comments and for providing us with preprints of their work.

Supplementary Material Available: Spectroscopic data and details of structure determination of **1**, including ORTEP, crystal data, data collection and refinement, positional parameters, temperature factor expressions, and selected bond distances and angles, and tables of positional parameters, temperature factor expressions, and selected bond distances and angles for **2** (32 pages). Ordering information is given on any current masthead page.

Synthesis of Self-Doped Conducting Polyaniline

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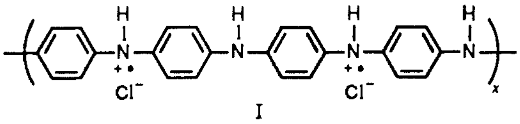
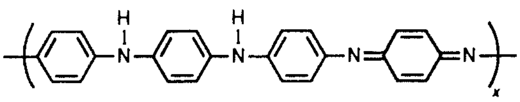
Polyaniline was the first conducting polymer whose electronic properties could be reversibly controlled by both protonation and charge-transfer doping.[1,2] We report the synthesis of sulfonic acid ring-substituted polyaniline, the first protonic acid self-doped conducting polymer. Without external doping, the polymer has a conductivity of ~0.1 S/cm, which is independent of pH when equilibrated with aqueous acid solutions of pH less than or equal to 7.

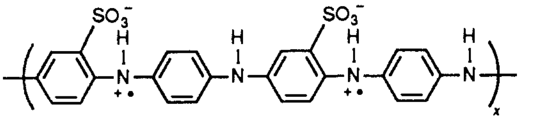


I

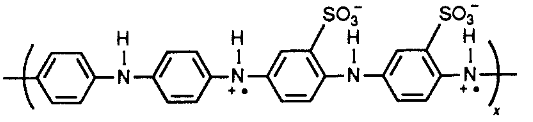


II

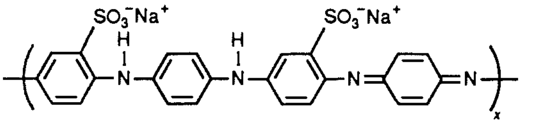
Emeraldine hydrochloride powder (I) was synthesized from an aqueous solution of aniline, $(NH_4)S_2O_8$, and HCl. It was then converted to analytically pure emeraldine base (II) via a previously described method.[3] Emeraldine base (0.5 g) was sulfonated by being dissolved in 40 mL of fuming sulfuric acid with constant stirring. The color of the solution changed from dark purple to dark blue during ~2 h at room temperature. The solution was then slowly added during ~20 min to 200 mL of methanol to precipitate most of the product, the temperature being held between 10 and 20 °C by an ice bath. Precipitation was completed by the addition of 100 mL of acetone. The green powder was then collected on a Büchner funnel, and the precipitate cake was washed at least 10 times with ~50-mL portions of methanol until the filtrate had a pH of 7 when tested by wet pH paper. The liquid level in the Büchner funnel was constantly adjusted so that it remained above the top of the precipitate in order to prevent cracking of the precipitate cake, which would result in inefficient washing. It was then permitted to remain under suction for approximately 10 min; the resulting precipitate cake was slightly soluble in water, giving a green solution. The filter cake then was transferred on the filter paper to a vacuum desiccator and dried under dynamic vacuum for 24 h. Elemental analyses[4] are consistent with structures given by compound IIIA or by compound IIIB containing two molecules of water of hydration. Either structure would give the polysemiquinone radical cationic (polaronic) structure, and both are consistent with presently available experimental data for a ring-sulfonated, protonated form of polyaniline in the emeraldine oxidation state.[5] The polymer is very soluble in dilute aqueous base, giving a blue-violet solution of the corresponding undoped (insulating) salt form, compound IV, or the alternate structure having the SO_3^- groups on adjacent rings.



IIIA



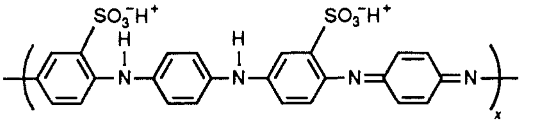
IIIB



IV

The sodium salt was synthesized by dissolving 0.5 g of compound IIIA,B in 20 mL of 0.1 M NaOH solution. Water was removed from the solution by slowly evacuating the vessel at room temperature. After most of the water had been removed, the product was transferred to a vacuum desiccator and dried under dynamic vacuum for 24 h. The polymer was obtained as a free-flowing dark purple powder.

