenylenediamine was present in the reaction mixture. The product was washed with a 0.1M hydrochloride solution. The product (silver in color) was recrystallized in toluene to afford pale pink crystals. (An unknown residue was left in the flask which was insoluble in toluene, but soluble in polar solvent such as acetone, THF, and DMF.) The pale pink crystals turned blue when exposed to air for several weeks.

Aniline tetramer was synthesized by palladium-catalyzed amination. This method has been widely used in the formation of aromatic C-N bonds. Different catalyst/ligand systems have been studied for this reaction. The most common system is Pd<sub>2</sub>(dba)<sub>3</sub> and BINAP. Here, palladium acetate was used in the coupling reaction. Compared with other catalysts, palladium acetate is more stable in the air and lower in price. The ligand, DPPPhos, was made by a two step, one pot reaction. It is easy to prepare, and stable in air. The catalyst system showed high efficiency in the coupling reaction of primary anilines and aryl bromides (18). Its application in the synthesis of higher aniline oligomers has not been reported. In our experiments, we found that the catalyst system is effective for the preparation of aniline trimer and tetramer. In this reaction, the NH group was protected as a tert-butyl carbamate, which is a widely used protecting group and can be readily removed by pyrolysis or chemical methods.

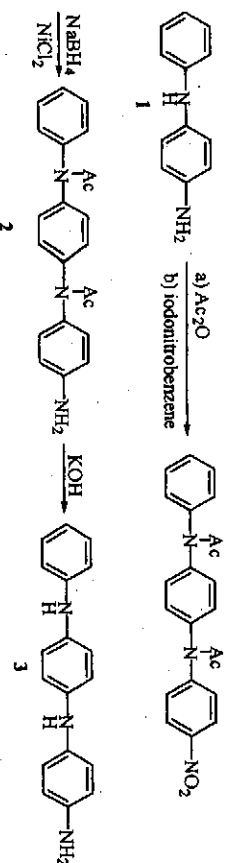


The introduction of *t*-Boc groups prevents oxidation of phenylenediamine units and the formation of triarylamines. The *t*-Boc group also improves the solubility of intermediates and products. The deprotection of the amine groups was carried out in the presence of palladium on carbon, which proved to be highly efficient. Compound 10 was heated to 190°C in an argon atmosphere for 10h and the proton NMR showed that the removal of protecting group was complete to afford tetraaniline. Aniline tetramer was reported to be synthesized by oxidation reaction of dimer with ferric chloride (19). The NMR spectra and DSC thermograms of tetramer made by these two methods were identical.

### Monomer Synthesis

Monomers were synthesized by the reaction between (meth)acryloyl chloride and the appropriate oligoaniline. Since there is more than one amine functionality in the oligomers, it is possible that multiple substitutions can occur. In our experiments, it was found that only the endgroup functionality underwent nucleophilic substitution when (meth)acryloyl chloride was used in slight excess. This may be due to the higher nucleophilicity and lower steric hindrance of the amine endgroup.

