effect of the quencher. In order for the pyrene to be quenched, it and/or the quencher must move in the particle or micelle. Reactant movement is not hindered in the CTAB only system, but movement is restricted in the latex particle systems. In the particle systems, only pyrene in the CTAB surface layer of the particles is quenched initially, the pyrene in the interior of the particles exhibiting no quenching by the CPC. More pyrene fluorescene quenching was observed in the smaller particle system than the larger, and this points to the fact that the smaller particles are less rigid. Similar effects have been observed previously with polymerized microemulsions.[2]

Conclusions

This work points to a relatively easy and convenient method of producing stable polystyrene latex particles which have a variety of useful properties. The 54-Å-radius particle is one of the smallest of these kinds of particles ever reported. The different size particles can be reproduced with accuracy and with narrow size distributions. It is noteworthy that the particles do not dissociate on dilution. This indicates a strong hydrophobic interaction between the polystyrene and the CTAB surfactant tails. These systems are convenient hosts for introducing hydrophobic photosystems into a hydrophilic environment.

Registry No. CTAB, 57-09-0; CPC, 123-03-5; AIBN, 78-67-1; polystyrene, 9003-53-6.

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Synthesis and Characterization of a Novel Conducting Coordination Oligomer

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ABSTRACT: Copper(I) chloride, 1,4-diaminoanthraquinone, and oxygen react to give a crystalline electrically conducting coordination oligomer. The oligomer is believed to consist of alternating 1,4-diaminoanthraquinone units connected by mainly (μ_2-dioxo)dicopper units and is of low molecular weight, DP = 2–4. The oligomer is oxidatively and thermally stable, insoluble, and infusible but possesses interesting electronic properties. It is an intrinsic p-type semiconductor having a conductivity of 0.10–0.60 S/cm and an activation energy of 0.090 eV. Various analogues of the coordination oligomer were made by replacing both the copper and the 1,4-diaminoanthraquinone in the oligomer synthesis. All of the analogues have lower conductivity and are p-type conductors except the copper(II) analogue which is n-type. The coordination oligomer is effective as a catalyst for the oxidative polymerization of 2,6-dimethylphenol to poly(2,6-dimethylphenylene oxide) of narrow molecular weight distribution (heterogeneity index = 1.1), and as an electrocatalyst in the oxychlorination of ethylene to give 1,2-dichloroethane.

Introduction

Conducting organic materials have received considerable attention several times in the past. In 1960 Acker et al.[1] discovered complexes of tetracyanoquinodimethane (TCNQ) and electron donors that form crystalline charge-transfer conductors. In 1964 Little[2] proposed the possibility of room temperature superconductivity with conjugated polymers. No room temperature superconductors were discovered and interest waned until MacDiarmid, using the Shirakawa method for polymerizing acetylene, oxidized polyacetylene films with arsenic pentafluoride.[3,4] The oxidized polyacetylene films had a conductivity of 200 S/cm, comparable to mercury on a weight basis. Since 1977 several polymers have been found to be highly conducting when oxidized and/or reduced. These include poly(*p*-phenylene),[5] poly(phenylene sulfide),[6] poly(pyrrole),[7] and phthalocyanine-containing polymers.[8–10] The oxidation and/or reduction produces charged species that are responsible for conductivity. At ambient conditions these highly reactive ions can react with moisture and/or oxygen destroying the conductivity.[11,12] Incorporation of oxidant or reductant into the polymer structure also reduces the conductivity-to-mass ratio.

Introduction of less reactive species into the conducting pathway which can exhibit multiple oxidation states was thought to be one method of producing a stable, intrinsically conducting polymer. The multiple oxidation state species could serve as an internal oxidant or reductant so the polymer would require no oxidation or reduction by external reagents to achieve a conducting state. Therefore the conductivity-to-mass ratio would be increased.

In this paper the synthesis and characterization of a novel conducting coordination oligomer, oligo[[(μ_2-dioxo)dicopper 1,4-diaminoanthraquinone]-*co*-[(μ_2-oxo)dichlorodicopper 1,4-diaminoanthraquinone]] (ODOD) having the proposed structure depicted in Figure 1, and some analogues will be discussed. The oligomer is stable at ambient conditions and is an intrinsic semiconductor and catalyst.

