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REVIEW

Electrically conducting organometallic polymers

Hari S. Nalwa*
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, USA

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Polyacetylene, which exhibits metallic-like electrical conductivity upon redox doping, led to the development of a new class of electronic materials. Metallic conductivity in polyacetylene originates from the mobility of charge-carriers along the highly conjugated π-electron carbon backbone. On the other hand, organometallic polymer backbones comprising transition-metal ions and highly conjugated ligands may themselves produce intrinsically conducting materials due to the increased molecular orbital interaction between metal atoms via ligands. For decades organometallic polymers have been the subject of great scientific interest due to their unique electrical properties and many potential uses. Following the discovery of polyacetylene, the cofacially joined metallophthalocyanine polymers emerged as a new class of electrically conducting polymers. This important class of conducting organometallic polymers now includes a wide variety of materials such as poly(metalyne), poly(metallophthalocyanines), metal poly(benzodithiolene), poly(metalloethylene tetrathiolate), poly(metal tetrathio-oxalate), etc. Depending upon the molecular structures, many organometallic polymers are intrinsic conductors while in others metallic-like conductivity is induced by a molecular doping process. The superiority of electrically conducting organometallic polymers is manifest in their excellent environmental stability and processability. Conducting organometallic polymers have a wide range of applications in electrocatalysis, photovoltaics, sensors and fuel-cell technology.

Keywords: Organometallic polymers, electrical conductivity, transition-metal ions, conjugated ligands, intrinsic conductors, environmental stability, processability, applications, electrocatalysis, fuel cells

*Present address: Department of Material Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.

INTRODUCTION

Organic polymers which have been considered important for decades as insulators in electronic industries have recently emerged as a new class of electronic materials. The discovery of polyacetylene, the prototype organic conjugated conducting polymer, attracted great attention in the scientific community in 1977.[1,2] From a structural viewpoint, polyacetylene consists of a highly conjugated carbon backbone comprising an array of alternating single and double bonds. The *cis-* and *trans-* isomers of pristine polyacetylene are insulating and semiconducting respectively but their electrical conductivity increases up to the metallic regime simply by redox doping.[3–5] Metallic-type conductivity in polyacetylene originates from molecular doping due to the extended delocalization of charge-carriers along the conjugated π-electron backbone.

Based upon similar fundamental ideas, enormous research activities were directed towards the discovery of new conjugated conducting polymers. A large number of conducting polymers have been developed over the last decade and the list is still enlarging with time.[6–8] Conjugated polymers possessing a very wide range of electrical conductivities could be generated upon molecular doping. Conductivities of conjugated organic polymers range from insulating to semiconducting to the metallic regime (Fig. 1). The best examples of an insulating and a conducting polymer could be given by nonconjugated polystyrene ($\sigma = 10^{-18}\,S\,cm^{-1}$) and conjugated polyacetylene ($\sigma = 10^{5}\,S\,cm^{-1}$) respectively. Good insulators are

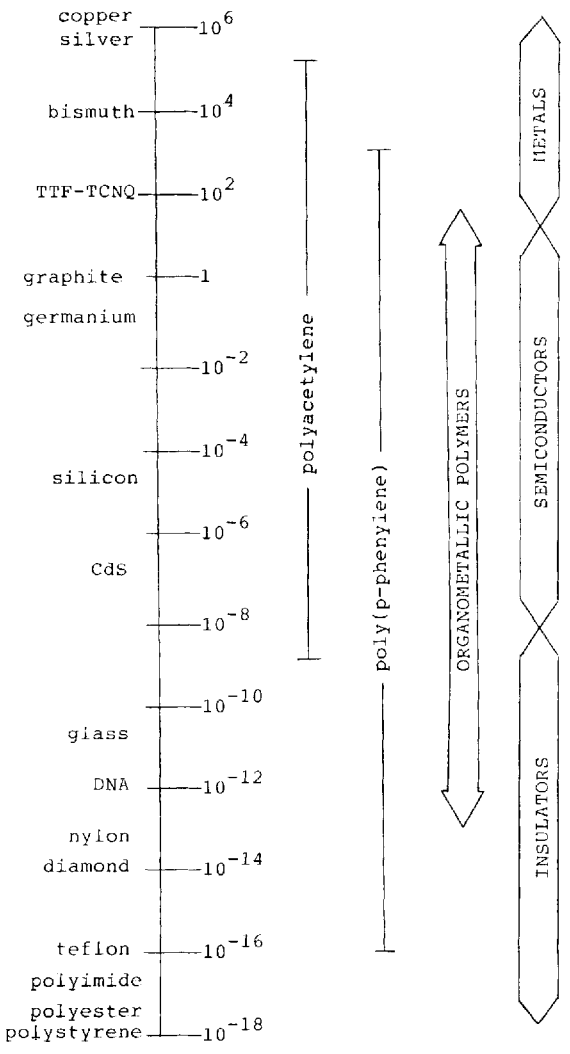

Figure 1 Conductivity scale of insulators, semiconductors and metals. Electrical conductivity is represented in S/cm unit.

polystyrene, poly(vinyl chloride), teflon, sulfur, quartz and wood, whilst copper, silver and aluminum are the best conductors. Inorganic materials such as silicon (Si), germanium (Ge), cadmium sulfide (CdS) and gallium arsenide (GaAs) are semiconductors.

