Coordination Chemistry Reviews, 53 (1984) 55–226
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COORDINATION AND REDOX CHEMISTRY OF SOME MACROMOLECULAR SYSTEMS

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(Received 7 March 1983)

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0010-8545/84/$51.60

LIST OF ABBREVIATIONS

A	acceptor
bipy	2,2′-dipyridyl
BQ	benzoquinone
CT	charge transfer
CTC	charge transfer complex
D	donor
DCIP	dichlorophenylindophenol
DDQ	dichlorodicyanoquinone
DPQ	diphenoquinone
DEAE-	diethylaminoethyl-
DHNA	dihydronicotinamide
DHP	dihydropyridine
dmg	dimethylglyoxime
DNA	deoxyribonucleic acid
EDTA	ethylenediamine tetracetic acid
en	ethylenediamine
FAD	flavin adenine dinucleotide
FMN	flavin mononucleotide
GO	glucose oxidase
HEC	hydrogen evolution catalyst
HQ	hydroquinone
MB	Methylene Blue
MV	methylviologen

NAD	nicotinamide adenine dinucleotide
o-phen	*o*-phenathroline
OEC	oxygen evolution catalyst
pol	polymer
PAA	polyacrylamide
PEO	polyethylene oxide
PEI	polyethyleneimine
PEG	polyethyleneglycol
PMA	polymethacrylic acid
PMAC	polymethacrylchloride
pmen	*N*,*N*′-bis(2-pyridylmethyl)-ethylenediamine
PMDAS	poly(dimethylaminostyrene)
PNVC	poly(*N*-vinylcarbazole)
PNVIM	poly(*N*-vinylimidazole)
PPG	polypropyleneglycol
PS	polystyrene
PPO	polyphenyleneoxide
PVA	polyvinylalcohol
PVAm	polyvinylamine
PVP	polyvinylpyridine
PVPr	polyvinylpyrrolidone
P2VP	poly(2-vinylpyridine)
P3VP	poly(3-vinylpyridine)
P4VP	poly(4-vinylpyridine)
PMST	phenazinemethosulphate
PVF	polyvinylferrocene
py	pyridine
Q	quinone
QPEI	quaternized PEI
QPMDAS	quaternized QMDAS
QPNVIm	quaternized PNVIm
QPVP	quaternized PVP
QP2VP	quaternized P2VP
QP3VP	quaternized P3VP
QP4VP	quaternized P4VP
RI	radical ion
RPEC	redox polymer electrode coating
RNA	ribonucleic acid
S	sensitizer
TAPC	4,4′,4″,4‴-tetraaminophthalocyanine
TCNE	tetracyanoethylene
TCNQ	tetracyanoquinodimethane

TCPC	4,4′,4″,4‴-tetracarboxyphthalocyanine
TEOA	triethanolamine
tetpy	2,2′,2″,2‴-tetrapyridyl
TPP	5,10,15,20-tetraphenylporphyrin
TSPC	4,4′,4″,4‴-tetrasulphophthalocyanine
TTF	tetrathiafulvalene
THF	tetrahydrofuran
vbpy	vinyl-bipyridine
VF	vinylferrocene

A. INTRODUCTION

Chemically active polymers that possess the physical properties of a high polymer and the chemical properties of an unattached reagent are a rapidly developing field in macromolecular science. The exploitable functional groups distributed throughout the polymers may be organic, organometallic or inorganic in nature. Polymeric reagents are often involved in the irreversible transfer of an atom or molecule to a particular substrate and thus the exchange process is not just a redox reaction. Several reviews on reactive polymers of this kind have appeared recently [1–15], which testify to the rapid development of both concepts and technology in polymer chemistry. Catalysts for various hydrogenation and hydroformylation reactions have also been supported in a polymer matrix [16–18]. The advantages of polymeric reactive species over low molecular weight reagents have been outlined in previous reviews. Polymers often lack many of the inconvenient properties of monomeric species, such as lability, volatility, toxicity and odour. Highly cross-linked polymers are generally insoluble in most solvents and this property facilitates isolation and separation of the catalyst from the products. Collection and recycling of heterogenized polymeric catalysts often compensates for the time and capital investment required in their preparation. The matrix of the polymers also allows the simultaneous use of several mutually isolated reactive species and the tailoring of specific steric and electronic effects which are mandatory for many catalytic processes.

One branch of chemically reactive polymers includes polymers that undergo reversible redox processes with oxidants and reductants. Such polymers are loosely termed “redox polymers”. These have the ability to be reduced by a reductant and subsequently reoxidized by an oxidant or vice versa, with an exchange of electrons and/or protons, but no other chemical entities. The reduction or oxidation of the functional group of the polymer may be induced by chemical, electrochemical or photochemical means and this review treats each of these types of electron transfer with an emphasis on the coordination chemistry of the active site and the relevance of these processes to chemical technology.

B. REDOX REACTIONS OF POLYMERIC SYSTEMS

(i) Classification of redox polymers

Attempts to produce heterogenized reduction systems began with the invention of the column reductor by Jones in 1889. This early reductor consisted of a column of amalgamated zinc, and a description of the modern equivalent is detailed by Vogel [19]. The Jones reductor, however, is limited to operations at very low pH and where the solutions are devoid of organic matter and most reducible metal ions which are easily reoxidized and contaminate the column. The 1940s saw the advent of heterogenized redox species that employed an insoluble synthetic polymer as the supporting matrix. According to Sansoni [20] patent claims appeared in 1944 for the preparation of redox active polymers from the polycondensation of quinones. Ion exchange resins were already 13 years old when Mills and Dickinson [21] treated polymeric anion exchange resins with copper and silver salts to obtain "redox ion exchangers" in 1949. By 1963 redox active polymers had found employment as analytical aids [22] and application to the quantitative oxidation and reduction of metal ions and organic substrates [23,24] via the columnar procedure devised by Jones. Nowadays, a plethora of oxidation and reduction processes are performed by redox polymers. Among the most interesting topics are the recent developments in biomimetic redox catalysis. The impact of redox polymers has not just been a technological novelty, rather, recent developments have acted as a philosophical lense. They have shown that enzymes are but biological polymeric catalysts which can be mimicked, and that the processes of nature can be modeled and understood.

The modes of preparation of the different types of redox polymers, and attempts at a structural classification and nomenclature have been dealt with elsewhere [16,25–27]. Briefly, a redox polymer can be prepared by: (1) the covalent attachment of a redox active species to a preformed polymer or the copolymerization of the redox active monomer with another monomer to form a redox active polymer (Type "C"); (2) the sorption of a metal ion or metal complex to a neutral coordinating moiety such as a N, S, P or O atom of the polymer (Type "S"); (3) the deposition from solution of a redox active species into an inert polymeric matrix so that the species is entrained within it (Type E); (4) the complexation of a charged redox active species with an oppositely charged group of a polymer via an electrostatic process (Type I); or (5) the nonspecific adsorption of aromatic or other molecules onto neutral polymers through van der Waals or hydrophobic interactions (Type N).

For the sake of clarity, the redox polymer type (C, S, E, I, N) will be indicated in tables when necessary.

TABLE 1

Some reactions of quinone–hydroquinone polymers

Redox active moiety	Polymeric matrix	Type	Reaction	Ref. [a]
Quinone/hydroquinone (Q/HQ)	Polymer of quinone, phenol and formaldehyde	C	Strecker degradation of alanine to acetaldehyde, and also of other amino acids. Oxidation of NADH to NAD^+	1
Q/HQ derivatives	Suspended in KeL-F powder (polytrifluorochloroethylene)	E	Columnar reduction of Fe(III), V(V) and Ce(IV) on oxidation of Sn(II), I^- or Cu(I) in analytical determinations for the ions	2
Tetrachloro-Q/HQ	as above	E	Columnar reduction of aqueous ferric chloride and ammonium vanadate as an analytical aid	3
Anthraquinone	Polyvinylanthraquinone	C	Reduction of metal ions in 1 M H_2SO_4 to the elemental metals Cu, Ag, Te and red Se. Reduction of Fe^{3+}, UO_2^{2+} to U^{4+}, and VO_2^+ to V^{3+} via VO^{2+}	1
Q/HQ	Poly(2,2′-disulphobiphenylenebenzoquinone)	C	Reoxidation of reduced ion-exchanged Pd(0) to Pd(II) in ethylene oxidation reactions. Reoxidation of the quinone performed by molecular oxygen	4
Various quinones	Bound to sulphochlorinated polystyrene	C	Reduction of Fe(III) solutions	5
Q/HQ	Methylstyrene–vinylhydroquinone copolymer	C	Columnar reduction of Fe(III) solutions as an analytical aid	6, 7
Q/HQ	Dispersion of polyvinylquinone in an albumin gel, celite or in paper	E	Columnar reduction processes and oxidant sensitive papers	8–10
HQ	Polymeric hydroquinones	C	Conversion of dissolved oxygen in water to H_2O_2, in the presence of metaphosphate	11, 12

HQ	HQ, formaldehyde, phenol copolymer	C	Removal of O_2 from water by reduction to H_2O_2 with subsequent reaction of the product with further poly-HQ to yield H_2O	13
Chloranil	Bound to cellulose pulp	C	Removal of O_2 from boiler-feed water	14, 15
Q/HQ	Polymer of quinone, phenol and formaldehyde	C	Dehydrogenation of cycloheptatriene, dihydronaphthalene, dihydrocarbazole, hydrazobenzene and other aromatics	1, 16
Q/HQ	Bound to chloromethylated polystyrene	C	Reduction of Fe(III) and Ce(IV), oxidation by iodine to remove O_2 from various liquids	17
Q/HQ	Polymer of quinone, phenol and formaldehyde	C	Dehydrogenation of cycloheptatriene, dihydronaphthalene, dihydrocarbazole, hydrozobenzene and other aromatics	1, 16

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[a] In this and subsequent tables the references refer to the table footnotes and not to the reference list.

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TABLE 2

Some reactions of thiol-containing polymers

Redox active moiety	Polymeric matrix	Type	Reaction	Ref.[a]
6-Mercaptopurine	Poly(9-vinylpurine-6-thiol)	C	Reduction of oxygen in alkaline solutions	1
Methionine	Poly-L-methionine	C	Reduction of polymer to poly-L-homocysteine with Na in liquid ammonia	2
Benzylthiol	Bis(*p*-vinylbenzyl)disulphide-chloromethylstyrene copolymer	C	Reduction of disulphide bond with diborane and reoxidation of I_2 or O_2. Investigation of cooperativity of thiol groups in redox processes	3
as above	Polythiolstyrene and thiolstyrene–methacrylate copolymer	C	Oxidation to disulphide derivative by I_2 or O_2 in alkaline solution. Reduction of disulphide with cysteine or thioglycollate. The reduced polymer could function as a coenzyme for urease	4, 5
as above	as above	C	Rate of oxidation of polymercaptan more rapid than model dithiol compounds	6, 7
Mercapto-acetic and proprionic acids	Anion exchange resins	I	Various redox studies	8
Lipoic acid (1,2-dithiolane)	Polyacrylamide	C	Reduction of polymeric disulphide with $NaBH_4$ to the corresponding dithiol, which was an active acyl transfer reagent	9, 10
Benzylthiol	Polythiolstyrene	C	Columnar reduction of the resin with $S_2O_4^{2-}$, S^{2-} and thioglycollic acid, reoxidation by aqueous I_2	11

Pendant $-CH_2SH$ groups	*N*-mercaptomethylpolyamides	C	Oxidation at the free SH group by molecular oxygen in solution	12
Cysteine	Poly-L-cysteine	C	Reduced form of polymer oxidized by aqueous iodine and molecular oxygen	13
Benzylthiol	Polystyrene or poly(bis-*p*-vinyl-benzyl-sulphide)	C	Reduction of polymeric moieties with $NaBH_4$, reoxidation with aqueous I_2. Cooperativity effects in reoxidation mechanism	14, 15
Thiosalicylic acid or mercaptocarboxylic acids $R-C_6H_4CH(SH)CO_2H$	Covalent attachment to PVA	C	Various electron exchange properties	16
1,2-dithiolane group	Polyurethanes from alkylene or arylene diisocyanates and 4,4-bis(hydroxymethyl)-1,2-dithiolane	C	Reduction of polymer with NaH in Me_2SO and $LiAlH_4$ in THF. The polymers were useful for reduction of protein thiol bridges	17
Thiopropane moiety	Agarose treated with epichlorohydrin and thiosulphate	C	Useful as a solid-phase reducing agent in biochemical applications and in covalent chromatography in enzyme purification. Available commercially as Thiopropyl-Sepharose 6B from Pharmacia	18, 19

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[a] See Table 1.

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TABLE 2 (continued)

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(ii) Miscellaneous applications of redox active macromolecular systems

The success of a particular reaction is very much dependent on the redox chemistry of the functional moiety of the macromolecule. The design of polymers with chemically active quinone/hydroquinone groups was once the center of an arena of vigorous competition between many chemists, and several reviews cover this field of macromolecular redox chemistry extensively [25,28–32]. However, there is very little interest in these polymers nowadays. The quinone groups can be easily reduced with ascorbic acid, various metal ions and complexes and reoxidized by aqueous I_2, or even by molecular oxygen, to yield H_2O_2 or in some cases H_2O. Reactions like these have been harnessed as an aid in several analytical and synthetic applications. In the wake of several comprehensive reviews it is sufficient in this instance to merely describe some of the more interesting applications of polymer pendant quinones that have appeared in the last few years. These are listed in Table 1.

In Table 2 are found some reactions of thiol-containing polymers [33]. Generally speaking, these polymers have never been the focus of very much attention and their redox properties have not been studied in too great a depth except when considered as models of thiol-containing proteins.

Polymers bearing nicotinamide, *N*-alkylpyridinium and nitrogen-containing heterocyclic dyes are currently receiving a lot of attention as models of enzyme-bound NAD^+ cofactors. Polymer-bound NAD^+ derivatives are also being studied with a view to constructing enzyme mimetic macromolecular systems [34–39] that are useful both as reusable oxidants/reductants for various industrial biocatalytic processes and various applications in affinity chromatography [40,41].

Further, immobilized flavins and related dyes are being successfully applied to diverse redox processes and sometimes studies as models of flavoproteins. The redox properties of synthetic macromolecular cofactors have been reviewed recently by Shinkai [42]. Other applications of nitrogen-containing heterocycles on polymers are presented in Table 3.

The coordination or complexation of metal ions and metal complexes to polymers bearing coordinating moieties or charged functional groups has given rise to an area of redox polymer chemistry whose breadth is without equal. This is an extremely fertile field of macromolecular chemistry and various transition metal and non-transition metal ions are often employed in reductive and oxidative processes. Chelated metal ions, such as the metallocenes, porphyrins, and phthalocyanines are popular electron-exchanging species and are described more fully in following sections. The coordination chemistry and some redox catalytic properties of polymer-complexed metal ions and complexes have been previously reviewed by Tsuchida [26] and

TABLE 3

Some reactions of polymeric nitrogenous heterocyclic groups and dyes

Redox active moiety	Polymeric matrix	Type	Reaction	Ref.[a]
N-(*p*-vinylbenzyl)-3-carbamoyl-1,4-dihydropyridine (DHP)	Polymerized vinyl monomer	C	Reduction of the dyes Methylene Blue and Malachite Green to their leuco forms and reduction of hemin to heme. Reoxidation of the polymer achieved with $Na_2S_2O_4$	1–4
N-ethyl-1,2-DHP	DHP moieties on reduced and partly quaternized P4VP derived from a borohydride reduction	C	Reduction of Fe(III) PPIX dimethyl ester in DMSO, DCIP in aqueous solution or columnar reduction of a toluene solution of the Fe(III) chelate	5–7
Alloxan	Polyvinylalloxan	C	Mediation of electron transfer between immiscible aqueous and organic phases	8
Nicotinamide	Bound to polystyrene (PS)		as above	
Dihydronicotinamide (DHNA)	Covalently coupled to chloromethylated polystyrene	C	Reduction of nicotinamide moiety with $Na_2S_2O_4$. Reduced polymer reduces Methylene Blue, thionine and benzoquinone	9
DHP, DHNA derivatives	Polyvinylalcohol and polystyrene	C	The pyridinium moieties once reduced with BH_4^- or $S_2O_4^{2-}$ can reduce Malachite Green and ferricyanide	3
1-Benzyl-1,4-dihydronicotinamide	Polystyrene	C	Reduction of solid benzoquinone–polystyrene polymer by solid dihydronicotinamide polymer mediated by alloxan in a liquid phase	10
Flavins	Covalently bound to a cationic polystyrene derivative	C	Oxidation of NADH and 1-benzyl-1,4-DHNA	11

NAD^+	Coupled to polysaccharides	C	Redox active polymeric cofactors for lactate dehydrogenase or yeast alcohol dehydrogenase	12, 13
NAD^+-N^6[*N*-(6-aminohexyl)-acetamide]	Coupled to Sepharose 4B	C	Exhibits cofactor activity in a three-enzyme system of malate dehydrogenase–citrate synthase–lactate dehydrogenase	14
6-(2-Hydroxy-3-carboxypropylamino)purine dinucleotide	Coupling to water-soluble polyethyleneimine, polylysine or insoluble aminohexyl Sepharose	C	Active cofactors for lactate dehydrogenase, alcohol dehydrogenase and alanine dehydrogenase	2, 15
Succinyl NAD	Coupled to polyethyleneimine (PEI) or agarose		Redox active cofactors for alcohol and lactate dehydrogenases immobilized on DEAE-cellulose	16
Acriflavin	Coupling to epoxy-substituted Sepharose	C	Oxidation of NADH and NADPH with reoxidation of the reduced flavin by molecular oxygen in various dehydrogenase systems	17
NADP	Coupled to cellulose	C	Columnar purification of glucose-6-phosphate dehydrogenase by allowing the enzymic catalysis to proceed in the presence of substrate and the macromolecular coenzyme	18
NAD^+	Coupled to a water-soluble dextran and bound within nylon-PEI microcapsules containing alcohol dehydrogenase and malic dehydrogenase	C	Polymer-bound cofactor recycling between alcohol dehydrogenase and malate dehydrogenase	19, 20
N-substituted dihydropyridines	Redox active moieties grafted onto chloromethylated polystyrene	C	Reduction of benzaldehydes, ketones and heterocyclic aldehydes to the corresponding alcohols	21, 22
Phenothiazine	Poly-2-vinylphenothiazine	C	Reduction of Fe(III)Cl_3 in THF	21

TABLE 3 (continued)

Redox active moiety	Polymeric matrix	Type	Reaction	Ref. [a]
Methylene Blue (MB)	Poly-2-vinyl-MB	C	Oxidation of titanous trichloride or bromine in aqueous solution	23
MB, Crystal violet	Dowex 50 strongly acidic and Amberlite IRC-50 weakly acidic cation exchange resins	I	Various redox studies	24
Thymol Blue, Alizarin, Thymolphthalein, Indigotetrasulphonate	Dowex 2 strongly basic and Dowex 3 weakly basic anion exchange resins	I	as above	24
MB, Thionine, Neutral Red	Cation exchange resins	I	as above	25
Variamine Blue	Cation exchange resins	I	The reduced dye would in turn reduce ferric ions in citrate solution, used as an analytical aid	26, 27
MB	MB, resorcinol and formaldehyde polymer in a filter paper matrix	C	Oxidant-sensitive papers	28
Viologen	Poly(viologen-methylstyrene)		Reduction of benzoquinone or ethylbenzoylformate mediated by the redox polymer	29

[a] See Table 1.

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TABLE 4

Selected reactions of polymer-bound metal ions and complexes

Redox active species	Polymeric matrix	Type	Reaction	Ref. [a]
Chelated Cu(II)	Poly(ε-carbobenzoxy-L-lysine)	S	Dehydrogenation of alcohols at 150–250°C by the heterogeneous macromolecular complex	1
Chelated Cu(II)	Polyhistidine	S	Oxidation of anionic or neutral substrates, hydroquinone or homogentisate more rapid than cationic substrate, arylammonium ions	2
Chelated Cu(II)	Q-PVP	S	Oxidation of salicyclic acid and tri-*t*-butylphenol more rapid than the cationic *p*-phenylenediammine	3
Chelated Cu(II)	Poly-4- or -5-vinylimidazole	S	Oxidation of hydroquinone and reoxidation of reduced catalyst with molecular oxygen	4
as above	Homopolymers and copolymers of ethylvinylsulphide and 4-vinylimidazole	S	Oxidation of hydroquinone. Coordination of Cu(II) to both amine and sulphide groups	5
as above	Polythiosemicarbazides	S	Oxidation of benzaldehyde and benzyl alcohol to benzoic acid, cyclohexanol to cyclohexanone or reduction of $KMnO_4$ to MnO_2, benzoquinone to hydroquinone, all in 100% yields	6, 7
Cu(II), Ag(I) salts	Cation exchange resin. Duolite A-3, containing amine-chelated moieties	I	Reduction of the metal ions with $S_2O_4^{2-}$, the heterogeneous polymer was used for removal of oxygen in gas analysis	8

Sn(II), Ce(IV), Ti(III), ions	Amberlite IR-120, Dowex-50 and Wofatit F cation exchange resin	I	Various redox studies	9, 10
Cu(II) ions	Polyvinylpyridine	S	Oxidative cleavage of 4-methylcatechol and *o*-phenylenediamine	11
Ti(II), Cr(IV), Cu(II) halides	Sulphonated polystyrene anion exchange resins	I	Oxidation and reduction of various inorganic species	12
Sn(II) ions	Strongly basic Lewatit MN cation exchanger	I	Columnar reduction of Fe(III) ions as an analytical aid in the determination of Fe(III)	13
Chelated Cu(II) ions	Poly(1-vinylimidazole) or polyethyleneimine	S	Oxidation of hydroquinone and re-oxidation of Cu(I) by molecular oxygen. Polymeric complex 20-times more active than cupric ions	14
Cobalt(II) acetate complexes	Sulphonated styrenedivinylbenzene copolymer	I	Oxidation of 2-propanol by molecular oxygen	15
V^{2+}, Mn^{2+} ions	Polymeric Schiff base complexes	S	Catalytic oxidation of Cumene to 2-phenyl-2-propanol and acetophenone at 100°C	16
Co(II) protoporphyrin IX	Ester-linked porphyrin on chloromethylstyrene graft polymerized onto a porous polyolefin matrix	C	Oxidation of hydroquinone and tetrachlorohydroquinone to their respective quinones	17
Fe(III) protoporphyrin IX	P4VP	S	Reduction of Fe(III)–polymer species by *N*-benzyl-1,4-dihydronicotinamide in DMSO. Reduction of $Na_2S_2O_4$ in DMF/H_2O mixtures	18
Hemin	P4VP	S	Reduction of hemin by dimethylamide —a degradation product of dimethyl formamide	19

TABLE 4 (continued)

Redox active species	Polymeric matrix	Type	Reaction	Ref. [a]
Fe(III) porphyrins	Bound through peptide to polyphenylalanine	C	Oxidative coupling of phenylene diammine. Catalytic activity of polymer twice that of monomer	20, 21
Ferrocene	Polyvinylferrocene	C	Reduction of ceric sulphate and reoxidation by ascorbate and other mild reductants	22

[a] See Table 1.

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Tsuchida and Nishide [27]. Other organometallic systems such as polymer-supported metallocenes [16,43] and heavy-metal systems [16] have been investigated for their hydrogenation and hydroformylation properties, but their redox properties remain largely uninvestigated.

Polymer-coupled metal ions and chelates whose catalytic properties are not discussed in later sections are outlined in Table 4.

Wholly inorganic oxidant and reductant species, such as BH_4^- and $HCrO_4^-$, have also been attached to a polymer and used as oxidants or reductants in homogeneous systems where the redox active species is not soluble, but becomes so by virtue of the attached macromolecule. The columnar oxidation and reduction of a number of organic and inorganic species is a common application of such reagents. Table 5 contains some examples of processes to which these polymers have been applied. At present there does not seem to be very much development of this type of polymer. The following sections deal with recent trends in the application of functionalized redox active polymers.

C. MACROMOLECULAR NITROGENASE MODELS

It has only been in recent years that the iron–molybdenum cofactor of nitrogenase from *Azobacter vinelandii* has been isolated [44,45]. This cofactor was reported to contain one Mo, eight Fe, six labile inorganic S groups and a polypeptide. The catalytic activity of this species towards the selective reduction of acetylene to ethylene with $NaBH_4$ has been established at about 8% of that of native nitrogenase. In an attempt to find a functional enzyme model the μ-dioxodi(oxomolybdenum(V)) complex coordinated by an L-cysteine ligand, $[Mo_2O_4(cys)_2]^{2-}$, was examined as a cofactor in the nitrogenase model reaction of the reduction of acetylene and dinitrogen [46–48]. Other organometallic compounds have been investigated for nitrogen fixation [49–54]. Nakamura et al. [55] reported recently that dioxo-molybdenum complexes having μ-disulphido bridge catalyzed the reductive cleavage of azobenzene with $NaBH_4$.

The last couple of years have witnessed the advent of similar polymer-bound active species which mimic the reactions of nitrogenase, such as nitrogen fixation and hydrocarbon reduction (Table 6) [56]. Oguni et al. [57] employed a binary catalytic system consisting of a polypeptide di-μ-sulphido-bis[thioxanthato(oxo)molybdenum] complex (**1**) and ferrodoxin

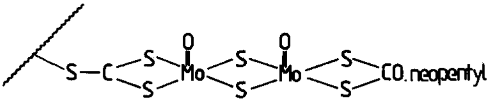
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TABLE 5

Some reactions of polymer-supported inorganic entities

Redox active species	Polymeric matrix	Type	Reaction	Ref.[a]
$S_2O_4^{2-}$	Sulphonated polystyrene anion exchange resins	I	Heterogeneous reduction of various metal ions, removal of oxygen from water	1, 2
Tungstosilicic acid	DEAE–Cellulose anion exchanging polymer	I	Reduction of Fe(III), Cu(II), TiO_2^{2+}, BrO_3^-, $Cr_2O_7^{2-}$ ions and $MeNO_2$, leuconic and crotonic acids in acidic solutions. Four of the 12 W atoms can be reduced from W^{6+} to W^{5+} with Cr(II) solutions and then have a reducing power between Ti(II) and Cr(II)	3
BH_4^-	Quaternary ammonium polystyrene derivatives	I	Reduction of benzaldehyde in ethanol solution	4
BH_3	Adduct formation with P4VP	S	Heterogeneous reduction of various aromatic aldehydes and ketones to the corresponding alcohols via batch and columnar processes	5
BH_4^-	Lewatit M-600 anion exchanger	I	Heterogeneous columnar reduction of various metal ions in solution	6
BH_4^-, $S_2O_4^{2-}$, $H_3PO_2^-$	Anion exchange resins	I	as above	7
$HCrO_4^-$	Quaternary ammonium derivative of polystyrene (Amberlyst A-26)	I	Oxidation of primary and secondary alcohols to carbonyl compounds in non-aqueous media. Conversion of alkylhalides to their aldehydes	8, 9

n-Butyltin dihydride	Bound through an Sn–C bond to polystyrene	C	Reduction of various aromatic aldehydes and ketones to their alcohols and several halides to the parent hydrocarbon. Regeneration of the –pol–$SnH_2 \cdot Bu$ species proved impossible	9
CrO_3	Polyvinylpyridinium-chlorochromate	I	Heterogeneous oxidation cinuamyl alcohol, 1-hexanol and cyclopentanol to their carbonyl derivatives with better than 90% conversion and no contamination of oxidant	10
BH_3	Polystyrene with pendant $MeSCH_2$ groups	S	Heterogeneous reduction of acetophenone to the corresponding alcohol	11

[a] See Table 1.

