New Polyarylates Prepared from 2,5-Bis(α-phenylisopropyl)-hydroquinone, Terephthalic Acid and Isophthalic Acid

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A new series of polyarylate copolyesters were prepared by melt polycondensation of 1,4-diacetoxy-2,5-(α-phenylisopropyl)benzene with mixtures of terephthalic acid and isophthalic acid in varying ratio. And their general properties such as the glass transition temperature, crystalline melting temperature, crystallinity and solubility were studied. The intrinsic viscosity values of the present polymers measured in a mixed solvent of phenol/p-chlorophenol/1,1,2,2-tetrachloroethane ranged from 0.45 to 0.66 depending on the composition and molecular weight. The copolyesters containing greater than 20 mole % of isophthalic acid were found to be amorphous, whereas the homopolymer derived from terephthalic acid was semicrystalline with a melting point of 414 ℃. The glass transition temperatures of the polymers ranged from 165 to 180 ℃ depending on the composition . The copolyesters containing 50 mole % and greater of isophthalic acid moiety were soluble at room temperature in such common solvents as tetrahydrofuran, chloroform and N,N-dimethlformamide.

Introduction

Polyarylates[1,2] are defined as wholly aromatic polyesters derived from aromatic diols and dicarboxylic acid. They belong to so-called a class of engineering plastics and are characterized by their inherent flame retardance, resistance to UV and relatively high glass transition temperatures (T_g). The copolyesters prepared from bisphenol-A (BPA), terephthalic acid (TPA) and isophthalic acid (IPA) are the representative examples of polyarylates. These polyesters are expected to find applications in transportations (interior panels for buses and aircrafts), glazing parts (solar collectors and appliances) and other optical uses.

In 1970's amorphous polyarylates, based on bisphenol-A and a mixture of isophthalic and terephthalic acids, were made available by Unitika in Japan (U-Polymer) and by Union Carbide Coporation (Ardel, acquired later by Amoco).[3] Since then several other companies also have introduced various polyarylates to the world market : Durel by Hoechst Celanese, Arylon by DuPont and APE by Bayer are some of the examples. Polymer blends based on polyarylates and other polymers such as poly(ethylene terephthalate), poly(butylene terephthalate), polycarbonate; poly(p-phenylenesulfide) and liquid crystalline polymers also are attracting a great deal of interests for improved performance and cost as well.

Bier[4] studied in detail the dependence of T_g, T_m, crystallinity and film toughness of polyarylates of BPA/TPA/IPA on the mole ratio of TPA and IPA in copolymers. He found that T_g tends to increase monotonously with increasing content of TPA moiety. The degree of crystallinity of the polymers, in general, was very low (≤3%) and those of containing 50-70 mole % IPA structure revealed lowest (~0.3%) degree of crystallinity. And the copolymers having the same level of IPA moiety formed very tough polymer films. Synthesis and properties of many other polyarylates have been the subjects of other investigations.[5-11]

There are several different preparation methods for the synthesis of polyarylates : 1) direct condensation between a aromatic diol(s) and a aromatic dicarboxylic acid(s) especially in the presence of a proper catalyst,[12-16] 2) interfacial polycondensation of diacid dihalide(s) with diol(s), 3) low temperature Schotten-Baunmann solution polycondensation[18-20] between diacid dihalide(s) and a diol(s) in the presence of an acid acceptor, 4) high temperature solution polycondensation[21,22] of a diacid dihalide(s) and a diol(s), 5) transesterification[5,6,23-25] of an aromatic dicarboxylic acid(s) with a diacetate of an aromatic diol(s) at a high temperature, and 6) polymerization of a diaryl (e.g. phenyl) ester[26,28] of an aromatic dicarboxylic acid(s) with an aromatic diol(s) via transesterification. All of the preparation methods possess certain advantages as well as disadvantages, and selection of a particular method is governed by factors such as economics, reliability of the process and product quality.