Results and Discussion

Synthesis and Characterization of ODOD. Planar coordination polymers consisting of difunctional ligand

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Table I
Conductivity, Elemental Assay, and Empirical Formula for ODOD Made in Dimethylformamide and Pyridine

solvent	σ, S/cm	elem assay C	H	N	O	Cl	Cu	empirical formula
pyridine	0.12	44.1	2.7	7.3	17.3	5.5	22.6	$C_{14}H_{10}N_2O_{4.2}Cl_{0.6}Cu_{1.4}$
pyridine	0.33	45.0	2.6	7.4	16.8	6.0	21.7	$C_{14}H_{10}N_2O_{4.0}Cl_{0.6}Cu_{1.3}$
DMF	0.18	49.1	2.9	7.9	N.D.	N.D.	22.0	$C_{14}H_{10}N_2Cu_{1.2}$

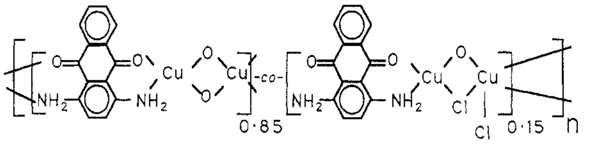
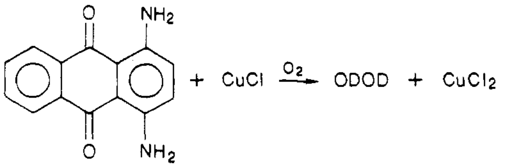


Figure 1. Proposed structure of ODOD where n = 2–4.

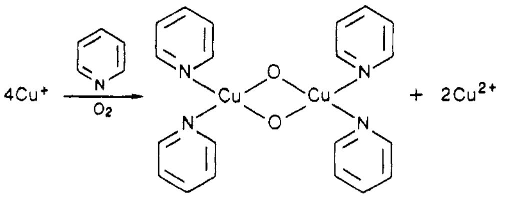
molecules linked by metal atoms are generally insoluble and precipitate from the reaction media as oligomers with DP's of less than 20 due to strong interactions between chains.[13] Several planar coordination oligomers possessing intrinsic electronic conductivity have been reported in the literature.[14–16] These oligomers are typical of planar coordination polymers in that they are insoluble, are infusible, and have DP's of 2–9 (based on metal content).

The synthesis reaction for ODOD is shown in eq 1. Oxygen or air is bubbled through a solution of copper(I)



(1)

chloride and 1,4-diaminoanthraquinone in pyridine, dimethylformamide, or dimethyl sulfoxide and the oligomer precipitates. The highest conductivity, 0.10–0.60 S/cm, is obtained when the initial copper(I) to 1,4-diaminoanthraquinone ratio is 2 and the temperature is −30 to 30 °C. The oxidation of copper(I) chloride in pyridine with oxygen has been extensively examined and is believed to have the initial products and stoichiometry expressed in equation 2.[17–22]



(2)

Equation 1 is similar to equation 2 with 1,4-diaminoanthraquinone replacing pyridine. However, increasing the ratio of copper(I) to 1,4-diaminoanthraquinone from 2 to 4 in the reaction media to ensure a complete reaction did not significantly change the DP and interestingly the ODOD conductivity decreased to 0.0054 S/cm. The DP is thus limited not by stoichiometry but by the fact that it crystallizes from solution at low DP, a finding that has been observed in other conducting coordination oligomers.[16]

ODOD is insoluble and infusible making characterization difficult. The oxidation state of the copper in ODOD was determined by using electron spectroscopy for chemical analysis (ESCA). The ESCA study shows the copper to be essentially copper(II) and that it may exist in several environments. The copper ($2p_{3/2}$) binding energy peak occurs at 933.6 eV, Figure 2, nearly the same as copper(II) oxide, 933.4 eV, and tails into its satellite peak indicating different copper chemical environments are present. A

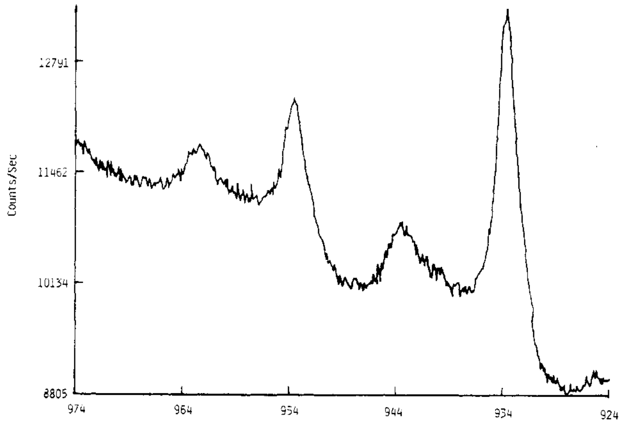


Figure 2. ESCA scan of ODOD. The Cu($2p_{3/2}$) binding energy peak of 933.4 eV indicates the copper is present as copper(II). The peak of 953 eV is the Cu($2p_{1/2}$) binding energy while the other two peaks are satellite peaks.

copper binding energy close to that of copper(II) oxide is expected due to the similarity between the copper environments in both copper(II) oxide and ODOD.

