New Polyaromatic Quinone Imines from Anthraquinone

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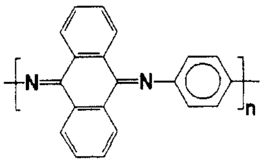
Introduction. Polyaniline, prepared by chemical or electrochemical oxidation of aniline, possesses in part a polyaromatic quinone imine structure. Its remarkable electrical, electrooptical, and tensile properties have drawn attention to the importance of this type of polymer.[1]

The oxidative synthesis of poly(quinone imines) is limited as to monomer structure. A polycondensation route would be preferable in order to allow a wider variety of monomers to participate and also to give a cleaner, better-defined polymer. An important step in this direction has been described by Wudl and co-workers using 1,4-dioxocyclohexane-2,5-dicarboxylic acid and an aromatic diamine.[2]



Our initial investigations[3] into the formation of aromatic quinone imines, involving reaction of anthraquinone (AQ) and aromatic diamines in poly(phosphoric acid) (PPA), led to black polymers which did possess the polyaromatic quinone imine structure according to elemental analysis and IR spectroscopy. However, these polymers were intractable and insoluble and upon doping did not display the high electrical conductivities associated with polyaniline.

This paper presents a clean synthesis of soluble, tractable, moderately high molecular weight poly(arylanthraquinone imines) via the condensation reaction between aromatic diamines and anthraquinone in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (Dabco). The synthesis was optimized by systematically varying the factors in the preparation of the model compound, *N,N'*-diphenylanthraquinone diimine, from anthraquinone and 2 equiv of aniline.

Experimental Section. General Methods. UV-visible spectra were recorded in chloroform on a Hewlett Packard 8452A diode array spectrophotometer. The NMR spectra were recorded at ambient temperature on a Bruker WM-250 NMR. The IR spectra (KBr pellets) were taken on a Perkin-Elmer 983 infrared spectrophotometer. Molecular weights were determined using a Beckman SEC equipped with a Beckman 160 UV detector and phenogel columns (10^3, 500, and 100 Å) in THF at ambient temperature. Molecular weight calculations were based on polystyrene standards. Inherent viscosities were measured in a #50 viscometer. The sample concentration was 0.10 g/10 mL in chloroform. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Fast atom bombardment mass spectrometry data were recorded on a MAT 311A mass spectrometer.

General Polymerization Procedure. Aromatic diamine (2.40 mmol) and 14.40 mmol of Dabco were dissolved in 10 mL of chlorobenzene while heating to 90 °C. Titanium tetrachloride (3.60 mmol) in 5 mL of chlorobenzene was added dropwise over 15 min. The addition funnel was washed with 5 mL of chlorobenzene. The quinone (2.40 mmol) was added to the system via a powder addition funnel, and the funnel was washed with 10 mL of chlorobenzene. After allowing the reaction to reflux for 24 h, the precipitate was filtered off and the filter cake was washed with hot chlorobenzene. Chlorobenzene was removed from the filtrate in vacuum, and the product was purified by dissolving it in chloroform and precipitating it into hexanes. Macrocyclic oligomers were isolated from the hexanes fraction. The polymerizations incorporating *p*-phenylenediamine were conducted in refluxing *o*-dichlorobenzene.

Polymerization of 4,4'-Thiodianiline and Anthraquinone. Yield: 92%. NMR (C_6D_6): δ 6.43 (m), 6.72 (m), 7.01 (m), 7.30 (m), 8.45 (m). IR: 1619 cm^{-1} (C=N). UV-vis: λ_{max} 424 nm (ϵ 8000 M^{-1} cm^{-1}). Elem anal. Calcd for $C_{26}H_{16}N_2S$: C, 80.39; H, 4.15; N, 7.21; S, 8.25. Found: C, 78.81; H, 3.99; N, 7.06; S, 7.75.

Polymerization of 4,4'-Methylenedianiline and Anthraquinone. Yield: 99%. IR: 1619 cm^{-1} (C=N). UV-vis: λ_{max} 410 nm (ϵ 7300 M^{-1} cm^{-1}). Elem anal. Calcd for $C_{27}H_{18}N_2$: C, 87.54; H, 4.90; N, 7.56. Found: C, 86.97; H, 5.01; N, 7.03. Macrocyclic oligomers' FAB mass spectrum: *m/e* (% relative intensity) 1942 (3), 1554 (13), 1166 (44), 777 (100).

