# Chiral Metals: Synthesis and Properties of A New Class of Conducting Polymers

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# CHIRAL METALS: SYNTHESIS AND PROPERTIES OF A NEW
## CLASS OF CONDUCTING POLYMERS

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Abstract

A new class of organic conductors, namely chiral conducting
polymers, were prepared by three approaches. The synthesis
of complexes incorporating either chiral polymer backbones,
chiral dopants or chiral solvating ligands (for dopant ions)
are described. Chiral complexes with conductivities as high
as 60 S/cm have been obtained, but resulting conductivities
are strongly dependent upon the structural nature of the
complexes.

## INTRODUCTION

Synthetic metals offer a wide variety of properties due to
the availability of many structural types and a large array of
dopant species. These materials possess yet another feature not
generally recognized or explored, namely the ability to be pre-
pared in chiral or "handed" forms. While the surfaces of conven-
tional conductors such as graphite have been chirally modified[1]
and used as catalytic electrodes for asymmetric reactions,[2]
inherently chiral conducting electrodes have not been prepared.
Because it is expected that the latter might offer superior per-
formance in electrochemical asymmetric reactions, and that chiral
conductors may possess other novel (magnetic and chiroptical)
properties, we attempted to prepare several inherently chiral
organic conducting polymers.

## CLASSES OF CHIRAL CONDUCTIVE POLYMERS

We envisioned several approaches to preparing at least three
different classes of chiral conducting polymer systems. Those
belonging to Class I are systems which incorporate a chiral
arrangement of atoms along the polymer backbone. Class II type
are those which incorporate a dissymmetric or asymmetric dopant
specie into an achiral conjugated polymer, and Class III systems
are those which incorporate chiral ligating solvents associated

with an achiral dopant ion in an achiral conjugated polymer. Of course, compositions can be derived which belong to any com-bination of these three classes. From the viewpoint of maxi-mizing the degree of induced asymmetry into a chiral conductor, the order of preference is probably Class I>Class II>Class III.

Systems Containing Chiral Polymer Backbones (Class I)
     Conjugated polymers containing chiral polymer backbones can be prepared by polymerizing suitably chiral monomers or by induc-ing a helical twist or coil of one "handedness" into an otherwise achiral polymer structure. The latter type might be derived from an asymmetric nickel-catalyzed[3] Grignard coupling of 2,5-dihalo-3-alkythiophene where the polymer backbone could be chiral by virtue of atropisomerism[4] (as long as adjacent rings never become completely co-planar). However, the extent of induced chirality in the polymer would be difficult to predict by this technique.
     The most straight-forward approach to Class I structures is to polymerize a chiral monomer by known techniques so that the existence of chirality in the resulting polymer is well-established. Pyrroles or thiophenes chirally substituted in the 3-position are attractive from the standpoint of obtaining highly conducting products by electrochemical polymerization.[5] Unfor-tunately, these chiral monomers are not readily available. A more expedient approach, but with an anticipated large trade-off in conductivity[9] (ca. $10^5$), is to prepare and polymerize pyrrole monomers which are N-substituted with chiral groups. Several such monomers were prepared and electrochemically polymerized. The results are shown in Table I. Neither good film quality

TABLE I   Conductivities of Electrochemically Polymerized
          Chiral Pyrroles



| R | $V_{app}$; Current Density | Results |
|---|---|---|
| H | 0.7V; 30 $\mu$A/cm$^2$ | Film, $\sigma$ = 114 S/cm |
| Ph<br>—⟨,,H<br>CH$_3$ | 0.62V; 50$\mu$A/cm$^2$ | Rubbery, flexible film; non-conductive |
| CH$_3$O ,,CF$_3$<br>—⟨·Ph<br>O | +1.1V; 200 $\mu$A/cm$^2$ | Powder in solution, no deposit on electrode |
| CH$_2$OAc<br>—⟨·H<br>CH$_3$ | 20$\mu$A/cm$^2$ | Film, $\sigma$~10$^{-6}$S/cm, {C$_9$H$_{11}$NO$_2$(BF$_4$)$_{0.64}$} |

nor the expected conductivity values were realized for these
poly(N-substituted pyrroles). Here, the large substituents prob-
ably force adjacent pyrrole rings severely out of co-planarity,
and in certain cases, may prevent formation of polymer with a
high degree of 2,5-linkages. Either of both occurrences would
severely compromise doped-polymer conductivity.[9] A more pro-
mising approach to polymers of this class is probably by poly-
merization of monomers chirally substituted in the 3-position.