In this investigation we have prepared a series of copolyesters by high temperature melt polymerization of 1,4-diacetoxy-2,5-bis(α-phenylisopropyl)benzene with mixtures of terephthalic acid and isophthalic acid in varying ratio:
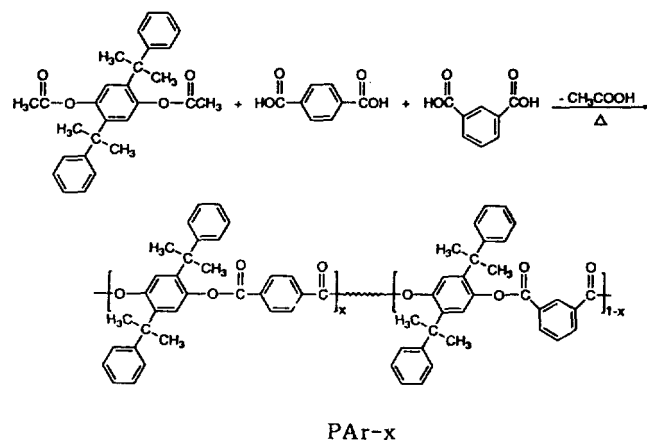
PAr-x

These copolymers are of random sequence, and x and $(1-x)$ in the above equation denote overall composition, not block length. And PAr-x stands for the polylate containtng x mole fraction of TPA unit. Thermal behavior of the polymers was examined on a differential scanning calorimetry and their

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crystallinity by wide-angle X-ray diffractmetry.

Experimental

Synthesis of Monomer[29]

2,5-Bis(α-phenylisopropyl)hydroquinone. Hydroquinone (22.02 g; 0.2 mol) and 1.8 g of p-toluenesulfonic acid were dissolved in 100 mL of tetraglyme. The mixture was heated to 140 ℃, to which 59.09 g (0.50 mole) of α-methylstyrene was added slowly over the period of 1 h. The mixture was heated to and maintained at 150 ℃ for 5 h. After being cooled to room temperature, the reaction mixture was thoroughly washed with 0.1 M NaOH. The product precipitate formed was washed with n-hexane. The crude product thus obtained was dissolved in acetone. The acetone solution was dropwise added to a cold dil-HCl solution with vigorous stirring. The precipiate obtained was collected on a filter. The final product was obtained through recrystallization from toluene/n-hexane (1/1 by volume). The product yield was 29 g (40%). mp 205 ℃ (lit.[30] value 195 ℃). ^{1}H NMR spectrum (CDCl$_3$); δ (ppm) 1.8 (s, 12H, 6CH$_3$), 4 (s, 2H, OH), 6.9 (s, 2H, aromatic), 7.2 (m, 10H, phenyl). IR-spectrum (KBr): 3415 (O-H stretching), 2955 (aliphatic C-H stretching), 1600 and 1645 (aromatic C-H stretching), 774 and 702 cm^{-1} (monosubstituted C-H out-of-plane bending).

1,4-Diacetoxy-2,5-bis(α-phenylisopropyl)benzene. The above prepared substituted hydroquinone (20.0 g; 58 mmole) was dissolved in 200 mL of acetic anhydride. The mixture was refluxed for 7 h. After being cooled to room temperature, the reaction mixture was poured into cold water. The precipitate was washed with water, 0.1 M Na$_2$CO$_3$ solution and then again with water. The crude product thus obtained was purified by recrystallization from toluene/n-hexane (1/1 by volume). The yield was 24 g (95%). mp. 200 ℃. ^{1}H NMR spectrum (CDCl$_3$): (ppm) 1.68 (d, 18H, 6CH$_3$), 7.15-7.3 (m, 12H, aromaric). IR-spectrum (KBr): 3512 (C=O overtone), 2940 (aliphatic C-H stretching), 1756 (C=O stretching), 1600 (aromatic C-H stretching), 1165 cm^{-1} (C-O stretching).

Preparation of Polymers

All of the polymers were prepared by the melt polymerizaion method. Since the preparation methods were similiar, only a representation synthetic process is given for the copolymer of TPA : IPA=30 : 70 (PAr-0.3). 1,4-Diacetoxy-2,5-bis (α-phenylisopropyl)benzene (1.500 g; 3.484 mmole), terephthalic acid (0.4057 g; 2.442 mmole), isophthalic acid (0.1739 g; 1.047 mmole) were placed in a polymerization tube equipped with a nitrogen inlet, a vacuum-sealed mechanical strrer and a distillation outlet. This tube was heated slowly in a salt bath to 280 ℃ over a period of 0.5 h. And then the mixture was heated at 290 ℃ for 1 h, at 300 ℃ for 0.5 h, at 310 ℃ for 1 h, at 320 ℃ for 1 h, and at 340 ℃ for 0.5 h. Afterwards, the nitrogen line was stopped and the pressure was reduced to 300 Torr. The reaction mixture was heated to and maintained at 350 ℃ for 0.5 h under this pressure. Finally, polymerization was conducted further at 350 ℃ for 0.5 h under 0.5 Torr of pressure. Polymer formed was dissolved in tetrahydrofuran (THF), and the solution was filtered through a filter. The filtrate was added to methanol precipiting the polymer, which was then washed