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TABLE 6

Some macromolecular nitrogenase models

Active species	Polymeric matrix	Type	Comments	Ref.[a]
Thioxanthate oxomolybdenum complexes (1)	L-Cysteine and γ-benzyl-L-glutamate copolypeptide	C	Catalytic reduction of phenylacetylene and azobenzene after reduction with $NaBH_4$, and in the presence of $Fe_4S_4(SPh)_4^{2-}$	1
Molybdenum(IV) complexes (2)	*p*-Mercaptomethyl substituted polystyrene	C	Reduction of acetylene and nitrogen in the presence of $Fe_4S_4(SPh)_4^{2-}$, accelerated in the domain of the polymer. Activity 1/100 of that of nitrogenase	2
MoO_4^{2-}	Bound to cysteine groups of reduced bovine insulin	C	Catalytic reductive cleavage of dinitrogen with $NaBH_4$	3, 4
Titanocene	Polystyrene and polycarboxyllic acid derivatives	C	Catalytic reduction of N_2 to NH_3 using lithium naphthalide as the ultimate reductant. Metal bound directly to polymer	5
Titanocene	Polystyrene	C	As above. Titanocene bound through cyclopentadienyl group to polymer	6, 7

Mo complexes	Polyvinylalcohol	S	Reduction of N_2 to N_2H_4 using phospholipids as cocatalysts	8
Methylene-bridged titanocene dichloride dimers (3)	Polystyrene	C	Conversion of N_2 to NH_3 using sodium naphthalide as reductant	9
Chelated Co(III)	Polymer pendant PPh_3	S	Coordination of nitrogen and reduction with lithium naphthalide and $TiCl_4$. Production of NH_3 greater in polymeric system than in the monomeric case	10

[a] See Table 1.

1 N. Oguni, S. Shimazu and A. Nakamura, Polym. J., 12 (1980) 891.
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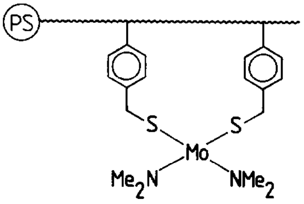
model complex, $Fe_4S_4(SPh)_4^{2-}$, for the reduction of phenylacetylene and azobenzene. The same authors [58] also investigated molybdenum(IV) complexes supported on partially *p*-mercaptomethyl-substituted cross-linked polystyrene (**2**) in conjunction with $Fe_4S_4(SPh)_4^{2-}$ for the reduction of acetylene and the reductive cleavage of dinitrogen. Other workers have used oxomolybdenum complexes coupled to insulin [59].



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The catalytic activity of the ferredoxin model compound, together with the polymeric species is 20-fold greater than the activity observed with the individual components and is due to an electron exchange between the two species in the catalytic process. The mechanism of reduction by these molybdenum complexes is typified by that for the polymeric species (**2**) as shown in Fig. 1, and serves to illustrate how dinitrogen reduction may occur. Although the exact oxidation state of molybdenum in nitrogenase remains ambiguous, Steifel [60] proposed Mo(II) should be considered for the lower redox state and most authors agree on a reduced state of molybdenum as the active species in these polymeric nitrogenase analogues. Schrauzer and Doemeny [46] proposed a mechanism in which molybdenum(IV) species react with acetylene to give ethylene on hydrolysis, and ethane is produced

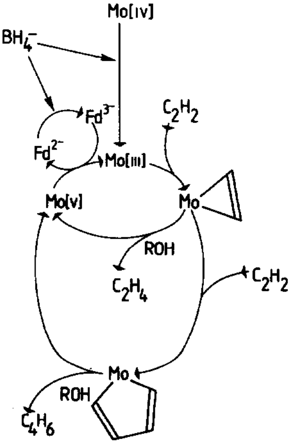


Fig. 1. Reduction mechanism of acetylenes by nitrogenase model polymers [58]. $Fd^{2-} = [Fe_4S_4(SPh)_4]^{2-}$; Mo = Mo unit of a polymer appended with–$(S)_2Mo\cdot NMe_2$.

through the intermediacy of a (μ-η^2-C_2H_2-)molybdenum(IV) species. Others [51] have reported that the electrolytic reduction of a Mo(V)–cysteine complex in the presence of acetylene yields a Mo(III)–acetylene complex. This reduced species readily interacts with acetylene to give a "side-on" (η^2) coordinated complex which affords ethylene on protonation by alcohol. The η^2-acetylene intermediate can also react with another molecule of C_2H_2 to give the molybdenacyclopentadiene species, which yields butadiene on subsequent protonation with alcohol leaving molybdenum oxidized to Mo(V). Oguni et al. [57,58] have also adopted this mechanism for their polymeric molybdenum complexes. Investigation of the reduction of dinitrogen as mimicking nitrogenase action has been dealt with by Denisov et al. [61]. Weathers et al. [59] reported the reduction of dinitrogen by catalysis of the insitu system of MoO_4^{2-} and insulin with $NaBH_4$ at a catalyst concentration as low as 10^{-6} mol l^{-1}. This system gave NH_3 in good turnover only for an initial short period. The results of Oguni et al. [58] with their polystyrene(methylthiol)$_2$Mo(NMe$_2$)$_2$/$Fe_4S_4(SPh)_4^{2-}$/$NaBH_4$ system were less impressive, as the amounts of hydrazine and ammonia produced were almost equivalent. The highest activity and best selectivity were observed with a system containing a random copolypeptide of L-cysteine-Mo(NMe$_2$)$_4$ and $Fe_4S_4(SPh)_4^{2-}$ [58].

One distinct advantage of these polymeric systems, despite their generally low activity, is that they enable greater rates of reaction and length of catalyst stability than is possible in homogeneous systems of this type. Perhaps the prevention of the catalytically inactive polynuclear Mo–Mo bonded species from forming is responsible for this effect [58].

Metal carbonyl complexes may be used to catalyze the reduction of N_2 to NH_3 and N_2H_2. It has been said that (η^5-cyclopentadienyl)dicarbonyldinitrogenmanganese, $CpMn(Co_2)_2N_2$ [62] has the potential of becoming an important nitrogen-fixing catalyst [63]. Polymer-bound dinitrogen complexes of poly-(η^5-vinylmethylcyclopentadienyl)tricarbonylmanganese analogues have been described by Kurimura et al. [64]. Dinitrogen complexes could be prepared by the oxidation of hydrazine coordinated to the polymer-bound manganese complexes, with hydrogen peroxide in the presence of cupric ions. Although catalytic reduction of coordinated N_2 was not achieved the manipulation of elementary technology vital to more fruitful endeavors has been demonstrated.

Reduced bovine insulin was found to bind oxomolybdenum species to the cysteine residues in the A and B chains of the polypeptide [59,65]. The bonding sites were provided by the four Cys residues in the A-chain and two in the B-chain. These macromolecular catalysts, generated in situ, catalyzed the reduction of acetylene and dinitrogen. The acetylene reduction reaction was used to shed light on the chemical behavior of the catalytic species. The reduction of C_2H_2 to C_2H_6 was typical of a binuclear intermolecular catalytic site which probably formed at high catalyst loading levels since the C_2H_2/C_2H_4 product ratio declined as the total catalyst concentration increased, the conversion of C_2H_2 to C_2H_4 proceding by a mononuclear active site [66]. The intramolecular formation of a dimeric species occurred to a greater extent with chain A than with chain B, as judged from the C_2H_4/C_2H_6 ratios. The stimulation of the reduction process by ATP parallels the findings of other authors [67] in their work with molybdenum/ PVA species in the presence of various phospholipids. It is thought that the phosphorous compounds specifically accelerate the reduction of the catalyst from the inactive oxidized state to the active reduced state with the electron donor ($NaBH_4$ or $Na_2S_2O_4$) [66].

The Mo–insulin complexes reduce N_2 with a turnover of about 2.5 mol of NH_3 per mol of Mo per min, which corresponds to 5% of the activity of native nitrogenase, and the macromolecular species are more active than simple molybdothiol complexes. It is thought that in this case N_2 is reduced

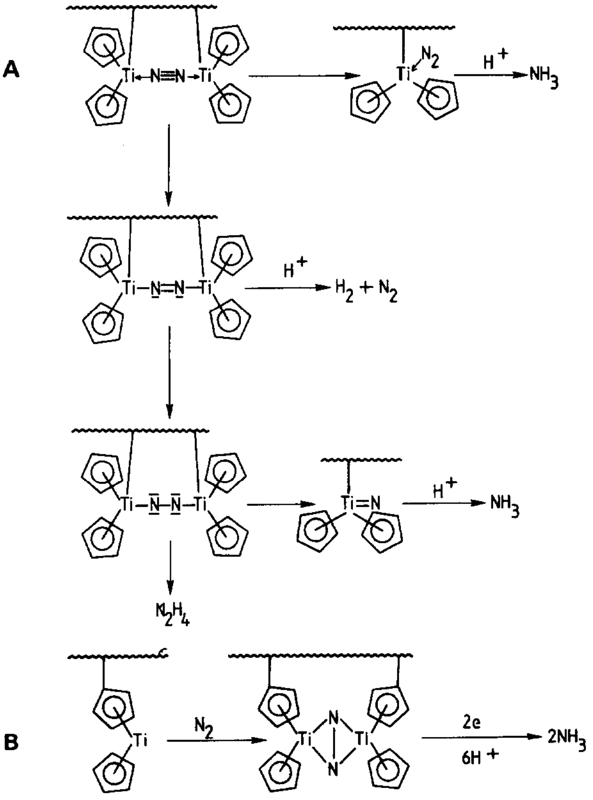
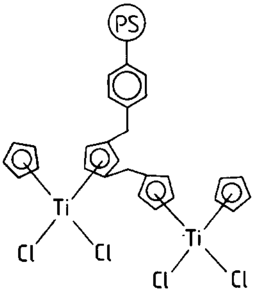


Fig. 2. Pathways of N_2 reduction with different macromolecular titanium catalysts.

to N_2H_2 which disproportionates to N_2 and N_2H_4, with subsequent conversion of the latter to NH_3 [65].

Titanocene complexes are widely recognized for their nitrogen-fixing ability [68,69]. Titanocenes bound to polystyrene can either be bound to the polymer through the cyclopentadienyl moiety or directly to the titanium center. Catalysts of the first type were employed by Kroll [70] and Chandrasekaran [71,72], however only very small quantities of ammonia were produced, as dimerization of the titanium centers to form the active species [73] was avoided by polymer attachment [74] (Fig. 2). Lau et al. [75] enjoyed greater success with polymer-bound methylene-bridged titanocene dimers (3)



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which enabled a modest conversion of N_2 to NH_3. Koide et al. [76] prepared polymeric catalysts with a σ-bond to the titanium metal center. Reduction of N_2 was performed using lithium naphthalide as the ultimate reducing agent and alcohols or acids as the hydrogen donors. In the absence of hydrogen-donating agents, dinitrogen complexes of the titanocene polymers could be identified by visible spectral measurements. Highly flexible and/or soluble polymeric systems were found to be much weaker catalysts than those with insoluble and/or less flexible polymeric backbones where it is thought the irreversible formation of binuclear titanium complexes was impaired.

Thus, it appears that these catalysts which have a direct bond from the metal center to the polymeric matrix operate by a different reduction mechanism (Fig. 2) and do not require a dimeric titanocene unit for efficient catalysis. Whatever the case it has not been clearly delineated whether N_2 reduction involves a transient reduced state of titanocene or whether direct reduction of the coordinated N_2 is involved.

D. OXIDATION OF ASCORBIC ACID AND MODELS OF ASCORBATE OXIDASES

Ascorbate oxidase (L-Ascorbate: O_2 oxidoreductase, EC 1.10.3.3) is a copper-containing enzyme that catalyzes the aerobic oxidation of vitamin C. The enzyme has a molecular weight of about 140 000 and contains 8–10

TABLE 7

Polymeric oxidants for ascorbic acid

Redox active group	Polymeric matrix	Type	Comments	Ref. [a]
Fe^{3+} ions	"Dowex" sulphonated PS-ion-exchange resin	I	Columnar oxidation of ascorbate to dehydroascorbate	1
trans-Fe(III)(tetpy)$(OH_2)^+$	Coordinated to poly-L- or -D-glutamate	I	Structure of ligands about catalytic center affects resultant catalytic activity. Reoxidation of Fe(II) center by H_2O_2	2
Chelated Cu(II)	Polymers bearing β-diketone groups	S/I	UV absorption data suggest a close relation between the catalytic activity and the electronic state of the ligand	3, 4
Chelated transition metal ions, M^{2+}	Poly-β-ketoesters (6)	S/I	Catalytic activity fell in the series Cu > Ni > Mn, Co, Fe, and increased as the distance between the catalytic sites was lengthened	5
Chelated Cu(II) ions	Poly(L-histidine)	S	Monomeric imidazole or histidine not catalytically active. Polymer complex more effective than cupric ions. Reoxidation of catalyst by molecular O_2, with the formation of H_2O_2	6–8
Chelated Cu(II)	Quaternized polyvinylpyridine (Q-PVP)	S	The polymer complex was 200–1500 times more active than cupric ions and monomeric complexes	9–12

Quinones	Entrapped within Kel-F (a polytrifluorochloroethylene powder)	C	Columnar oxidation of ascorbate. Rapid electron exchange	13
Quinone	Hydroquinone derivations of phenol–formaldehyde polymers	C	Columnar oxidation of ascorbate	14–16
Ferrocene	Polyvinylferrocene	C	Oxidized form of the polymer can be reduced by ascorbic acid	17

[a] See Table 1.

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copper atoms per molecule [77]. The enzyme is made up of two identical sub units, each sub unit consisting of two polypeptide chains of molecular weights between 30000 and 40000 [78]. There are several instances where metal ions and complexes supported in a synthetic polymeric matrix emulate the catalytic nature of ascorbate oxidase and these are outlined in Table 7. Conversely, the complexities of ascorbate as a reducing agent have been discussed by Creutz [79].

Barteri et al. [80] employed *trans*-Fe(III)(tetpy)$(OH)_2^+$ (tetpy = 2,2′,2″,2‴-tetrapyridyl), which formed an inner-sphere complex with poly-L-glutamate or poly-D-glutamate in the oxidation of L(+)-ascorbate. These catalysts were found to possess stereoselective properties. At low complex-to-polymer-residue molar ratios ($C/P < 0.015$) the α-helical fraction of the polypeptide matrices was low and the configurational disymmetry was unable to impart any stereoselective effects. However, by increasing the C/P ratio above 0.02 the amount of α-helicity in the polymer rose and the stereoselectivity of the catalytic sites also increased. Under those conditions the second-order rate constants for the oxidation of ascorbate by the macromolecular D and L isomers dropped markedly, but that of the L isomer more so than that of the D isomer ($k_D/k_L = 4.0$). Pecht et al. [81–83] studied poly-L-histidine–Cu(II) complexes. Since imidazole residues are often suggested as ligands for the active site of copper-containing oxidases it was thought that an understanding of these macromolecular Cu(II) complexes might shed some light on certain enzymic oxidase activities. It turned out that the poly-L-histidine matrix enhanced the oxidation of negatively charged substrates, such as ascorbate and hydroquinone anions, but served to inhibit the oxidation of cationic species, such as tetramethyl-*p*-phenylenediammonium and 1-(2,5-dihydroxyphenyl)isopropylammonium cations, by the coordinated Cu(II). Unlike the monomeric Cu(II) species, the polymer–Cu(II) complex-catalyzed reaction became zero order in substrate concentration at relatively low concentrations of substrate and exhibited Michaelis–Menten kinetics. It was thought that the polycationic catalyst concentrated the negatively charged substrate within the domain of the polymer and hence facilitated the coordination of the substrate to the copper(II) site. A moderate concentration of inert electrolyte, however, neutralized this electrostatic effect. A similar effect was observed by Dadze and Khidekel, [84] and Vengerova et al. [85] with partially alkylated Cu(II)–polyvinylpyridine complexes.

The copper(II) poly-L-histidine complexes, however, can vary in their configuration of the catalytic site at extreme ends of the pH range. From circular dichroism and ESR measurements it was concluded that at pH 5 the Cu(II) ion is bound to three imidazoles and one peptide nitrogen, whereas at pH 14, it can be discerned that four consecutive peptide nitrogens occupy a distorted coordination square and one imidazole group binds at an axial site [83]. Unlike the oxidases, however, reoxidation of the copper(I) species by molecular oxygen yields hydrogen peroxide and not water.

E. DECOMPOSITION OF HYDROGEN PEROXIDE AND MODELS FOR CATALASE

Enzymes immobilized on an inorganic or organic polymer matrix are widely used as heterogeneous catalysts in batch or columnar synthetic processes [86,87]. The group of enzymes known as the oxidoreductases are often subject to deactivation by hydrogen peroxide, a by-product of the oxidative reaction [88]. Activated carbon [89,90], metallic oxides [91–93], especially those of manganese [92,93], are efficient catalysts for the decomposition of H_2O_2. The deactivation of various enzymes by H_2O_2 under catalytic circumstances can be minimized by attaching the enzyme to just such a manganese oxide [94] or activated carbon matrix [89,95].

In living organisms the enzyme catalase acts as a catalyst for the decomposition of H_2O_2. Catalase is a heme iron protein having a molecular weight of about 250000 and containing four hemin groups per molecule, each hemin moiety consisting of high-spin iron(III) in a protoporphyrin IX ring [96]. The deactivation of supported glucose oxidase by H_2O_2 [97,98] may be kept to a minimum by cosupporting bovine liver catalase with the glucose oxidase [99]. Co-immobilization of xanthine oxidase with superoxide dismutase and catalase improved the operational stability of the heterogeneous catalyst [100]. The effectiveness of catalase as a scavenger of H_2O_2 is known to be improved upon attachment to an organic polymer. In Table 8 co-immobilized enzyme assemblies containing catalase are presented.

The covalent attachment of bovine liver catalase to polyethyleneglycols results in an enhanced circulating life of the enzyme in the blood of acatalasemic mice during repeated intravenous injection [101]. Further, the attachment of polyethyleneglycols to such biological macromolecules renders the protein envelope incapable of eliciting an immune response in their presence [102].

The time is fast approaching when biomimetic polymers of catalase will see commercial application in conjunction with the heterogeneous enzymic catalysts.

It is well established that many metals and metal ions catalyze the decomposition of H_2O_2 into water and oxygen [103,104].

$$2\,H_2O_2 \xrightarrow{\text{catalyst}} 2\,H_2O + O_2$$

The activities of metal ions in a Y-type zeolite were found to form the order Pd(II) < Fe(III) < Ni(II) < Ag(I) > Mn(II) > Co(II) > Co(III) > Hg(II)

TABLE 8

Examples of polymer-bound catalase in peroxide decomposition

Immobilized enzyme system	Comments	Ref. [a]
Catalase	Cross-linked with glutaraldehyde	1
	Coupled with cyanuric chloride to cellulose fibers	2
	Electrostatically adsorbed onto DEAE-cellulose fibers	3
	Covalently coupled to DEAE-cellulose fibers	4
	Diazonium coupling to cellulosic derivatives	2
	Coupling of enzyme and CNBr-treated dextran matrix	5, 6
	Polyethyleneglycol coupled to 4,6-dichloro-5-triazine derivative of catalase. For medicinal use as an enzyme supplement	7, 8
	Diazonium derivatives of synthetic pulp used to couple with enzyme	9
	Incorporation into oxygenator membranes	10
	Microencapsulation of the enzyme in an inert polymeric matrix. For medicinal use as an enzyme supplement	11
Glucose oxidase and catalase	Covalently bound to a polyacrylamide matrix. Synergic activation of both enzymes	12
	Covalently coupled with glutaraldehyde to silanized silica–alumina	13
	Adsorption of both enzymes onto nickel impregnated silica–alumina pellets treated with α-aminopropyltriethoxysilane	14
	Coadsorption of both enzymes onto titania and alumina. The activity of the combined heterogeneous system depends upon the pore size of the matrix	15–17
Milk xanthine oxidase, superoxide dismutase and catalase	Covalent attachment to CNBr-activated Sepharose 4B and adsorption onto *n*-octylamine-substituted Sepharose 4B. More efficient conversion of xanthine to uric acid	18
L-Amino acid oxidase and catalase	Bound to polymeric matrix for the production of α-ketoacids for medical use	19
	Coimmobilization onto glass beads for use in an analytical device for the determination of L-leucine	20

[a] See Table 1.

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> Cu(II) > Cr(III) > Zn(II), and on alumina [105] the order of activity Ag > Pt > Pd > Au has been established. Similarly, the catalytic activities of several metalloporphyrins were very sensitive to the nature of the supporting oxide matrix [106].

The decomposition of H_2O_2 by metal ions of variable valency was studied by Haber and Weiss [107] who proposed that metal ion catalysts underwent both oxidation and reduction [108] during the dismutation process, i.e.,

$$H_2O_2 + M^{n+} \rightarrow OH^- + M^{n+1} + OH^{\cdot}$$

$$H_2O_2 + M^{n+1} \rightarrow H^+ + M^{n+} + HO_2^{\cdot}$$

Not only does the metal need to be redox active, but the ion or complex must be coordinatively unsaturated for efficient catalysis [109]. A number of polymer–metal complexes which possess these characteristics have been reported to mimic the behavior of catalase. These biomimetic redox polymers are summarized in Table 9.

Several purely organic polymers have also been found to catalyze the disproportionation of hydrogen peroxide [110–113]. For example, pyrolized polyacrylonitrile [114] behaves much like a polyquinone, capable of reversible electron transfer. With the technological advances in the use of

TABLE 9

Examples of polymeric species which hasten decomposition of H_2O_2

Redox active moiety	Comments	Type	Ref. [a]
Fe(III) and Cu(II) ions	Polyvinylalcohol matrix containing either one, or both, metal ions. Distorted chelate structure of bimetallic system enhances the activity of the catalyst	S	1, 2
cis-Fe(III)(pmen)$(OH)_2^+$ and *trans*-Fe(III)(tetpy)$(OH)_2^+$	Coordination to poly(L-glutamate)	I	3–5
Fe(III) amine complex	Coordination to polyacrylic acid partially amidated with diethylenetriamine or with ethylenediamine	I/S	6, 7
Fe(III) ions	Coordination to polyacrylic acid (PAA) or polymethacrylic acid (PMA)	I	6
Fe(III)en_2	PAA or PAA/PMA copolymer	I	8–10
	Coordination to polyethyleneimine (PEI)	S	9
M^{2+}, transition metal ions	Complexed to poly(β-ketoesters)	S	11–13
Fe(III) ions	Coordinated to PEI	S	14
Cu(II) ions	RNA and DNA–copper(II) matrix. Some degradation of the biopolymer occurs during the catalytic cycle	I	15
Co(II)$(dmg)_2$	Bound to P4VP	S	16
	or a 4-vinylpyridine–acrylamide copolymer	S	17
Cu(II) ions	Complexation with homopolymers of L-lysine, L-glutamic acid or glycine	I	18
Cu(II) ions	Coordination of polyvinylalcohol (PVA)	S	19
$Cu(II)_2Cl_2$	Poly(vinyldiphenylphosphine) matrix. Decomposition of *t*-butylhydroperoxide in benzene. Cu–Cl–Cu bridges constitute the active center	S	20
Cu(II) ions	Polymeric hydroxamic acids, acrylohydroxamic acids and α-chloroacrylohydroxamic acids	S	21–23

TABLE 9 (continued)

Redox active moiety	Comments	Type	Ref.[a]
Co(II)en$_2$	Complexed to a sulphonated styrene–divinylbenzene ion-exchange resin	I	23
Co(II) acetate complexes	Sulphonated styrene–divinylbenzene copolymer	I	24
Cysteine	Polycysteine	C	25
Hydroquinone (HQ)	Hydroquinone/formaldehyde polymers	C	26
Hydroquinone and catechol	Styrene–divinylbenzene copolymer with pendant organic functional groups	C	27
HQ	Hydroquinine groups bound to chloromethylated polystyrene	C	28
$S_2O_4^{2-}$	Commercial ion-exchange resin as matrix	I	29
Aromatic groups of undetermined character	Polyacrylonitrile		30, 31
	Polyamino-quinones		32
	Vulcanized analine-black		33, 34
	Pyrolized chlorinated PVC		35

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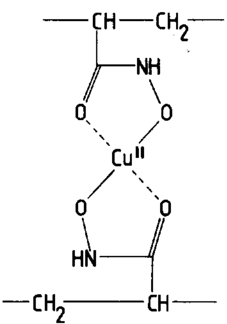
industrial biocatalysts, such redox polymers may find a use as inexpensive replacements for catalase in the stabilization of oxidoreductase assemblies.

It has been shown that polymer–metal ion chelates exhibited profound catalase-like behavior, whereas metal complexes of the monomer from which the polymer was derived were found to possess little or no catalytic activity. For instance, polymeric ligands of the β-diketone type complexed with Cu^{2+} were shown to be much more catalytically active for the decomposition of H_2O_2, whilst the copper chelate of dibenzoylmethane, one of the simplest ligands of the β-diketone type, was inactive. Similar observations were reported for cupric chelates of polyhydroxamates (**4**) [115,116]. From the infrared and electronic absorption spectra it was concluded that the catalytic activity of the chelated polymers was inversely proportional to the bond strength between the ligand and the Cu^{2+} ion as the molecular weight of the polymer increased. These conclusions were justified when it was later shown that at increasingly higher molecular weights of the polymeric ligand, the stability constants of the Cu^{2+}–macromolecular chelate decreased [115,116].