The uniqueness of conjugated polymers lies with the fact that their electrical conductivity could be maintained in any range by an appropriate concentration of an electron-acceptor or electron-donor species. For example, the conductivity of poly(p-phenylene) increases by 18 orders of magnitude from 10^{-16} to 500 S cm^{-1} upon doping with arsenic pentafluoride.[9] Among conducting polymers, polyacetylene shows the highest conductivity ($\sigma = 1.47 \times 10^5$ S cm^{-1}) matching the conductivity of copper metal.[10] Conjugated organic polymers that could be doped to a conducting regime by treatment with appropriate dopants all possessed a highly delocalized π-electron system like polyacetylene (Table 1). Since the electrical conductivity of these conjugated polymers strongly depends on the density of the charge-carriers and their mobilities, therefore high conductivity could be achieved by doping and extended conjugation in order to facilitate the mobility of the charge-carriers.

Although both organometallic and organic polymers have the common structural feature of a conjugated backbone, an important characteristic that distinguishes between them is their molecular nature. In organometallic polymers, molecular orbital interactions between metal atoms via ligands generally yield intrinsically conducting materials. In common conjugated organic polymers, such as polyacetylene, extension of electrical conductivity is associated with molecular doping or impurities whilst, in general, conducting behavior in organometallic polymers originates from electronic states of the pure bulk material due to the overlapping of π-orbital electrons of partially filled or vacant metal *d*-orbitals.

Since the molecular structural arrangement of the

Table 1 Electrically conducting conjugated organic polymers[7–14]

Polymer	Structure	Conductivity (S/cm)
Polyacetylene		10^5
Polyphenylene		500
Poly(phenylenesulfide)		100
Poly(phenylenevinylene)		3
Poly(1,6-heptadiyne)		0.1
Polythiophene		100
Polyaniline		5
Poly(phenyleneoxide)		10^{-3}
Polypyrrole		100
Poly(phenylquinoline)		50

organometallic system plays a significant role in determining the conducting behavior of the polymer, therefore, in some cases, molecular doping may even affect conductivity adversely. Some polymers show an increase in conductivity on doping. Organometallic polymers exhibit excellent thermal stability in anaerobic atmospheres; therefore high conductivity may also be induced by pyrolysis (e.g. of polyacrylonitrile).[15]

Various aspects of the electrical conductivity of organometallic polymers are discussed in this review, which mainly covers electrically conducting organometallic polymers which have emerged as an important class of electronic materials only in the last few years.

POLY(METALLOPHTHALOCYANINES)

A valuable class of electrically conducting organometallic polymers is the metal-containing phthalocyanine polymers in which monomeric units are connected together by a variety of bonding arrangements.[16] These are as follows.

(1) Polymers in which adjacent phthalocyanine rings are bonded together by sharing a benzene ring in common, generally forming a linear or two-dimensional structure. These polymers are prepared by condensation polymerization and are referred either as *ladder* or *sheet-type* polymers.
(2) In *stacked* metallophthalocyanine polymers, adjacent phthalocyanine units are linked together through central metallic atoms via bridging ligands.
(3) Finally, adjacent phthalocyanine units can be connected together via benzene rings, either by single bonding between rings or by the substituents attached at the peripheral sites of the benzene rings.

Metallophthalocyanine polymerization to $(MPc)_n$ imparts the highly conjugated π-electron system necessarily required for high conductivity. The versatility of the phthalocyanine system facilitates the incorporation of a very wide variety of metal atoms making it easier to establish a structure–property relationship. Furthermore, $(MPc)_n$ polymers also offer the advantages of exceptional thermal and chemical stability. Only two kinds of $(MPc)_n$ polymers, i.e. stacked and sheet-type, have been reviewed with respect to conductivity.

Linear stacked metallophthalocyanine polymers

Although cofacially joined, stacked $(MPc)_n$ polymers have been known since 1960, studies made by Marks *et al.*[17] in 1979–1980 led them to a new class of electrically conducting polymers. An approach to control the molecular stacking in a face-to-face configuration by covalent bonding was developed. Such a molecular arrangement was achieved by bridging the central metal atoms of phthalocyanine rings via suitable bidentate ligands. Oxygen-bridged stacked $(MPc)_n$ polymers were obtained from dihydroxy compounds $MPc(OH)_2$, where M = silicon, germanium and tin; Pc = phthalocyanine.[18] Dehydration of dihydroxy compounds at elevated temperatures under vacuum gives oxygen-bridged stacked polymers $[M(Pc)O]_n$ (Fig. 2). These stacked polymers are soluble in strong acids and their degree of polymerization, estimated by end-group analysis, ranges between 70 and 120.[19] Oxidation of $[M(Pc)O]_n$ polymers with halogens [Br_2

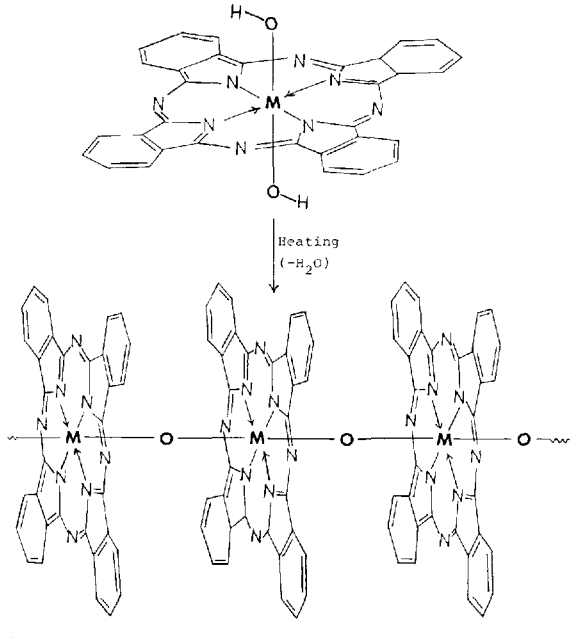

Figure 2 Synthesis and structure of a linear stacked phthalocyanine polymer having oxygen-bridging. (After Ref. 19, reprinted with permission from *J. Am. Chem. Soc.*, 1983, 105:1539, Copyright (1983) American Chemical Society and also reprinted from Ref. 30, by courtesy of Marcel Dekker Inc.)