Table 1. Polymerization Conditions

| IPA/TPA	Temperature (℃)/Pressure (torr)/Time (min)
100/0	220/760/10→260/760/10→280/760/30→
80/20	290/760/60→300/760/30→310/760/60→
70/30	320/760/60→340/760/30→350/300/30→
50/50	350/0.5/30
30/70	
20/80	220/760/10→260/760/10→280/760/30→
0/100	290/760/60→310/760/60→340/760/60→
	360/760/60→365/300/30→365/0.5/30

with acetone and ethanol. The weight of obtained polymer was 1.2 g (70%). The copolyesters prepared from TPA/IPA= 7/3 (PAr-0.7), 8/2 (PAr-0.8) and 10/0 (PAr-10) were not soluble in THF and other common solvents. Therefore, these polymers were simply washed with acetone and ethanol. Table 1 summarizes the polymerization process of the present series of polyesters.

Characterization of Intermediates and Polymers

Elemental analyses were performed by the Korea Basic Research Center, Seoul, Korea using a Carlo Erba 1108 elemental analyzer. Melting points and other thermal transitions were measured on a Fisher-Jones melting point apparatus and on a differential scanning calorimeter (DSC) (DuPont 910 or Mettler 3000 DSC instrument). DSC analyses were usually conducted under nitrogen atmosphere at the heating rate of 10 ℃/m. The H NMR and IR spectra were recorded on a Varian Gemini 300 MHz instrument and Bomen MB FT-IR spectrophotometer, respectively. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max III$_a$ instrument using a nickel-filtered Cu-K$_a$ (λ=1.542 Å) radiation. The solution viscosity values were measured at 25 ℃ for the solution of 0.2 g/dL in a mixted solvent of phenol/p-chlorophenol/1,1,2,2-tetrachloroethane (25/40/35 by weight).

Results and Discussion

Sythesis of 1,4-Diacetoxy-2,5-big(α-phenylisopropyl)benzene Monomer. The substituted hydroquinone could be synthesized by Friedel-Crafts type reaction between hydroquinone and α-methylstyrene in the presence of p-toluenesulfonic acid.[29] The diacetylated monomer was prepared in very high yield by reaction of 2,5-bis(α-phenylisopropyl)hydroquinone with acetic anhydride at a refluxing temperature. The whole synthetic route is sohwn in the following scheme.

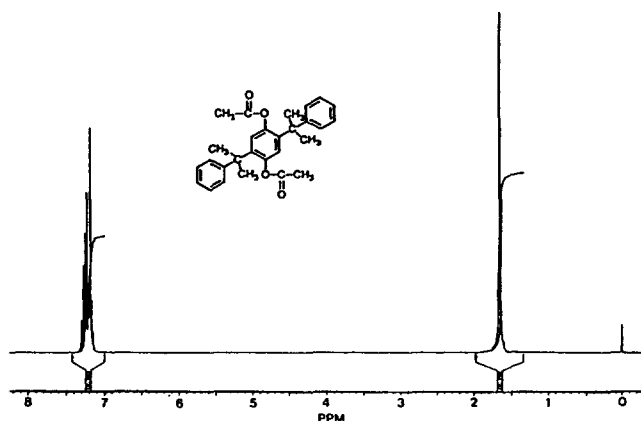*Polyarylates of 2,5-Bis(α-phenylisopropyl)hydroquinone*