The elemental analysis, infrared and electron spin resonance spectra, and conductivity are consistent with compound IIIA,B with UV-vis polaron band transitions[6] at 435 nm (2.85 eV) and 850 nm (1.46 eV), a π-π^* transition[7] at 320 nm (3.88 eV), and an intense ESR signal of line width ~0.4 G. This self-doped polymer can be regarded as being formed hypothetically via the initial formation of the strong acid, compound V, which then immediately protonates ("dopes") the imine nitrogen atoms to give the conducting polymer in an analogous manner to the protonation of the parent emeraldine base polymer by HCl.[8] Treatment of compound IIIA,B with aqueous NaOH yields the corresponding nonprotonated sodium salt, compound IV, an insulator, analogous to emeraldine base (II).



V

It is implicit from the structure of compound IIIA,B that, under the experimental conditions employed, only half the rings are sulfonated. This is consistent with the fact that only half the rings

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[1] (a) MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173-180. (b) Epstein, A. J.; MacDiarmid, A. G. *Proc. Int. Winter School On Electronic Polymer Properties*; Kirchberg, Austria; March 1989; *Solid State Science* **1989**, *91*, 282-289; Kuzmany, H., Ed.; Springer-Verlag: Berlin. (c) MacDiarmid, A. G.; Epstein, A. J. *Trans. Faraday Soc.*, in press.

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[4] Elemental anal. Found for compound IIIA or compound IIIB: C, 52.12; H, 3.98; N, 10.13; S, 11.18; O, 22.59. (Oxygen by difference.) Calcd for $C_{12}H_9N_2SO_3(H_2O)_{0.98}$: C, 51.67; H, 3.96; N, 10.04; S, 11.49; O, 22.83.

[5] Copolymerization of 2-aminobenzenesulfonic acid and aniline yields a similar product. However, attempts at polymerization of 2-aminobenzenesulfonic acid alone were unsuccessful.

[6] (a) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, W. R.; Woo, H. S.; Tanner, D. B.; Richter, A. F.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303-309. (b) Stafstrom, S.; Brédas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464-1467.

[7] (a) Euler, W. B. *Solid State Commun.* **1986**, *57*, 857-859. (b) Boudreaux, D. S.; Chance, R. R.; Wolf, J. F.; Shacklette, L. W.; Brédas, J. L.; Thémans, B.; André, J. M.; Silbey, R. *J. Chem. Phys.* **1986**, *85*, 4584-4590.

[8] MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285-290.

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need to be sulfonated in order to produce the stable polysemiquinone form of the polymer. Indeed, additional sulfonation and consequent protonation of amine nitrogen atoms would convert some of the $-(NH)-$ to $-(NH_2^+)-$ groups and hence destabilize the polymer by reducing the extent of its π conjugation. The absorption maxima at 1080, 700, and 620 cm^{-1} in the FTIR spectrum of compound IIIA,B are consistent with the presence[9] of SO_3^- groups attached to the aromatic rings. The absorption maxima at 820 and 870 cm^{-1} indicative of 1,2,4-trisubstitution of the rings are out-of-plane bending of aromatic hydrogens. These absorptions are not present in the 1,2-disubstituted emeraldine base (II), from which compound IIIA,B was synthesized.

The solubilities of compounds IIIA,B and IV differ markedly from those of the corresponding protonated and nonprotonated forms, respectively, of parent polyaniline. Compound IIIA,B dissolves appreciably in aqueous 0.1 M NH_4OH or NaOH to give the corresponding salts whereas emeraldine hydrochloride when treated in this manner is converted to the insoluble emeraldine base form (II). The anionic (SO_3^-) groups are presumably largely responsible for its solubility in water. Compound IIIA,B partly dissolves in DMSO, giving the dark green color of the protonated polyaniline, but is apparently deprotonated when it dissolves in *N*-methyl-2-pyrrolidinone (NMP), in which it has a blue-violet color, characteristic of compound IV.