Systems Incorporating Chiral Dopant Ions (Class II)
    Since certain conducting polymers such as polyacetylene[10]
and polyquinoline[11] can be donor-doped with the inclusion of
tetraalkylammonium counter-ions, chiral complexes could be
readily obtained with these polymers by incorporating appropriate
chiral "onium" ions. A few chiral ammonium and phosphonium ions
were prepared from readily available, optically active precur-
sors, and attempts were made to electrochemically insert them
into polyacetylene films using the cell shown in Figure 1.



| R | Mol % Doping | σ (S/cm) |
|---|---|---|
| (structure: tetrahydrofuran with CH$_2$– and H) | 4 | 11 |
| | 5.8 | 52 |
| | 8.0 | 60 |
| (d,l) (structure: tetrahydrofuran with CH$_2$– and H) | 5.8 | 48 |
| (structure: CH$_3$, H, Ph) | Unstable | — |
| (structure: cyclohexane with P Ph$_2$CH$_3$ and CH$_3$) | Unstable | |

Anode: $yNa(Hg) \rightarrow yNa^+ + ye^-$
Cathode: $(CH)_x + ye^- + yRNMe_3{}^+I^- \rightarrow [CH^{y-}(RNMe_3{}^+)_y]_x + yI^-$

$y Na(Hg) + (CH)_x + y RNMe_3{}^+I^- \rightarrow y Na^+I^- + [CH^{y-}(RNMe_3{}^+)_y]_x$
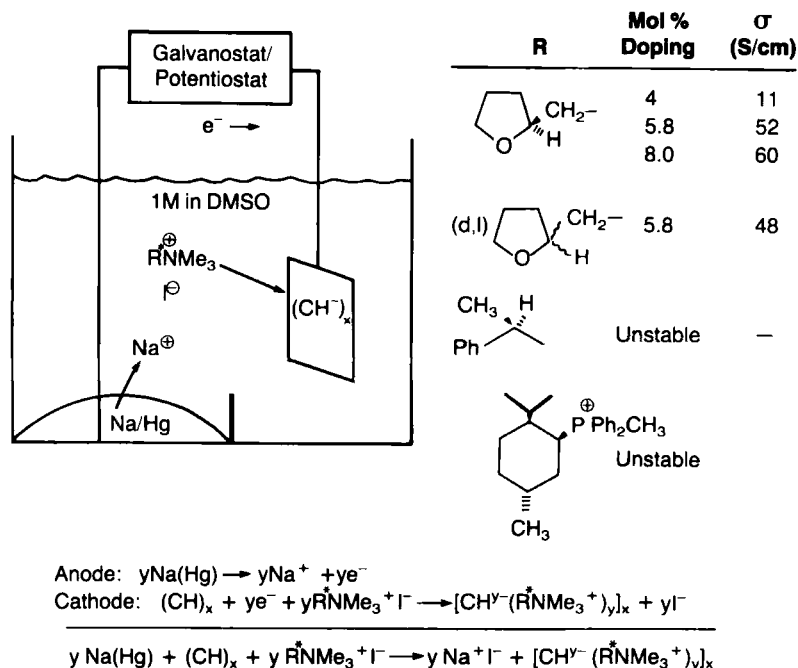
FIGURE 1    Electrochemical doping cell and conductivities of
            various chiral alkylammonium ion and phosphonium ion-
            doped polyacetylene films.