Scheme 1

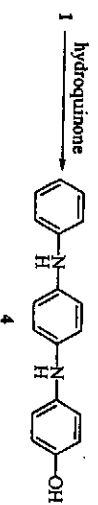


### Polymer Synthesis

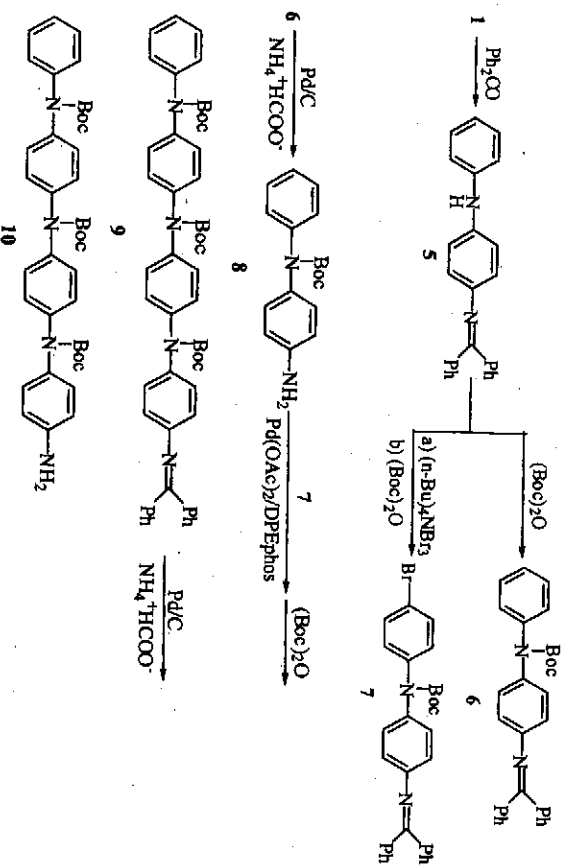
Diphenylamine has long been known as a radical inhibitor. When the diphenylamine reacts with radical species, the hydrogen is abstracted by the radical. The resulting aminyl radical may couple to other radicals, thus eliminating the radical species. Aminyl radicals can undergo self-coupling to form a neutral compound (20).

Previous research regarding the polymerization of monomers M1 and M2 showed that only azo-initiators were able to initiate the polymerization. Other radical initiators such as dibenzoyl peroxide and cumene hydroperoxide failed (21). In this work, AIBN was used in all polymerization reactions. Monomers

Scheme 2



Scheme 3



of the aniline dimer (M1-M4), (meth)acrylamides and (meth)acrylates, could be polymerized under standard conditions. For those monomers made from the aniline trimer, the polymerization reactivities were different. Monomer M5 polymerized under standard conditions, however, M6 only gave polymer of lower molecular weight and lower yield. Polymerization of M9 is completely inhibited. When the NH groups on trianiline were blocked by acyl groups (M7, M8), the polymerization occurred readily. This indicates that the diaryl amine NH does inhibit the polymerization and it is necessary to block the NH groups in the longer oligoaniline-based monomers. Research on protected M1 and M2 showed that the introduction of acyl groups lowered the solubility of the resulting polymers. However, to obtain electroactive polymers, protective groups need to be removed after the polymerization. Hydrolysis of the amide groups requires vigorous reaction conditions, which can also break the amide bonds connecting the backbone and side chains.

The structure of the polymers was confirmed by proton NMR. The characteristic proton peaks of the carbon-carbon double bond in the monomer disappeared after the polymerization reaction. All other peaks attributed to the side chains remained unchanged indicating that polymerization occurred through the addition of carbon-carbon double bonds. The properties of the polymers are summarized in Table I.

The polymers (M1-M6) are soluble in polar solvents, such as THF, DMSO, DMF and NMP. Polymers M7 and M8 did not dissolve in THF, but were soluble in the other solvents. Thin polymer films were cast from solvents, but the films were brittle. This may be due to the low molecular weights and rigidity of the oligomer side chains. The incorporation of aniline oligomers directly onto the backbone as side chains led to polymers with  $T_g$ 's in the range of 73-208° C.

t-Boc protected compounds showed good solubility. Monomer M10 was soluble in dichloromethane, ethyl acetate, chloroform, DMSO and THF. The thermal stability was studied by TGA. A two-step weight loss was observed. In the first step, t-Boc group was removed. The calculation from the TGA weight loss showed that the removal was quantitative. This was further confirmed by proton NMR. Unprotected compound was stable and no weight loss was observed until the sample decomposed at higher temperatures. The t-Boc protected monomer M10 was polymerized under the similar reaction conditions as the other monomers.

### Polymer Characterization

Thermal properties of polymers were measured by TGA and DSC in nitrogen at heating rates of 20 and 10 °C/min, respectively. All polymers began to lose weight at temperatures higher than 250°C as measured by the temperature at which the polymers lost 5% of their original weight. It is clear from the data in Table I that the polyacrylates have lower  $T_g$ 's than

polyacrylamides. Also, polyacrylamides and polyacrylates showed lower  $T_g$ 's than the corresponding polymethacrylamides and polymethacrylates.