In concentrated sulfuric acid ODOD hydrolizes to give a red-brown solution from which, after neutralization, 1,4-diaminoanthraquinone precipitates and is recovered with a yield of 61.3%. If the 1,4-diaminoanthraquinone units are linked by copper(II) ions instead of oxodicopper bridges, chloride ion will be present to balance the charge on the copper(II) ion. Elemental analysis (Table I) shows a chlorine concentration of only 5.5–6.0%, thus the majority (85%) of bridging copper units are of the dioxodicopper type while a minority (15%) are copper(II) ions and/or (μ_2-oxo)dichlorodicopper units. The elemental analysis and corresponding empirical formulas of samples made in pyridine and dimethylformamide are given in Table I. The analysis indicates low degrees of polymerization (assuming the polymers are end capped with 1,4-diaminoanthraquinone) are obtained in pyridine (DP $\leq$ 4) and dimethylforamide (DP $\leq$ 2) before the oligomer precipitates. From the C, H, and N assay of the sample made in pyridine, a calculated 1,4-diaminoanthraquinone content of 62.4% is obtained, in agreement with the observed value 61.3%. The empirical formulas show the expected 1–2 copper atoms (a value of 2 is not obtained because the oligomer precipitates at low DP's) per 1,4-diaminoanthraquinone but more oxygen than expected, 0.8 extra oxygens/copper. Copper(III) was not found in the ESCA study suggesting the extra oxygen is in the −1 or zero valent state, otherwise a charge imbalance between the copper, chloride ion, and oxygen would exist. Kim et al. have also observed extra oxygen in conducting metal diaminobenzenedithiol coordination polymers and have attributed it to coordinated molecular oxygen (O_2),[15] and molecular oxygen is known to coordinate with other copper complexes.[23] Another possibility that could account for the high oxygen content is (μ-diperoxo)dicopper bridges between the quinone units. This seems unlikely as such bridges have not been observed in the analogous pyridine copper(II) oxygen complexes (eq 2) and if present a room temperature EPR signal would be expected but none is

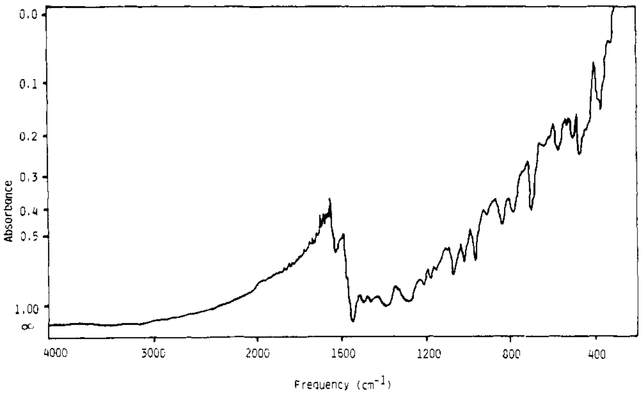


Figure 3. Infrared spectrum of ODOD dispersed in a KBr pellet.

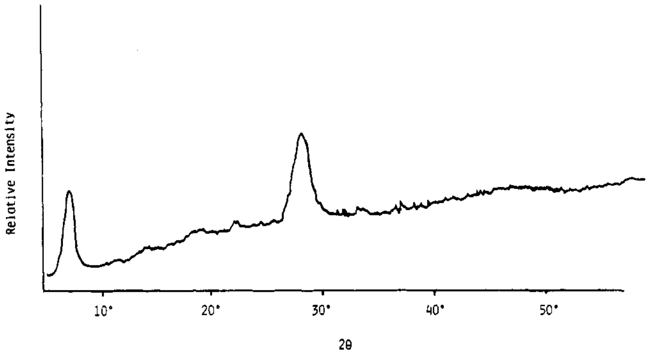


Figure 4. X-ray powder diffraction pattern of ODOD.

observed. So although the chemical nature of the extra oxygen in the ODOD structure is not definately known, it could be due to molecular oxygen coordination. In the infrared spectrum of ODOD, Figure 3, a large very broad absorption peak is observed from 4000 to 1700 cm^{-1}. An absorption of this type is frequently encountered in electrically conducting organic materials and is due to electronic transitions involving the valence and conduction bands.[24] The remainder of the spectrum is a multitude of minor peaks and two major peaks at 1635 and 1550 cm^{-1}. The 1635-cm^{-1} peak is believed to be the quinone carbonyl and is shifted from 1600 cm^{-1} where it appears in 1,4-diaminoanthraquinone.