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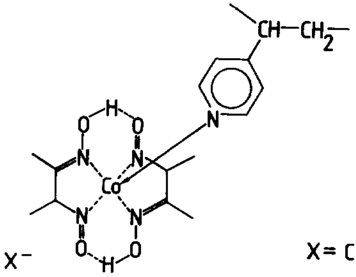
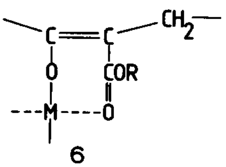
The catalytic activity of cobalt dimethylglyoxime complexes of P4VP (5) is also known to be subject to the magnitude of the metal–macromolecular



X= Cl^-, CN^-

5



6

ligand interaction [117]. The complex with the chloro axial ligand was more active than when a cyanide axial ligand was present, for both the monomeric and polymeric chelates. The electron-withdrawing CN^- group enriches the positive charge on the cobalt atom resulting in a stronger Co–N interaction between the chelate and the polymer. Furthermore, the macromolecular chelate was more active than the monomeric pyridine complexes. The basicity of the P4VP pyridine group is considerably less than pyridine itself. The trend emerging from all these findings is the weaker the coordinate base or ligand, the stronger the catalytic activity becomes [118].

Other workers have described bis(ethylenediamine)iron(III) complexes of polyacrylic acid (PAA) [119–123]. The macromolecular complexes are almost as active as catalase [119,123]. The activity of the $Fe(III)(en)_2$ complexes is partly due to the incorporation of the carboxyl groups of the polymer into the coordination sphere of the Fe(III) chelate [123]. It is generally agreed that the presence of primary or secondary amines augment the catalytic reaction. It has been suggested that H_2O_2 is activated prior to

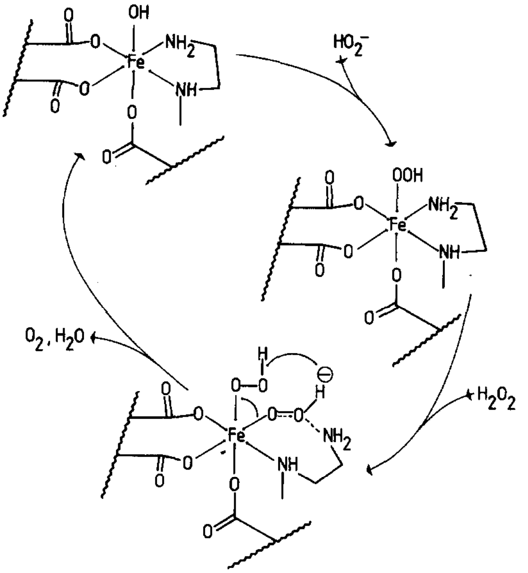


Fig. 3. Decomposition of H_2O_2 by polymer-supported Fe(III).

decomposition [104,124] where one carboxyl and one amino group of the enzyme participate in forming hydrogen bonds to one molecule of H_2O_2 [121]. By this mechanism, a second H_2O_2 molecule would then form a complex with the first one at the active site. A working model of such a scheme was developed by Pshezhetskyi et al. [119] in which spontaneous decomposition of H_2O_2 was performed by an Fe^{3+} complex of PAA partly amidated by diethylenetriamine. The energy of activation for the decomposition reaction was as high as 25 kcal/g mol for liver catalase and as low as 23 kcal/g mol for the Fe^{3+} macromolecular complex. A simplified version of the catalytic mechanism is presented in Fig. 3. The catalytic process is pH dependent and the maximum rate of reaction is observed above pH 10.7. The acid–base dissociation of the substrate [122], and subsequent coordination of HO_2^- to the metal complex are believed to be responsible for this.

The findings of studies on Cu^{2+}–PVA complexes at different pH suggest that different mechanisms may operate at opposite ends of the pH scale [125]. At pH 6.6–8.2, H_2O_2 is the sole coordinating substrate to the copper center, whereas at a pH above 8.2, the coordination of HO_2^- to the metal center predominates.

F. OXIDATION OF THIOSALTS BY MOLECULAR OXYGEN

Polythionates are a waste product from sulphide-ore milling operations. These compounds originate in the alkali-flotation circuits used to process the ore and their safe disposal is often a cause of concern [126,127]. The irresponsible elution of tailings water creates a severe drop in pH of nearby streams and is extremely harmful to aquatic life. The acidity build-up is a result of their conversion to sulphuric acid by bacterial action. Though ozone and hydrogen peroxide have been used to oxidize waste polythionates, the ability of suitably complexed copper(II) ions to catalyze the oxidation of thiosulphate to sulphate in aqueous solutions by molecular oxygen [128–130] has prompted the investigation of certain redox polymers as heterogeneous oxidation catalysts [131–135] for the conversion of such species as sulphite, SO_3^{2-}; thiosulphate, $S_2O_3^{2-}$; dithionite, $S_2O_4^{2-}$; disulphite, $S_2O_5^{2-}$; trithionate, $S_3O_6^{2-}$ and tetrathionate, $S_4O_6^{2-}$, to sulphate. Catalysts of this type described recently involve the complexation of copper(II) ions to poly(4-vinylpyridine) [131,133,134] and quaternized P4VP [132], and covalently bound copper(II) bipyridine-type complexes to porous polystyrene [135]. Other types of redox polymers employed in thiosalt oxidation are presented in Table 10.

The copper(II)–PVP catalysts have been thoroughly studied. Though the initial rate of thiosalt oxidation (as measured by oxygen consumption) is higher for monomeric 4-vinylpyridine-copper(II) complexes than their polymeric counterparts, upon prolonged exposure to oxygen they exhibit a loss in activity. The polymeric catalysts, however, have excellent stability and are not subject to such deactivation [134]. Like the monomeric complex, the macromolecular copper(II) PVP catalyst is subject to disassociation at either extreme of pH.

Though copper(II) can undergo one to six coordination with pyridine, Nishikawa and Tsuchida [136] have shown it forms one to four coordinate complexes with PVP. The stepwise formation constants, K_1 to K_4, in contrast to the monomeric pyridine–Cu(II) system,

$$\mathrm{Cu(II)} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{Cu(II)L}$$

$$\mathrm{Cu(II)L} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{Cu(II)L_2}$$

$$\mathrm{Cu(II)L_2} + \mathrm{L} \overset{K_3}{\rightleftharpoons} \mathrm{Cu(II)L_3}$$

$$\mathrm{Cu(II)L_3} + \mathrm{L} \overset{K_4}{\rightleftharpoons} \mathrm{Cu(II)L_4}$$

where L is a pyridine moiety within the PVP matrix increase with the number of coordinated ligands in the PVP matrix and the four-coordinate copper(II) complex is by far the predominant species formed. This is because of chain contraction and consequent steric hindrance in PVP gels, and restriction of chain mobility due to associative cross-linking formed by the pyridine–Cu(II) interaction.

TABLE 10

Polymeric catalysts for thiosalt oxidation

Redox active species	Polymeric matrix	Type	Comments	Ref. [a]
Cu(II) ions	Quaternized P4VP	I	Oxidation of $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	1
Cu(II) ions	Various ion-exchange resins	I	Oxidation of $S_2O_4^{2-}$	2–4
Cu(II) and Ag(I) ions	Duolite A3 aminated ion exchanger	I	as above	4
Cu(II) ions	P4VP	S	Oxidation of $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	5, 6
Cu(II) complex of bipy, 4,4′-dimethyl bipy, 4,4′-diphenyl bipy, *o*-phen, and other ligands	Copper complexes covalently bound to porous polystyrene particles	C	Oxidation of $S_2O_3^{2-}$ to sulphate, tetrathionate and triothionate	7
$Cr_2O_7^{2-}$	Diphenylcarbazide polymer	S	$S_2O_4^{2-}$ oxidation	8
Fe(III) mesoporphyrin IX	Bound through isocyanate side chain to poly(2-hydroxyethylmethacrylate) and Sephadex LH-20	C	Oxidation of $S_2O_4^{2-}$	9
Methylene Blue (MB)	Condensation polymer of MB, resorcinol and formaldehyde	C	Reduction with $S_2O_4^{2-}$	10, 11
MB	Amberlite IR 20 and Dowex 50 sulphonated PS ion exchangers	I	as above	12
Malachite Green	Copolymer of styrene, divinylbenzene and 4-vinylmalachite green	C	Reduction with $S_2O_6^{2-}$ and reoxidation with Fe^{3+}	13
Indigoid dyes	Polyamino styrene and polymeric indigo	C	Reduction with $S_2O_4^{2-}$	14, 15
1,4-Dihydronicotinamide	Reaction product of nicotinamide and chloromethylated PS	C	as above	16–18
Viologen	Polyviologens adsorbed on an insoluble ion-exchange resin	I	$S_2O_4^{2-}$ oxidation	19

Viologen	Polymerized vinyllic viologens	C	as above	20
Viologen	Condensation product of bis(aminoalkyl)viologens with acid chlorides		as above	21
Quinone, benzoquinone	Grafted onto a chloromethylated styrene–divinylbenzene copolymer	C	Reduction of polymer with sulphite, bisulphite and dithionite	22
as above	Polyvinylquinone	C	as above	4
Thiophenol	Polythiolstyrene	C	Oxidation of $S_2O_4^{2-}$, S^{2-}	23

[a] See Table 1.

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Thus the four stepwise formation constants, log K_i, are successively 1.1, 1.6, 2.7, and 4.7 for the polymeric system (average MW 11 000) compared with 2.5, 1.9, 1.3 and 0.8 for the complexation of copper(II) ions by pyridine under similar conditions.

Catalysts prepared from the complexation of copper(II) ions with PVP are known to exhibit maximum catalytic activity at a copper content between 11 and 14% by mass, and the activity diminishes significantly as higher copper/polymer levels are approached. Chanda et al. [133] have calculated that the fraction of four-coordinate polymeric complex increases, and that of the one-coordinate complex decreases monotonically with a rise in the ligand/copper(II) ratio, whilst both the two-coordinate and three-coordinate species pass through a maximum. They concluded that only the two- and three-coordinated PVP–Cu(II) complexes were catalytically active for the oxidation of thiosalts such as $S_2O_3^-$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$.

Partially quaternized PVP–copper(II) macromolecular complexes have also been investigated as oxidation catalysts for the conversion of thiosalts to sulphate [132]. Partial quaternization and cross-linking (~ 33%) of the pyridine groups in PVP with 1,4-dibromobutane alters the effect that the relative copper content has upon the rate of oxidation. Quaternization strongly activates the macromolecular catalyst for the oxidation of $S_2O_3^{2-}$, but deactivates it towards $S_3O_6^{2-}$ and $S_4O_6^{2-}$.

Cupric complexes of PVP, partly quaternized by methylbromide or dimethylsulphate, were found to contain predominantly the tetrapyridinate-copper(II) species [137], much the same as unquaternized PVP. The ESR spectra of Cu(II)/PVP complexes quaternized and cross-linked with 1,4-dibromobutane (4–12% quaternization) are typical for the square planar Cu(II)(py)$_4$ complex with the magnetic parameters $g_\parallel$, 2.3; $g_\perp$, 2.1; and $A_\parallel$, 150 ± 10 G. At 31% quaternization and higher, the parallel component of the spectrum is shifted to higher magnetic field. This result indicates the approach of a distorted tetrahedral structure of polymerized pyridine groups about the copper(II) center at the higher levels of quaternization and cross-linking [138]. It is perhaps this change in geometry of the catalytic site that alters the catalytic selectivity of highly quaternized Cu(II)/PVP complexes over unquaternized ones.

Catalysts consisting of copper(II) bipyridine and terpyridine-type complexes covalently attached to porous polystyrene have also been studied [135]. The Cu(II)–terpyridine based catalyst is less active in thiosalt oxidation that the Cu(II)–bipyridine derived catalytic system. This was explained as arising from strong copper–nitrogen interactions in the terpyridine chelate, which enhanced the stability of the Cu(II)–terpyridine based catalyst over the Cu(II)–bipy catalyst, but consequently proved detrimental to the activity of the former. Both heterogeneous catalysts were less active than their homogeneous counterparts.

For each of the catalyst types outlined, a different reaction pathway exists for the copper(II)-catalyzed oxidation of thiosulphate as summarized in Fig. 4. In each case, however, the initial rate of oxidation of such species as $S_2O_3^{2-}$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$ is explained by a Langmuir–Hinshelwood-type rate law [131–135].

Studies of Cu(II) amine complexes as homogeneous catalysts for thiosulphate oxidation have shown that the coordination of molecular oxygen and substrate to the copper(II) center is fundamental to the catalytic process [128–130], and that the molecular oxygen in this ternary complex assists in the electron transfer between thiosulphate and copper(II) [130,139]. The copper(II)–PVP complexes are believed to behave similarly.

The initial concentration of $S_2O_3^{2-}$ influences the reaction mechanism and the product distribution pattern, a lower concentration favoring its oxidation to SO_4^{2-} over that to $S_4O_6^{2-}$. Two alternate pathways have been proposed for the oxidation of $S_2O_3^{2-}$; one involving electron transfer from $S_2O_3^{2-}$ to Cu(II) and another involving electron transfer from $S_2O_3^{2-}$ to O_2 through the central Cu(II) atom in a $Cu(py)_n(S_2O_3^{2-})(O_2)$ complex. The latter mechanism may predominate at lower thiosulphate concentrations and may account for the different distribution of products found under such conditions.

The polymeric analogues of 1,4-dihydropyridine have also been found to form an oxidation–reduction polymer capable of thiosalt oxidation. The reduction of a typical 1,4-dihydronicotinamide type polymer by sodium

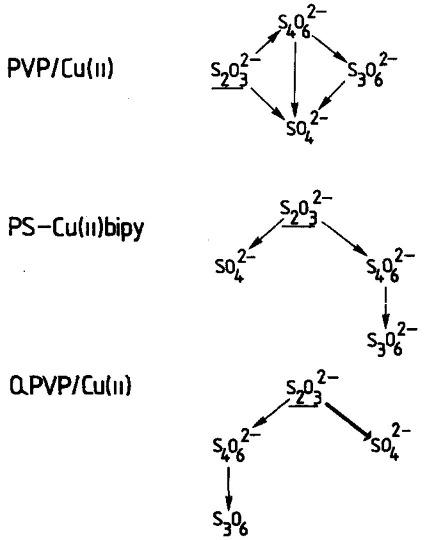


Fig. 4. Some reaction pathways of thiosalt oxidation followed by macromolecular copper(II) catalysts.

dithionite [140–142] has been shown to proceed by the formation of a sulphinate adduct [137,143,144], without the formation of a stable free-radical intermediate [145], as might be expected.

G. MACROMOLECULAR OXIDATIVE POLYMERIZATION CATALYSTS

(i) Types of oxidative coupling

Organic compounds with reactive hydrogens, such as phenols [146–152], aromatic amines [153–156] and acetylenes [156–158], may be oxidatively coupled in the presence of a metal complex to form oligomeric and polymeric compounds. Typically, these catalysts are copper(II) amine type complexes which undergo a reductive step in catalytic reaction, with subsequent reoxidation to the divalent copper species by molecular oxygen. The last decade has seen the appearance of a number of polymer-attached metal ions and complexes as oxidative polymerization catalysts.

The oxidative coupling of terminal acetylenes in the presence of oxygen and copper salts [159] is an established process. It has been reported that the oxidative dimerization of ethynylbenzene may be catalyzed by copper(II) chloride coordinated to partially amidated polystyrene [159]. It is believed that the catalytic species responsible for the homogeneous polymerization process is a hydroxy-bridged dinuclear copper(II) species [158,160]. Polymeric catalysts are thought to function similarly [161].

The catalytic mechanism of acetylene polymerization is outlined by Fig. 5.

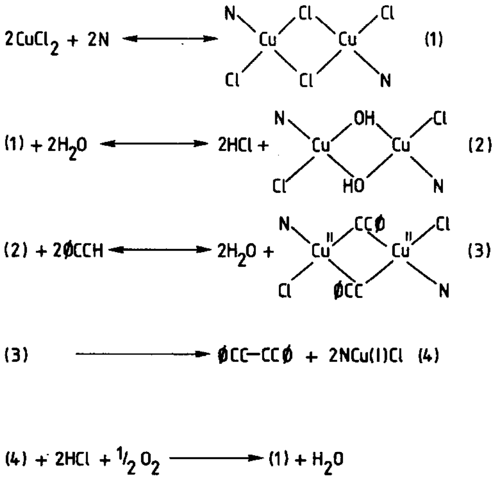
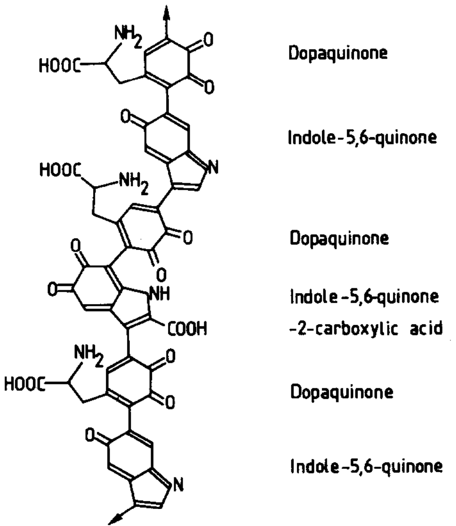


Fig. 5. Mechanism of oxidative coupling of ethynyl benzene by CuCl$_2$ supported on a polymer [161].

The polymerization of acetylenes may proceed by a somewhat different route than phenols. Catalysts which cause polymerization of phenols result in the dimerization of ethynyl benzene [160].

As outlined earlier, the oxidative coupling of phenolic compounds catalyzed by copper(II) complexes is a widely observed phenomenon. The catalytic behavior of copper(II) complexes in this respect resembles that of the copper oxidases. The enzymatic oxidation of phenols is an important pathway in the biosynthesis of plants, and "lignin" is a natural product formed from the catalytic polymerization of coniferyl alcohol and sinapyl alcohol by enzymes such as laccase [162]. The electropolymerization of phenols to produce the bulk polymer, and as a means of passivation of metal surfaces, is a rapidly developing field [163,164]. Previous reviews [165–167] on polymeric redox catalysts for phenol polymerization outline the reactions involved. The salient features of recent developments in this area are summarized in Table 11.

The behavior of macromolecular polymerization catalysts [156,168–172] for the biomimetic formation of melanin and its precursor compounds [173] from 3,4-dihydroxyphenylalanine (dopa) have been described. Melanin is a quinoid polymer (7) [173a] formed by the oxidation and oxidative polymerization of dopa which is the hydroxylation product of tyrosine by tyrosinase (see Fig. 6). Natural melanin is isolated as the pigment protein complex where the melanin is linked to the protein by means of cysteine units [174]. Melanin plays a major role in the protection of epidermal tissues against prolonged exposure to UV light, which initiates photodynamic reactions [174]. The route to the formation of the melanin polymer initially involves



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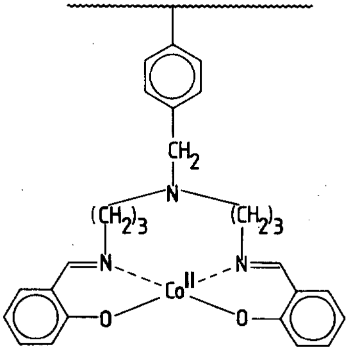

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TABLE 11

Polymeric catalysts for phenol oxidation

Active species	Polymeric matrix	Type	Comments	Ref. [a]
Cu(II) complex	Partially dimethylaminomethylated polystyrene	S	Polymerization of 2,6-diphenyl- and 2,6-dimethyl-phenol	1–6
Cu(II) complex	Poly(4-vinylpyridine) (P4VP)	S	Polymerization of 2,6-xylenol is slower with a polymeric catalyst and more rapid by monomeric copper(II) pyridine complexes	7–10
Cu(II) complex	Partially quaternized P4VP	I	Polymerization of phenols accelerated by the positive electrostatic field of the polymer	11–18
Cu(II) complex	Styrene, vinylpyridine copolymer attached to silica spheres pretreated with *p*-nitrobenzyltrichlorosilane	S	Phenol polymerization. Heterogeneous catalyst more active than homogeneous polymeric catalyst	19
Cu(II) complex	Styrene, vinylpyridine copolymer	S	Polymerization of 2,6-dimethylphenol	20–22
Cu(II) complex	Styrene, *N*-vinylimidazole copolymer	S	Ligand to copper(II) ratio of catalyst determines whether C–O (polymerization) or C–C (dimerization) coupling occurs	23–24
Co(II) SalDPT (**8**)	Functionalized chloromethylated polystyrene bearing the Schiff base	C	Oxidation of 2,6-dimethylphenol predominantly to the *p*-quinone and some residual C–C coupled dimer	25, 26
Co(II) SalDPT (**8**)	as above	C	Oxidation of di-tertibutyl phenol to the *p*-quinone and some residual C–C coupled dimer	27

Cu(II) complex	Poly(L-lysine)	I/S	Selective oxidation of D-dopa over L-dopa. Oxidation of D-dopa involves a bifunctional coordination of the catechol and amino acid residues to copper(II) ions	28–30
Cu(II) complex	Poly(L-lysine) and copoly(D,L-lysine)	I/S	Asymmetric selective oxidation of dopa dependent on the helical nature of the polypeptide catalyst	31–32
Binuclear Cu(II) complex	Poly(4-vinylpyridine/styrene), dimethylaminomethylated polystyrene	S	Oxidative coupling of 2,6-diphenylphenol, and polymerization of 2,6-dimethylphenol. Catalytic activity of the macromolecular species at high loading levels of copper was hindered due to steric factors	33

[a] See Table 1.

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TABLE 11 (continued)

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the oxidation of dopa to the corresponding quinone by tyrosinase in the melanosome of the skin. With horseradish peroxidase-catalyzed oxidation of tyrosine it has been observed that D-tyrosine is more readily oxidized than L-tyrosine [175]. Contrarily, the enzyme lactoperoxidase catalyzes the oxidation of L-tyrosine more readily than the D isomer.

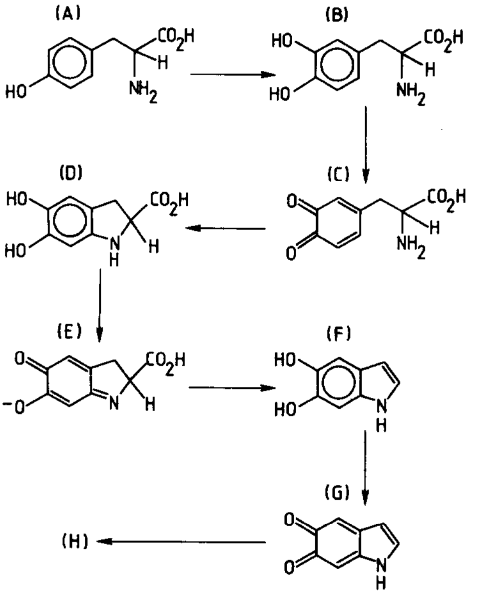

Fig. 6. Enzymatic pathway for the formation of melanin from dopa [174]. (A) tyrosine; (B) dopa; (C) dopaquinone; (D) leucodopachrome; (E) dopachrome; (F) 5,6-dihydroxyindole; (G) indole-5,6-quinone; (H) melanin polymer.

The oxidation of dopa by copper(II) complexes of poly(L-lysine) and poly(D,L-lysine) can proceed with appreciable asymmetric selectivity [168,169,172]. The helical structure of the amino acid residues about the catalytic site favors the binding of D-dopa over the L isomer. Possible factors which influence this specificity include the electrostatic field exerted by the polymer, its molecular weight and the helical content of the Cu(II)–polyamino acid complexes [171]. In comparison, the catalytic activity of these macromolecular copper(II) complexes exceed that of bis(ethylenediamine)copper(II) complexes in solution at both pH 6.9 and 10.5 [172]. An interesting facet of the catalytic process is that the oxidation of phenol may proceed by either the coordination of the catechol end groups to the copper(II) catalyst or through a bifunctional process whereby both the amino acid and the catechol end groups are coordinated to Cu(II) ions. It is through the latter process that selective oxidation of D-dopa proceeds [170].

(ii) Mechanisms of polymerization

Depending upon reaction conditions, catalyst composition and specific substituent (R) of 2,6-disubstituted phenols, polymerization of the monomeric phenol may occur through C–O and/or C–C coupling resulting in a 2,6-disubstituted polyphenylene oxide (PPO) and/or a tetrasubstituted diphenoquinone (DPQ), respectively (Fig. 7). The search for the mechanism of polymerization of phenols has resulted in some controversy in the literature. The circumstances favoring C–C or C–O coupling were not entirely clear some years ago [147,176], especially since the conditions favoring C–O coupling for 2,6-dimethylphenol result in C–C coupling for 2,6-diphenylphenol and vice versa [177,178]. Ditertiary butyl phenol is known to yield the C–C coupled product exclusively, diphenylphenol mostly the diphenoquinone and dimethylphenol mostly the C–O coupled polymer [179]. The Hammets σ value of the substituent of the phenol is proportional to the oxidation potential of the phenol, and the electron-transfer step is rate determining [150]. It has been suggested [147] that a radical mechanism operates in dimer formation and an ionic one for the polymer, whereas others [180,181] preferred the converse. Recent studies have done much to delineate the mechanistic pathways. It is now held that the copper(II) complex catalytic site is subject to a chemical transformation that explains the observations once considered incongruous.

Several workers have found that the presence of hydroxide in the catalytic system containing copper(II) chloride, whether in the homogeneous or polymer-supported phase, can profoundly affect the rate and specificity of the polymerization reaction [160,182–187]. It is currently thought that two

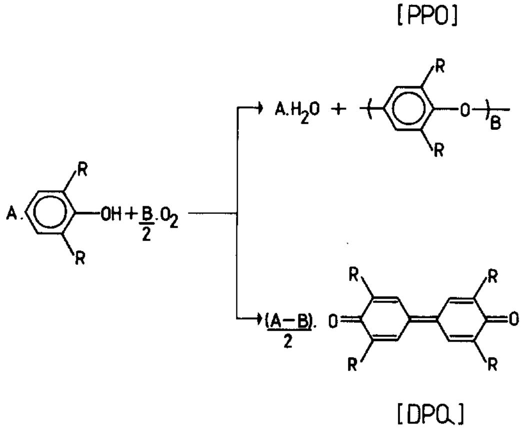

Fig. 7. Oxidative coupling of phenols.

types of catalytic sites exist; a copper(II) (nitrogenous base) chloro species and a copper(II) (nitrogenous base) hydroxy species. The two species are identified by their electronic absorption spectra [184], the former appearing as a blue and the latter as a green species in solution.