and I_2) leads to high conductivity. Electrical conductivities of undoped and doped polymers with different stoichiometric ratios are listed in Table 2. Doping of oxygen-bridged stacked polymers with iodine and bromine leads to the formation of a mixed-valence phthalocyanine π-radical cation intercalated with I_3^- or Br_3^- counterions. The conductivity of the $[Sn(Pc)O]\ I_{1.76})_n$ complex is lower compared with Si and Ge polymers, resulting from the longer interplanar distance 382 pm in (Sn—O—Sn) to 333 pm in (Si—O—Si) between phthalocyanine rings.[20] Conductivity arises from charge-carrier mobility via $\pi-\pi$ overlap of phthalocyanine rings through the M—O—M stack.

Oxygen-bridged stacked polymers having alkyl groups at the peripheral sites of the benzene ring have also been synthesized.[21] Although these polymers are highly soluble in common organic solvents, their electrical conductivities upon iodine doping did not reach the level of peripherally unsubstituted polymers.

Stacked polymers (Fig. 3) having the structural formula $[R_4M(Pc)X]_n$ (where R = H, M = Al, Ga and Cr; X = F^-; as well as R = H, tBu, M = Si, Ge, Sn; X = S^{2-}) have also been reported.[17–32] Conductivity for a $[(PcAlF)I_{3.3}]_n$ polymer was reported to be 5 S cm^{-1}, the highest among these stacked polymers.[22]

A very wide variety of stacked polymers having ligands (L) such as cyanide, acetylene, pyrazine, bipyridine or di-isocyanobenzene, which can bridge a variety of metal atoms, have been reported by Hanack *et al.*[23–27] and others.[28–30]. A fluorine-bridged iron phthalocyanine polymer shows a conductivity of 5×10^{-3} S cm^{-1} on doping with iodine.[31] Another iron-containing phthalocyanine polymer having

Table 2 Compaction electrical conductivities of halogen-doped [Metal(phthalocyaninato)O]$_n$ polymers[20]

Polymer	Conductivity (S cm^{-1})
$[Si(Pc)O]_n$	5.5×10^{-6}
$([Si(Pc)O]Br_{1.12})_n$	9.5×10^{-1}
$([Si(Pc)O]I_{1.55})_n$	1.4
$[Ge(Pc)O]_n$	2.2×10^{-10}
$([Ge(Pc)O]I_{1.08})_n$	1.1×10^{-1}
$[Sn(Pc)O]_n$	5.2×10^{-7}
$[(Sn(Pc)O]I_{1.76})_n$	6.5×10^{-7}

(Reprinted with permission from *J. Am. Chem. Soc.*, 1983, 105:1551, Dirk *et al.*, Copyright (1983) American Chemical Society)

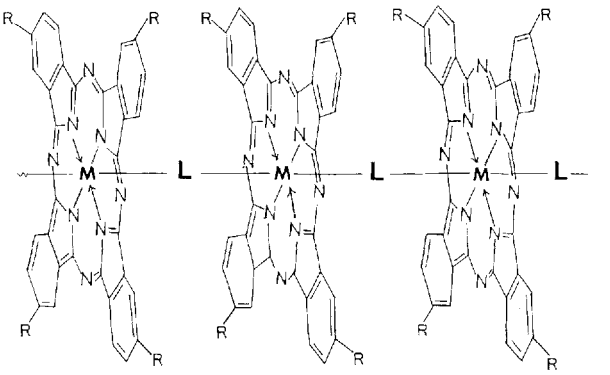

Figure 3 Stacked metallophthalocyanine polymers. (Reprinted from Ref. 30 by courtesy of Marcel Dekker Inc.)

pyrazine-bridging ligands exhibits conductivity *ca* 10^{-1} S cm^{-1} when doped with iodine.[29] A cobalt phthalocyanine stacked polymer containing cyanide-bridging ligands (—C≡N→) shows intrinsic conductivity *ca* 0.01 S cm^{-1} (undoped state).[32] Treatment of this polymer with base molecules such as pyridine, piperidine, 2-methylpyrazine and n-butylamine results in monomeric complexes having conductivity six to 10 orders of magnitude lower. Coordination polymers having macrocyclic ligands of the type $[M(Pc)(L—L)]_n$, where M = Iron, ruthenium, rhodium and cobalt and L—L = pyrazine, bipyridine, di-isocyanobenzene and *s*-tetrazine have been reported.[26,33] Analogous to these polymers, a series of $[M(OEP)(L—L)]_n$ coordination polymers of iron, ruthenium and osmium octaethylporphyrin bridged by the ligands pyrazine, 4,4′-bipyridine, and 1,4-diazobicyclo[2.2.2]octane have been prepared by Collman *et al.*[34,35] The electrical conductivities of these polymers are strongly influenced by the nature of the bridging ligands, and the central transition metals. Undoped polymers are insulators ($\sigma = 10^{-11}$ S cm^{-1}). These polymers having pyrazine (pyz) ligands exhibit conductivities *ca* 2.1×10^{-5}, 1.4×10^{-2}, and 2.3×10^{-2} S cm^{-1} for $[Fe(OEP)(pyz)(PF_6)]_n$, $[Ru(OEP)(pyz)I]_n$ and $[Os(OEP)(pyz)(PF_6)]_n$, respectively.[35] Conductivity of $[Os(OEP)(pyz)]_n$ increases by 10^3-fold on exposure to an oxygen atmosphere, similarly to other polymers reported earlier. Infrared (IR) spectral studies

demonstrate that bridging ligands contribute in the conduction process rather than porphyrin π-electrons.