The X-ray diffraction pattern of ODOD, Figure 4, shows it to be crystalline with two major *d* spacings. The most intense diffraction peak *d* spacing is 3.2 Å and the other *d* spacing is 13 Å. The crystallite size can be estimated from the peak broadness by using the Scherrer formula[25] and is 60–90 Å. Crystalline materials containing planar aromatic groups typically display a spacing at ~3.4–3.5 Å due to layer diffractions with a minimum of 3.35 Å observed for graphite.[26] The 3.2-Å spacing seen in ODOD is too small for layer diffractions, unless the layers are capable of packing more closely than in graphite which seems unlikely, but both ODOD spacings do correspond to the expected copper atom distances. If the spacings are due to copper distances, it appears the ODOD molecules pack well side by side in the plane do not stack on top of one another in a orderly fashion. The average number of repeat units/crystallite calculated from the crystallite size and the 13-Å spacing is 4–7.

The differential scanning calorimeter (DSC) thermogram of ODOD is shown in Figure 5, curve 1. Three freatures are observed: (A) a broad endotherm between 40 and 140 °C; (B) another endotherm between 220 and 260 °C; (C) a large exotherm between 340 and 370 °C due to the thermal decomposition of ODOD. Endotherms A and B disappear if the sample is preheated to 280 °C, Figure 5, curve 2. A 10% weight loss also occurs during the preheating to 280 °C but no loss in conductivity is observed so the reactions responsible for the DSC endotherms and weight loss do not effect the conductive pathway.

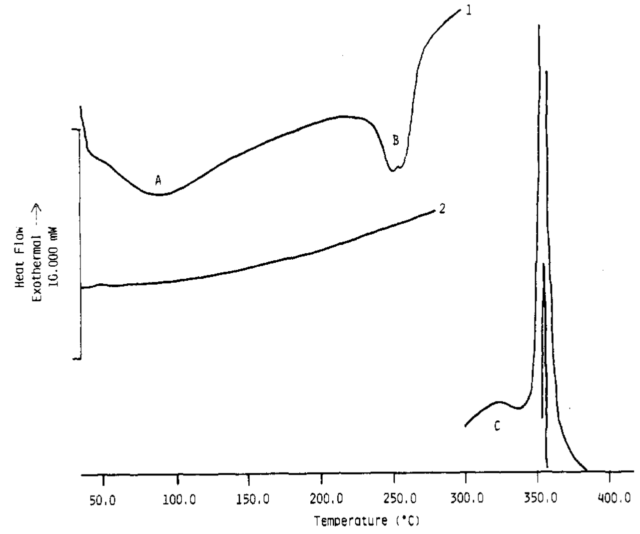


Figure 5. DSC thermogram of ODOD. Curve 1 has no preheat treatment while curve 2 shows the effect of preheating to 280 °C; notice features A and B disappear.

ODOD contains copper(II) which has an unpaired electron and is expected to be EPR active. This was found to be the case but at −196 °C where the EPR *g* value is 2.100 and a line width of 240 G is observed. The signal disappears upon warming probably due line broadening caused by electron exchange between close copper atoms.[27,28] The absence of a room temperature EPR signal suggests the copper is not present in isolated copper(II) ion or (μ_2-diperoxo)dicopper bridges where the coppers would be too distant to exchange electrons but rather it is in μ_2-dioxodicopper or (μ_2-oxo)dichlorodicopper bridges.

The conductivity of ODOD, measured on compressed powder pellets by a two-probe method, is 0.1–0.6 S/cm. The stability of conductivity is good, as a sample stored in air at ambient conditions for 4 years shows no decrease (within experimental error) in conductivity. Interparticle resistance generally lowers the powder conductivity by 2 orders of magnitude so the conductivity of single crystal ODOD is expected to be 10–60 S/cm.[29] The activation energy and conduction mode (metallic or semiconductor) are obtained from the plot of ln (conductivity) versus inverse temperature, Figure 6. The plot between −77 and 25 °C is linear with a negative slope. The negative slope (conductivity decreases with decreasing temperature) is indicative of a semiconductor and gives an activation energy of 0.090 eV. Room temperature thermal energy should be sufficient to promote electrons to the conduction band so no photoconductivity is expected at room temperature and no measurable amount was observed. A positive potential is developed across a ODOD sample in a temperature gradient, indicating the majority of charge carriers are holes, thus ODOD is a p-type semiconductor.