The chloro copper(II) (nitrogenous base) complexes are known to react with 2,6-dimethylphenol, yielding mainly the C–C coupled dimeric product and cannot be reoxidized by molecular oxygen to their original state [182,184,188,189]. The introduction of hydroxyl ligands to the catalytic center results in a change of the specificity of the catalytic center towards the

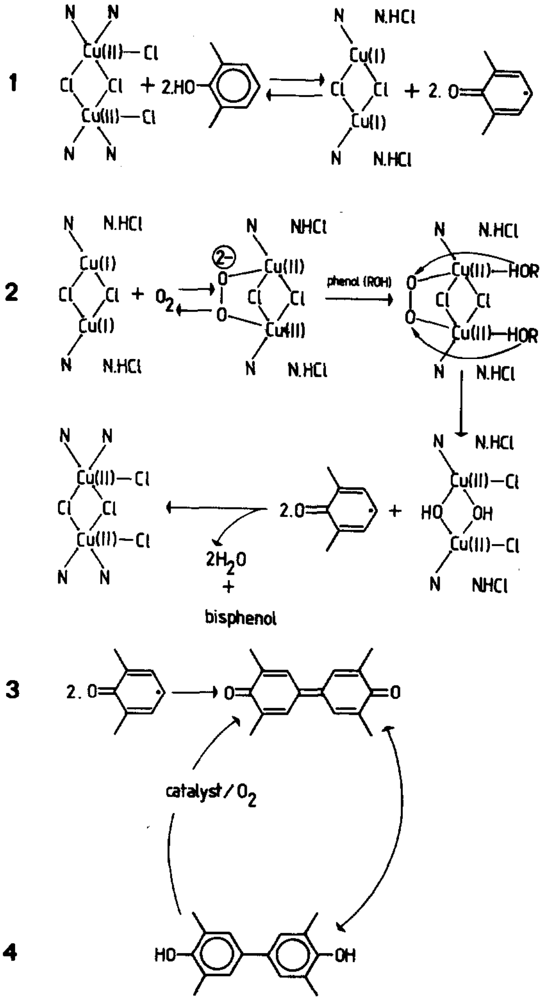

Fig. 8. Oxidative dimerization of phenols by polymer-supported $CuCl_2$ complexes [191]. "N" represents a nitrogenous base attached to the polymer.

production of the C–O coupled polymer [160,184,190]. Further, the catalytic site then becomes reoxidizable by oxidation with molecular oxygen.

An interesting observation is that the copper(II) catalytic center is undoubtedly a dimeric copper species. The possible manner in which the species reduces dioxygen has already been compared with that of the type-3 copper in laccase and the copper–copper pair in tyrosinase [191].

The monomeric chloro copper(II) nitrogenous base complexes [160,192], like their hydroxy counterparts [158,193,194], are known to exist as the chloro- and hydroxy-bridged dinuclear species, respectively. Not unexpectedly, the polymer-supported copper(II) catalytic center from chemical considerations [160], UV absorption [182] and ESR [160,182,191] data has also been established as a bridged dinuclear species. Other workers have also reported on dinuclear copper(II) species in a polymeric matrix [191,195].

With such a dinuclear catalytic site in mind, Challa et al. [184,190,191] favor an ionic polymerization mechanism and a radical process for the formation of the dimer. For 2,6-dimethylphenol, at least, it appears that the dinuclear hydroxy-bridged species catalyzes polymerization, and the dinuclear chloro-bridged species, dimerization (Figs. 8 and 9).

At present, the mechanism of the regeneration of the copper(II) complex by molecular oxygen is not completely understood, nor is it known whether the same mechanism is applicable to both the chloro- and the hydroxy-bridged dinuclear complexes. Kinetic data indicate that the reduction of oxygen proceeds through an intermediary peroxo complex [149,196,197] containing the catalyst, dioxygen and the substrate to produce water [191].

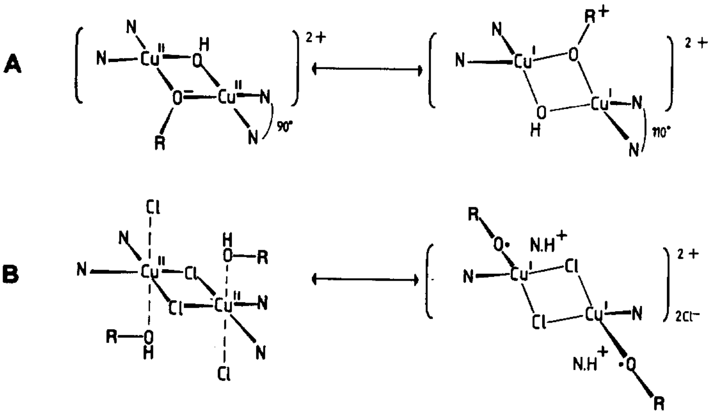

Fig. 9. Schematic representation of the different electron-transfer processes in the catalytic oxidative coupling of 2,6-dimethylphenol [184]. (A) polymeric hydroxo-bridged complex is acting as the catalyst; (B) polymeric chloro-bridged complex is acting as the catalyst. "N" represents a nitrogenous base within the polymer.

However, it has been pointed out that if hydrogen peroxide was the reduction product of O_2, the hydrogen peroxide itself is capable of oxidizing the copper(I) dinuclear catalytic species and yielding water in the process [184].

(iii) Influence of the polymeric matrix on the catalytic process

The rate and product distribution pattern of a catalyzed phenol coupling reaction may be strongly affected by the morphological characteristics of the polymeric matrix in which the catalyst is embedded. The polymeric redox catalysts enable a more rapid rate of oxidative polymerization [160,167,188, 189,192,198–200]. In some instances where the opposite trend is observed [183,198,199], steric hindrance imposed by the polymer about the catalytic center is believed to prevent the rapid coordination of the phenolate anion to the copper(II) species.

Tsuchida et al. [199] have observed that polymers which exert a non-polar field about the catalyst induce a more rapid reoxidation of the reduced copper species than polar matrices. The presence of non-polar groups such as styrene and benzene, either incorporated into the polymer or in the solvent blend, enhanced the overall catalytic activity. The wavelength of maximum absorption (λ_{max}) of the *d–d* transitions in the electronic absorption spectra of the copper(II) center was observed to decrease as the polarity of the polymeric ligand decreased (i.e. Cu(II)–Styrene, vinylpyridine copolymer, 700 nm; Cu(II)–polyvinylpyridine, 710 nm; Cu(II)–pyridine complex, 722 nm). From such evidence it was reasoned that in a less-polar matrix, the cupric state of the polymeric species was stabilized and the rate of oxidation of the reduced catalyst is therefore facilitated.

The polymeric copper(II) complexes of polyvinylpyridine may be partially quaternized to yield oxidative polymerization catalysts of a higher activity [167,199–201] than either the unquaternized polymeric or monomeric copper(II) complexes. The kinetic and thermodynamic parameters of the quaternized polymeric catalyst differ significantly from those of the monomeric species. The enhanced activity of the former may be viewed as the manifestation of a significant decrease in the activation enthalpy [167,192,199–202] and has been discussed more fully elsewhere [165,166].

The higher activity of the quaternized polymeric complex results from the electrostatic attraction between the copper(II)–QPVP polyelectrolyte and the substrate [167,202]. However, depending upon the solvent system employed, the selection of the quaternizing agent can be crucial to the resultant activity of the polymeric catalyst [199]. It has been observed that reagents which introduce non-polar N-substituted groups in the vicinity of the active site aid the catalytic process.

The favorable effects of the electrostatic charge of the quaternized species on the catalytic rate may be offset by the addition of such salts as $NaClO_4$, which shields the charges of the positively charged ligands and hinders the concentration of ionized anionic substrate near the cationic domain of the active center. The enhancement of a catalytic rate due to the operation of such a substrate concentration mechanism is not a new concept and has been observed in several other catalytic circumstances [81,203,204]. The association of substrate with unquaternized pyridine complexes [205,206] has been observed spectroscopically by a shift in the absorption spectrum of the substrate in the presence of the pyridine polymer [184].

The viscosity of a copper(II)–QPVP solution is inversely proportional to the percentage of copper(II) incorporated into the polymer, quite unlike its unquaternized counterpart. The presence of copper(II) ions causes a contraction of the polymeric coils due to intramolecular chelation. Upon reduction of the copper catalyst, increased viscosity and uncoiling of the polymer is observed. It appears likely that the coordinate bonds between the polymer ligands and the Cu(II) ion are weakened by the strain produced by the introduction of electrostatic repulsion within the polymeric matrix.

During the electron-transfer step, the rearrangement of a contracted copper(II)–QPVP to an uncoiled copper(I)–QPVP is aided by the strain within the polymer, and an enhancement of the overall catalytic process results.

The influence of the effects of the polymeric matrix on the thermodynamic and catalytic aspects of the oxidative coupling reaction for styrene/4-vinylpyridine and styrene/*N*-vinylimidazole copolymers have been investigated by Challa et al. [160,184,190]. The fraction of nitrogenous base units incorporated into the copolymer, α, was found to influence the behavior of the macromolecular catalyst in several ways. For instance, the solubility of the complexes and their copper complexes in various solvent systems decreases markedly with values of α greater than about 0.4. The factor α, however, has not been observed to exert any great influence on the specificity of the catalytic process.

The initial rate of the catalytic reaction is known to fluctuate as α is increased. A typical plot of "initial rate of reaction" versus "α" for an *N*-vinylimidazole/styrene macromolecular catalyst [190] is presented in Fig. 10. A similar curve is observed for a 4-vinylpyridine/styrene matrix [184], though in this case three maxima, instead of two, are observed.

The activation of the binuclear copper(II) complex involves a primary deformation of the binuclear substrate–copper(II) species, prior to the electron-transfer step, into a tetrahedral-like configuration [192].

As the magnitude of α increases, the conformation of the polymer about the active center changes, as represented in Fig. 11. Initially, the steric interaction between bridged-coordinated substrate and an intermediate chain

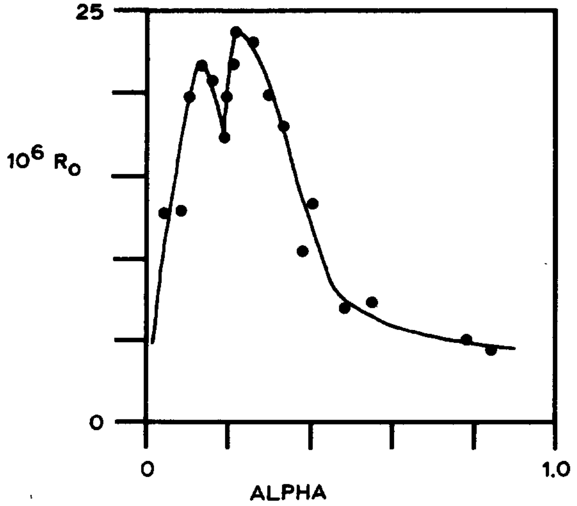

Fig. 10. Dependence of the initial rate of phenol polymerization (R_0) on "α" for an *N*-vinylimidazole/styrene copolymeric copper(II) catalyst [190]. R_0 is in units of mol O_2 dm^{-3} s^{-1}.

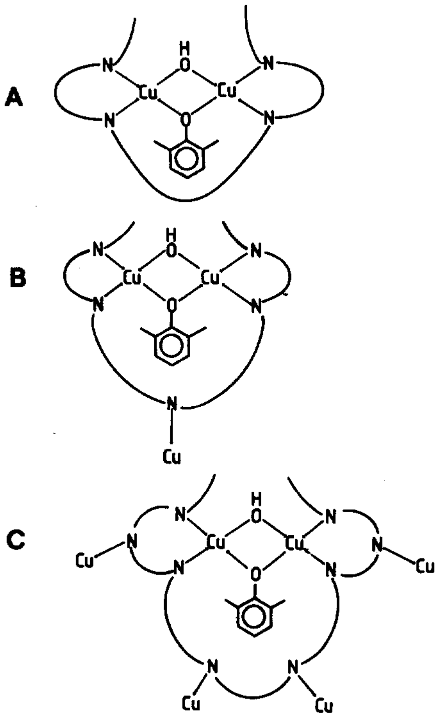

Fig. 11. Schematic representation of the coordination of a vinylpyridine/styrene copolymer with a binuclear copper–substrate complex throughout different fractions (α) of the functional comonomer vinylpyridine [184]. (A) $\alpha = 1/10$; (B) $\alpha = 1/6$; (C) $\alpha = 1/3$. "N" represents the vinylpyridine unit of the macromolecule.

segment between two coordinated nitrogenous groups in the polymer increases with an increase in α (decreasing segment length). The reaction rate is enhanced by this interaction, because the tetrahedral-like transition state becomes more favored over the original configuration.

At higher values of α, a neighboring nitrogenous residue in the polymeric coil has to be skipped in favor of the next adjacent group as the intermediate chain segment becomes too short to afford simple complexation. This trend results in dense coils that are intramolecularly cross-linked by the copper(II) binuclear species, and consequently becomes less soluble in the reaction medium. Problems of diffusion in and out of the polymeric matrix then limit the number of active sites to those located at the surface of the macromolecular complex [184,190]. The maxima and minima in catalytic activity throughout the spectrum of α values reflect the geometry of the polymeric chain about the active center.

H. AUTOXIDATION OF THIOLS

(i) Petroleum sweetening

Thiols (mercaptans) are frequently present in natural gases and in hydrocarbon distillates including kerosine and fuel oil. The thiols have corrosive properties [207,208] and adversely affect the octane number and tetraethyl lead response of automotive fuels, where the depressant effect of thiols is generally greater than that of the corresponding disulphides [209]. The major objection to the presence of thiols in fuels is concerned with their combustion to SO_2 and SO_3 which form the respective acids on contact with water.

The removal of thiols from gasoline fractions ("sweetening") is usually effected by scrubbing with aqueous sodium hydroxide whilst the amount of thiols in the caustic solution are converted to disulphides by either of several techniques of catalytic oxidation [210–213].

Among the most powerful oxidation catalysts for this process are cobalt(II) salts [210–214], cobalt(II) Schiff-bases [215,216] and cobalt(II) phthalocyanines [217–219].

Heterogeneous catalysts consisting of a cobalt(II) phthalocyanine supported on activated carbon have recently been employed to catalyze the autoxidation of thiols in petroleum fractions and caustic waste solutions [220–224] as outlined in Fig. 12.

$$4RSH + (1 + a)O_2 \xrightarrow[\text{base}]{\text{catalyst}} 2(1 - a)H_2O + (2a)H_2O_2$$

A highly successful process of petroleum sweetening is the U.O.P. Merox process [225,226]. Prior to 1980, it was estimated that more than 1000 Merox

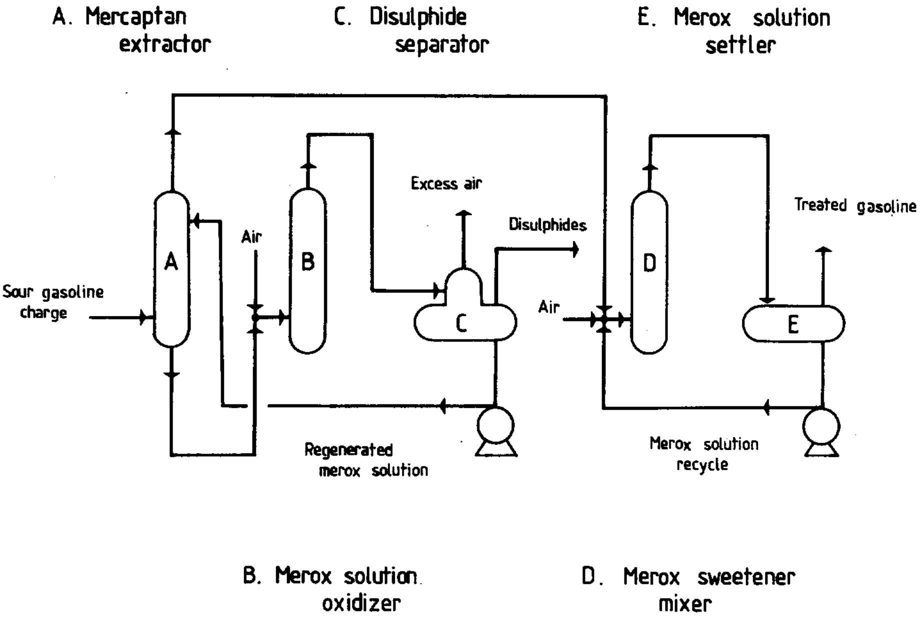

Fig. 12. Diagrammatic representation of the UOP merox process [225].

units were operating worldwide, processing in excess of 9 million barrels of oil per standard day [225]. This process employs a catalyst, usually a cobalt(II) phthalocyanine, on activated carbon to aid the autoxidation of thiols to disulphides in alkaline media. The Merox process (Fig. 12) functions by removing base-soluble thiols in a caustic scrub and thereafter converts the remaining thiols in the hydrocarbon fraction and those in the alkaline solution to disulphides.

Light hydrocarbon distillates usually undergo a caustic scrub whereas higher-boiling fractions with a lower thiol content are processed without undergoing the alkaline scrubbing operation.

(ii) Polymeric thiol oxidation catalysts

Recently, there has been some interest in polymer-supported thiol oxidation catalysts. The composition of these catalysts is presented in Table 12. The mode of attachment of the cobalt(II) phthalocyanines (**9**) to polymers has proceeded by covalently coupling the phthalocyanine annulus to the polymeric backbone, by coordinating the central cobalt(II) ion of the chelate to a pendant nitrogenous base in the polymer or by the sorption from solution of a water-soluble cobalt(II) sulphophthalocyanine onto an ion-exchange resin.

TABLE 12

Polymeric thiol oxidation catalysts

Redox active species	Polymeric matrix	Type	Comments	Ref. [a]
Cobalt(II) TPP	Covalent linkage through carboxy and amino groups of porphyrins to polystyrene beads	C	Oxidation of β-mercaptoethanol	1
Cobalt(II) TAPC	Coupling of the tetraamino phthalocyanine (TAPC) by means of cyanuric chloride to chloromethylated PS	C	as above	2
	or to polyacrylamide with aniline-substituted acrylamide groups	C	as above	2, 3
Cobalt(II) TCPC	Polyvinylamine (PVAm) or PVAm grafted onto polystyrene	S	as above	3–5
	Coupling by means of dicyclohexylcarbodiimide to PVAm or PVAm grafted polystyrene	C	as above	3–5
	Sephadex-DEAE dextran ion-exchange resin	I	Autoxidation of β-mercaptoethanol in aqueous and non-aqueous media by heterogeneous catalyst	6
Cobalt(II) TSPC	PVAm	S	Oxidation of β-mercaptoethanol	3, 7, 8
	Polyacrylamide(PAA) with pendant bis(3-aminopropyl)amine groups	S	as above	7
	Polyethyleneimine (PEI)	S	as above	7
	Sephadex-DEAE dextran ion-exchange resin	I	as above	6

Cobalt(II) phthalocyanine monosulphonate	Amberlyst A-21 and A-26 basic anion-exchange resins	I	Industrial-scale oxidation of mercaptans in aqueous caustic and non-aqueous media	9
Cu(II), Co(II) ions	Synthetic cation-exchange resins	I	Conversion of thiols to disulphides in aqueous solution	10, 11
Br_2	Bromine adduct of poly(2-vinylpyridine)	S	Oxidation of various thiols and cysteine for synthetic purposes	12
Benzoquinone	Polyvinylbenzoquinone	C	Oxidation of cysteine	13
Thiophenol	Polythiolstyrene	C	Columnar oxidation of thioglycollic acid or cysteine	14, 15

[a] See Table 1.

1 L.D. Rollmann, J. Am. Chem. Soc., 97 (1975) 2132.
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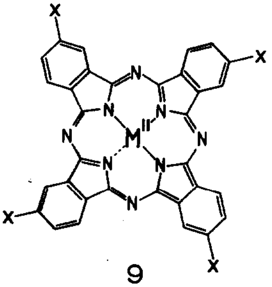
In several instances it has been found that polymer-supported cobalt(II) phthalocyanines catalytically oxidize thiols to disulphides more actively than the corresponding chelates in homogeneous solution as in the case of cobalt(II) tetraaminophthalocyanine (Co(II)TAPC) covalently coupled to water-insoluble polymers such as polystyrene and polyacrylamide [227]. The observation of a lower rate of thiol oxidation, as catalyzed by the cobalt(II) TSPC chelate in homogeneous solution, is thought to result from the formation in solution of the dinuclear species.



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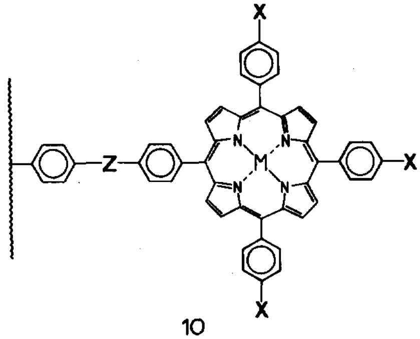
$RS^- \cdot TSPCCo(III) \cdot O_2^{2-} \cdot Co(III)TSPC \cdot {}^-SR$

It is thought that the formation of the latter species is prevented by covalent or coordinative attachment of the phthalocyanine catalysts to a polymer. The main evidence for the formation of the less-reactive dinuclear species in aqueous solution arises from the observation that the rate of thiol oxidation (as measured by oxygen consumption) decreases with an increase in oxygen pressure [228].

Solubility and flexibility of the supporting matrix in the reaction medium endows the polymer with morphological characteristics that offer less resistance to the transport of materials about the catalytic site. For example, the coordination of cobalt(II) TSPC to the amine moieties of the water-soluble polymers polyvinylamine (PVAm), polyacrylamide (PAA) and polyethylenimine (PEI) resulted in a 100–200-fold increase in the activity of the cobalt(II) chelate, even in the absence of alkali. Cross-linking of the polymer chains to a large extent may render the polymers less soluble in the reaction medium and consequently the catalytic rate of oxidation of thiol may be sharply reduced.

(iii) The state of the catalysts in the polymeric matrix

The covalent attachment of phthalocyanines and porphyrins to polymer matrices results in a monomolecular distribution of the chelates. Rollmann [229] managed to obtain magnetically dilute copper(II) tetraphenyl porphyrins in polystyrene (**10**). The ESR spectra of the latter showed distinct nitrogen and copper(II) hyperfine structure at room temperature, whereas solid or aggregated porphyrins do not exhibit such behavior [230]. Zwart and Van Wolput [231] also claim that with cobalt(II) tetraaminophthalocyanines covalently bonded to a cross-linked polyacrylamide resin, mononuclear catalytic sites can be isolated within the matrix. The good resolution of the ^{59}Co hyperfine structure in the parallel region supports their argument; however, swelling of the catalyst in water resulted in a considerable increase of the signal intensity due to the mononuclear cobalt centers. They estimated that in such a swollen state the fraction of truly mononuclear sites was about 30%. The remaining cobalt(II) species remain in an aggregated state and would therefore be ESR silent [232]. It is not yet known whether the extent of such intermolecular association affects the catalytic reaction to any degree.



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The association of monomeric metal–phthalocyanine complexes in aqueous solution [232,233] and in the polymer phase of wool [234,235] is well documented. From the electronic absorption spectra of cobalt(II) TSPC on PVAm ($\bar{P}_n = 570$), Schutten et al. [236] have demonstrated that the cobalt(II) chelate is more aggregated within the polymeric matrix than in aqueous solution alone. Their UV-VIS spectral results indicate that the cobalt(II) TSPC is sorbed onto the polymer in the strongly associated form even when the molar ratio of coordinating amine groups to chelate (N/C) is quite high.

The specific catalytic activity of cobalt(II)TSPC/PVAm complexes, at constant catalyst levels, was found to increase with an increase in the ratio, N/C. This effect was thought to arise partly from an increasingly monomolecular distribution of the catalyst within the polymer as N/C became greater. Skorobogaty et al. [237,238] have clearly shown the ability of water-soluble phthalocyanine chelates of copper(II), nickel(II), cobalt(II) and oxovanadium(IV) to vary in their degree of solute–solute interactions when sorbed onto an hydrophilic ion-exchange resin. The chelates can exist in an aggregated form on the resin, but may be dispersed in a distribution of monomeric forms by treatment of the chelate on the resin with aqueous solutions containing polar organic solvents or solutions at high pH.

(iv) The catalytic cycle

Interest in thiol oxidation catalysts for petroleum sweetening has put cobalt(II)phthalocyanines into the limelight. Many of the key investigations into the chemical behavior of these compounds have been performed on water-soluble derivatives, such as cobalt(II)tetrasulphophthalocyanine (Co(II)TSPC). The catalytic activity of these chelates is closely related to their ability to bind extraplanar ligands, undergo reversible reduction and reoxidation, and to act as carriers of molecular oxygen.

Kundo et al. [239–241] showed that the oxidation of cysteine by cobalt(II)TSPC operated by a reduction of the cobalt chelate with subsequent reoxidation by molecular oxygen. Dolansky et al. [242] thought the catalytic cycle involved the formation of a ternary complex, cysteine–Co(II) TSPC–O_2, and that no reduction of the chelate occurs. Cookson et al. [243], by means of ESR spectroscopy, demonstrated that effective catalytic oxidation of cysteine proceeds only in the pH range 4.0–9.0. Above pH ~ 9.5, oxygenation of cobalt(II)TSPC occurred, as well as a reversal of the catalytic cycle.

$$\text{pH } 4.0\text{–}9.0\ \text{Co(II)TSPC} \xrightarrow{\text{cysteine}} \text{Co(I)TSPC} + \text{cystine} \xrightarrow{O_2} \begin{array}{l}\text{Co(II)TSPC}\\ +\,\text{cystine}\end{array}$$

$$\text{pH } 9.5\text{–}12.0\ \text{Co(I)TSPC} \xrightarrow{\text{cystine}} \begin{array}{l}\text{Co(II)TSPC}\\ +\,\text{cysteine}\end{array} \xrightarrow{O_2} \begin{array}{l}\text{Co(III)TSPC}\cdot O_2\\ +\,\text{cysteine}\end{array}$$

In the oxidation of β-mercaptoethanol by cobalt(II)TSPC in aqueous alkaline solution, Zwart [228] discerned that the catalytic cycle proceeded by the initial reduction of the cobalt(II) chelate to the cobalt(I) species, which was subsequently reoxidized by molecular oxygen present in solution, to yield cobalt(II) TSPC, the corresponding disulphide, water and hydrogen peroxide. A schematic representation of the catalytic mechanism is presented in Fig. 13. In addition, this reaction was found to be of negative order with respect to oxygen. The reason for this is explained by considering two cycles in the catalytic reaction; one which involves a modestly active diamagnetic dinuclear species

$$RS^-\cdot \text{TSPCCo(III)}\text{–}O_2^{2-}\text{–Co(III)TSPC}\cdot RS^-$$

and involves the majority of the members in solution (the OXIDATIVE cycle), the second (the REDUCTIVE cycle) represents only the minority of species in solution, but accounts for nearly all of the observed catalytic

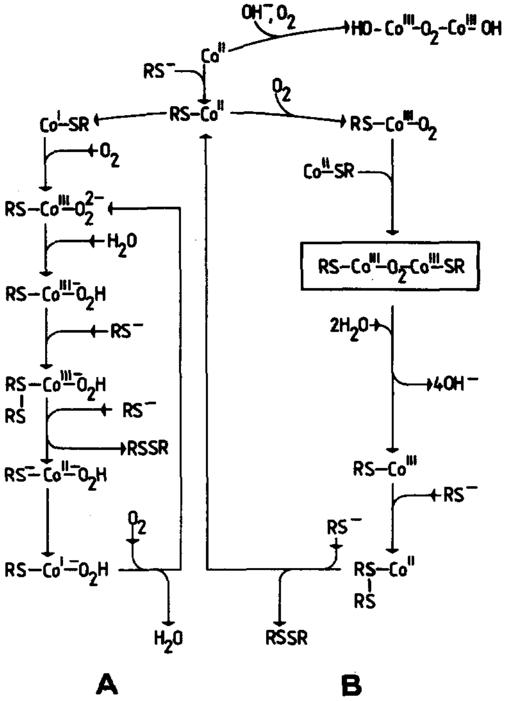

Fig. 13. Mechanism of thiol oxidation by cobalt(II)TSPC [228]. (A) Reductive cycle; (B) oxidative cycle.

activity. The reaction proceeds by the reduction of the cobalt(II) complex to the diamagnetic cobalt(I) TSPC. In the polymeric matrix, the chelates operate in a similar manner, though in certain cases isolating the reactive units can prevent the formation of the dinuclear peroxo species, as discussed earlier. The reduction and reoxidation steps are still observed in the polymer matrix. The oxygenation of cobalt(II) TSPC [237,244,245] and other complexes [246] within a polymeric matrix has been described.