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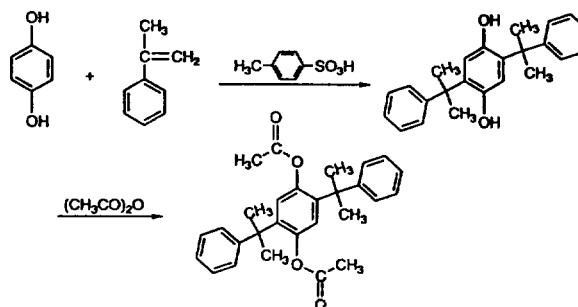
Figure 1. ¹H NMR spectrum of 1,4-diacetoxy-2,5-bis(α-phenyliso-propyl)benzene (in CDCl₃).
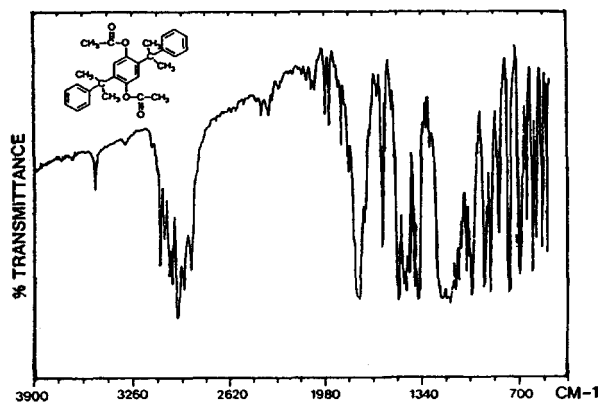
Figure 2. IR spectrum of 1,4-diacetoxy-2,5-bis(α-phenyliso-pro-pyl)benzene (KBr).

Table 2. Properties of Polymers

Feed Ratio (IPA/TPA)	Actual Ratio[a] (IPA/TPA)	η_inh[b]	Tg (°C)	Tm (°C)
1/0	1.00/0.00	0.66(0.73)	180	–
0.8/0.2	0.68/0.32	0.50(0.56)	169	–
0.7/0.3	0.64/0.36	0.45(0.81)	167	–
0.6/0.4	0.61/0.39	0.55(0.68)	167	–
0.5/0.5	0.47/0.53	0.52(0.54)	167	–
0.3/0.7	–	0.61(0.65)	166	–
0.2/0.8	–	0.60(0.61)	166	–
0/1	–	ins[c]	170	414

[a] Calculated from NMR data. [b] Viscosity was measured for 0.2 g/dL solutions is phenol/p-chlorophenol/1,1,2,2-tetrachloroethane (w/w/w=25/40/35) mixture at 25 °C. Values in the parenthesis are the viscosities measured after 3 hours of annealing at 180 °C. [c] Insoluble.

Table 3. Solubility of polymers in common organic solvents

IPA/TA	THF	CHCl₃	Phenol	DMF	Acetone	MeOH
100/0	+ +	+ +	+ +	+ +	+	–
80/20	+ +	+ +	+	+ +	–	–
70/30	+ +	+ +	+	+ +	–	–
60/40	+ +	+ +	+	+ +	–	–
50/50	+ +	+ +	+	+ +	–	–
30/70	–	+	+	–	–	–
20/80	–	+	–	–	–	–
0/100	–	–	–	–	–	–

(+ +) very solube; (+) soluble; (−) insoluble

The ¹H NMR spectrum of this compound is shown in Figure 1. One sharp peak appears at δ 1.68 ppm and a multiplet over δ 7.15-7.3 ppm. The integrated areas of these peaks are in the ratio of 3 : 2, which is in a complete agreement with the ratio expected for the diacetoxy compound. It is rather surprising that the methyl protons in the acetoxy and and isoproplidene groups reveal the exactly same chemical shift. The IR spectral data (Figure 2) given in Experimental also are in agreement with the expected structure.

Synthesis and Properties of Polymers. As shown by the chemical equation given in Introduction and as described in Experimental, the present polymers were prepared by melt polymerization of 1,4-diacetoxy-2,5-bis(α-phenylisopropyl)benzene with mixtures of terephthalic acid (TPA) and isophthalic acid (IPA) in varying ratio. The actual compositions of the obtained polymers were determined by the analysis of their H NMR spectra obtained in CDCl₃. Since terephthaloyl moiety shows a characteristic resonance peak at δ 7.6 ppm, relative peak area at this position gives us its molar content in the copolymers. The results are included in Table 2. In general, copolymers tend to contain higher levels of TPA structure than in feed when use level of IPA in feed is high. This can be most probably ascribed to the higher volatility and thus loss of IPA during polymerization. But copolymer compositions are practically same as feed co-

mpositions when TPA level in feed is 40 mole % or higher. The compositions of the two copolymers PAr-0.7 and PAr-0.8 containing 70 and 80 mole % TPA moiety respectively could not be determined spectroscopically due to their insolubility in common NMR solvents. It is, however, our conjecture that their actual compositions are not very far from the feed compositions as observed for other copolymers.