(The Na/Hg anode was chosen since the ammonium and phosphonium
ions, as well as the solvent (DMSO) were found to be unstable at
pure lithium and sodium electrodes. All doping reactions were
performed in an Argon-filled dry box). The phosphonium ion was
found to be reductively unstable at the potential where donor-
doping of polyacetylene begins (ca +1.8V vs. Li$^+$/Li). Similar
results were observed with the  -phenethylammonium ion - not
surprising in light of the ease with which benzylic ammonium ions
are cleaved. A completely aliphatic chiral ammonium ion, derived
from resolved tetrahydrofurfurylamine, proved stable. Polyacety-
lene films coulometrically doped with this ion to the 8 mol %
level were bright gold, flexible, and had conductivities as high
as 60 S/cm (four-point probe technique). The doped films were
amorphous by X-ray. No solvent (DMSO) was incorporated into the
film since doping levels determined by weight uptake (after
washing in fresh DSMO, then THF, and drying under vacuum) gave
the same values as determined coulometrically ($\pm$2%). Figure 1
summarizes the conductivity data on films doped to various levels
with both the chiral and racemic forms of the trimethyltetra-
hydrofurfuryl ammonium ion. Absorption spectra on polyacetylene
films (500Å thick) doped to various levels with the chiral ammo-
nium ion are shown in Figure 2. The spectra are very similar to
those obtained on alkali-metal-doped polyacetylene films.[12,13]

Chiral polymer systems belonging to this class have thus far
enjoyed the most success in terms of conductivity levels and ease
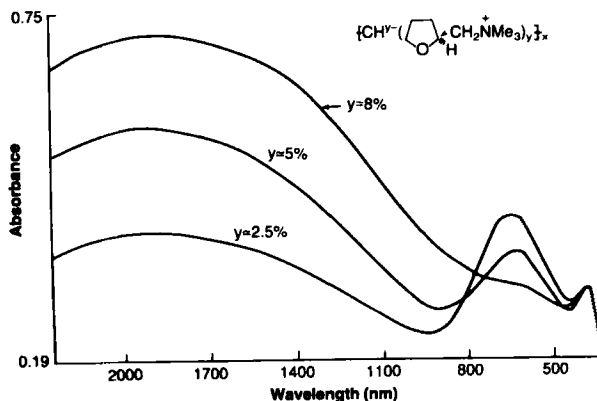of   preparation. Acceptor-doped chiral complexes should also be



FIGURE 2   Absorption Spectra of a Chiral, Donor-Doped Polyacety-
lene Complex at Various Doping Levels

readily obtainable by electrochemical polymerization of pyrroles
and thiophenes with chiral anionic dopants (e.g. chiral alkyl
sulfonic acid salts). Unknown at this time is the extent to
which the chiral counterions induce both molecular and electronic
asymmetry into the conjugated system. Circular dichroism (CD)
studies in the near infrared region on similar films used to
generate the absorption spectra shown in figure 2 are underway to
try and answer this question.

Systems Containing Chiral Solvating Ligands (Class III)
      A third, and perhaps the least attractive, approach to a
chiral conducting complex is through the incorporation of chiral
solvating ligands on the dopant-ions. By taking advantage of the
tendency for alkali-metal-ions, especially lithium ions, to be
heavily solvated when inserted into donor-doped polyacetylene,[14]
we have prepared compositions belonging to this class by insert-
ing a chiral ligand which is good for lithium ion solvation,
(+)-2,3-dimethoxy-1,4-bis(dimethylamino) butane (DMBDMB),[15] into
lithium-doped polyacetylene films. In a first attempt, polyace-
tylene films were doped with lithium-naphthalide using DMBDMB as
the solvent. The doped films had a conductivity of 1 S/cm, con-
tained 8 mol% lithium per CH unit (by elemental analysis), but
the amount of chiral ligand incorporated was far below this
value and corresponded to only one ligand per six $Li^+$ ions.
A second approach utilized polyacetylene films pre-doped with
phenyllithium - a doping agent which we found gives crystalline,
highly conducting, heavily lithium-doped polyacetylene (11-14 mol
% Li per CH repeat unit) containing no solvating ligands.[16] Pre-
doped films ( =140 S/cm) on exposure to DMBDMB liquid for 3 hr.,
then pumped visually dry, dropped in conductivity (to 119 S/cm),
swelled by 7.3%, but contained only one ligand for every 20 Li-
ions in the complex. Diffusion of the solvent into the complex
is apparently very slow; longer contact times probably being
necessary for complete solvation. At this time, this approach
seems to be the least attractive to chiral conducting complexes
due to their lability and non-stoichiometric nature.