(v) Ageing of the polymeric catalysts

The loss in the activity of polymer-attached cobalt(II) phthalocyanines in successive catalytic trials has been shown to be related to the extent of accumulation of hydrogen peroxide [247,248]. Rollmann [229] has noted that an "ageing" of polymer-attached porphyrins during the catalytic autoxidation of thiols occurs, and has ascribed this deactivation of the catalyst to the decomposition of the porphyrin by free-radical processes.

Various workers have shown that hydrogen peroxide may react with thiols to generate the corresponding disulphides [249–253] and small amounts of sulphur oxo-acids [254]. Thiols can also be converted to disulphides by hydroperoxides in the presence of alkylamines [251–253]. Alkylamines may react with the hydroperoxides to form alkylammonium peroxides which then oxidize the thiol. The "inhibitor sweetening" of distillate fuels relies upon such a process [210,211]. In the cases where cobalt(II) phthalocyanines are coordinated to amine-containing polymers, poisoning of the catalytic site probably results from the reaction of the amine groups in the polymer with sulphur oxo-acids and hydrogen peroxide. The inability of the amine groups proximal to the cobalt(II) chelate to participate in the promotion of the catalytic cycle results in a decline in the activity of the macromolecular catalyst.

The disproportionation of H_2O_2 to oxygen and water is catalyzed by various metal ions and complexes [225,256]. In biological systems the decomposition of H_2O_2 is performed by the enzyme catalase, which is a heme iron-protein containing four hemin groups per molecule [256]. The catalase-like activity of a number of metallophthalocyanines was investigated in recent years because of the structural similarity of phthalocyanines to the naturally occurring porphyrins. The phthalocyanine chelates of iron(III) [257], cobalt(II) [258], copper(II) [259] and oxovanadium(IV) [260] are known to catalyze the disproportionation of H_2O_2, iron(III) phthalocyanines being the most active.

Schutten and Beelen [254], and Skorobogaty and Smith [237] have shown that cobalt(II)TSPC in aqueous solution is irreversibly decomposed by H_2O_2 at acidic pH. In PVAm, cobalt(II)TSPC is less susceptible to such degradation, though at the same time, the catalase activity of the chelate is also impaired [254]. The catalase-like activity of certain *trans*-cobalt(II) and iron(III) complexes can also be severely inhibited when only one of the two available coordination positions is blocked by a ligand not displaceable by H_2O_2 molecules [261,262]. In an ion-exchange resin [237], cobalt(II)TSPC enjoys no such protection by the polymeric matrix and the chelate is subsequently decomposed.

It has been claimed [263] that manganese phthalocyanines can be used to decompose H_2O_2 produced in the industrial petroleum sweetening process, in conjunction with a cobalt(II) phthalocyanine catalyst.

The concept of a bifunctional polymeric catalyst, one with both a catalytic center to oxidize the thiol and another center to destroy the peroxide formed during the sweetening process, has been explored by Schutten [264]. Iron(III)TSPC, when used in conjunction with cobalt(II)TSPC in a PVAm matrix, as a dual thiol oxidation catalyst, does not improve the stability of the cobalt chelate. Presumably the thiolate anion competes successfully with H_2O_2 for coordination to a ferric center and prevents the catalytic decomposition of hydrogen peroxide.

I. ENZYME-MODIFIED ELECTRODES

The application of enzymes to electrochemical processes has developed rapidly over the last decade. A major development in this sphere has been the development of the enzyme electrode. The enzyme electrode consists of a normal conductive electrode coated with a layer of adsorbed, entrapped or bound enzyme to that the layer imparts a selectivity for a specific substrate to the electrode system as a whole. Primarily, the immobilized enzyme does not operate by an electrocatalytic mechanism, but rather occupies a secondary role in acting upon organic substrates to either consume or produce another compound, ion or gas which is sensed by the underlying electrode. There are a large number of variations on this theme and several reviews [265–274] and texts [275–282] tabulate the various types of enzyme electrodes, as well as discuss their application to analytical chemistry.

Enzyme electrodes are also finding application in various areas of bioelectrocatalysis, which encompasses the various phenomena associated with the acceleration of electrochemical reactions occurring at an electrode surface in the presence of specific enzymes [282]. The interest in bioelectrocatalysis has been stimulated considerably by the possibility of creating electrochemical transformers that oxidize different fuels and generate an electrochemical potential [283–285]. The class of enzymes known as the oxidoreductases operate by a redox mechanism during their biological function and these are particularly well suited for the catalysis of electrochemical reactions [286]. For some of these enzymes the number of elementary acts occurring at the catalytic site during catalysis can range between 10^6 and 10^8 per second. The chief problem in the bioelectrocatalysis of various reactions is not the activity of the enzyme itself but the coupling of the enzymatic and electrochemical processes. This problem has been solved by two fundamentally different strategies. Firstly, electrons have been transferred from the active site to the electrode by low-molecular-weight redox-active mediators, and secondly by tailoring the enzyme–electrode interface so that direct electron transfer between the electrode and the active site is possible (Fig. 14). Often, some kind of surface modification of the electrode is necessary for this to occur. The reversible heterogeneous reduction and oxidation of sperm whale myoglobin ($E^{0\prime}$ 0.046 V) at a gold minigrid electrode proceeded only very slowly unless the gold surface was modified with a layer of methyl or benzyl viologen ($E^{0\prime}$ -0.358 V) [287] which enabled electron transfer to the Fe(III) center of the enzyme. Spinach ferrodoxin behaves similarly at a gold electrode [288]. In the absence of the viologen surface modification, ferrodoxin is reduced or oxidized heterogeneously very slowly and is irreversibly denatured. Often, electrochemical reactions of enzymes on metal electrodes are irreversible. The electrochemical behavior of most enzymes on mercury electrodes is composed primarily of the redox reactions of thiol and disulphide moieties of the protein [289,290].

$$2H^+ + RSSR + Hg \rightarrow (RS)_2Hg + 2H^+ \underset{-2e}{\overset{+2e}{\rightleftharpoons}} 2RSH + Hg$$

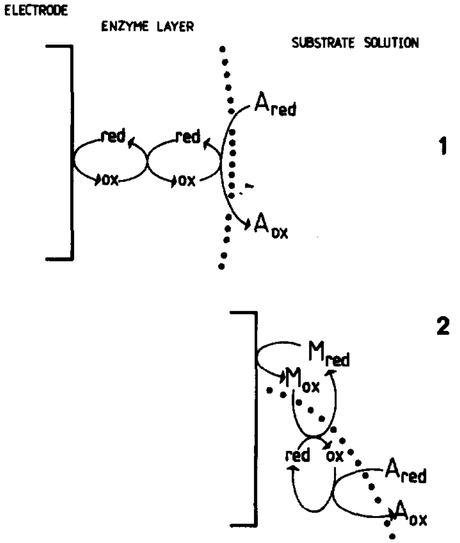

Fig. 14. Pathways of enzyme-mediated electrochemical reduction and oxidation. (1) Direct electron transfer through the enzyme layer to the electrode; (2) electron transfer from the enzyme to the electrode requires an electroactive mediator. A represents a substrate. B represents a free electron mediator. Ox and Red refer to the oxidized and reduced forms of the active site in the enzyme layer.

and even the interior SH groups of the protein can participate in this process [291,292].

The examination of the electrochemical behavior of enzymes in solution at the surface of an electrode have yielded much information about the redox and conformational behavior of enzymes as they might function in an enzyme electrode prepared by simple adsorption techniques. Where there is a simple adsorption of an enzyme onto a polarized carbon or metal surface, the outcome of adsorption of the first molecular layer is irreversible denaturation of the enzymes' ternary and quaternary structure [292–295]. The protein matrix becomes partly unfolded due to a flattening under the electrochemical potential [292–294], but this prevents the denaturation of the second adsorbed layer and electron exchange proceeds by way of the first adsorbed layer [295,296] or through pores in the coverage of the first layer. The process of protein flattening in the first adsorbed layer can in some cases lead to an improved contact of coenzyme groups (FAD, FMN) within the protein matrix with the electrode surface, but this phenomenon is very much a function of the secondary structure of the enzyme. The monolayer protein film is an insignificant obstacle for the discharge of small electroactive molecules such as riboflavin or hemin [293] at the electrode surface, and the kinetics of intermolecular (enzyme–enzyme or enzyme–coenzyme) electron transfer are known to depend on such factors as buffer concentration, screening of charged groups and channels of matrix conduction [296,297].

The techniques associated with the immobilization of enzymes onto various surfaces in electrochemical devices and biochemical reactions have been thoroughly dealt with in previous reviews [298–305]. Enzymes immobilized in polymeric matrices or copolymerized with suitable cross-linking agents are also capable of undergoing reversible electron transfer with an electrode surface by either the direct or mediated schemes discussed earlier.

Direct electron transfer from an electrode to an enzyme layer without the need for redox mediators has been demonstrated successfully. The cyclic voltmetric characteristics of urease adsorbed onto a thermistor mercury electrode have been studied [306]. The reduction and oxidation peaks (-0.58 V vs. SCE) of the adsorbed enzyme appear to be characteristic of insulin and albumin proteins and more specifically, of disulphide bonds in the enzymes' protein envelope. This reduction of the enzymes' disulphide bridges denatured the enzyme and the drop in the thermistor temperature signalled the destruction of the enzyme activity. Reoxidation of the enzyme restored the catalytic activity, which remained unaltered after several cycles of reduction and reoxidation. Galactose oxidase contains a single copper ion and is inactive when the copper is in the reduced form, Cu(I), and active when the Cu(II) state prevails [307]. Johnson et al. [308] found that they could control the oxidation state of immobilized galactose oxidase in a thin layer cell by the mediation of the ferricyanide–ferrocyanide couple. Tungstocyanide, 2,6-dichlorophenolindophenol, tetracyanomonophenanthzoline ferrate and cobalt terpyridine complexes also proved to be reliable. Enzymes have been coupled to synthetic polymers and used as electrocatalysts in various electrode processes. Several examples of these are shown in Table 13.

Several groups have investigated the electrocatalytic oxidation of molecular hydrogen by immobilized hydrogenase enzymes [283]. In such systems one may organize the electrochemical oxidation of hydrogen by transforming the chemical energy of the fuel into an electrochemical potential The mechanism of bioelectrocatalysis in this instance involved the enzymatic reduction of methylviologen by molecular hydrogen with electrochemical reoxidation of the viologen mediator [283–285,309–311]. The reversible electrochemical oxidation and reduction of the mediator at pyrographite electrodes, though kinetically hindered by the diffusion of the reagent

TABLE 13

Electrocatalysis by polymer-coupled oxidoreductase enzyme electrodes

Enzyme	Immobilization technique	Application	Comments	Stability	Ref. [a]
Lactate dehydrogenase (EC.1.1.1.27)	(1) Covalent coupling of the enzyme and NAD to a cellulosic dialysis membrane with glutaraldehyde. Resultant membrane fixed onto carbon electrode or	Analytical detection of lactate by conversion of lactate to pyruvate $CH_3 \cdot CHOH \cdot CO_2^- \rightarrow CH_3 \cdot CO \cdot CO_2^- + \text{pol-NAD}^+ + \text{pol-NADH} + H^+$	Non-linear response profile in phosphate buffer, pH 8. Determination of as little as 4×10^{-6} M substrate	50% loss of activity in 55 h	1
	(2) entrapment of agarose-bound NAD^+ at electrode surface by enzyme-laden dialysis membrane	as above			
Laccases	Irreversible adsorption onto pyrographite, glassy carbon or carbon black electrodes	Reduction of oxygen to water in the range +1.20–0.60 V	Enzyme electrocatalysis inhibited by azide and fluoride ions	Little decrease in activity up to 50 h	2–4
Alcohol dehydrogenase (EC.1.1.1.1.) Lactate dehydrogenase (EC.1.1.1.27) Glutamate dehydrogenase (EC.1.4.1.3)	Solution of the enzyme, mediator and dextran–NAD^+ polymer held over a Pt disc by a dialysis membrane	Determination of ethanol, lactate and glutamate by measuring current developed upon oxidation of substrates	Linear calibration curves for glutamate, lactate and ethanol were linear to 0.5., 1.5 and 100 mM respectively	Alcohol and lactate sensitivity decrease by 50% within 60 h, and that of glutamate in 6 h	5

Lactate dehydrogenase (EC.1.1.1.27)	(1) Constraint of enzyme solution and agarose-bound NAD^+ over glassy carbon electrode by dialysis membrane or (2) covalent coupling of enzyme and NAD^+ to cellulosic membrane by glutaraldehyde	Determination of lactate by measurement of current produced upon oxidation of substrate	Measurement of substrate in the range 0–4.5 mM. Electrode (1) was usable at lower applied potentials	50% decrease of activity in 50 h	6
Glucose oxidase (EC.1.1.3.4)	Photopolymerization of enzyme with acrylamide into a gel on a Pt gauze electrode	Oxidation of glucose to gluconic acid and H_2O_2	Linear zero-current potential pH characteristics		7
	Covalent coupling of enzyme to a cyanuric chloride modified graphite electrode	Differential pulse voltametric study	Peak potential (−0.5 V) of bound enzyme, 100 mV more positive than free enzyme in solution		8
	Electroinitiated polymerization of enzyme with glutaraldehyde at 0.4 V on a Pt screen or photopolymerization of enzyme with acrylamide and FAD into a gel on a Pt screen	Oxidation of glucose (0–140 nM) to glucanolactone	Half-cell potentials of electrodes depend upon manner of immobilization	Stable over 10-day period	9
Peroxidase	Adsorbed onto a carbon electrode	Reduction of H_2O_2 and *o*-dianisidine	Rate of process is both pH and substrate concentration dependent		10, 11

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[a] See Table 1.

1 I.V. Berezin and S.D. Varfolomeev, Appl. Biochem. Bioeng., 2 (1979) 259.
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through the enzyme layer at the electrode surface, enables a reversible redox hydrogen potential at the electrode to be established and makes it possible to perform hydrogen electro oxidation or evolution. The kinetics of the redox processes in the enzyme film have been discussed at length by Varfolomeev et al. [286,309,312]. The activation of molecular hydrogen by hydrogenase involved the heterolytic splitting of the hydrogen molecule accompanied by the transition of two electrons to the enzymes' iron–sulphur cluster active site. This enzymatic reaction is energetically more advantageous (33 kcal/mol) than homolytic splitting of the molecule (104.5 kcal/mol) [284]. Varfolomeev et al. [313] designed an hydrogenase electrode with a view of realizing mediatorless electron transport between the electrode and the catalytic site. Hydrogenase was immobilized in a polymer-gel having semiconducting properties and the polymer–protein matrix was active in the electrocatalysis of molecular hydrogen evolution. The reduction of molecular oxygen in water takes place at a high over-voltage even on platinum group metals which are the most active catalysts of this reaction. Depending on the material and on the surface condition of the electrode, molecular oxygen can undergo reduction directly to water or through the formation of H_2O_2.

The electrocatalytic cathodic reduction of oxygen by enzyme electrodes is being rapidly developed. Although direct electron transfer from hemoprotein to a mercury electrode is known [296], the electrochemical behavior of peroxidase at mercury electrodes appears to involve only reduction and oxidation of the protein disulphide bonds [314]. Yaropolov et al. [315] were unable to induce direct electron transfer between horseradish peroxidase and pyrographite electrodes. The cathodic reduction of oxygen to H_2O_2 was mediated by manganese ions and quinone/hydroquinone in the presence of the enzyme, and these effected a shift in the reduction potential of oxygen by about 300 mV to the positive region. Similar results have been obtained using cytochrome-*c* oxidase in conjunction with tetramethylparaphenylenediamine [316].

Mediatorless electron transfer from the electrode to the enzyme active site during oxygen electroreduction has been noted for tyrosinase and laccase adsorbed onto carbonaceous electrodes [284,285,317–319]. Adsorbed laccase was more efficient in oxygen reduction than tyrosinase, the latter requiring mediators such as caffeic acid before it approached the activity of laccase [285]. Tarasevich et al. [317,318] have further shown that laccase adsorbed on carbon-black electrodes shifts the potential towards the positive side and accelerates O_2 electroreduction to H_2O in the 1.2–0.6 V range. The potential can reach 1.2 V, which is close to the oxygen equilibrium potential. The oxygen reduction mechanism at the cathode varied with the electrode potential and the proposed reaction scheme for oxygen reduction by laccase supported on an electrode is outlined in Fig. 15. At polarizations less than

0.6 V, the enzyme underwent partial inactivation, probably as a result of H_2O_2 formation on the carbon-black electrode. That laccase does not practically catalyze the anodic oxidation of water except at potentials close to 1.2 V may arise from the oxidation of the copper atoms at the active center [318]. The biomimetic electroreduction of O_2 to H_2O_2 has also been achieved by Ru(III) histamyl [320] and cobalt(II) complexes [321,322] in a polymer matrix on carbon electrodes. The direct electron transfer between the enzyme's active site and the electrode surface has also been demonstrated for some flavoenzymes (containing flavin adenine dinucleotide, FAD, or flavin mononucleotide, FMN) via alternating current and differential pulse polarography [323–325]. In these systems adsorption of the enzyme onto the mercury metal aided in the reduction process due to protein flattening and the concomitant exposure of the active center to the electrode surface. Direct electron transfer to FAD in glucose oxidase (GO) covalently coupled to a cyanuric chloride modified graphite electrode has also been demonstrated [323]. The binding of the electroactive prosthetic group to the protein matrix of the enzyme generally causes steric hindrance of the electron exchange with the electrode and so a number of authors have found that flavoproteins such as GO cannot be reduced at the electrode surface [326,327], probably as a result of the particular absorption or immobilization technique.

$$L + O_2 \longleftrightarrow LO_2$$

$$LO_2 + e^- \longleftrightarrow LO_2^-$$

$$LO_2^- + H^+ \longrightarrow LO_2H \quad (\Delta U = 1{\cdot}15 - 1{\cdot}11\ V)$$

$$LO_2H + 2e + H^+ \longrightarrow LO^- + H_2O \quad (\Delta U = 1{\cdot}20 - 1{\cdot}15V)$$

$$LO^- + e^- + H^+ \longrightarrow LOH^-$$

$$LOH^- + H^+ \longrightarrow L + H_2O$$

Fig. 15. Oxygen reduction mechanism by a Laccase-electrode system [317]. L represents the enzyme laccase.

Many enzyme electrodes used in analytical devices have no renewable source of coenzyme and thus the development of systems with enzymatic regeneration of coenzymes [328] were designed to overcome this shortcoming. The feasibility of electrochemical recycling of NAD^+ and other coenzymes associated with bioelectrochemical cells [329–331] provided the impetus towards the creation of polmeric NAD^+, a macromolecular coenzyme [34–40] that mediated electrogeneration of the active site of several oxidoreductases. Several authors [332,333] have recently used polymeric NAD^+ to mediate electron transfer to lactate dehydrogenase, glutamate dehydrogenase and alcohol dehydrogenase in an enzyme electrode assembly.

$$AH_2 + \text{pol-NAD}^+ \rightarrow A + \text{pol-NADH} + H^+$$

$$\text{pol-NADH} \underset{\text{Pt electrode}}{\rightarrow} \text{pol-NAD}^+ + H^+ + 2e$$

Malinauskas and Kulys [332] coupled succinyl-NAD$^+$ to 8-amino-octyl dextran with the use of dicyclohexylcarbodiimide. However, in their construction of a Pt/dextran-NAD$^+$/dehydrogenase electrode, they found that reoxidation of pol-NADH occurred very slowly and at potentials too high for any kind of substrate selectivity to operate. The use of a second electron relay, phenazine methosulphate (PMS$^+$), enabled a rapid reoxidation of the polymeric NAD$^+$ and thus of the enzyme itself.

Other approaches to the problem of electrochemical regeneration of an enzyme immobilized on an electrode have included the co-immobilization of riboflavin with glucose oxidase (GO) and catalase in a polyacrylamide gel [334,335], FAD with GO in polyacrylamide gels or by cross-linking with glutaraldehyde [336]. Similarly, the construction of a lactate-sensitive electrode was made possible by the co-immobilization of LDH and NAD$^+$ onto a cellulosic membrane coating the electrode surface or by trapping a layer of agarose-bound NAD$^+$ between the electrode surface and a cellulosic film containing the enzyme [333]. The importance of these accomplishments, however, should not overshadow the potential of enzyme electrode fuel cells that operate without the need for polymeric electron mediators to the enzyme. Drake [337] has studied the use of glucose oxidase in a fuel cell operating on glucose and oxygen. The poor electron transfer between the carbonaceous electrode and the enzyme remains an obstacle. Wingard et al. [338] circumvented this problem of poor electron transfer to immobilized GO in an analytical cell for the determination of blood glucose by measuring the potential difference between an enzyme electrode–reference electrode combination and a blank electrode–reference electrode couple. Their method proved sensitive enough to determine glucose concentrations to at least 3×10^{-4} M. Once again, the successful fabrication of glucose-sensitive electrodes with direct electron transfer to GO in a polyacrylamide gel on Pt gauze by Wingard et al. [339] is a petition for continued investigation into mediatorless enzyme electrodes.

J. REDOX POLYMERS IMMOBILIZED ON ELECTRODES

(i) Electrocatalysis

The coating of electrodes with both monomeric redox active species and electroactive polymers is rapidly developing. With the recent wave of interest

TABLE 14

Some applications of polymer-coated electrodes

Electroactive moiety attached to polymer	Polymeric matrix	Type	Comments	Ref. [a]
Ferrocene	Polyvinylferrocene (PVF) on a Pt electrode	C	Reference electrode	1–3
Nitrobenzene	Polyvinylnitrobenzene	C	Reference electrode	4
Ru(III) histamyl complex and a Cu(II) phenanthroline complex	Ru(III) histamyl–acrylic acid copolymer incorporating sorbed Cu(II) (*o*-phen)$_2$ species (**12**)	C, I	Electroreduction of O_2 to H_2O_2. Cu(II) complex aids the decomposition of H_2O_2 to H_2O	5
Cobalt(II) phthalocyanine	Phthalocyanine pendant polystyrene	C	Reduction of oxygen to H_2O_2	6
Cobalt(II) ions	Modified polyacrylonitrile	I	Electroreduction of oxygen in acidic and alkaline media	7
Ru(II)(bipy)$_2$Cl$_2$	Poly(4-vinylpyridine) (P4VP)	S	Catalytic reduction of aqueous Ce(IV) and oxidation of aqueous Fe(III) ions	8
Ir(IV)Cr_6^{2-}	Protonated P4VP on a graphite disk electrode	I	Catalytic oxidation of aqueous Fe(III)	9
Ru(II)edta complex	P4VP on a graphite disk electrode	S	Catalytic reduction of $Fe(CN)_6^{3-}$	9
$Fe(CN)_3^{3-}$	Polymerized silane monomer $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$ on a Pt electrode	I	Electrocatalytic oxidation of ascorbic acid	10
Alanine, lysine	60% Lysine, 40% alanine copolymer	C	Catalytic reduction of *n*-propyl-3,5-dinitrobenzamide and ferrocene	11
Nitrobenzene	Poly-*p*-nitrostyrene	C	Catalytic reduction of *meso*-1,2-dibromo-1,2-diphenylethane to *cis*- and *trans*-stilbene	12, 13

as above	as above	C	Catalytic electroreduction of oxygen in acetonitrile	4
Dopamine	Dopamine pendant polymethacryloylchloride on a carbon electrode (13)	C	Electrooxidation of NADH	14
Viologen	Electropolymerized viologen on a gold Minigrid electrode	C	Catalytic reduction of spinach ferrodoxin and sperm whale myoglobin	15, 16
as above	Viologen–silane polymer based on the monomer (14)	C	Polymeric bilayer electrode with poly Ru(II) (vinyl–bipy)$_3$ for the analysis of trace dioxygen in solution	17
Vinyldiquat (22)	Polyvinyldiquat	C	Electrocatalytic reduction of dibromo diphenylethane	17
Viologen	Binary polymeric electrolyte consisting of poly(xylylviologen) and poly(styrenesulphonate)	C	Reduction of $Fe(CN)_6^{3-}$ and possible use as an electrochromic film	18
as above	Poly(*N*-vinylviologen) on a gold electrode	C	Catalytic reduction of horse heart ferricytochrome C	19
Eugenol [2-methoxy-4-(2-propenylphenol)]	Vinyllic monomer electropolymerized onto a glassy carbon electrode	C	Catalytic reduction of NADH and oxidation of ascorbic acid	20
Pyrrole	Electropolymerized pyrrole on a Pt electrode	C	Oxidation of ferrocene and halides at low electrode potentials	21, 22
$(bipy)_2py \cdot RuO^{2+}$	P4VP on glassy carbon, reticulated vitreous carbon electrodes, Au and Pt disk electrodes	S	Catalytic oxidation of 2-proponol, *p*-toluic acid and mixed xylenes	23
$IrCl_5(acetonato)^{2-}$	Plasma-polymerized P4VP film on glassy carbon electrodes	I	Catalytic oxidation of ascorbic acid	24
Cobaltocene	Polyethyleneimine coupled moieties dip coated onto a glassy carbon electrode	C	Reduction of benzaldehyde and benzophenone to the radical ion which dimerize to yield pinacol	25

TABLE 14 (continued)

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[a] See Table 1.