The high concentration of protons in the vicinity of the polymer backbone due to the presence of the attached SO_3^- groups is not only responsible for the retention of doping of the polymer at the higher pH values, where the parent emeraldine base polymer (II) is essentially a (nondoped) insulator, but is also consistent with the observed faster electrochemical redox reactions of compound IIIA,B in aqueous media.

Acknowledgment. The authors are grateful to Prof. A. G. MacDiarmid for valuable comments and stimulating discussions. This research has been supported in part by the Defense Advanced Research Projects Agency through a grant monitored by the U.S. Office of Naval Research.

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Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by (Salen)manganese Complexes

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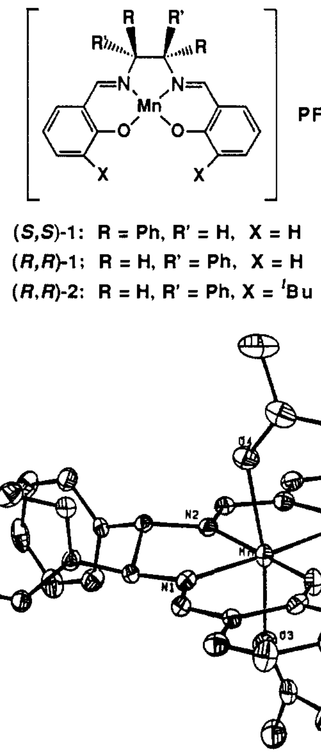
The development of catalysts that mediate enantioselective group transfer to unfunctionalized olefins is an important goal in organic chemistry.[1] Catalytic systems that are effective for *directed* epoxidation[2] and hydrogenation[3] have been discovered, but the substrates must bear specific functional groups to achieve the precoordination required for high enantioselectivity. This restriction is lifted when stereoselectivity relies solely on nonbonded interactions, and in these cases the pool of potential substrates could in principle be unlimited. We report here that manganese complexes of chiral Schiff bases catalyze epoxidation of alkyl- and aryl-substituted olefins with the highest enantioselectivities reported to date for nonenzymatic catalysts.[4]



(*S*,*S*)-1: R = Ph, R' = H, X = H
(*R*,*R*)-1: R = H, R' = Ph, X = H
(*R*,*R*)-2: R = H, R' = Ph, X = ^{t}Bu

Figure 1. Structure of catalysts **1** and **2**. ORTEP view of the cation of (*S*,*S*)-**1**·[acetone]$_2$.

Epoxidation catalysts **1** and **2** (Figure 1) were prepared in three steps and in 68–74% overall yield from readily available (*R*,*R*)- or (*S*,*S*)-1,2-diamino-1,2-diphenylethane[5] and the appropriate salicylaldehyde derivative.[6,7] The X-ray crystal structure of the bis(acetone) adduct of (*S*,*S*)-**1** (ORTEP diagram included in Figure 1)[7] reveals that the tetradentate ligand adopts a near-planar geometry with the phenyl groups of the diphenylethylene unit residing in pseudoequatorial positions.

The reactions were carried out in air with iodosylmesitylene as the oxygen atom source and 1–8 mol % catalyst.[8] Our data summarized in Table I along with the best results previously

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(1) Epoxidation: (a) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (b) Tani, K.; Hanafusa, M.; Otsuka, S. *Tetrahedron Lett.* **1979**, 3017. (c) Curci, R.; Fiorentino, M.; Serio, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 155. (d) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728. (e) Naruta, Y.; Tani, F.; Maruyama, K. *Chem. Lett.* **1989**, 1269. (f) O'Malley, S.; Kodadek, T. *J. Am. Chem. Soc.* **1989**, *111*, 9116. Hydroboration: (g) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. Dihydroxylation: (h) Jacobsen, E. N.; Markó, I. E.; Mungall, W. S.; Schröder, G. W.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968. (i) Wai, J. S. M.; Markó, I. E.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123. Hydrogenation: (j) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105.

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(7) Experimental procedures for the epoxidation reactions, physical and experimental data for the catalysts and their precursors, and details of the structure determination are provided as supplementary material.

(8) Preliminary studies indicate that sodium hypochlorite is also an effective oxidant. With undiluted commercial bleach, 0.3–2 mol % catalyst may be used under phase-transfer conditions with no reduction in enantioselectivity or yield. Zhang, W.; Jacobsen, E. N., work in progress.