Metallophthalocyanine sheet polymers

Reaction of 1,2,4,5-tetracyanobenzene with cuprous chloride in *N*-methylpyrrolidone (NMP) produces dark blue poly(copper octacyanophthalocyanine) (Fig. 4) as reported by Lin and Dudek.[36] This polymer shows excellent thermal stability in an inert atmosphere. It has an electrical conductivity of 6.7×10^{-6} S cm^{-1} at room temperature. When the pristine polymer is doped with triethylamine, its conductivity increases by over 10^3-fold. Thermal treatment of the polymer carried out under an inert atmosphere produces a material possessing a conductivity *ca* 5–8 S cm^{-1}.[37] The thermal treatment leads to an extended conjugated system and generates charge-carriers by the formation of free radicals. Therefore the high conductivity originates from strong π-orbital overlapping and the ease of charge-carrier mobility. Likewise, on thermal treatment, polyacrylonitrile (PAN) yields a conducting material (20 S cm^{-1}); similarly, cyclization of cyano groups in this phthalocyanine polymer gradually increases conductivity depending (like PAN) upon the pyrolysis temperature.[38] Deposition of tetracyanoethylene in the solution phase onto metal surfaces at 200 °C produces black adhesive films of conductivities of 10 S cm^{-1}, as reported previously.[39]

Metallophthalocyanine sheet polymers possessing peripheral carboxylic acid functional groups have been prepared by Achar *et al.*[40] These blue-to-purple polymers are soluble in sulfuric acid, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and dimethylacetamide (DMA). These polymers are also highly stable in an anaerobic atmosphere. Electrical conductivity measurements conducted by the author (HSN) show a semiconducting nature and yield materials of 8.57×10^{-2} S cm^{-1} upon electron acceptor doping,[41] see Table 3. Magnetic susceptibility studies demonstrate their paramagnetic behavior. Lower conductivity on doping probably results from carboxylic (—COOH) groups that act as carrier traps. However, pyrolysis produces conducting

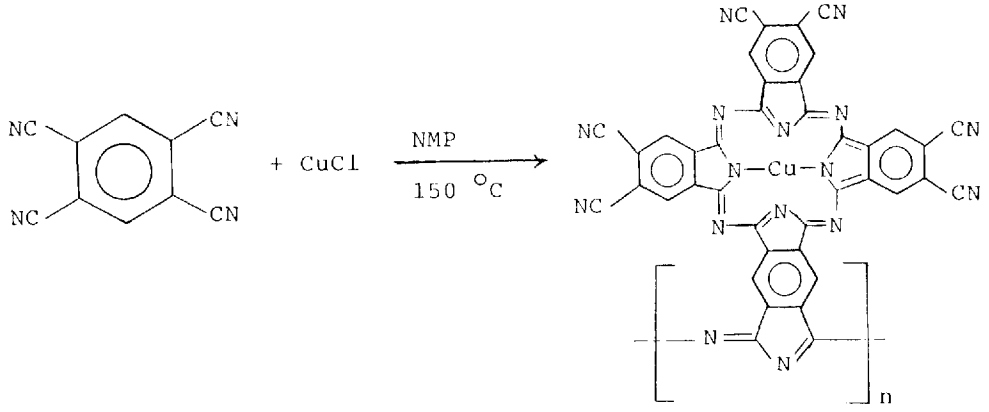

Figure 4 Synthesis of poly(copper octacyanophthalocyanine) (from Ref. 36).

Table 3 Electrical conductivity and magnetic susceptibilities (Xg) of nickel and copper containing phthalocyanine sheet (MPc-S) polymers[41]

(MPc-S) polymers	Conductivity in doped state at room temperature* (S cm^{-1})	Xg† (cmu/g)		
		6K	75K	300K
(NiPc-S)	8.57×10^{-2}	1.422×10^{-4}	6.191×10^{-6}	7.045×10^{-7}
(CuPc-S)	3.26×10^{-3}	3.271×10^{-5}	3.042×10^{-6}	5.062×10^{-7}

*metallophthalocyanine sheet polymers were doped with sulfuric acid

†Xg represents the gram susceptibility values recorded by the superconducting quantum-interference device (SQUID) technique

polymers of 2.3 S cm^{-1} due to the decarboxylative reaction resulting into the formation of a highly conjugated network of phthalocyanine moieties.[42]

POLY(METALYNES)

The development of an organometallic polymer containing a transition metal in the poly(yne) carbon backbone was first reported by Okamoto and Wang.[43] The coordination polymers of arylethyl copper as shown in Fig. 5 form charge-transfer complexes with iodine. These iodine-doped polymers are highly conducting and show stability in an aerobic atmosphere. In the doped state, conductivity of poly(*p*-toluenylethynyl copper) is about 100 times higher than poly(phenylethynyl copper). Recently, Krikor *et al.*[44] further investigated poly(phenylethynyl copper) and confirmed that the linear coordination polymer has a chemical composition $(C_6H_5—C\equiv C—Cu)_n$. Electrical conductivity of this polymer increases by about 13 orders of magnitude from 10^{-12} to 14 S cm^{-1} upon iodine doping. Metallic type conductivity in this polymer originates from the partially filled copper *d*-orbitals and from enhanced molecular interaction due to metal–metal bonding and cofacial stacking of copper atoms.