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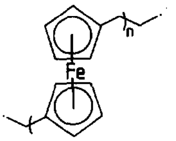
in electrocatalysis and organic electrosynthesis [340,341], redox polymers are finding their niche in the various endeavors associated with chemically modifying electrodes [342–345].

In electrocatalysis, the electroactive moiety attached to the electrode may act as a fast electron-transfer mediator for a substrate dissolved in the contacting solution and only very slowly reduced or oxidized by the bare electrode. Polymeric electrode coatings are appealing on several counts. The electrochemical response of the immobilized redox polymer on the electrode does not usually require as much chemical sophistication as the preparation of monolayers of the electroactive moiety on the electrode's surface.

Although the art of constructing redox polymer electrodes is well advanced, their practical utility is only in its infancy. In Table 14 a summary of the applications of redox polymers in electrocatalysis is presented. Andrieux et al. [345] have devised a kinetic model for stationary voltametric techniques, such as rotating disc voltametry, used to probe the catalytic activity of redox polymer film electrodes. Besides the diffusion of the substrate from the bulk of the solution to the film–solution interface, three kinetic factors determine the magnitude of the catalytic current: transport of electrons from the electrode surface to the film–solution interface; diffusion of substrate in the opposite direction; and the rate of the rate-determining step of the catalytic reaction.



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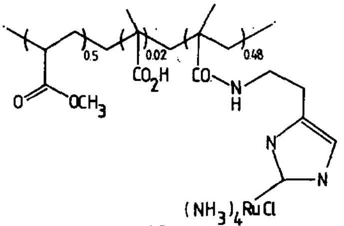

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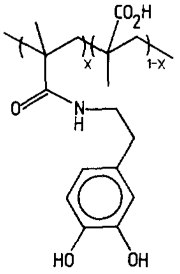

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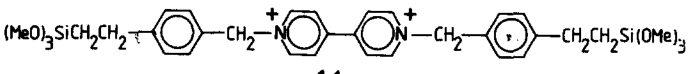

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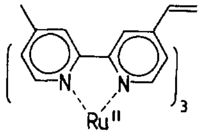

15

(ii) *Conduction of electrons through a redox polymer*

The transfer of electrons through a redox polymer to a species in solution can transpire through electron or hole conduction in the valence band of the polymeric film or by the continuous electron exchange between electroactive species of the polymer to the polymer–solvent interface, whether that be in a zone within the actual film (a channel or pore) or external. The latter mode of electron transfer from the electrode predominates among the type of electroactive films now being investigated and has been described theoretically by Laviron [346]. The process of electron transfer between the electroactive species in solution and the polymer surface may be described by current theories of interfacial electron transfer [347].

That redox polymers actually participate in mediated electron-transfer processes between the electrode surface and the substrate in solution has already been demonstrated successfully [288,348–354]. In some cases where the morphology of the polymer permits, electron transfer between the polymer and the substrate occurs within the redox film and even at the electrode surface. The experimental evidence for this phenomenon [350,351,355,356] has been described in theoretical terms by Peerce and Bard [355]. Experimental strategies employed in probing charge transport in redox polymers have included the variation of temperature [351,357], solvent [358,359], supporting electrolyte [360,361], extent of cross-linking [362] and layered film effects [363]. Others have investigated the effects of the concentration of charge carriers in the redox film on the electron conduction process [364,365]. Recent attempts to describe mathematically the electrochemical behavior of redox active macromolecular assemblies [349,355,366–369] have culminated in the successful digital simulation of the cyclic voltametric behavior of redox polymeric electrode coatings [361].

The electron hopping mode of electron transport through an electroactive polymer has been studied extensively in ferrocene-containing polymers. Ferrocene–ferrocinium polymers [370,371] conduct electrons by a metal to metal hopping process without participation of the organic framework. In a situation where a metal complex is supported in a polymer matrix, the metal complexes adopt a geometry peculiar to their particular oxidation state and constraints to changes in geometry upon oxidation or reduction adversely affect the conductivity of the polymer [372]. Biologically conducting polymers which transport electrons through metalloproteins with metal sites 2.5–5.0 nm apart avoid this problem as the geometry of the metal complex is usually a compromise between the oxidized and reduced states [373,374]. The importance of polymer chain motion to the redox process of polymeric anthraquinones on a mercury electrode has been discussed by Degrand and Miller [375]. Polymers with a higher loading of anthraquinone units become more inflexible and the charging of the bulk of the coating is more difficult. After continuous cyclic oxidation and reduction of electropolymerized films of Ru(phen)_3^{2+}, it was observed that the cathodic peak gradually became less reversible. It is thought that this results from a slow conformational change of the polymer about the redox active center which causes an inhibited counterion efflux from the film [376].

The transport processes which are necessary for the electrochemical activity of redox polymer electrode coating (RPEC) are strongly dependent on the morphology of the polymer matrix. The morphological characteristics of a polymeric film are manifested in such quantities as the free volume content of the film and its sensitivity to swelling by solvents.

The electrochemical production or destruction of fixed charged sites in an RPEC is accompanied by movement of electrolyte counter ions to maintain electroneutrality. The generated osmotic pressure creates a solvent flow within the polymeric film which at equilibrium is counterbalanced by the opposing energetics of expansion (or contraction) of the polymeric lattice [377]. The degree of swelling of the RPEC in a particular solvent can determine the accessibility of the redox sites in the matrix and affect the kinetics of electron hopping and counter-ion flow. Generally, swelling of a polymeric film is promoted by a solvent of similar polarity to the polymer, by the presence of fixed ionic sites, but can be opposed by a swelling-induced decrease in configurational entropy [378].

Several workers [35,358,379,380] have demonstrated that a redox polymer, though electroactive in one solvent, may not be active in another. Ru(III)edta/PVP for example, though electroactive in aqueous media, is completely inactive in solvents such as dimethylsulphoxide.

Cyclic voltammograms of redox polymers on electrodes may show nonsymmetrical waveshapes due to the different morphological and solubility characteristics between the oxidized and reduced forms of the polymeric coating [352,379,380]. The different degrees of broadening of anodic and cathodic cyclic voltammetric waves in a particular solvent is typified by the behavior of PVF(**11**). Smith et al. [380] found that the cyclic voltammogram of PVF in methylene chloride displayed a larger current-voltage peak for the reduced species. This asymmetric distortion of the peak intensities for the oxidized and reduced species of polyvinylferrocene was believed to arise from the poor swelling and solubility properties of PVF^+ in the solvent. In hexamethylphosphoramide however, such behavior was not observed.

The rates of permeation of electroactive solutes through thin films of redox polymers on electrodes, and the relevance of this phenomena to electron self-exchange reactions within the film has been discussed by Ikeda et al. [381].

Schroeder and other workers [352,379,380,382,383] have shown that the rate-limiting process during the oxidation of several ferrocene- and pyrazoline-containing polymers was the transport of counter ions to the charged moieties in the polymer phase. The rate of oxidation of phenoxy-tetrathiafulvalene (phenoxy-TTF) polymers in 0.1 M solutions of tetraalkylammonium salts in acetonitrile was examined chronoamperometrically and was

TABLE 15

Some electroactive polymers bound to electrodes

Electroactive moiety attached to polymer	Polymeric matrix	Type	Comments	Ref. [a]
Ferrocene	Polyvinylferrocene (PVF)	C	Plasma discharged monomer onto Pt or oxide free glassy carbon electrode	1–6
Ferrocene	PVF	C	Electrodeposition of prepolymerized PVF onto a Pt electrode	7–10
	PVF	C	Photodeposition of PVF onto a Pt electrode	11
Ferrocene	Vinylferrocene–styrene copolymer	C	Spin coating of polymer solution onto a Pt disk electrode	12
Ferrocene	Polymethacrylchloride (PMAC) with pendant ferrocene groups	C	Covalent bonding of PMAC to SnO_2 electrode, followed by attachment of hydroxymethylferrocene to the PMAC film	13
Ferrocene	as above	C	Electrodeposition of PMAC-ferrocene onto an SnO_2 electrode	13
Ferrocene	Vinylferrocene–acrylonitrile copolymer	C	Electrodeposition onto a Pt electrode	10
Ferrocene	PVF	C	Absorption of PVF onto a Pt/poly-Ru(vinyl–bipy)$_3$ electrode to form a redox polymer bilayer film	14–16
Cobaltocene	PEI-bound chlorocarbonyl cobaltocinium hexafluorophosphate	C	Dip coating of glassy carbon electrode	17
η^5-$C_6H_5 \cdot Fe$-$\eta^6 C_6Me_6$	Bound to a polystyrene matrix	C	Adsorption onto mercury electrodes for polarographic studies	18

Ru(II)(bipy)$_3$ type complex	Poly[tris-(4-methyl-4′-vinyl-2,2′-bipyridine)Ru(II)] perchlorate	C	Electrochemical polymerization of the monomer onto a Pt disk electrode	1
Ru(III)edta	Polyvinylpyridine (PVP)	S	Dip coating of performed PVP–Ru(III) complex onto graphite electrode	19–22
as above	PVP	S	Methanol–PVP solution evaporated on a graphite electrode. Complex adsorbed into film from solution	23, 24
Ru(II)(bipy)·Cl$_2$	PVP	S	Dip coating of various types of elemental electrodes with the precomplexed polymer	25
Cobalt(II) ions in polymer matrix	Polyacrylonitrile containing decomposed Co(II) (acac)$_3$	S/I	Glow discharge polymerization of cobalt(II)(acac)$_3$ and acrylonitrile onto carbon surface	26
[Cobalt(III)·(en$_2$py·Cl)]Cl$_2$	PVP	S	Dip coating onto graphite electrode	19
Ru(II)(vinyl–bipy)$_3^{2+}$ (**15**) and Fe(II)(vinyl–bipy)$_3^{2+}$ and other vinyl bearing Ru–bipy chelates	Electropolymerized monomer	C	Polymerization onto a Pt disk electrode, vitreous carbon SnO$_2$ and TiO$_2$ electrodes	14–16, 27
(bipy)$_2$py·RuO^{2+} (terpy)py·RuO^{2+}	PVP	S	Evaporation of the metal complex–polymer species from an ethanol solution onto Pt, Au or carbon electrodes. $E^{\circ\prime} = 1.2$–1.3 V	28, 29
Ru(II)(*o*-phen)$_3$	Electropolymerized monomer	C	Polymerization onto silanized Pt electrodes	30
Ru(II)(NH$_3$)$_6^{3+}$, MV^{2+}, Cr(III)(bipy)$_3^{3+}$	Coelectropolymerized styrene sulphanate with γ-methacryloxypropyltrimethoxysilane	C	Electrostatic entrapment of the ionic species in the polymer (**17**) on a Pt electrode	31

TABLE 15 (continued)

Electroactive moiety attached to polymer	Polymeric matrix	Type	Comments	Ref. [a]
$Fe(CN)_6^{3-}$	QPVP	I	Dip coating of polymer onto graphite electrode. Redox species sorbed from solution into the polymeric coating	32
$Ru(NH_3)_6^{3+}$	Polyacrylic acid, polystyrene-sulphanate and polyvinylsulphate	I	Dip coating of polymer–metal complex onto graphite electrode	32, 33
$Ir(Cl)_6^{3-}$	*N*-protonated PVP	I	Methanol–PVP solution evaporated onto a graphite disk electrode. Redox species adsorbed into film from solution	23, 33
$Fe(CN)_6^{3-}$	Protonated form of an alkylamine–siloxane polymer	I	Spin coating of the siloxane polymer onto Pt disks, followed by absorption of the redox species from solution	34
$Ir(Cl)_6^{3-}$, $Fe(CN)_6^{3-}$	Copolymer of vinylpyridine and γ-methacryloxypropyltrimethoxysilane (**16**)	I	Films prepared by slow evaporation of a solution of the polymer–metal complex onto superficially oxidized Pt disk electrodes	35
$Ru(bipy)_3^{2+}$, $Ru(NH_3)_6^{2+}$	Electropolymerized polystyrene converted to the sulphonic acid derivative with chlorosulphonic acid	I	Ion exchange of complexes onto preformed polymer coated electrode. Polymer can undergo electron exchange with vinylferrocene	36
Nitrostyrene	Polynitrostyrene	C	Dip coating of graphite on Pt electrode	37–39
Tetrathiafulvalene (TTF)	TTF–styrene copolymer	C	Spin coating onto a Pt disk	12, 40
Triaryl-Δ^2-pyrazolines (TAP)	TAP–styrene copolymer	C	Evaporation spin coating onto a Pt disk	12, 41

Anthraquinone	Polymer of 2-anthraquinonecarbonylchloride and PEI (**18**)	C	Dip coating onto vitreous carbon or mercury drop electrode	42,43
Benzidine-type dimer from (**19–21**)	Polystyrene backbone with pendant active groups which dimerize upon oxidation	C	Spin casting of polymers from THF solution onto 500 nm Pt-coated quartz disks	44
Viologen	Viologen–silane polymer based on the monomer	C	Electropolymerization of the monomer onto the Pt disk electrode	45
Vinyldiquat	Polyvinyldiquat	C	as above	14, 45
Viologen	Polymeric form of viologen	C	Electrodeposited onto a gold electrode	46
N-vinylcarbazole (NVC)	Poly NVC	C	Electropolymerization of NVC onto Pt and Au electrodes	47
Pyrrole	Polypyrrole	C	as above	48, 49
Azobenzene (5–95% of polymer)	Condensation product of *p*-phenylazobenzoyl chloride and PEI	C	Adsorbed onto a glassy carbon or hanging mercury drop electrode	50

[a] See Table 1.

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found to be highly dependent upon the particular supporting electrolyte employed. The polymers were completely inactive in *p*-toluene sulphonate and no clear relationship between the size of the counter ion and electrochemical oxidation rate was discerned. On the contrary, the activity of pyrazoline- and ferrocene-modified polymers was not impaired in *p*-toluene sulphonate. Thus the design of potential redox polymer electrode coatings for a given system of solvent and electrolyte is often approached empirically. Schroeder and Kaufman [379] have related the morphological characteristics to the electrochemical behavior of several redox polymers in electrolyte solutions. The diffusion coefficient, D [375], of the dye Sudan III in a polymer was employed as a relative measure of the free volume content of various RPECs.

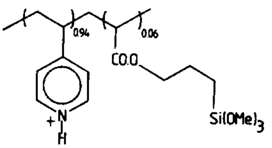
The quantity l^2/η, where l represents the thickness of the RPEC and η the oxidation overpotential, is often used as an electrochemical parameter to represent the relative rates of oxidation among different polymeric materials. It was observed that films with a large value of D (cm^2 s^{-1}) had a large value of l^2/η. Thus large overpotentials for oxidation, due to slow ion transport within polymers, are greatly decreased in ionized, swollen films.

There are cases where the morphological characteristics and thus the electrochemical behavior of the RPEC are sensitive to changes in pH. For example, the electroactivity of Ru(III) edta/PVP prepared by Oyama and Anson [351] was found to increase upon lowering the pH of the solution in contact with the electrode. Protonation of the pyridine residues within the polymer is thought to produce a more swollen film due to the coulombic repulsion of protonated pyridine groups, facilitating the migration of counter ions into the polymer phase.

(iii) Techniques associated with the coating of electrodes with electroactive polymers

The coating of electrodes with thin films of electroactive polymers is an art which has borrowed much from other technologies. The most common methods for coating electrodes with such polymers involve some absorption techniques, spin casting, plasma discharge polymerization, electro- or photo-deposition of the polymer onto the electrode or a glow discharge technique. Several examples of the different methods used to apply RPECs to electrodes are contained in Table 15.

Many polymers adsorb to solids producing films containing hundreds or thousands of molecular layers. The application of a film of the redox polymer onto the electrode can involve dipping the electrode into a solution of the redox polymer with subsequent drying of the polymer coating. The



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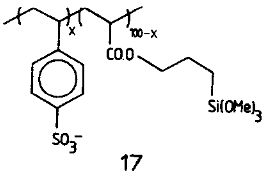

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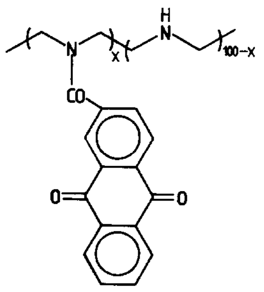

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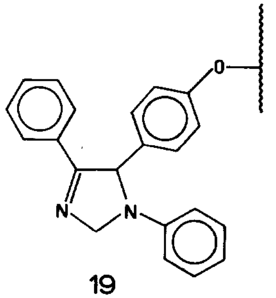

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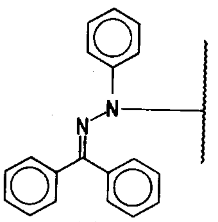

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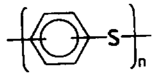

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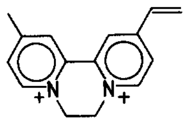

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coated electrode is employed in a solvent in which the redox polymer has negligible solubility. Another method involves placing a drop of the polymer solution on the electrode and evaporating it until a dry uniform film is obtained.

With polymers such as PVP, the polymer may coat the electrode first and then electroactive groups are adsorbed into the RPEC [350,351,359,384,385] or the PVP–metal chelate complex may be formed prior to coating the electrode [349,386,387].

The spin casting of electroactive films onto electrodes is often employed (Table 15). Thin films of redox polymers may be applied to platinum disks to form a working electrode in an electrochemical cell. Thin films of the polymer may be formed by dropping a small quantity of a solution of the polymer onto the substrate, such as the disk electrode, and then spinning at several thousand r.p.m. The techniques for the production of thin organic films by centrifugal spinning are adapted largely from methods employed to prepare photoresists [388,389].

As the liquid layer thins during centrifugal spinning, evaporation of the solution increases the concentration of the solids causing increased viscosity and the formation of a solid film. Emslie et al. [390] showed that for a Newtonian fluid, the solution of the hydrodynamic equations leads asymptotically to a layer of uniform thickness independent of the liquid profile at the start of the rotation. For non-Newtonian fluids, however, films of

TABLE 16

Conductivity studies of selected polymeric charge-transfer and radical-ion polymers

Donor	Acceptor	Description	σ ($\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$)	Ref.[a]
TYPE 1				
QPVP	I_2 (75–90% w/w)	Used in long-life batteries for implantable pacemakers	10^{-3} (max)	1–2
Quaternized (poly(1-alkyl-2-vinylpyridine)	$(TCNQ)_2^-$/polymer (1 : 1)	Conductivity depended on whether the polymer was atactic or isotactic and on the nature of alkyl group	$< 2.14 \times 10^{-5}$	3
QPVP and styrene-1-butyl, 2-vinylpyridine copolymer	$TCNQ^{\dot{-}}$/TCNQ	Conductivity improves with increasing levels of TCNQ and degree of quaternization	10^{-10}–10^{-3}	3–8
QPNVIm (100% quaternized)	$TCNQ^{\dot{-}}$ (15% w/w)		2.1×10^{-3}	4, 5
QPDMAs (75% quaternized)	$TCNQ^{\dot{-}}$ (15% w/w)		2.1×10^{-3}	4, 5
QP2VP QP3VP QP2EP QP3EP	$TCNQ^{\dot{-}}$/TCNQ	Conductivity varies with size of alkyl groups and is greater in isotactic than in atactic polymers	—	9
P2VP P4VP	I_2	Complexes stable to 147°C	10^{-7}–10^{-4}	10
Diphenylamine polymer	I_2 Chloranil TCNE	D/A (1 : 1.50) D/A (1 : 0.25) D/A (1 : 1)	3.3×10^{-6} 4.2×10^{-10} 5.9×10^{-8}	11

Ionene (**38**)	TCNQ$^{\dot{-}}$/TCNQ^0 (1:1)	Activation for conductance dependent on chain length and ratio of TCNQ$^{\dot{-}}$ to TCNQ^0	—	12, 13
Ionene (**27**)	TCNQ$^{\dot{-}}$/TCNQ^0	ESR absorption intensity proportional to T^{-1} (°K) below 210°K	—	13, 14
Heterocyclic ionenes (**39**)	TCNQ$^{\dot{-}}$	Conductivity of polymer CT complex greater than that of monomer	—	15
Ionene (**30**)	TCNQ$^{\dot{-}}$/TCNQ^0	Simple salts complex salts	10^{-8}–10^{-6} 10^{-3}–10^{-2}	16 17, 18
Polymer formed from polyepichlorohydin and substituted pyridines	TCNQ$^{\dot{-}}$/TCNQ^0	Simple salts complex salts	10^{-7} 10^{-2}–10^{-1}	19
Ionene (**29**)	TCNQ$^{\dot{-}}$/TCNQ^0	Conductivity varies x/y ratio and decreases with increasing x and y	3.1–10^{-9}–5.0×10^{-3} 10^{-5}–10^{-2}	20–23 24–26
Ionene (**40**)	TCNQ$^{\dot{-}}$/TCNQ^0	Conductivity increases with increasing TCNQ$^{\dot{-}}$/TCNQ^0 ratio	6.7×10^{-7}–1.1×10^{-2}	27
Ionene (**28**)	TCNQ$^{\dot{-}}$/TCNQ^0		1.96×10^{-6}–1.3×10^{-2}	27, 28
Ionene (**41**)	TCNQ$^{\dot{-}}$/TCNQ^0 (1:1)		6×10^{-2}	28
Polybipyridyl ionene (**31**)	TCNQ$^{\dot{-}}$/TCNQ^0	simple salts complex salts	2.67×10^{-8}–1.38×10^{-8} 9.17×10^{-5}–4.48×10^{-2}	29
Ionene (**25**)	TCNQ$^{\dot{-}}$/TCNQ^0 and Br^-	Conductivity varies with TCNQ$^{\dot{-}}$/TCNQ^0 ratio and depends upon whether derivative is ortho, meta or para type	1.86×10^{-6}–2×10^{-2}	30

TABLE 16 (continued)

Donor	Acceptor	Description	σ ($\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$)	Ref. [a]
Polytriethyldiammonium ionene (**26**)	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}^{0}$	Conductivity of simple salts of pol/$\mathrm{TCNQ}^{\dot{-}}$ increased by doping with TCNQ^{0} to give complex salt		29
		simple salts	9.62×10^{-7}–1.95×10^{-7}	29
		complex salts	7.41×10^{-5}–6.67×10^{-4}	29
		CuBr salts	1.4×10^{-5}	31
4,4′-Bipyridinium–PPG copolymer	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}^{0}$	Highly flexible ionene polymers with extended storage life	3.75×10^{-2}	32
1,2-Bis(4-pyridyl)ethylene–PPG copolymer	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}$		4.03×10^{-2}	32
Piperazine–PPG ionene (**42A**)	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}^{0}$	Stress-strain relationship influenced by, and conductivity proportional to, the $\mathrm{TCNQ}^{0}/\mathrm{TCNQ}^{\dot{-}}$ ratio	2.04×10^{-9}–3.13×10^{-7}	33
Ionene (**42B**)	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}^{0}$	67% w/w TCNQ/polymer	1.7×10^{-4} (max)	34
Polymers based on dicyclohexylmethane (**38**)	$\mathrm{TCNQ}^{\dot{-}}/\mathrm{TCNQ}^{0}$		1.2×10^{-3}–4×10^{-2}	35
PNVC (**32**)	I_2 (77% w/w)	Conductivity increases proportionally with I_2 content	10^{-5} (max)	36, 37
PNVC		Used as an electrolyte in a solid state electrochemical cell		38
PNVC	*N*-methylacridinium–TCNQ salt		0.95×10^{0}	8

PNVC	$SbCl_5$		4×10^{-11}–5×10^{-6}	37
Halogen derivatives of PNVC	TCNE and 2,4,7-trinitro-fluorenone	Conductivity varies with type of halogen and position of substitution in carbazole unit		39, 40
Polyvinylacetate bearing donor functions	$(TCNQ^{-})_2Et_3NH^{+}$, $TCNQ^0$	Conductivity dependent upon donor strength of polymeric donor, and the stoichiometry of the TCNQ species		41
TCNQ–TTF copolymer (**43**)	I_2		2×10^{-8}–2×10^{-6}	42
Poly(aryliminodiethanol bisphenol-A carbonate)	DDQ	D/A (1:1)	$<10^{-11}$	43
Polymer (**44**)	DDQ (**24**)		4×10^{-9}	44
Polymer (**45**)	Tetranitro fluorenone (**45**)		10^{-11}	45
Quaternized urethane rubbers	$TCNQ^{-}/TCNQ^0$	No change in conductivity upon dilation of material		46, 47
Sulphur-containing hydrocarbon polymer (**47**)	$TCNQ^{-}/TCNQ^0$	Conductivity of the complex salt is proportional to the degree of methylation of the sulphur units in the polymer	4.90×10^{-3}–4.59×10^{-2}	48
Various ferrocene-containing polymers		Highly thermastable polymers	$<10^{-8}$	49
Poly(1,1′-ferrocenylene), ferrocene-*o*-anisaldehyde polymer	BQ DDQ	50% Fe(III)/Fe(II) 73% Fe(III)/Fe(II)	4.2×10^{-11} 2×10^{-6}	50, 51
Polyferrocenylene, PVF, polyethynylferrocene	DDQ, I_2 and TCNQ	Conductivity maximized in the region Fe(III)/Fe(II) 35–65%		52, 53

TABLE 16 (continued)

Donor	Acceptor	Description	σ (ohm^{-1} cm^{-1})	Ref. [a]
Polyamino acid with -pyrenyl or -phenothiazine pendant groups (**48**)	TCNQ, I_2	TCNQ complex I_2 complex TCNQ complex I_2 complex	3.3×10^{-11} 1.1×10^{-7} 1.4×10^{-9} 1.7×10^{-7}	54
PVA or PVAm Cu(II) complexes	I_2	Surface conductivity of film dependent upon degree of neutralization of the polymeric chelate	3.06×10^{-6}–2.5×10^{-5}	32, 55–57
TTF–polyurethane	I_2		2×10^{-6}	42
Poly(3-vinylbisfulvalene di-iron)	I_2		10^{-3}	58
Polyvinylpyrene	I_2 TCNE TCNQ	D/A (16:3) (15:2) (15:2)	7.69×10^{-9} 2.22×10^{-13} 9.09×10^{-15}	59
Polyvinylphenylene	I_2		10^{-4}	60
Poly(*p*-phenylene)	AsF_5		1.45×10^{2}	61, 62
Poly(*m* or *p*-phenylene sulphides) and analogues	AsF_5	Conductivity proportional to concentration of dopant and subject to doping conditions	10^{-3}–1.0	63–68
Polydiacetylene	I_2		10^{-6}	69
Polyphenylacetylene (*cis* and *trans*)	I_2	Conductivity proceeds by an ionic mechanism, rather than electronic	10^{-4}	70
Polymethylacetylene polypropacrylchloride	I_2		10^{-3}	71, 72

Polyacetylene	AsF_5		1200	73
trans-Polyacetylene	Cl_2, Br_2I_2	Only I_2 does not react chemically with conjugated structure		74, 75
		I_2 doped material	$30–10^3$	
		Br_2 doped	0.5	
cis- and *trans*-polyacetylene	AsF_5, Cl_2, Br_2I_2 or Na	Doping with mixed species i.e.,		76, 77
		cis-$[CH(1.Br)_{0.15}]_x$	4.0×10^2	
		trans-$(Na_{0.28}CH)_x$	8×10^1	
		cis-$[CH_{0.82}Br_{0.13}$-$(AsF_5)_{0.12}]_x$	12.0	78
cis-Rich polyacetylenes	AsF_4^-, ClO_4^-, I^-	*n*-Type doping by electrolysis in counterion solution $[CH(ClO_4)_{0.0645}]_x$	970	79
cis-Rich polyacetylenes	BF_3	Determination of conductivity via electrical and spectroscopic methods		80–82
Polypyrrole	BF_4^-	Prepared by electrolytic oxidation of monomers in a suitable electrolyte	100	83, 84
TYPE 2				
Polyacetylene$^-$	Na^+ (as naphthalide)	28% Na^+ (mol/mol fundamental unit)	80	51, 76, 85
Polyphenylene$^-$	K^+ (as naphthalide)	57.1 K^+ (mol/mol fundamental unit)	7	62, 73
TYPE 3				
Arylaminoethanol polymers	Polynitroisophthalates		$1.5\times10^{-17}–4\times10^{-18}$	86
PNVC (32)	Polymeric acceptors (36)		10^3	87–89

TABLE 16 (continued)

Donor	Acceptor	Description	σ (ohm^{-1} cm^{-1})	Ref.[a]
TYPE 4				
Emeraldine–polyamino-styrene grafted polymer. Oxidized units (**37**)	Unoxidized units of polymer	Polymer used as a battery electrode	5×10^{-2}	90
Oxidized units of polymer (**33**)	Neutral moieties of polymer (**33**)	neutral state cation radical form	1.3×10^{-7} 4.3×10^{-5}	91
Oxidized polymer moieties (**34**)	Neutral units of polymer (**34**)	neutral state cation radical form	5.5×10^{-10} 2.0×10^{-9}	91
Phenylene units in a phenyleneaminochloranil copolymer	Chloranol units in the copolymer	Unequal distribution of paramagnetic intramolecular CT centers affects ESR characteristics and mechanism of electronic conductivity		92
Pyridine units in a 4VP–trinitrostyrene copolymer	Trinitrostyrene units of the copolymer	1:1 ratio of D/A	$<10^{-10}$	93
Pyridium units of copoly-(styrene, 1-butyl-2-vinylpyridinium TCNQ)	Free TCNQ^0 units (15%) and polymer-bound TCNQ		10^{-3}	4, 7
Ferrocene units in a TCNQ–ferrocene polyurethane (**49**)	TCNQ moieties of the polymer		3×10^{-3}	62, 94
TTF units in a TTF–TCNQ polyurethane (**43**)	TCNQ moieties of the polymer		1.66×10^{-7}	62

[a] See Table 1.