The solution viscosity values (Table 2) of the polymers ranged from 0.45 to 0.66 for the original samples, but the values increased to 0.54-0.81 when the polymers were annealed at 180 °C for 3 hours under vacuum. Solubility of the polymers is summarized in Table 3. The compositions containing 50 mole % and higher level of IPA unit are soluble in such common solvents as tetrahydrofuran, chloroform and N,N-dimethylformamide. Those containing higher than 50 mole % of TPA show poor solubility. All of the polymers are soluble in mixed solvents consisting of phenol, p-chlorophenol and 1,1,2,2-tetrachoroethane. Compositions of 30-70 mole % of the TPA unit formed transparent tough films.

Figure 3 compares the wide-angle X-ray diffractograms of the polymers and shows that crystallinity decreases rapidly with inclusion of IPA units in the copolymers. The copolymers containing 30 mole % and higher level of IPA moiety are amorphous. Even the homopolyester derived form IPA appears to be of very low degree of crystallinity. In contrast, the homopolymer prepared from TPA is highly crystalline.
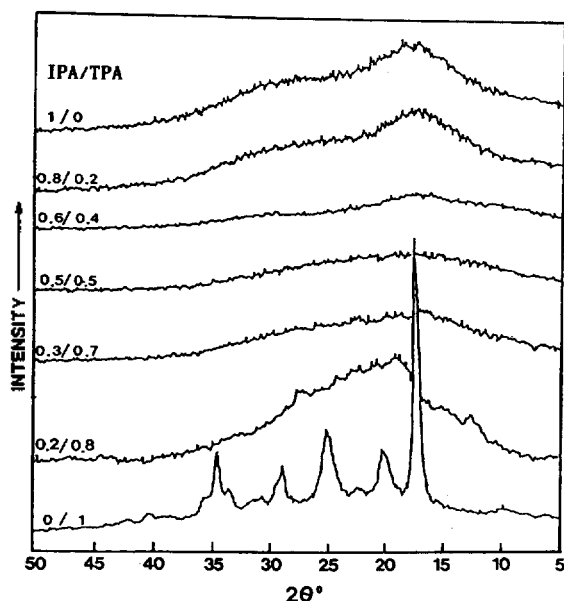
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Figure 3. Wide-angle X-ray diffractograms of the polymers obtained before annealing.

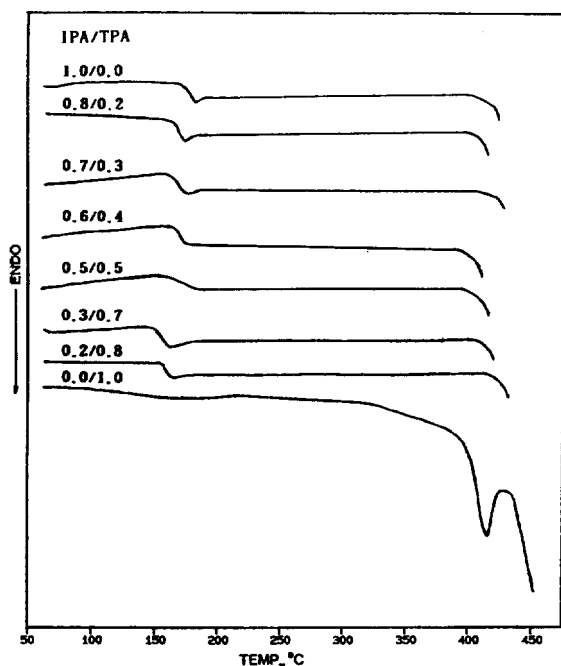**Figure 4.** DSC thermograms of the polymers (N₂ atmosphere, heating rate; 10 ℃/min).

This observation is born out by the DSC thermograms shown in Figure 4. All of the polymers exhibit glass transitions clearly between 165 ℃ and 180 ℃, with all of the copolymers' Tgs lying around 167 ℃ (see Table 2). The glass transition of the TPA homopolymer (PAr-1.0) is very weak as demonstrated by a small inflection near 170 ℃, which must be due to the fact that this polymer has a very higher degree of crystallinity as reflected by its X-ray diffractogram in Figure 3. The relatively high Tg values of the present polymers must be the result of the rigidity of the main chain together

with fact that the hydroquinone ring carries two bulky substituents. These values, however, are lower by 15-20 ℃ than those of the correspoding polyarylates[4] prepared from bisphenol-A in place of the present diol monomer.