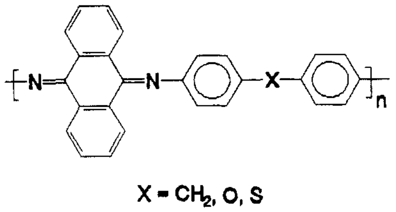
Polymerization of 4,4'-Oxydianiline and Anthraquinone. Yield: 64%. IR: 1619 cm^{-1} (C=N). UV-vis: λ_{max} 432 nm (ϵ 11 500 M^{-1} cm^{-1}). Elem anal. Calcd for $C_{26}H_{16}N_2O$: C, 83.85; H, 4.33; N, 7.52; O, 4.30. Found: C, 84.45; H, 5.02; N, 7.57.

Polymerization of *p*-Phenylenediamine and Anthraquinone. Yield: 88%. IR: 1619 cm^{-1} (C=N). Elem. anal. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.32; N, 9.90. Found: C, 81.96; H, 4.65; N, 10.28.

Polymerization of *p*-Phenylenediamine and 2-*tert*-Butylanthraquinone. Yield: 97%. IR: 1619 cm^{-1} (C=N). Elem anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 83.41; H, 5.90; N, 8.47.

Model Compound. The synthesis procedure was similar to the polymerization. Aromatic diamine is replaced with aniline (4.80 mmol), and toluene is the solvent used. Yield: 99%. Characterization was identical to that reported in ref 3.

Results and Discussion. The model compound *N,N'*-diphenylanthraquinone diimine was prepared from AQ and 2 equiv of aniline in the presence of titanium tetrachloride and Dabco in toluene. The reaction proceeded efficiently when 50% excess titanium tetrachloride and 6 equiv of Dabco were used. Dabco was the tertiary amine of choice because it gave no side reactions such as those observed between titanium tetrachloride and other tertiary amines such as triethylamine.[4] The reaction was conducted in toluene at reflux for 18 h. The order of addition of the reactants was critical. The optimum yield (99%) of the model compound was obtained when the reactants were added to the solvent at 90 °C in the following order: aniline, Dabco, titanium tetrachloride, and anthraquinone.



X = CH₂, O, S

Table I. Condensation Polymers Prepared from AQ and Diamines

diamine	η_{inh} (dL/g)[b]	SEC data: % high MW	SEC data: M_w
MDA	0.19	93	14 600
SDA	0.12	69	15 400
ODA	0.19	85	15 400
p-phenylenediamine	0.08	13	21 400
p-phenylenediamine[a]	0.12	62	18 600

[a] Anthraquinone is replaced with 2-*tert*-butylanthraquinone. [b] Concentration is 0.10 g/10 mL in chloroform.

For the synthesis of the polymer with AQ, several diamines were used, namely 4,4′-methylenedianiline (MDA), 4,4′-oxydianiline (ODA), 4,4′-thiodianiline (SDA), and *p*-phenylenediamine. Since fully conjugated systems typically have low solubilities, the polymerization methodology was developed using MDA in hopes of preparing a soluble polymer. Another objective of incorporating the methylene spacer unit in the polymer backbone was to allow a more detailed spectroscopic analysis than was possible with the insoluble poly(quinone imines) previously prepared in this laboratory.[3]

Polymers were initially prepared from anthraquinone and 4,4′-methylenedianiline utilizing reaction conditions identical to those employed for the model compound. The polymer, isolated in 51% yield as a red powder, was soluble in organic solvents such as chlorobenzene, tetrahydrofuran, and chloroform. The isolated polymer formed a transparent red film upon slow evaporation of solvent.

To obtain quantitative yields in the polymerization, the effect of the solvent was investigated. The polymerization yield increased from 51 to 99% when the solvent was changed from toluene to chlorobenzene. We postulate that the improved reaction was not a function of solvent selectivity but instead was due to the increased reaction temperature; chlorobenzene has a reflux temperature 21 °C higher than toluene. The increased reaction temperature results in increased solubility and reactivity of the monomers and growing polymer chains. The same methodology was used successfully to synthesize polymer with ODA and SDA.