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TABLE 16 (continued)

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non-uniform thickness may result [391]. Meyerhofer [392] has found that for spin cast films, the thickness, h, is dependent on the rotation speed, f, initial viscosity, V_0, and evaporation rate, e,

$$h \propto f^{-2/3} \cdot V_0^{1/3} \cdot c^{1/3}$$

where e is proportional to $f^{1/2}$. The thickness of the resulting film may be accurately gauged from mechanical surface profile measurements using commercially available equipment [383]. Typically, the films have a thickness ranging from 5 to 1000 nm.

The introduction of various monomers into radiofrequency plasma discharges is known to initiate the polymerization of the monomer on exposed surfaces placed within the plasma chamber [370,393,394]. The rate of surface deposition of the plasma polymeric film is dependent upon the geometry of the chamber, radiofrequency power and substrate temperature [395,396].

Regarding RPECs, this technique has, so far, only been applied to vinylferrocene (VF). A film of plasma-polymerized vinylferrocene may be formed by exposing a bed of solid vinylferrocene monomer to a low-pressure Ar plasma with the electrode surface facing the bed and about 5 mm distant, for typically 1–3 min.

The plasma-polymerized vinylferrocene is not composed entirely of polymerized monomer. Elemental analysis of such films reveals a composition, $C_{9.7}H_{10.6}O_{1.7}Fe$ [351] or $C_{11}H_{12.6}O_2Fe$ [356], as opposed to the ideal composition, $C_{10}H_{12}Fe$. Broad infrared bands at 1600 and 3400 cm^{-1} arise from the stretching modes of OH and C=O groups of an undetermined structural character. The degradation of ferrocene sites in the film is minimized when the rate of deposition is increased. Fe $2p_{3/2}$ X-ray photoelectron spectroscopy (XPS) shows a ferrocene (708.5 eV) 5–10 times more intense than the 711 eV peak due to a mixture of ferrocinium and non-electroactive Fe(III) decomposition product within the polymer [397].

Although the chemical composition of plasma-polymerized VF and PVF films differ, their electrochemical properties are qualitatively similar [357].

The thickness of plasma-polymerized films of VF are typically 100 nm compared with 5–1000 nm of spin cast films. Surface electron microscopy (SEM) has shown that more-uniform film surfaces are obtained with plasma-polymerized VF [356].

Electro- and photo-deposition techniques for polymer immobilization are summarized in Table 15. In the earliest voltammetric studies of PVF in acetonitrile and methylene chloride, electrooxidized polyvinylferrocene (PVF^+) was found to deposit on the anode owing to the poor solubility of PVF^+ in the solvent media [380]. The electrodeposition of polyvinyl ferrocenes and their derivatives onto electrodes [355,380,397–399] results in an RPEC which is a salt containing the supporting electrolyte [355].

The polymer-coated electrode can be removed from the PVF solution, shaken to remove any adhering solution and employed in a test solution which has no tendency to dissolve the polymeric coating in its oxidized or reduced forms. Films of PVF so produced can be between 20 [355] and 2000 nm [399] thick, as estimated from the charge consumed in completely reducing the film [355].

Ferrocene is known to become photooxidized in chlorinated solvents [400] and PVF may also become photooxidized in CH_2Cl_2. Like electrodeposited PVF films, photooxidized PVF precipitates from the CH_2Cl_2 solution [359,382] and this phenomenon has been employed to coat electrodes with thin films of PVF [382]. Though polymeric electroactive films can be deposited on electrodes by cathodic glow discharge polymerization, there are few examples of RPECs being manufactured by this method [322,401,402].

Polymeric metal complexes have been formed by the polymerization of metal acetylacetonates and acrylonitrile. The formation of the polymeric film is initiated by applying a high voltage to a glow discharge reactor containing the monomeric vapors at an elevated temperature in the presence of the electrode.

A large number of different metal complex/polymer combinations can be conceived, and it is thought that redox polymers so produced may find applications in fuel cells.

The introduction of electroactive species into non-conductive polymers bound to an electrode surface is another method of preparing electroactive RPECs. These techniques can involve the sorption of a charged metal complex to oppositely charged polycationic or polyanionic polymers. Typical polycations contain the pyridinium moiety (protonated or alkylated [364,403]), and polyanions such as nafion (perfluorinated polymer with $-SO_3$-anionic moieties) [404], styrene sulphonate polymers [405] or polyacrylicacid [360] have also been used. This electrostatic trapping process has a number of advantages including the simultaneous incorporation of several different types of electroactive species into a given polyionic film [404,406]. Ion-exchange RPECs also have the potential technological advantage of being regenerable by replacement of "aged" electroactive species with fresh redox catalyst. One disadvantage of the electrostatic trapping process is that the exchange process is reversible to some degree and leaching of the electroactive species after many oxidation/reduction cycles can occur. Further, the rate of charge transport through the polymer and the permeability of the film to other species can decrease at high loading levels of electroactive catalyst [406]. Such a permeability effect has been rationalized in terms of electrostatic cross-linking of the film by the redox ion, and under such conditions the mobility of the electroactive species (which can influence the conduction process) also falls.

Redox active species can also be introduced into neutral polymeric electrode films such as polyvinylpyridine by the coordination of metal complexes to the nitrogen-containing moiety of the polymer [407,408]. Redox active polymeric electrode films of this type offer similar advantages (and disadvantages) to the films prepared by electrostatic trapping.

K. BILAYER POLYMERIC ELECTRODES

The most recent development in redox polymer science is the bilayer film electrode. The bilayer redox polymer electrode is comprised of two electroactive films each of a different reduction potential; the outer layer being exposed to the surrounding solution, the inner layer being in direct contact with the electrode surface and acting as a mediator to the outer layer. Abruña et al. [363] first demonstrated the principle of unidirectional current flow based on a conductor electrode coated with two physically discrete layers of electroactive materials of different redox potentials. In this case, the bilayer was constructed by sequential electropolymerization of two different ruthenium polypyridyl complexes bearing pendant vinyl groups onto Pt, vitreous carbon, SnO_2 and TiO_2 electrodes. Typical bilayer films were

inner layer: poly-Ru(II)$(bipy)_2$$(vinyl\text{-}py)_2$ (A)
outer layer: poly-Ru(II)$(bipy)_2$(vinyl-py)Cl (B) and
inner layer: poly-Ru(II)$(bipy)_2$(vinyl-bipy) (C)
poly-Fe(II)$(vinyl\text{-}bipy)_3$ (D) and
inner layer: (C)/outer layer: PVF.

In the (A)/(B) bilayer film the outer film (B) redox sites were not oxidized at +1.0 V (vs. SSCE), but as the potential increased to +1.3 V a small population of Ru(III) states in (A) arose and Ru(II) sites in (B) were oxidized through the catalytic electron-transfer mediation at the (A)/(B) interface. At +1.5 V (vs. SSCE) the entire bilayer was in the oxidized state. When the potential scan was reversed the reduction of the Ru(III) states in (A) was observed, but the Ru(II) sites in the inner film were thermodynamically incapable of mediating the reduction of the Ru(III) sites in the outer film (B), and the latter remained trapped in the oxidized state. Thus the electron transfer across the (A)/(B) interface was unidirectional for the outer ruthenium sites, mimicking an *n*-type semiconductor.

Overlap of the energy distribution between the inner and outer film redox states has a strong bearing on the lifetime of the trapped outer states. For example, $\Delta E^{0'}_{C,D}$ was only 0.1 V and the trapped oxidized outer states of Fe(III) quickly dissipated, whereas $\Delta E^{0'}_{A,B}$ was 0.47 V and the lifetimes of the trapped outer states was considerably prolonged.

Similarly, Denisevich et al. [409] have studied the rectifying behavior of the bilayer films:

inner layer: poly-Ru(II)(4-methyl, 4-vinyl-bipy)$_3$, (E)/outer layer: PVF
inner layer: (E)/outer layer: poly-Fe(II)(4-methyl, 4-vinyl-bipy)$_3$, (F)
inner layer: (E)/outer layer: poly-benzylviolagensilane, (G)
inner layer: (E)/outer layer: poly-vinyldiquat, (H), and
inner layer: (H)/outer layer: PVF on Pt electrodes

and have developed a theory of the electrochemical action of bilayer electrodes. The conductivity of bilayer redox polymer assemblies has been termed "redox conductivity" to distinguish it from the more familiar but different "electronic conductivity", since redox conductivity permits electrons to flow within the film only at energies centered around the formal potentials of the electroactive species and in redox conductivity an exhaustive redox transformation of the film is possible.

Schneider and Murray [405] have constructed bilayer films from copolymerized styrene sulphonate–siloxane/PVF couples. The styrene sulphonate–siloxane ion exchanger (17) could absorb MV^{2+}, $Ru(NH_3)_6^{3+}$ and $Cr(bipy)_3^{3+}$ from solution. In this particular case redox conductivity in the inner film was provided entirely by mobile redox ions, Br^- and $Ru(NH_3)_6^{2+}$, rather than fixed sites employed by others.

Charge trapping reaction: $Br_2 + 2PVF \rightarrow 2Br^- + 2PVF^+$
Untrapping reaction: $Ru(NH_3)_6^{2+} + PVF^+ \rightarrow Ru(NH_3)_6^{3+} + PVF$

Willman and Murray [410] have gone a step further and explored the practical utility of inner layer: poly-Ru(II)(vinyl-bipy)$_3$/outer layer: (H) and inner layer: poly-Ru(II)(vinyl-bipy)$_3$/outer layer: (G) bilayer films on Pt and SnO_2 electrodes. It was found that a cyclical negative potential scan ($0 \rightarrow -1.7 \rightarrow 0$ V) trapped the viologens in the outer layer in the zero-valent state. A gradual untrapping or discharge of the highly reduced outer film to the contacting solution was detected when a second similar cyclical potential sweep measured only a portion of the original trapped states. In this instance, it was thought that the principal oxidant was dissolved oxygen.

As the rectifying characteristics of semiconductor solution interfaces [411], and the application of electroactive films to photoelectrochemistry [412] is currently receiving much attention, the same authors [410] have also demonstrated photoreductive trapping of the outer layer in an SnO_2/inner layer: poly-Fe(II)(vinyl-bipy)$_3$/outer layer: poly-benzylviologensilane electrode assembly. Irradiation of this electrode with a xenon lamp for 30 min, followed by a potential scan from 0 to +1.4 V (vs. SSCE), revealed an enhanced oxidation current at the poly-Fe(II)(vinyl-bipy)$_3$ oxidation potential which corresponded to the untrapping reaction of the reduced viologen. Since 45% of the viologen states in the outer film were reduced by one electron as a result of the irradiation, the application of these electrodes for trapping and storage of radiant energy may be realized in the near future.

L. ELECTRON TRANSFER IN RADICAL-ION AND CHARGE-TRANSFER POLYMERS

(i) Types of charge-transfer polymers

The electrical conductivity (σ) of most organic materials at room temperature is quite small ($\sigma < 10^{-10}$ ohm^{-1} cm^{-1}). Over the last two decades the synthesis of organic molecules with electrical properties approaching those of metals have been the focus of considerable attention [413–418]. Because organic polymers generally have elasticity, strength and plasticity, they offer significant advantages over non-polymeric materials in the manufacture of electronic materials. Many macromolecular substances can now be tailored to perform as semiconductors or even as organic metals. This technological explosion has been well described in several monographs [418,419] and recent reviews [420–433].

One of the most promising areas in this field is that of the organic charge-transfer (CT) and radical-ion (RI) polymers. These are formed by the interaction of two valency-saturated molecules: an electron donor D and electron acceptor A. The former possess a filled molecular orbital of quite high energy but low ionization potential, whilst the latter has a vacant relatively low energy molecular orbital with considerable electron affinity. Formally, the radical-ion polymers can be considered as macromolecular CT complexes in which total electron donation has occurred. The classification and electronic theory behind monomeric and polymeric CT complexes has been discussed previously by Peredeeva et al. [422]. The mechanism of electron transport in these polymers has been amply dealt with in previous reviews [413,417,420,424] and can involve the migration of discrete redox states. Whether charge transport involves delocalization and mobility along the crystal stack of donor and/or acceptor molecules, or migration by alternate electron transfer from donor to acceptor, or both has not yet been clearly resolved.

Charge-transfer polymers can be grouped into four basic categories.

(1) An intermolecular CT complex is found between the donor moieties of poly-D and a monomer A.

(2) Intermolecular CT complexes are formed between the acceptor moieties of poly-A and a monomer D.

(3) Intermolecular CT complexes are formed between the acceptor moie-

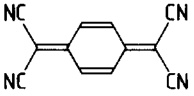
ties of poly-A with the donor functions of poly-D.

(4) Intramolecular CT complexes are formed between the acceptor and donor moieties of a polymer containing both groups, copoly-A/D.

Other than this superficial classification according to the macromolecular structural types, Mulliken [434] classified donor and acceptor molecules into three groups, n, σ, π and υ, σ, π, respectively. For donors the energetically highest orbital in the first group is a lone pair of n-electrons of a heteroatom (R_2S, R_3N, etc.), secondly an electron pair forming a σ-bond (e.g. R–halogen), followed by a pair of π-electrons in an unsaturated or aromatic compound. With acceptors, the lowest molecular orbitals are υ-valent orbitals of a metal atom (metal halides, organometallic compounds), followed by non-bonding σ-orbitals (e.g. molecular halides, X_2) and a π-bond system of aromatic or unsaturated compounds containing electron-accepting substituents.

(ii) Type 1 CT polymers

The construction of macromolecular complexes from poly-donors and monomeric acceptor molecules is by far the most popular route to conductive macromolecular charge-transfer complexes. The polymeric donors are often polymeric polycations having a quaternary amino function within the polymer which enables the complexation of anionic acceptor molecules. Tetracyanoquinodimethane (TCNQ) (**23**) is a powerful π-molecular acceptor



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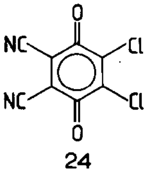
whose radical forms organic semiconductors with a variety of cations. Its use in promoting the conductivity of organic compounds is presently the center of a great deal of attention [413,417]. Some of the other acceptors used in conductive with poly-donors are halides (Cl_2, Br_2, I_2), tetracyanoethylene (TCNE) dichlorodicyanoquinone (DDQ) (**24**) and chloranil (tetrachloroquinone). The macromolecular semiconducting complex may be formed by the addition of a solution of the cationic polymer to a solution of a metal



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salt of the anionic donor, from which the polymeric CT complex often precipitates.

The electrical conductivity (σ, ohm^{-1} cm^{-1}) of the macromolecular salts is governed by the relation

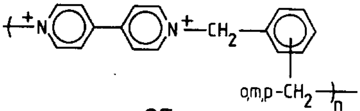
$$\sigma = \frac{1}{\rho} = \sigma_0 \exp(-E_a/kT)$$

where E_a is the activation energy of the conduction process and σ_0 is a constant.

Polyvinylpyridines have a conductivity of the order of 10^{-15} Ω^{-1} cm^{-1} at 300 K [435], and this figure is typical of most other nitrogenous polymers. Quaternization of the nitrogenous moiety and doping these with acceptor molecules by the coprecipitation method can lead to an increase in the conductivity of the macromolecule by several orders of magnitude, i.e. from 10^{-15} up to 10^{-3} Ω^{-1} cm^{-1} by doping PVP with I_2 [436]. Kuwata et al. [437] using diphenylamine polymers have shown that the conductivity of the poly-donor/acceptor complex, using iodine and chloranil as acceptors, increases in proportion to the percentage of acceptor dopant in the macromolecular chelate. With TCNE as an acceptor, molar ratios of acceptor to donor moieties above 0.33 actually proved detrimental to the conductivity.

In the early 1960s it was realized that materials of good conductivity could be prepared by exchanging the anionic halide acceptors for $TCNQ^{\dot{-}}$ by mixing a solution of the polycation–halide complex with a solution of Li TCNQ. A careful selection of solvents enabled the immediate precipitation of the exchanged species, poly-$D^{+} \cdot TCNQ^{\dot{-}}$. Close inspection of these polymeric salts revealed that many samples also contained neutral $TCNQ^0$, arising from the disproportionation of $TCNQ^{\dot{-}}$ to $TCNQ^0$ and *p*-phenylenedimalonitrile in the presence of polymer-bound acid remaining from the solvolysis of the alkylating agent during the quaternization of the uncharged polymer [438]. In the initial experiments, where $TCNQ^0$ was formed unintentionally, conductivities of about 10^{-5} Ω^{-1} cm^{-1} were frequently observed. Extraction of the neutral $TCNQ^0$ in hot benzene lowered the conductivity of the polymer complexes to $\leqslant 10^{-10}$ Ω^{-1} cm^{-1}. Thus it was shown that the polycation–$TCNQ^{\dot{-}}$ polymers were actually poorly conducting, and that the presence of $TCNQ^0$ was central to the conductivity of the polymeric salts, and such is the case with monomeric TCNQ/donor complexes [417].

The conductivity of the $TCNQ^{\dot{-}}$/poly-D complexes (simple salts) can now be adjusted by the introduction of $TCNQ^0$ into simple salts to form mixed-valence species (complex salts) yielding values as high as 10^{-3} Ω^{-1} cm^{-1} [438–460]. Complex salts are prepared by dissolving the simple salt and TCNQ in dimethylformamide and then evaporating the dimethylformamide under reduced pressure. The motor ratios of both TCNQ$^{\dot{-}}$ to poly-D$^+$, and TCNQ^0 to TCNQ$^{\dot{-}}$ determine the electrical characteristics of the resultant polymer [446,453,454,459–464]. For example, Kamiya and Shinohara [464] have shown that the conductivities of typical ionene-type simple salts of (**25**), (**26**) and (**27**), of 7.14×10^{-9}, 2.3×10^{-8}, 7.7×10^{-6} were increased to 2.1×10^{-3}, 2.2×10^{-2} and 4.0×10^{-2} Ω^{-1} cm^{-1}, respectively, by constructing complex salts (TCNQ^0/TCNQ$^{\dot{-}}$, 1 : 1) at the same TCNQ loading level as the simple salts. The activation energies for conduction fell from 0.33, 0.30 and 0.25 to 0.069, 0.089 and 0.074 eV, respectively.



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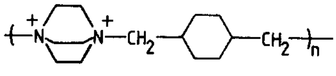

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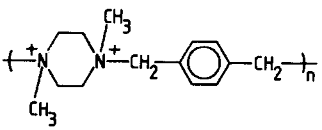

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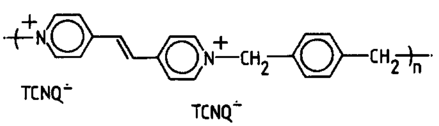
Other authors have performed similar comparisons which agree with these observations [459–461].

The nature of polymeric donors can severely affect the electrical properties of the macromolecular charge-transfer complex. For example, the resistivity of the complex of polyphenylene with iodine is 10^4 Ω cm^{-1}, several times larger than that of iodine alone and much lower than a simple admixture of the polymer and iodine [465]. Simple TCNQ complexes of the ionene (**28**) are slightly less conductive than the corresponding monomeric species [446]. The distance between the quaternary ammonium centers of ionene-type poly-donors plays an important role in conditioning the conductivity of TCNQ CT complexes. An increase in the polymethine units, $(CH_2)_y$, in the simple and complex salts of the polymers (**29**) [456–459] and



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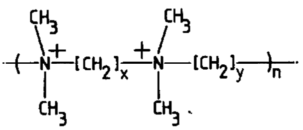

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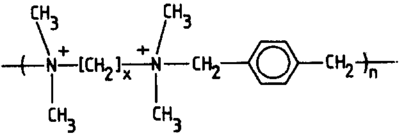

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(**30**) [452] resulted in an increase in the value of E_a of the simple salts, but a decrease in the case of the complex TCNQ salts. The conductivity of simple and complex salts of the ion (**29**) displayed a minimum at $x = y = 6$ and increased as the chain length increased ($x = 6$, $y = 16$) [459]. Hadek et al. [459], from their X-ray diffraction studies, concluded that the variations in σ and E_a of the various CT complexes arise from the changing conformations of the polymethylene chains in the solid state; the high conductivity resulting from electron delocalization in one-dimensional TCNQ columns. Kamiya et al. [461,464] found that simple and complex TCNQ charge-transfer complexes of the ionenes (**30**) and (**36**), respectively, exhibited enhanced conductance when the number of CH_2 units (y) was even compared with those with an odd number of units. It was concluded that high conductivity is observed when the polymeric chain is most linear, offering the least hindrance to the formation of a one-dimensional TCNQ column and in this regard they are in agreement with other workers [438,466]. The conductivity of polyvinylpyridinium/TCNQ complex salts are also subject to steric factors. Boniface et al. [441] have shown that the conductivity of the isotactic poly-1-methyl-2-vinylpyridinium complex ($2.15 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$) exceeds that of the atactic polymer complex ($1.04 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$). Similar effects have also been observed for atactic and isotactic polyacetylenes [467] and in polyvinylnaphthalene-TCNE complexes [468]. The isotactic materials behave much as polycrystalline samples of monomeric materials of intermediate conductivity, having similar energy gaps (E_a) and conductivities. In crystals of complex salts of monomeric bases [469] the separation between cations is exactly twice that between TCNQ molecules to accommodate face-to-face stacking of TCNQ beside the cations and maintain the stoichiometry, $R^+(TCNQ)_2^-$. In the polyvinylpyridines the bases recur ~ 0.3 nm along the chain, which is too close to permit the formation of a parallel stack of TCNQ molecules with half this separation, thus a non-linear array, especially in the atactic case, is not possible. Besides steric factors the polarizability of the cationic moiety in the polymer is important in determining the electrical behavior of the polymeric CT complex. Klandermann and Haesterey [470] proposed that the polarizability of cations in a CT complex should be assigned in proportion to the largest wavelength $\pi \rightarrow \pi^*$ transition. Kamiya et al. [460] demonstrated that the value of E_a of various monomeric derivatives of pyridinium $-(TCNQ)_2^-$ decreased with an increase of $\lambda_{\max}$ of the cation, which means the conductivity of the TCNQ complex salt decreases as the polarizability of the cations increases. Similar results were obtained for polymeric CT complexes. According to LeBlanc [471] the activation energy for conduction can be described by the equation

$$2E_a = C - \Delta$$

where C is the coulombic repulsion between adjacent unpaired electrons [414] and Δ represents the bandwidth of energy states of the conducting electron (0.1 eV), which is related to the intermolecular transfer integral, t. The magnitude of t is related to the nearest neighbor intermolecular overlap, S, which is estimated to be $S \simeq \exp(-a/a_0)$ where a is the intermolecular spacing and a_0 the radius of the $2p_z$ carbon wave function. Thus the bandwidth is affected by the spacing of the TCNQ molecules relative to one another, and Δ can often contribute significantly to E_a [464]. Even so, the activation energy is due mainly to the electrostatic component, C, and if this energy is less than the bandwidth then metallic behavior can be expected.