The TPA homopolymer (PAr-1.0) reveals a sharp melting endotherm at 385 ℃, whereas other polymers do not exhibit any melting transition on their DSC thermograms due to their amorphous nature. The crystalline melting point of PAr-1.0 is noted to be higher than 350 ℃ [6] reported for the polyester prepared from bisphenol-A and TPA. Although thermogravimetic thermograms are not given, all of the present polymers start to loose their weight at about 410 ℃, when they were heated at 20 ℃/min under nitrogen atmosphere. Maximum decomposition rates were observed around 450 ℃. And they were self-extinguishing in air.

Conclusion

A series of new aromatic polymers were prepared from 2,5-bis(α-phenyl-isopropyl)hydroquinone, terephthalic acid and isophthalic acid. Copolymers containing equal to and more than 50 mole % of isophthalic acid unit are soluble in common organic solvents. Most of the copolymers were amorphous and their glass transition temperatures were about 167 ℃. The compositions containing 30-70 mole % of isophthalic or terephthalic acid unit produced tough films. The polymers were found to be stable up to about 400 ℃. Although photochemical studies have not been performed, it is conjectured that the photochemical Fries rearrangement[11] would not easily occur with the present polymers owing to the presence of the two extremely bulk α-phenylisopropyl substitutent on the hydroquinone phenylene ring.

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Electrochemical Reduction of Oxygen

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Electrochemical Reduction of Oxygen at Co(II)-3,4-bis (salicylidene diimine)toluene Complex supported Glassy Carbon Electrode

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Electrochemical reduction of oxygen has been carried out at glassy carbon electrode and carbon ultramicroelectrode, the surface of which is modified with a new Co(II)-Schiff base complex, Co(II)-3,4-bis(salicylidene diimine)toluene in 1 M KOH solution. The results obtained from cyclic voltammetric and chronoamperometric experiments are consistent with the formation of the reasonably stable superoxide ions as a primary electron transfer reaction product. The exchange rate constant obtained for oxygen reduction is about 0.02 cm/s.

Introduction

Reduction of dioxygen species in both aqueous and nonaqueous solutions has been receiving a great deal of attention due to its implications in practical applications such as fuel cells and batteries, as well as biological reactions.[1,2] It is well established that the first species generated upon reducing oxygen is superoxide ion.[2] The generation of superoxide ions in nonaqueous solutions has been demonstrated electrochemically[2-4] as well as spectroscopically.[5] While evidence has been presented for the presence of superoxide ion in aqueous solution by monitoring ESR signals during the electrochemical reduction of oxygen at low temperature,[6] it is generally very difficult to observe its generation due to its high reactivity with water. This is true even in strong alkaline solutions.

We have been studying the oxygen reduction because the reaction is used as a cathode reaction in fuel cells and metal air batteries.[7-8] Because the oxygen reduction occurs *via* several intermediates including generation of superoxide ions during the first step, which reduces overall coulombic efficiencies of the reaction, many transition metal chelate based catalysts have been studied with hopes to reduce the intermediate steps.[9-16] Phthalocyanines or porphyrins of cobalt and iron are known as effective catalysts for oxygen reduc-

tion. Carbon based oxygen electrodes are modified by the adsorption of these macromolecular compounds, which mediate the electron transfer. Oxygen is reduced to hydrogen peroxide and/or water at these modified electrodes *via* a two- or four- electron transfer reaction. Collman *et al.*[16-18] and Anson *et al.*[15,19-21] have synthesized and characterized cobalt cofacial porphyrin derivatives as oxygen reduction catalysts in an effort to reduce the intermediate step during the oxygen reduction since the rate of the overall reaction is often limited by one or more steps of the reduction. As a result, some of these compounds were found to reduce dioxygen species directly to water *via* a four- electron transfer reaction.[16-26]

In our present report, we describe Co(II)-Schiff base complex, Co(II)-3,4-bis(salicylidenediimine)toluene, Co(II)(o-BSDT)(H$_2$O)$_2$, which is shown to catalyze the oxygen reduction *via* predominantly a single electron, rather than multielectron, transfer reaction. The catalytic effect is large and the reaction occurs *via* one- electron transfer to produce superoxide ions. The superoxide ion produced at the Co(II) (o-BSDT)(H$_2$O)$_2$ modified electrode shows a reasonable stability in aqueous KOH solution.

Experimental

Pyridine (Fischer Scientific), potassium ferricyanide (Mal-