Synthesis and Characterization of Some Analogues of ODOD. Copper(II), nickel(II), and silver(I) ions can also react with 1,4-diaminoanthraquinone to give conducting materials. Synthesis with nickel(II) and silver(I) ions requires the presence of triethylamine to make conducting materials. The triethylamine may deprotonate the 1,4-diaminoanthraquinone, making it a better chelator. The conductivity, majority charge carriers, elemental analysis, and empirical formulas of metal ion substituted

Table II
Conductivity, Elemental Assay, Majority Charge Carriers, and Empirical Formulas for Some ODOD Analogues

metal ion[a]	σ, S/cm	elem assay C	H	N	O[b]	M	Cl	major charge carrier	empirical formula
Cu(II)	1.32×10^{-2}	56.8	3.86	9.10	16.8	5.7	7.7	electrons	$C_{15}H_{12}N_2O_3Cl_{0.7}Cu_{0.3}$
Ag(I)	4.72×10^{-3}	38.6	2.06	6.12	13.2	40.0	ND	holes	$C_{15}H_9N_2O_{3.8}Ag_{1.7}$
Ni(II)	7.9×10^{-3}	51.3	3.76	9.38	15.8	17.2	2.6	holes	$C_{13}H_{11}N_2O_3Cl_{0.2}Ni_{0.9}$

[a] Metal ion used in synthesis. [b] Calculated by difference.

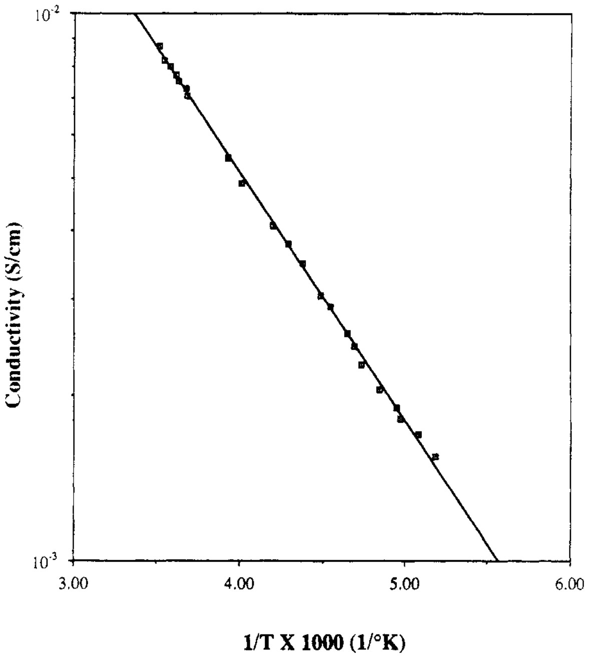


Figure 6. Arrhenius plot of conductivity for ODOD. A conductivity activation energy of 0.090 eV can be calculated from the slope.

materials are shown in Table II. The materials containing copper(II) and nickel(II) appear to be monomeric complexes based on the stoichiometry while the silver(I) compound has a similar stoichiometry as ODOD and suggests the silver is present as silver(II). The conductivities of the metal ion derivatives are 10–100 times lower than that of ODOD. The copper(II)/1,4-diaminoanthraquinone compound is unusual in that the copper content is low but its conductivity is high and it is the only n-type material synthesized in this work.

Many other aminoanthraquinones could be substituted for 1,4-diaminoanthraquinone in the reaction with oxygen and copper(I) chloride. Among those that gave conducting compounds are 2,6-diaminoanthraquinone, 1-amino-4-hydroxyanthraquinone, and 1,4,5,8-tetraminoanthraquinone. In general these materials have conductivities 10–1000 times lower than that of ODOD. Nitrogen substituted aminoquinones such as 1,4-bis(methylamino)anthraquinone and 1,4-bis(acetylamino)anthraquinone do not give conducting materials. Presumably, the substituent sterically hinders the copper coordination. Some other quinones that also do not give conducting materials are 1,4-dihydroxyanthraquinone, 1,2-diaminoanthraquinone, and 2-aminoanthraquinone.

Various substituted 1,4-diaminoanthraquinones give conducting materials after reacting with oxygen and copper(I) chloride. Chlorinated 1,4-diaminoanthraquinone works well but the conductivity decreases as the degree of chlorination increases. This is illustrated in Figure 7 where the conductivity is plotted against the degree of chlorination of 1,4-diaminoanthraquinone used in the synthesis.