Matsuda *et al.*[45] synthesized poly(butadiyne copper) by the reaction of butadiyne with corresponding copper salts. Depending upon the synthetic procedures, two kinds of poly(butadiyne copper) are obtained. Both

$[C_6H_5—C\equiv C—Cu]_n$ $[CH_3—C_6H_4—C\equiv C—Cu]_n$

Figure 5 Organometallic poly(yne) systems.

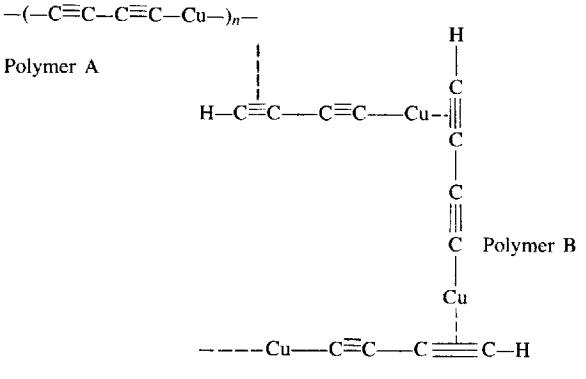

Figure 6 Poly(butadiyne copper) polymers.

polymers are black powders and exhibit insolubility and infusibility. A three-dimensional polymer is produced by the reaction of butadiyne with cuprous chloride in *N, N′*-dimethylacetamide under an argon atmosphere. A linear chain polymer is obtained by reacting butadiyne with cupric chloride in ammonia/methanol solution. Both polymers (Fig. 6) are insulating in the undoped state. Electrical conductivities of 10.2 S cm^{-1} for polymer A and 6.3 S cm^{-1} for polymer B were obtained upon doping with iodine. Iodine-doped poly-yne without metal, i.e. $—(—C\equiv C—C\equiv C—)_n—$, showed a conductivity of 2.1×10^{-4} S cm^{-1}. The metal-containing polymers exhibited metallic behavior as evidenced by temperature-dependent conductivity studies. These iodine-doped polymers do not show any metal–insulator transition down to 7 K.

POLYMERIC METAL COMPLEXES OF TETRATHIOLATOPYRAZINE AND TETRATHIOLATOBISDITHIINOPYRAZINE

Clark *et al.*[46] recently reported a series of polymeric metal complexes derived from divalent transition-metal cations and 2,3,5,6-tetrathiolatopyrazine (ttp) or 2,3,7,8-tetrathiolatobis-1,4-dithiino(2,3-*b*:2′,3′-*e*) pyrazine (ttdp). Polymeric complexes with stoichiometry M[M(ttp)]; where M = nickel, copper, palladium and platinum, or M[M(ttdp)] polymers possessing nickel and copper have been synthesized (Fig. 7). Among the polymeric complexes, nickel- and copper-containing M[M(ttp)] polymers exhibited the highest conductivities of 1×10^{-2} and 7×10^{-2} S cm^{-1} respectively. When these polymeric complexes were oxidized with iodine in the solution phase, their electrical conductivity remained unchanged. The nickel and copper polymeric complexes of M[M(ttdp)] have conductivity six orders of magnitude lower than those of M[M(ttp)] polymers. Probably bulky ttdp ligands having more sulfur atoms than ttp ligands hinder the conduction process. Clark *et al.*[46] have proposed a planar ribbon-type structure for the polymeric complexes M[M(ttp)], in which ribbons are connected together through coordination of the sulfur atoms to the metal cations outside the polymer chain. Based on a planar two-dimensional sheet structure, formation of ribbon-type structures of polymeric metal complexes has also been suggested

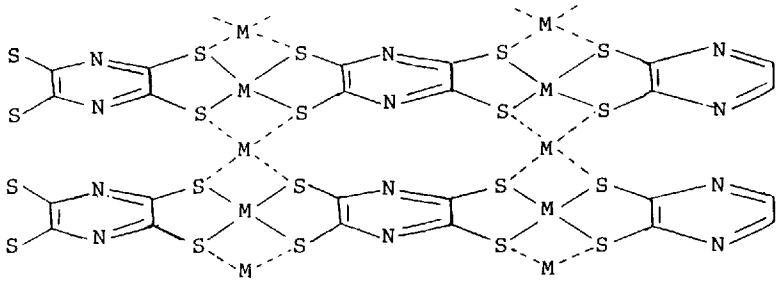

Figure 7 Structure of polymeric metal complexes based on 2,3-dithiolatoquinoxaline where M is Cu or Ni (from Ref. 46).

by Alvarez *et al.*[47] The reaction of nickel(III) and copper(II) chlorides with 2,3-dithiolatoquinoxaline yields only semiconducting monomeric complexes having conductivities in the range of 10^{-6} to 10^{-7} S cm^{-1}.