PROPERTIES OF CHIRAL METALLIC CONDUCTORS

      It is difficult to predict at this time what unusual proper-
ties chiral conducting polymers may display. Interest in these
materials will most likely come from a combination of features
such as high conductivity and novel chiroptical and magnetic
properties. An added dimension is their ability for ion inser-
tion and removal with external applied voltages which allows for
a continuous variation of properties. The existence of chiral
donor-doped conducting polymer complexes now opens up the possi-
bility of utilizing these as inherently chiral electrodes for
(catalytic) asymmetric reductions (for example, of prochiral

ketones, imines, epoxides, and vic-dihalides). Attempts to
realize this intriguing possibility, as well as characterization
of the chiroptical and magnetic properties of several chiral
conductors, are now in progress.

## REFERENCES

1.  S. Abe and T. Nonaka, Chemistry Letters, 1541 (1983).
2.  S. Abe, T. Fuchigami, and T. Nonaka, Chemistry Letters,
    1033, (1983).
3.  T. Hayashi, M. Fukushima, M. Konishi, and M. Kumada,
    Tetrahedron Letts., 79 (1980).
4.  Atropisomers are conformational isomers which can be iso-
    lated or observed in enantiomeric forms. Atropisomerism is
    most commonly observed among the biphenyls.
5.  3-Methylthiophene,[6] 3-methylpyrrole,[7] and 3,4-dimethyl-
    pyrrole can be electrochemically polymerized to give poly-
    mers with conductivity values nearly as high as those
    obtained with the unsubstituted polymers.
6.  G. Tourillon and F. Garnier, J. Electroanal. Chem., 135, 173
    (1982).
7.  M. Salmon, A.F. Diaz, A.J. Logan, M. Krounbi, and J. Bargon,
    Mol. Cryst. Liq. Cryst., 83, 265 (1982).
8.  T.C. Clarke, J.C. Scott, and G.B. Street, IBM J. Res.
    Develop., 27, 313 (1983).
9.  A.F. Diaz, J. Castillo, K.K. Kanasawa, J.A. Logan, M.
    Salmon, and O. Fajardo, J. Electroanal. Chem.
    Interfacial Electrochem., 133, 233 (1982).
10. D. MacInnes, Jr., M.A. Druy, P.J. Nigrey, D.P. Nairns,
    A.G. MacDiarmid and A.J. Heeger J.C.S. Chem. Comm., 317
    (1981).
11. Y.S. Papir, V.P. Kurkov, and S.P. Current, Electrochem. Soc.
    Extended Abst., 83-1 #543.
12. T.-C. Chung, F. Moraes, J.D. Flood, and A.J. Heeger, Phys.
    Rev. B, 29, 2341 (1984).
13. H. Eckhardt and S.W. Steinhauser, Mol. Cryst. Liq. Cryst.,
    105, 219 (1984).
14. B. Francois and C. Mathis, J. de Physique, Coll. C3, 44,
    21 (1983).
15. D. Seebach, H. Kalinowski, B. Bastani, G. Crass, H. Daum, H.
    Door, N.P. DuPreez, V. Ehrig, W. Langer, C. Nussler, H. Oei,
    and M. Schmidt, Helv. Chim. Acta., 60, 301 (1977).
16. R.L. Elsenbaumer and G.G. Miller, unpublished results.