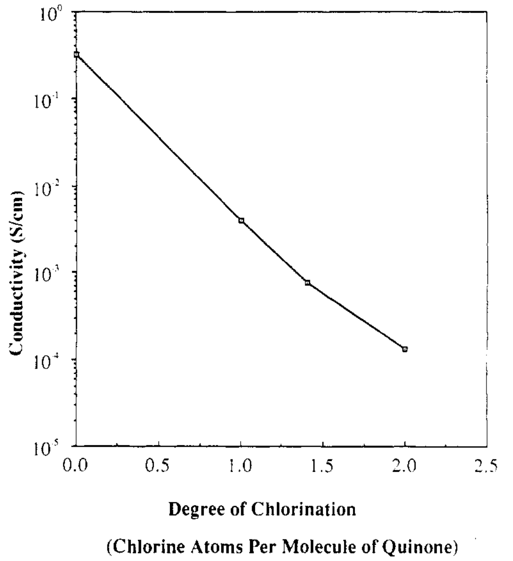


Figure 7. Graph of conductivity versus monomer degree of chlorination for oligomers made from 2,3-dichloro-1,4-diaminoanthraquinone, 2-chloro-1,4-diaminoanthraquinone, and 1,4-diaminoanthraquinone.

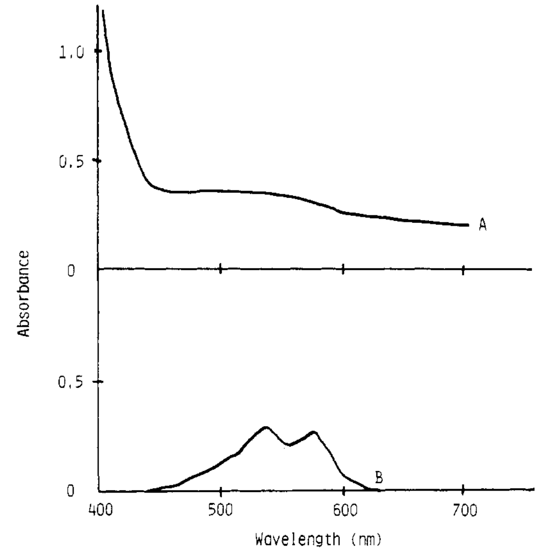
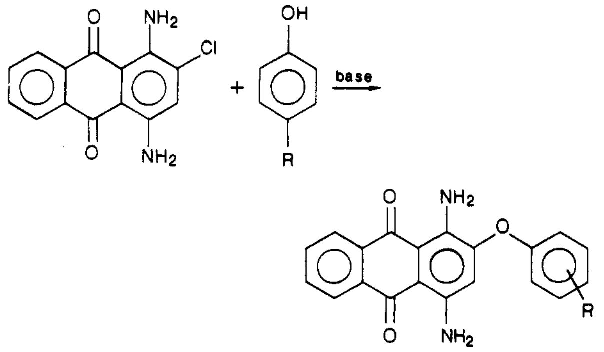


Figure 8. Visible spectra of (A) the conducting oligomer made from quinone III and (B) quinone III.

The chlorine in 2-chloro-1,4-diaminoanthraquinone is labile and can be displaced by phenoxide anions as shown in eq 3. The coordination oligomers made by using quinones I–IV are p-type semiconductors with conductivities of 0.01–0.10 S/cm. A conducting film can be made by mixing quinone III and copper(I) chloride in deoxygenated solvent and casting onto a glass or Teflon plate. The liquid gels as air diffuses into the solvent and a brittle film forms upon drying. The visible spectrum of a film cast upon a microscope slide and that of unreacted quinone III are shown in Figure 7. The conducting oligomer



(3)

R = H (I), CH_3 (II), CH_2CH_2OH (III), and $C_{12}H_{25}$ (IV)

spectrum is a broad band, with a peak at 550 nm, that extends well into the infrared region indicating a high degree of electron delocalization for the oligomer while that of unreacted quinone III shows two peaks, 535 and 575 nm, that quickly drop to zero absorbance past 600 nm.

ODOD as a Catalyst. The structural similarity between ODOD and the copper catalyst used in the oxidative polymerization of 2,6-dimethylphenol[20-22] suggested ODOD might also have similar catalytic properties. Indeed, poly(2,6-dimethylphenylene oxide) with a narrow molecular weight distribution (heterogeneity index 1.1) is formed by using ODOD as the catalyst. The heterogeneity index of 1.1 is much lower than the usual value of 2.2 cited in the literature.[30] However, both the yield (12.5%) and molecular weight (M_w = 4800 g/mol) are low but might be improved by optimization of the reaction conditions which was not attempted in this work.

The presence of potential substrate binding sites provided by the copper and the electrical conductivity make ODOD and its analogs good candidates as electrocatalysts. One electrochemical reaction ODOD catalyzes is the oxychlorination of ethylene. In this application the high conductivity of ODOD makes possible thicker catalyst coatings on the electrode than nonconducting catalysts and the ODOD is relative stable in aqueous media resulting in a long lived electrode.[31]

Experimental Section

Materials. The 1,4-diaminoanthraquinone (Aldrich) was recrystallized from acetone, m.p. 265 °C, before use. The white copper(I) chloride was prepared by the method of Stathis.[32] All other chemicals were reagent grade or better and used as received.