POLY(METAL TETRATHIO-OXALATE)

The reaction of difunctional tetraethylammonium tetrathio-oxalate with nickel(II), copper(II) and palladium(II) salts in a 1:1 stoichiometry yields linear poly(metal tetrathio-oxalate)s.[48] A polymerization reaction using nickel(II) nitrate as an example is represented by a metallopentacycle polymer chain (Fig. 8). Transition-metal complexes of tetrathio-oxalates are oligomers having a degree of polymerization between 3 and 8. $(Mc_2S_4)_n$ complexes are insoluble black powders and show stability in aerobic atmospheres. Oligomers of $(NiC_2S_4)_n$ have electrical conductivities ranging from 5 to 20 S cm^{-1}, whilst $(CuC_2S_4)_n$ and $(PdC_2S_4)_n$ both have a conductivity of 1 S cm^{-1}. Molecular doping with iodine results in a 10- to 1000-fold decrease in conductivity due to the compensation effect. These $(MC_2S_4)_n$ complexes are n-type semiconductors, as demonstrated by their low negative thermoelectric coefficients.

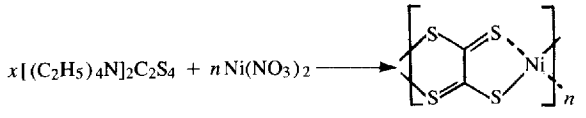

Figure 8 Poly(metal tetrathio-oxalate) compounds (from Ref. 48).

Recently, a series of organometallic polymers, $(MC_2S_4^{x-})n$ with M = nickel, palladium, platinum, and gold, have been prepared from the ethyltetrathiolate anion.[49] These organometallic polymers have a compaction conductivity ranging

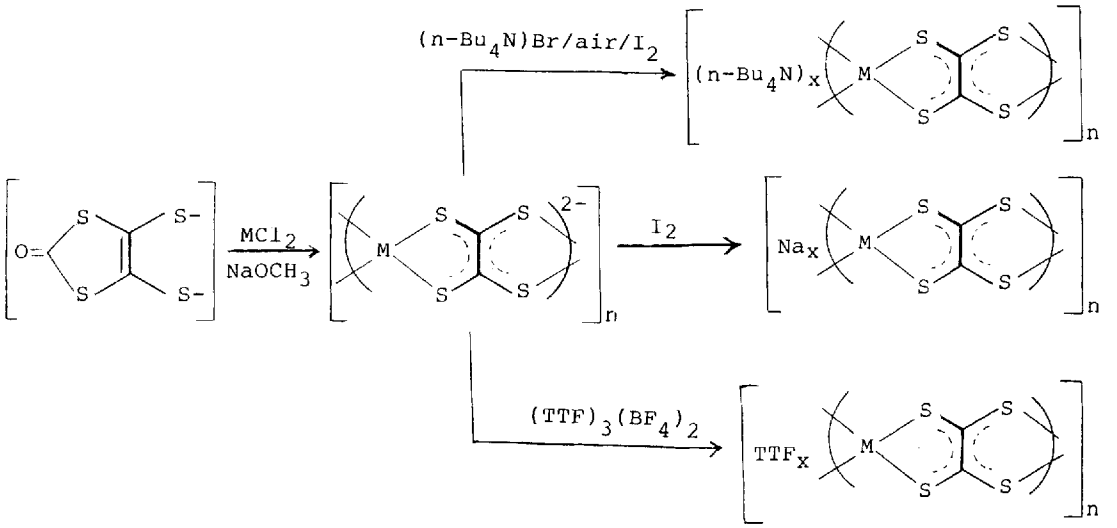

Figure 9 Poly(metal ethyltetrathiolate) systems (from Ref. 49,; reprinted with permission from Elsevier Sequoia S.A.)

Table 4 Electrical conductivity of organometallic polymers derived from the ethylene tetrathiolate anion (from Ref. 49, reprinted with permission from Elsevier Sequoia, S.A.)

Polymer	Metal atom	Conductivity (S cm^{-1})
$[Na_x(MC_2S_4)]_n$	Ni	3.8
	Pd	6.4×10^{-2}
	Pt	1.9
	Au	3.3
$[TTF_x(MC_2S_4)]_n$	Ni	3.9
	Pd	–
	Pt	0.2
	Au	1.2
$[(n\text{-}Bu_4N)_x(MC_2S_4)]_n$	Ni	0.9
	Pd	8×10^{-2}
	Pt	0.3
	Au	0.4

from 5 to 10^{-5} S cm^{-1} (Table 4). A polymer of $Na_{0.31}(NiC_2S_4)_n$ is found to be the most conducting and exhibits metallic conductivity as evidenced by temperature dependence studies. The conductivities of these organometallic polymers are related to the degree of partial oxidation and may be increased further by controlled oxidation.

METAL POLY(BENZODITHIOLENES)

Coordination transition-metal poly(benzodithiolenes) have been reported by Dirk *et al.* (Fig. 10).[50] These organometallic polymers obtained from benzene 1,2,4,5-tetrathiol and divalent transition-metal salts have a linear chain structure containing the metal in the polymer backbone. These coordination polymers consist of the divalent transition metals iron, cobalt, nickel and copper in the polymer chain. They are paramagnetic and exhibit conductivities in the range $0.2-10^{-5}$ S cm^{-1}. Iron poly(benzodithiolene) shows the highest compaction conductivity of 0.2 S cm^{-1}, in which iron exists in the iron(III) oxidation state as evidenced by Mössbauer spectroscopy. The iron-containing polymer has an effective magnetic moment of 2.23 μ_B at room temperature which decreases to 1.15 μ_B at 6 K. Magnetic susceptibility results also confirm the iron(III) oxidation state of iron in the polymer.