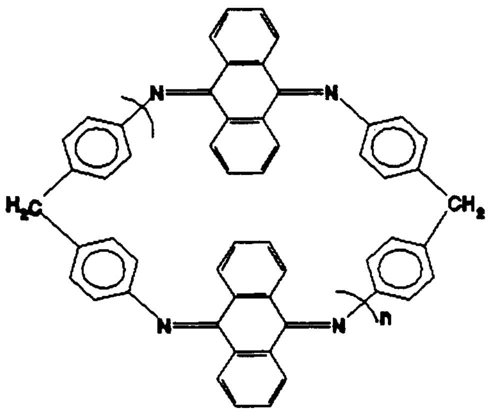
In an attempt to prepare a fully conjugated polymer, *p*-phenylenediamine and AQ were used. A red powder was isolated in high yield but only a small fraction of this material possessed high molecular weight (Table I). A higher molecular weight fully conjugated polymer was prepared by replacing anthraquinone with 2-*tert*-butylanthraquinone. The higher molecular weights are attributed to an increased solubility of the polymer due to incorporation of the *tert*-butyl groups. Therefore, the *tert*-butyl groups prevented premature oligomer precipitation, allowing higher molecular weights to be obtained.

IR, ^{1}H and ^{13}C NMR, UV–vis, and elemental analysis were used to assist in the structural confirmation of the poly(quinone imines). The imine peak was detected in the IR spectrum at 1619 cm^{-1} just as in the model compound. The end groups of the poly(arylquinone imine), amino and carbonyl, display characteristic peaks in the IR spectrum which should be readily observed at 3300 and 1688 cm^{-1}, respectively. However, no end group peaks were detected, indicating that a polymer of significant molecular weight was prepared.

The ^{1}H and ^{13}C NMR confirmed that the polymer backbone was similar to the model compound since the chemical shifts of the polymer peaks correlated well to those of the model compound. No detailed information could be obtained from the broad peaks in the spectra.

The UV–vis spectra of the polymers exhibited an absorption maximum at 420–430 nm, which is shifted 20–30 nm higher in wavelength than the corresponding *N,N′*-diphenylanthraquinone imine model compound. The polymers containing 4,4′-thiodianiline and 4,4′-oxydianiline exhibit an increase in the wavelength of maximum absorbance over the polymer containing 4,4′-methylenedianiline. The extinction coefficients of the model compound and polymers are of the same order of magnitude, namely, 8.0×10^4 M^{-1} cm^{-1}. These data indicate that the incorporation of the oxo or thio linkage in the dianilines results in increased conjugation from the lone pair electrons.

Relative molecular weights were determined by SEC and the inherent viscosities of the polymers. The results are listed in Table I. The SEC data revealed that the majority of the sample was high molecular weight polymer while the remaining fraction was a series of low molecular weight components. The high and low molecular weight materials could be separated chromatographically or by precipitating the polymer into hexanes, the oligomers remaining soluble in hexanes. It was not possible to fractionate the low molecular weight product into individual oligomers. There was no detectable difference in the IR and NMR of the high and low molecular weight fractions. The fact that no end groups were detected in the high molecular weight fraction could be explained by the molecular weight of the sample effectively diluting the end groups to a point where they were not detected, but the lack of end groups observed in the low molecular weight fraction was unexpected.



Oligomeric macrocyclic structures would explain the lack of the end groups in the low molecular weight fraction. Fast atom bombardment mass spectrometry (FAB-MS) analysis of the oligomers indeed confirmed that the low molecular weight fraction was a mixture of macrocycles where $n = 1–4$.

The above polymers were exposed to poly(phosphoric acid), and this resulted in intractable black materials which were similar to those previously reported.[3]

Investigations are continuing into the synthesis and properties of these and other novel polyaromatic quinone imines by our new synthesis.

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References and Notes

(1) Prasad, P. N., Nigam, J. K., Eds. *Frontiers of Polymer Research*; Plenum: New York, 1991.
(2) Vachon, D.; Angus, R. O., Jr.; Lu, F. L.; Nowak, M.; Liu, Z. X.; Schaffer, H.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *18*, 297.
(3) Everaerts, A.; Roberts, S.; Hall, H. K., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1703.
(4) Maier, M. E.; Brandstetter, T. *Tetrahedron Lett.* **1991**, *32*, 3679.