Equipment. A Varian EM-360A spectrometer was used to obtain the proton NMR spectra. Uncorrected melting points were determined on a Thomas Hoover capillary melting point apparatus. Infrared spectra were obtained with a Perkin-Elmer 598 spectrometer. A Mettler TA3000 differential scanning calorimeter was used to make thermograms. X-ray powder diffraction patterns were recorded on a Phillips scanning diffractometer using Cu Kα radiation and a 2 deg/min scanning rate. Silica gel thin layer chromatography plates which were sometimes used in the identification and purification of the aminoquinones were purchased from Analtech. The aminoquinones are intensively colored, making development of the plates after methylene chloride elution unnecessary. Conductivities were determined by a two probe method on disks (1.90 cm diameter × ~0.2 cm thick) that were under 13.8 MPa of pressure. A Varian 4502 spectrometer was used to obtain the ESR spectra. Visible spectra were recorded on a Cary 118 spectrophotometer.

Photoconduction was determined by using a conducting glass plate. The indium-doped tin oxide coated glass plate, 2 in. × 2 in., is scratched down the middle, removing the conducting layer and creating an insulating gap, ~1 mm, between the conducting surfaces. A sample is placed over the gap and a nonconducting glass cover is clamped on. The plate is inverted and light is directed through the conducting glass to the sample interface and the resistance is measured. The resistance is then measured in the dark with differences between the light and dark resistance indicating photoconduction. This apparatus is also useful in determining, quickly and with small amounts, whether a material is conducting.

Synthesis of ODOD. White copper(I) chloride (20.0 g) is dissolved in deoxygenated pyridine (1.0 L). The 1,4-diaminoanthraquinone (23.8 g) is added and oxygen bubbled through the mixture for 18 h. The mixture is then filtered and the filtrate washed successively with acetone, water, acetone, and finally methylene chloride to remove unreacted starting materials and copper(II) chloride. The yield is 19.6 g of a dark blue-black powder having a conductivity of 0.1–0.6 S/cm. Conducting materials containing other aminoquinones are made in a similar manner by replacing the 1,4-diaminoanthraquinone with the desired aminoquinone.

Synthesis of 2-Chloro-1,4-diaminoanthraquinone.[33] A mixture of thionyl chloride (320 g) and 1,4-diaminoanthraquinone (20 g) is refluxed 24 h. The mixture is then cooled and poured on to crushed ice. The resulting precipitate is filtered, dried, and recrystallized from carbon tetrachloride. The yield of 2-chloro-1,4-diaminoanthraquinone is 50% (11.4 g): mp 207–210 °C; NMR (deuterated trifluoroacetic acid) δ 8.1 (m), 7.9 (m), 7.5 ppm (m).

Synthesis of 2-(*p*-(Hydroxyethyl)phenoxy)-1,4-diaminoanthraquinone. A solution of dimethyl sulfoxide (50 mL), water (5.0 mL), 2-chloro-1,4-diaminoanthraquinone (5.0 g), sodium hydroxide (1.0 g), and *p*-(hydroxyethyl)phenol (3.4 g) is heated at 100 °C for 4 h. The mixture is then cooled and diluted with water until a precipitate forms. The precipitate is collected, washed, dried, and recrystallized from carbon tetrachloride. The yield of 2-(*p*-(hydroxyethyl)phenoxy)-1,4-diaminoanthraquinone is 24% (1.7 g): mp 224–227 °C; NMR (deuterated trifluoroacetic acid) δ 8.2 (m), 7.8 (m), 7.3 (q, J = 1 Hz), 6.85 (s), 4.7 (m, 1), 3.2 ppm (m, 1). In the same manner 2-phenoxy-1,4-diaminoanthraquinone is prepared from phenol, 2-(methylphenoxy)-1,4-diaminoanthraquinone is prepared from *p*-cresol, and 2-(dodecylphenoxy)-1,4-diaminoanthraquinone is prepared from dodecylphenol.

Synthesis of Copper(II)/1,4-Diaminoanthraquinone Complex. Copper(II) chloride dihydrate (0.71 g) is dissolved in dimethylformamide (30 mL) and 1,4-diaminoanthraquinone (1.00 g) is added. The mixture quickly turns into a paste that is filtered and washed with methylene chloride before drying. The dry filtrate is then washed with water, acetone, and methylene chloride and dried at 25 °C in vacuo overnight. The product (0.86 g) is a dark blue powder having a conductivity of 1.32×10^{-2} S/cm. Anal. C, 56.84; H, 3.86; N, 9.10; Cu, 5.7; Cl, 7.7.