Transition-metal coordinated polymers from bis(bidentate) ligands containing sulfur- and nitrogen-donor ligands also exhibit conducting behavior. Recently, Kim *et al.*[51] have prepared polymeric transition-metal complexes from 2,5-diamino-1,4-benzenedithiol reacting with metal(II) chlorides in aqueous ammonia (NH_4OH) solution (Fig. 11). These square planar ladder polymeric complexes are crystalline and show paramagnetic behavior. The cobalt(II) complex exhibits the highest conductivity of 1 S cm^{-1}, whereas conductivities of other transition-metal complexes were 1.6×10^{-2} S cm^{-1} for iron(II), 1.2×10^{-3} S cm^{-1} for copper(II) and 4.8×10^{-6} S cm^{-1} for nickel(II). Among polymeric transition complexes derived from *S*-donor ligands, nickel(II) generally exhibited the highest conductivity, unlike the present case. Molecular doping of these polymers causes a decrease in conductivity, probably due to the depletion of charge-carriers, a phenomenon usually observed in intrinsically conducting organometallic polymers.

TETRATHIAFULVALENE–METAL BISDITHIOLENE OLIGOMERS

Reaction of tetrasodium tetrathiafulvalene tetrathiolate with transition-metal salts (ML_n) of nickel(II), copper(II), iron(II), platinum(II) and palladium(II) yields insoluble, amorphous powders having a metal:ligand ratio of *ca* 1:1.[52] These transition-metal complexes are oligomers possessing

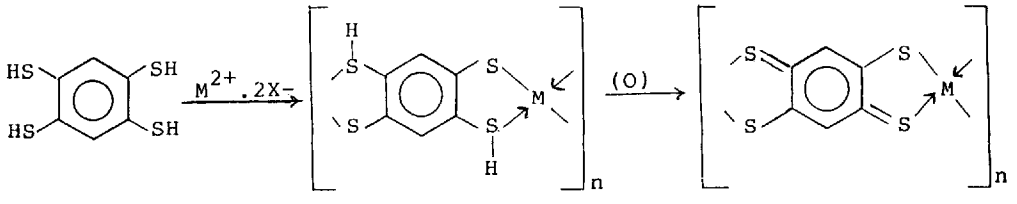

Figure 10 Metal poly(benzodithiolenes) (from Ref. 50).

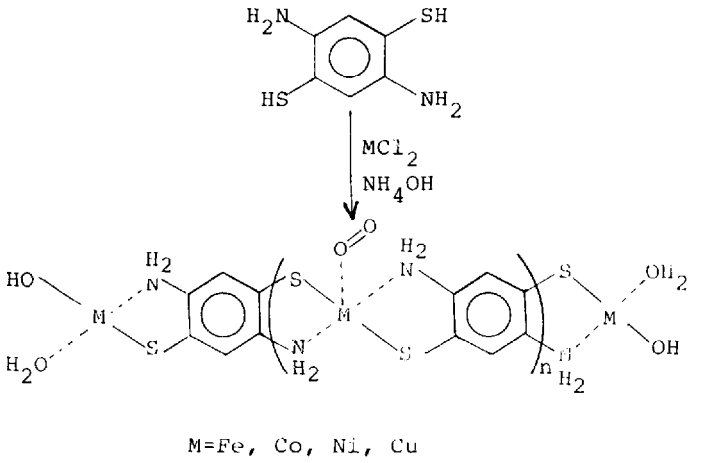

Figure 11 Poly(metal 2,5-diamino-1,4-benzenedithiol) systems (from Ref. 51).

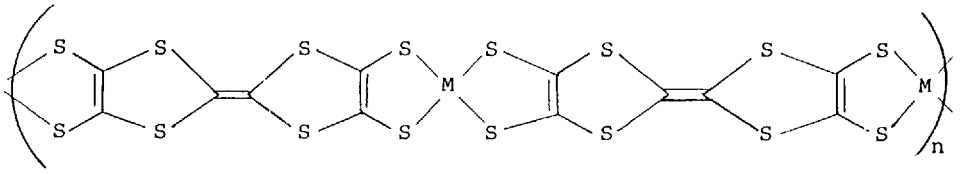

Figure 12 Tetrathiafulvalene–metal bisdithiolene oligomers (from Ref. 52).

tetrathiafulvalene–metal bisdithiolene repeating units in the backbone (Fig. 12). The nickel(II) oligomer showed the highest conductivity of 30 S cm^{-1}, whilst other oligomers had lower conductivities, viz. 10^{-1}, 10^{-2}, 10^{-3} and 10^{-5} S cm^{-1} for copper(II), platinum(II), palladium(II) and iron(II) transition-metal complexes.

OLIGO{[(μ_2-DIOXO)DICOPPER 1,4-DIAMINOANTHRAQUINONE]-co-[(μ_2-OXO)DICHLORODICOPPER 1,4-DIAMINOANTHRAQUINONE]} (ODOD)

Planar coordination polymers, or oligomers having difunctional ligand molecules connected through metal atoms, exhibit intrinsic electronic conductivity. Recently, Rickle[53] reported the preparation of an ODOD oligomer from 1,4-diaminoanthraquinone, copper(I) chloride and oxygen (Fig. 13). The oligomer has a degree of polymerization between 2 and 4, and consists of alternating 1,4-diaminoanthraquinone units connecting by (μ_2-dioxo)dicopper units. It is insoluble and infusible and shows good environmental stability; it possesses intrinsic conductivity in the range of 0.10–0.60 S cm^{-1}. The oligomer and its analogues are p-type conductors with the exception of the copper(II) analogue which is of the n-type. Its analogues containing copper(II), nickel(II) and silver(I) have conductivities 10–1000 times lower than that of the copper-containing ODOD oligomer. The copper ODOD oligomer can be used as an electrocatalyst in the oxychlorination of ethylene to produce 1,2-dichloroethane.