The polymers were prepared under the same, non-optimized polymerizations conditions (70°C, 24h,  $N_2$ ). Moderate number average molecular weights were obtained in the range of 11,000–58,000 daltons.

The UV-Vis spectra were recorded for polymer M5 in DMF (Figure 3). The reduced colorless polymer exhibited a single strong absorption at 311nm ( $\epsilon_{max} = 2.3 \times 10^4$ ). After oxidation in the air, the blue polymer solution showed a sharp peak at 300nm ( $2.2 \times 10^4$ ) and a broad band at 578nm ( $6.3 \times 10^3$ ). The higher energy band is believed due to the  $\pi \rightarrow \pi^*$  transition of benzenoid ring, and the lower energy is due to the charge transfer from benzenoid ring to quinoid ring (22, 23). The solution turned green when doped with sulfuric acid. There were three peaks in the spectrum, 292nm, 396nm and 830nm. Thus, the characteristic absorptions of polymer M5 are similar to that of polyaniline as reported in literature.

Polymer M5 powder was doped with iodine for a week, and pressed into pellet. The conductivity was measured by the four-point probe method. The conductivity was low,  $5.6 \times 10^{-7}$  S/cm. Further work on the doping and conductivity of these new polymers is planned.

## Conclusions

New meth(acrylate) and meth(acrylamide) monomers containing oligoaniline side chains were designed and synthesized. The polymerization of these monomers was studied using standard free radical polymerization techniques. Monomers containing dimer aniline units were readily polymerized. For longer aniline oligomers, protection of diphenylamine moiety was necessary to prevent the polymerization inhibition. Polyacrylates displayed lower  $T_g$ 's than polyacrylamides. Polyacrylates and polyacrylamides displayed lower  $T_g$ 's than corresponding polymethacrylates and polymethacrylamides. The polymers were soluble in polar solvents and possessed good thermal stabilities with decomposition temperatures above 250°C. UV-vis spectra of polymer M5 were similar to that of polyaniline. This polymer showed low electrical conductivity when doped with iodine. Further doping experiments will be conducted to fully explore the redox properties and conductivity of these new polymers.

Polymer properties will be further tailored by copolymerization with commercially available monomers. These copolymers will be spray-coated onto metal coupons such as mild steel and aluminum for laboratory testing. Promising candidates will be scaled up and subjected to outdoor corrosion testing.

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Table I. Properties of polymers

Monomer	IV (dl/g)	Mn (10 <sup>3</sup> )	Mw (10 <sup>3</sup> )	PDI	T <sub>5%</sub> (°C)	T <sub>g</sub> (°C)
M1	0.26	30.1	80.3	2.67	250	116
M2	0.12	13.3	24.4	1.83	269	73
M3	0.27	58.4	134.9	2.31	263	184
M4	0.25	28.4	—	broad	280	155
M5	0.14	14.7	31.3	2.16	290	110
M6	—	11.0	16.0	1.50	—	—
M7	0.29	—	—	—	324	208
M8	0.10	—	—	—	291	184

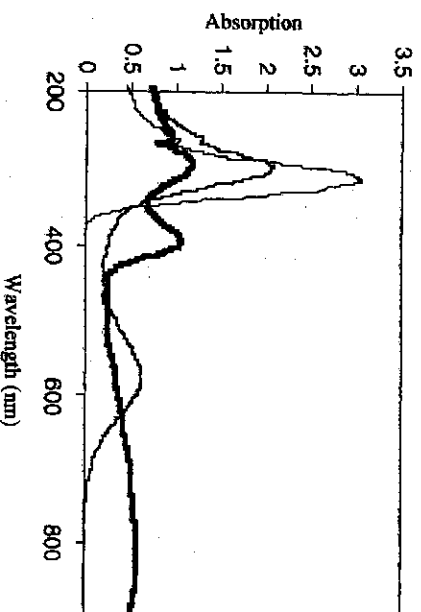


Figure 3. UV-vis spectra of polymer M5: a) reduced state (---); b) oxidized state (—); c) oxidized state doped with sulfuric acid (—).

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