Synthesis of Nickel(II)/1,4-Diaminoanthraquinone Complex. Nickel(II) chloride hexahydrate (0.50 g) is dissolved in dimethylformamide (25 mL) containing 1,4-diaminoanthraquinone (0.50 g) and triethylamine (0.84 g). A precipitate forms and is collected, washed with methylene chloride until the washings are colorless, and then dried. The precipitate (0.66 g) is a dark blue-black powder having a conductivity of 4.72×10^{-3} S/cm. Anal. C, 59.34; H, 3.76; N, 9.38; Ni, 17.2; Cl, 2.6.

Synthesis of Silver/1,4-Diaminoanthraquinone Complex. Silver(I) nitrate (0.71 g) is dissolved in acetonitrile (25 mL). Triethylamine (0.3 mL) and 1,4-diaminoanthraquinone (0.50 g) are added and a precipitate forms immediately. The precipitate is collected and washed with acetonitrile, dimethylformamide, acetonitrile, and finally methylene chloride before drying. The product is a dark blue-black powder having a conductivity of 7.9×10^{-3} S/cm. Anal. C, 38.6; H, 2.06; N, 6.12; Ag, 40.1.

Polymerization of 2,6-Dimethylphenol. 2,6-Dimethylphenol (7.2 g) was added to a mixture of pyridine (35.0 mL), nitrobenzene (100.0 mL), and ODOD (1.2 g). Air was then bubbled through the mixture for 24 h. The mixture was filtered to remove ODOD catlayst and then evaporated to remove solvent and unreacted monomer. The residue (4.5 g) is purple and was readily dissolved in methylene chloride (100 mL). The methylene chloride solution was added dropwise to methanol (1.0 L) and a light blue precipitate formed which was collected, washed, and dried, this procedure was repeated to give a light blue powder (0.90 g) whose infrared and proton NMR spectra are consistent with those of poly(2,6-dimethylphenylene oxide). The polymer GPC (based on polystyrene standards) M_n is 4400 g/mol while M_w is 4800 g/mol.

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Registry No. III, 107259-31-4; HO-*p*-C_4H_4–CH_2CH_2OH, 501-94-0; 2-chloro-1,4-diaminoanthraquinone, 54841-24-6; 2,6-dimethylphenol, 576-26-1; poly(2,6-dimethylphenylene oxide), 24938-67-8; ethylene, 74-85-1.

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Zwitterion Polymerization of 1-[(4-Carboxyphenyl)methyl]tetrahydrothiophenium Hydroxide Inner Salt

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ABSTRACT: The zwitterion 1-[(4-carboxyphenyl)methyl]tetrahydrothiophenium hydroxide inner salt was synthesized from tetrahydrothiophene (thiolane) and 4-(chloromethyl)benzoic acid and characterized by NMR and IR spectroscopy. Bulk polymerization of the zwitterion over the temperature range 70–200 °C gave linear polymer in 88–96% yield. The polymer was identified as a random copolymer containing oxycarbonyl-1,4-phenylenemethylene and oxycarbonyl-1,4-phenylenemethylenethiotetramethylene repeat units based on NMR, IR, and elemental analysis. Size-exclusion chromatography showed the number-average molecular weight to vary with temperature in the range 5100–41 000. Solution polymerization in DMF gave lower polymer yields (38–69%), lower polymer molecular weights (3000–7400), and higher oligomer yields (31–62%). HPLC fractionation coupled with NMR identified the oligomer fraction as consisting of a range of linear and cyclic oligomers of varying molecular size. The polymer end groups were identified by ^1H NMR as OH and COOH. When methanol was present during polymerization, the COOH end group was replaced by $COOCH_3$. Polymerization proceeded by ring-opening nucleophilic attack of carboxylate anion on the benzylic carbon and α-carbon of the tetrahydrothiophenium (thiolanium) ring to incorporate the two different types of repeat units into the polymer. Termination involved cyclization and reaction of propagating centers with water (and methanol, when present).

Introduction

Zwitterions have been proposed as reactive intermediates in polymerizations involving various pairs of electrophilic and nucleophilic reactants (e.g., β-propiolactone or acrylic acid with 2-methyl-2-oxazoline).[1,2] Zwitterion polymerizations involving stable (isolable) zwitterions have received relatively less attention. We recently reported the thermally initiated zwitterion polymerization of tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt which proceeds via ring-opening nucleophilic