POLY(3-VINYLBISFULVALENEDI-IRON)

Organometallic polymers having sandwich-type configurations form another class of semiconducting materials. A sandwich-type polymer based on the fulvalene di-iron system (Fig. 14) exhibits electrical conductivity of *ca* 10^{-2} S cm^{-1} after 71% oxidation with tetracyanoquinodimethane (TCNQ). This polymer had the highest known conductivity amongst organometallic polymers when reported by Krogmann in

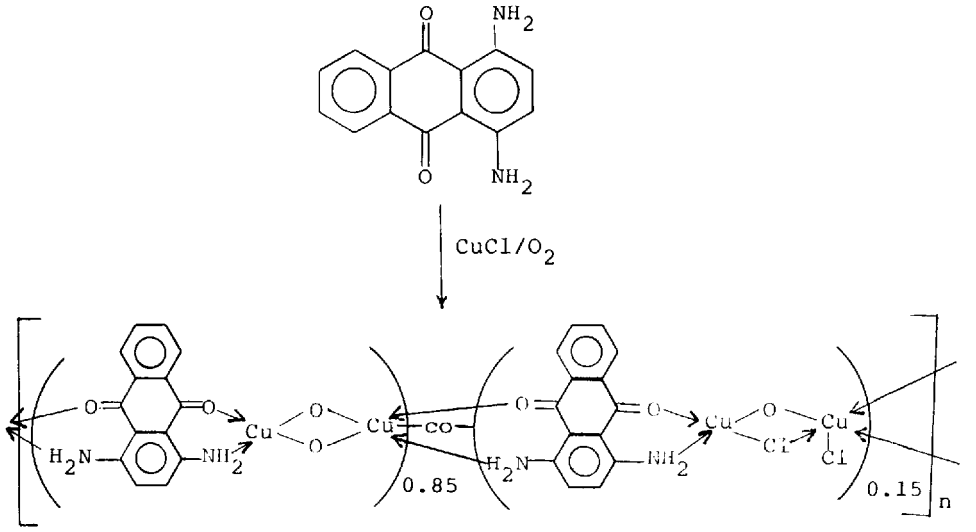

Figure 13 Copper 1,4-diaminoanthraquinone oligomer (from Ref. 53).

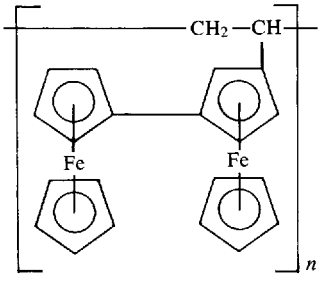

Figure 14 Fulvalene di-iron sandwich polymer.

1969.[54] Other sandwich-type polymers such as poly(ferrocenylene) and poly(ethynylferrocene) have low conductivity. The maximum conductivity of the iodine-doped poly(ethynylferrocene) could reach to 10^{-4} S cm^{-1} as reported by Polzonetti *et al.*[55] in a recent study. X-ray photoelectron spectroscopy of iodine-doped polymers demonstrates an increase of conductivity according to the number of I_5^- species or by the oxidation reaction of iron(II) to iron(III).

Chelation of the tetrathiosquarate dianion with the transition-metal ions nickel(II) and palladium(II) yields semiconducting organometallic polymers having a degree of polymerization of 10 and 25 respectively.[56] The nickel- and palladium-containing polymers have conductivities of *ca* 10^{-4} S cm^{-1}. A platinum-based polymer with a Pt:C_4S_4 ratio of 1:1 shows a conductivity of 6×10^{-7} S cm^{-1}.

Recently, coordination polymers of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) with terephthalaldehyde bis (*S*-benzyldithiocarbazate) have been reported.[57] These chelate polymers doped with iodine produce semiconducting materials of electrical conductivy ranging from 10^{-7} to 10^{-9} S cm^{-1} at room temperature.

Polymeric chelates having tetra-aza annulene ligands prepared from tetra-aminobenzene or diaminobenzidine, propynal (HC≡C—CHO) and divalent transition-metal salts [copper(II), nickel(II), cobalt(II), iron(II)] show a semiconducting nature.[58,59] The conductivities of these polymers were found in the range 10^{-10} – 10^{-12} S cm^{-1} in the undoped state.

Recently, Sielcken *et al.*[60,61] reported the synthesis of crown-phthalocyanines. A poly(oxysilicon phthalocyanine) containing 15-crown-5 subunits shows an electrical conductivity of 10^{-7} S cm^{-1} at room temperature.

Stacked tetracyanoplatinate complexes having an

analogous structure to metallophthalocyanine polymers have also been studied. These one-dimensional structures exhibit conductivities greater than 1 S cm^{-1}, even though they possess no macrocyclic ligands.[62]

Electrical conductivities in organometallic polymers can therefore be tailored from a semiconducting to a metallic regime. Generally, these polymers are intrinsically conducting, and their conductivity could be raised either by molecular doping or thermal treatment. Conducting organometallic polymers should have commercial applications parallel to conjugated organic polymers. Their practical applications may span from solid-state technology to biomedical engineering. At present the potential of conducting organometallic polymers has been considered for photovoltaic cells, fuel cells, functionalized electrodes, chemical sensors, electrocatalysis, photoelectrocatalysis, catalysis, semiconductors and opto-electronic technology.[63,64] Although many strategies of developing new organometallic polymers possessing even metal-like conductivities exist theoretically, intense synthetic efforts still await full realization of potential.

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