LeBlanc [471] considers that the role of the cation is to reduce the effective repulsion by a polarization mechanism, by a factor of $1-(\alpha/r^3)$, where α is the polarizability of the cation and r the effective distance between the cation and anion.

From known crystal structures and conductivity anisotropy of monomeric salts it is clear that conductivity arises from the motion of odd π-electrons among TCNQ sites. The TCNQ molecules are arranged in face-to-face stacks such that π-orbital overlap within a stack is considerably larger than that between any other near neighbors. Conductivity states arise from the introduction of defects into an ordered ground state configuration induced by an applied potential. An electron is removed from $TCNQ^{\dot{-}}$ leaving $TCNQ^0$ and is transferred by a hopping mechanism to successively more distant $TCNQ^{\dot{-}}$ molecules to give $TCNQ^{2-}$. The propagation of these "electrons" ($TCNQ^{2-}$) and "holes" ($TCNQ^0$) is greatest in the direction normal to the planes of these stacks. For simple salts, this process involves an increase in the electrostatic energy, C, but for complex TCNQ salts when both $TCNQ^{\dot{-}}$ and $TCNQ^0$ are present, C and consequently E_a are much lower and the conductive properties of these salts is several orders of magnitude greater than for simple salts [471].

Since both holes and electrons contribute to the conductivity of a material, σ is best expressed as

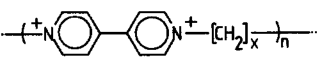
$$\sigma = (n_+\mu_+ + n_-\mu_-)e$$

where e is the electronic charge, n_+ and n_- (carriers/cm^3), and μ_+ and μ_- (cm^2/V) the density and mobility, respectively, of the positive and negative carriers. The determination of the sign of the majority carriers and their individual mobilities is performed less often than measurements of σ, probably as a result of the intrinsic experimental difficulty involved in such undertakings. Hall effect studies [420], which measure the potential developed by current displacement of mobile carriers in a magnetic field, determine the magnitude of μ, and the sign of the majority carrier can be ascertained from thermoelectric studies and the resultant Seebeck coefficient, Q (mV/°C).

There have been a few studies of Hall effects and the measurement of Seebeck coefficients in polycation–TCNQ charge-transfer complexes [441,446,450,459]. Hadek et al. [459] observed only positive values of Q for simple salts of (**29**) and poly-methylenebis(trimethylammonium), which indicated hole-type conductivity. With the corresponding complex salts the magnitude of Q was generally smaller than for the simple salts, however both positive and negative Seebeck coefficients were observed. Boniface et al. [441] found positive Seebeck coefficients for atactic polyvinylpyridinium–TCNQ complex salts, but negative coefficients for the isotactic isomers even though the sign of the majority carries from Hall mobility data was negative in both cases. Although the disagreement between the sign of the majority carrier obtained from Seebeck and Hall measurements in the isotactic polymer is difficult to explain it is to be understood that in this instance a change in the mode of conduction has occurred.

Rembaum et al. [446] found only positive Seebeck coefficients for simple and complex TCNQ salts of the ionene (**28**). The simple salts followed a singlet-triplet model for paramagnetism in which the ESR intensity, I, was proportional to $T^{-1} \cdot \exp(J/kT + 3)^{-1}$, J representing the singlet-triplet separation energy. Other workers have noted a similar effect [450]. Rembaum et al. [446] found that the concentration of holes was about 8 orders of magnitude below the concentration of ESR spins, which means that the carriers are not the spin excitations themselves, which is in agreement with previous studies of PNVC–I_2 complexes [472].

Macromolecular CT complexes of poly(N-vinylcarbazole) (**32**) are currently under investigation. The polymeric donor–acceptor complexes in some cases are as conductive as the monomeric complexes [473] and the polymers have the advantage of excellent mobility [472,473]. These complexes are of interest because of their utility in various photochemical and photoconductive processes [420,474,475]. Polymeric charge-transfer complexes between PNVC and various monomeric acceptors differ from polycation-$\text{TCNQ}^{\dot{-}}$ complexes in that the radical moiety resides on the polymer itself in the form of a cation radical. Mizoguchi et al. [476] found conductivities as high as 1 Ω^{-1} cm^{-1} for complexes of poly(N-vinylcarbazole) (PNVC) and $\text{TCNQ}^{\dot{-}}$. Related conductivity studies are listed in Table 16. Yamamoto et al. [473] found that PNVC–$SbCl_5$ complexes were more conductive than the corresponding iodine complexes by a factor of about 10^5, although their ESR investigations showed that the number of unpaired electrons in the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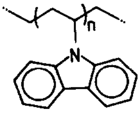
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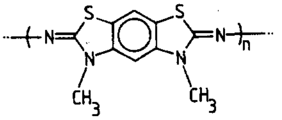
$SbCl_5$ complex is about one-tenth of the number of molecules of the acceptor in the macromolecular complex, whereas in the case of the I_2 complex, the spin concentration exceeds the carrier concentration by about 10^4 [472,473]. Since the band model of conductivity cannot apply to complexes with such low mobilities (0.5 cm^2/V) it is thought that these results are more or less consistent with a hopping model for conduction.

The investigations of Hermann and Rembaum [472] on the transport properties of PNVC–I_2 have not really resolved the nature of the majority carrier. The Hall coefficients were negative but the Seebeck coefficient positive. The Dember voltage supported *n*-type conduction as found in the Hall effect. It was believed that discrepancy arose from the interference of anomalous surface states which control both the Hall and Dember voltages.

Other workers have shown that polymers based on the violene redox system, (**33**) and (**34**), can be oxidized to the radical cations, which are significantly more conductive than the neutral polymers. Related polymers of interest are the poly-*m*- or -*p*-phenylenesulphides (**21**) [424,477–481], polydibenzothiophenesulphides (**35**) [478] and poly-*p*-phenyleneoxides [477],



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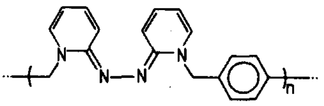

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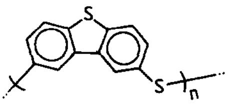

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which can be rendered conductive by the incorporation of AsF_5 (or SbF_5) by exposure of the polymers to an atmosphere of the halide gas at a pressure of ~ 400 torr at various temperatures and exposure intervals. These polymers are highly melt-and-solution-processible and upon doping may have conductivities as high as $10^0\ \Omega^{-1}\ cm^{-1}$ [477,478]. Unlike TCNQ salts they are inert towards atmospheric O_2 but deteriorate in the presence of water vapour [321].

The exact degree of conductivity is proportional to the temperature and pressure at which doping proceeded, that is, the amount of dopant incorporated into the polymer. The doping process results in the oxidation of the aromatic moieties to the radical cations with the concomitant formation of AsF_3 [477].

$$2e(pol) + 3AsF_5(g) \rightarrow 2AsF_6^-(pol) + AsF_3(g)$$

Heavy exposure to AsF_5 considerably alters the processing characteristics of the conducting polymer by altering the chemical nature of the polymeric backbone [478,482]. The formation of simple poly-cation radical/AsF_6^- salts(A) (Fig. 16) predominates over intrachain (B) or interchain (C) cross-linking at doping temperatures between −78 and −10°C. High dopant concentrations (> 0.5 mol AsF_6^- per monomer unit) favor intrachain and interchain cross-linking, the latter coupling being the least common. Thermoelectric studies of AsF_5-doped polyphenylene sulphides give positive Seebeck coefficients indicating *p*-type conductivity (holes). The conductivity obeyed the relation $\sigma \propto \exp(-a/T^{1/2})$ instead of the Arrhenius expression $\exp(-E/kT)$ and this behavior is consistent with a conduction mechanism in which carriers tunnel between conducting particles in an insulating matrix [478]. The synthesis and conductivity of polymers with extensive π-electron systems such as polyacetylene, polyphenylene etc., have been dealt with elsewhere [420–424,428,483]. The emphasis of recent developments in this area has centered on the doping of polyunsaturated conjugated polymers with strong electron acceptors such as AsF_5 or the weaker I_2. Selected examples of those are found in Table 16.

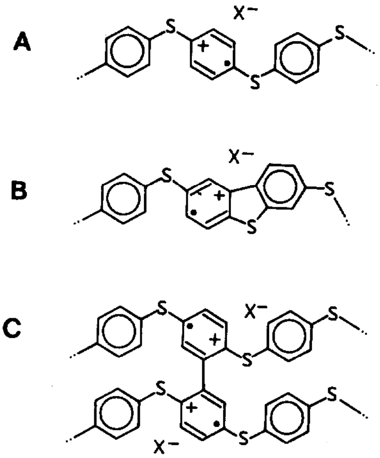


Fig. 16. Products of the reaction of AsF_5 dopant with poly(*p*-phenylene sulphide). X^- represents AsF_6^-.

(iii) *Type 2 CT polymers*

Highly conjugated polymers such as polyacetylene and polyphenylene can be doped with alkali metals such as lithium or sodium, resulting in a situation where the reduced polymer acts as a poly-acceptor [423]. Other workers [484,485] have shown that the reduction of polyacetylene with sodium naphthalide in THF solvent yields a complex

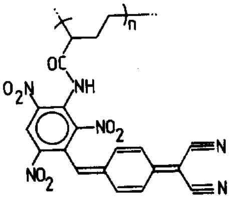
$$(\mathrm{CH{=}CH})_n + \mathrm{R}^{\cdot -}\mathrm{Na}^+ \rightarrow \mathrm{R} + (\mathrm{CH{=}CH})_n^{\cdot -}\,\mathrm{Na}^+$$

(where R represents naphthalene)

with a conductivity of $\sim 80\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Shacklette et al. [486,487] also achieved high conductivity with complexes derived from polyphenylene and potassium naphthalide. Studies on related oligomeric components have shown that the reduction process in solution leads to the formation of both the radical anion and the dianion of the aromatic species [488]. Baughmann et al. [423] have discussed recent developments in the elucidation of the structural aspects of these compounds.

(iv) Type 3 CT polymers

Very few examples of type 3 conducting polymers have been reported. Naarman [489–491] has potential complexes formed from PNVC and a polymeric acceptor species (**36**), which form films with conductivities as high as $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$. These polymeric donor–polymeric acceptor complexes are much more conductive than the polynitrophthalates/polyarylaminodiethanol complexes studied by Sulzberg and Cotter [492].



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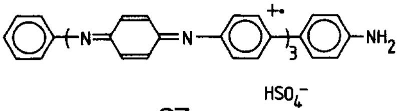
(v) Type 4 CT polymers

Polymers which possess both donor and acceptor moieties incorporated into the polymeric chain can have two different donor/acceptor species that form a charge-transfer complex with each other or only donor moieties which upon oxidation to the radical cation, form intramolecular charge-transfer complexes with unoxidized donor functions, which in this instance occupy the role of an acceptor moiety. One such example is emeraldine (**37**)



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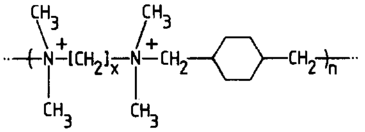

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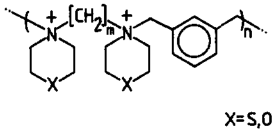

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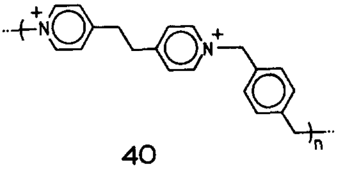

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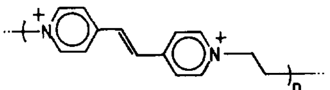

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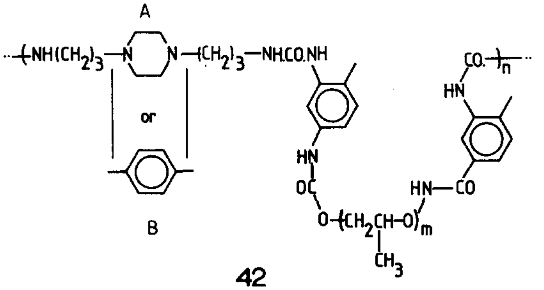

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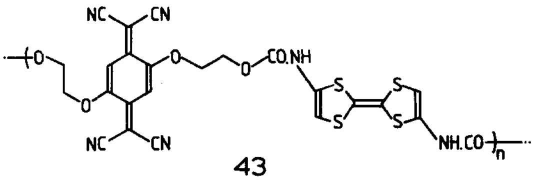

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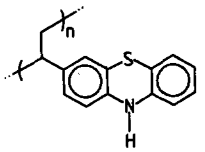

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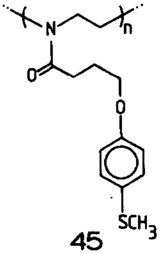

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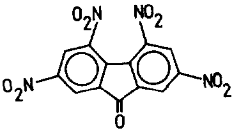

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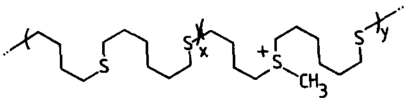

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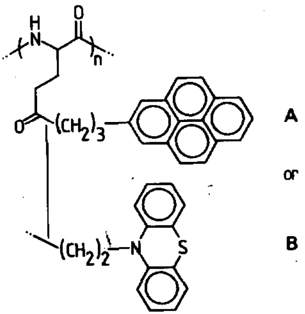

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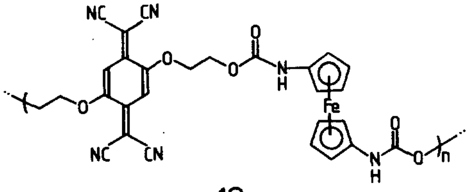

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bound to polystrene. Attempts have been made to use it as a battery electrode [493]. Manecke and Kautz [494] have also prepared polymers containing cation radicals based on the violene redox systems (**33** and **34**). Further examples of cation radical polymers and mixed poly(D/A) species are listed in Table 16.

M. ELECTROCHROMIC POLYMERS IN DIGITAL DISPLAY DEVICES

The use of electrochromic materials is one of the methods by which display devices may be constructed [495–497]. Redox polymers are presently finding applications in such devices. A colorless polymer may be reduced at an electrode to yield a highly colored derivative which can be "erased" upon electrochemical oxidation back to the leuco form.

Viologens are colorless 4,4′-bipyridinium salts (Fig. 17) which may be chemically or electrochemically reduced [498] through two separate reduction stages. The first reduction (E_1) yields a deep violet radical cation and the second (E_2) forms a neutral red 1,1′-dialkyl-1,1′-dihydro-4,4′-bipyridyl. Typically, E_2 is more negative than E_1, and for benzyl viologen the values are −0.57 and −0.79 V vs. SCE, respectively. Both reduction states are rapidly reoxidized by molecular oxygen [499,500] to the non-reduced V^{2+} species. Recently, there have been several attempts to utilize viologens in electrochromic display devices [501–504] of the seven-segment display type [501]. The use of viologens in electrochromic displays have been successful enough to warrant several patent applications [505–507].

Monomeric viologens, however, precipitate upon reduction to the radical cation species in electrolyte solutions [501,508,509]. It is known that the cation radicals of viologens associate to form dimers [498]. The dimers may

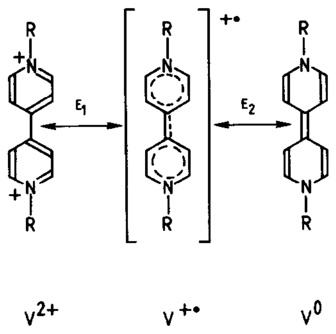


Fig. 17. Reduction states of viologen.

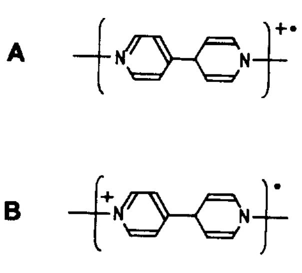


Fig. 18. States of the viologen cation radical [511, 512]. (A) Ion-pair state; (B) ion-bonding state.

be either monocation dimers or dication dimers,

$$V^{+\cdot} + V \rightarrow V_2^{+\cdot} \text{ or } 2V^{+\cdot} \rightarrow V_2^{2+}$$

Various structures for the dimers have been proposed [498] and it seems that the deterioration [510] of the electrochromic characteristics can be attributed to a transformation from the ion-pair state to the non-bonding state [511,512] (Fig. 18) during some strong intermolecular interaction.

Further, the second reduction step in monomeric viologens is often irreversible and results in poor display performance [502,503]. To overcome some of the problems inherent in systems using monomeric viologens, polymers based on viologens have been investigated. Spectroscopic analysis of polyviologens suggests that in the polymeric state there is still some intermolecular interaction between the radical cations of the reduced polymer. Ageing of polyviologens, however, does not appear to be as pronounced as that observed for the monomeric species, and there are several claims for the superiority of memory stability in the former [511–515].

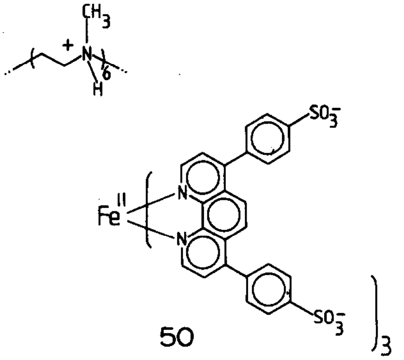
The polymeric viologens have a lower E_1 value than viologen monomers [498,513,516,517], and generally a larger value of ΔE, where $\Delta E = E_2 - E_1$. The impedance of electrochromic devices is quite low as they contain electrolyte solutions, and more than several milliamperes of current is applied to the device. The electrodes within the display often have a high resistance and an ohmic drop comparable to ΔE may occur within the electrode. In overcoming this, operating at a higher potential often means that the second reduction occurs. Electrochromic materials with a wider separation of the two reduction steps are desirable [518] and are realized in the use of polyviologenic compounds. The lower E_1 values of these polymers allows the display device to operate at lower potentials than would be possible with the monomeric compounds.

Electrochromic polymers containing tetrathiafulvene [519–522] and pyrazoline dyes [520,523,524] have not yet been seriously considered for use in electrooptic recording devices. The color change upon electroreduction is usually yellow to green; not as visually striking as the color change apparent upon electroreduction of viologens or deposited films of prussian blue [525].

Macromolecular ionic complexes between the polycation quaternized PVP, quaternized polyethyleneimine (PEI) and polyethylmethocrylatetriethylammonium chloride with metal–bathophenanthroline disulphonate (BPS^{2-}) chelates have been studied both as modifying polymers for electrodes and for their spectroelectrochemical properties over transparent SnO_2 electrodes in seven-segment electrochromic display devices [526]. It was found that a macromolecular complex of the cationic polymer and the anionic ligand formed a precipitate which was only soluble in a ternary solvent blend of conc. HCl, H_2O and dioxane. The polymeric complexes could then be spin coated onto disk electrodes and immersed into ammonium ferrous sulphate so that formation of the deep red $\mathrm{Fe(II)(BPS)_3}$ chelate within the polymer could occur. The polymer complexes are colorless upon oxidation

$$\underset{\text{red}}{\mathrm{QPEI}\cdot\mathrm{Fe(II)(BPS^{2-})_3}} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\text{clear}}{\mathrm{Fe(III)(BPS^{2-})}\cdot\mathrm{QPEI}}$$

Electrochemical investigation of the $\mathrm{(QPEI)^+\cdot Fe(II)(BPS^{2-})_3}$ complex (**50**)



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revealed an anodic wave at about +0.95V vs. SCE and a cathodic peak at about +0.85 V which arose from a continuous repetition of scanning of the electrode potential. Continuous scans of > 50 cycles yielded a steady-state voltammogram; several potential sweeps are required for the TTF polymer electrode to give a steady-state voltammogram [519]. The reason for the absence of a cathodic peak in the first scan is probably due to an electron-transfer reaction from uncoordinated Fe(II) to coordinated Fe(III). The uncoordinated Fe(II) ions are located mainly at the surface of the polymeric film, as evidenced by the absence of an oxidation wave due to Fe(II) even in the first scan, and the excess of uncoordinated Fe(II) in the domain of the polymer is soaked out during such repeated scanning.

The $\mathrm{(QPEI)\cdot Fe(II)(BPS^{2-})/SnO_2}$ electrodes, having a film thickness of 180 nm after reaching steady-state conditions, have the anodic and cathodic peak currents directly proportional to the scan rate up to 0.2 $\mathrm{V\ s^{-1}}$. Apparently, these electrodes have much faster responses than polyviologen-modified electrodes where, in a previous paper [527], the deviation of the peak anodic and cathodic currents was observed at scan rates $< 0.2\ \mathrm{V\ s^{-1}}$ at a film thickness of only 40 nm.

Recent progress in display technology has also touched upon the use of conductive polymers in other parts of the electrochromic cell. Electrochromic systems based on amorphous tungstic oxide ($\mathrm{WO_3}$) films employ liquid proton conducting media containing sulphuric acid [528]. However, it is now recognized that these amorphous films are not sufficiently stable in these electrolytes to permit the construction of a truly long-life display device

[529]. Polymeric electrolytes have found an application in electrochromic displays as semi-solid conducting media between the electrochromic film and the counter electrode [530]. The ionic conductivities and chemical stabilities of polystyrenesulphonic acid (PSSA), polyethylenesulphonic acid (PESA), poly-2-acrylamido-2-methylpropanesulphonic acid (PAMPS) and perfluorosulphonic acid ('Nafion') have been investigated and found suitable for use as polymeric electrolyte media in WO_3-based electrochromic devices, with PAMPS generally being the most tractable [531]. The conductivity of the polymer levels-off at $\sim 5 \times 10^{-2}$ ohm^{-1} cm^{-1} as the water content of the electrolytes reaches 6–10 H_2O equivalents, compared with H_2SO_4 at $\sim 8 \times 10^{-1}$ ohm^{-1} cm^{-1} under similar circumstances, although the conductivity of the polyelectrolytes is inferior to sulphuric acid. Many of the problems inherent with acidic electrolyte solutions are overcome and the efficiency of the display devices do not seem to be impaired [531].

N. PHOTOREDOX PROCESSES IN MACROMOLECULAR ASSEMBLIES

(i) Aspects of the photoredox process

The photoredox behavior of macromolecules, and ways in which polymers influence the photoconversion process in various light-driven redox systems, have been the subject of a number of investigations. Photoredox reactions of polymers have been studied as models of photosynthesis in plants, the aim being the utilization of solar energy for production of primary substances necessary for human survival. Foremost among the aims of recent endeavors are the photoinduced splitting of water [532–534] to hydrogen and oxygen. Other efforts have centered on the construction of photovoltaic devices [535,536]. In light-harvesting reactions involving polymeric assemblies, the polymer can assume either a primary or secondary role, that is, the polymer contains the chromophore or it participates in the light transduction process by means of a sensitizing agent. The photosensitization process involves a sensitizer, S, an acceptor, A, and a donor, D. The sensitizer absorbs a quantum of light and subsequently undergoes an electron-transfer process with an accompanying shunting of electrons from D to S to A in an oxidative quenching process, or from A to S to D in reductive quenching of the sensitizer [537,538] (Fig. 19). However, no spontaneous electron transfer can occur between the ground state of any of the species.

By suitable choice of the donor/acceptor couple, the initial conversion efficiency, i.e. the standard free energy of reaction divided by the threshold photon energy, may be higher than 90% [539]. In homogeneous solutions the forward electron transfer is followed by a rapid thermally induced back reaction, for example

$$\mathrm{A} + \mathrm{D} \underset{(\Delta)}{\overset{(h\nu,\, S)K_q}{\rightleftharpoons}} \mathrm{A}^- + \mathrm{D}^+$$

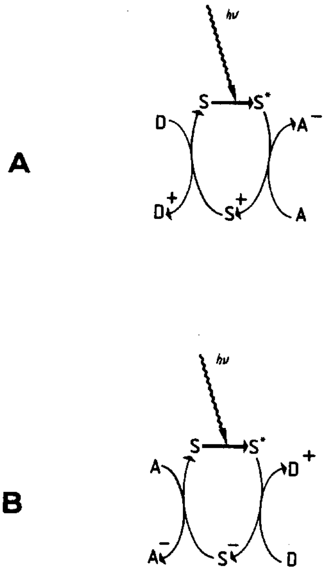

Fig. 19. Sensitization of photoinduced ternary electron-transfer reactions [537]. (A) By oxidative quenching of the sensitizer; (B) by reductive quenching of the sensitizer.

Microheterogeneous systems such as micellar aggregates [540,541] in aqueous solutions have been successfully employed to inhibit the undesirable back reaction [539,542–544], and similar effects can be obtained by incorporation into liposomes [545] or polymers.

A kinetic model of simple photoinduced electron transfer in a reductively quenched donor/acceptor couple

$$\mathrm{A}^* + \mathrm{D} \underset{K_q}{\rightarrow} \mathrm{A}^- + \mathrm{D}^+$$

where the donor is contained within the micelle, has been developed by Grätzel [539]. It was assumed that the donor distribution over the micelles followed Poisson's law

$$\frac{M_i}{M} = \frac{m_i}{i!} \cdot E^{-m}$$

Considering the elementary intramicellar photoredox reactions

$$\mathrm{A}^* \xrightarrow[K_{nr}+K_f]{} \mathrm{A} \quad \text{non-reductive deactivation of the acceptor (sensitizer)}$$

$$\mathrm{A}^* + (i \times \mathrm{D}) \xrightarrow[i \times K_q]{} [(i-1) \times \mathrm{D}] + \mathrm{D}^+ + \mathrm{A}^- \quad \text{reductive quenching}$$

$$[(i-1) \times \mathrm{D}] + \mathrm{D}^+ + \mathrm{A}^- \xrightarrow[K_b]{} (i \times \mathrm{D}) + \mathrm{A} \quad \text{back reaction}$$

where M_i is the number of micelles having i donor molecules, M is the total number of micelles and m the average occupancy, it can be shown that the time rate law for the decay of excited acceptor after excitation with a light pulse is given by

$$[\mathrm{A}^*](t) = [\mathrm{A}^*](0) \cdot \exp\left\{ -(K_f + K_{nr})t + n \cdot \left[\exp(-K_q t) - 1\right] \right\}$$

where [A*](0) represents the concentration of excited acceptor immediately after the light pulse, and K_f and K_{nr} are the rate constants for the radiative and non-radiative deactivation competing with the reductive quenching process.

From this expression it may be shown that micelles enhance the rate of the electron-transfer reaction compared with that in a homogeneous solution, owing to a close concentration of the reactants. It also follows, however, that the yield of quenched products may be less in a surfactant rather than a homogeneous solution.

(ii) Polymeric sensitizers

Polymeric sensitizers are formed by well established methods and applications of polymeric sensitizers are summarized in Table 17. The adsorption of a sensitizing dye onto an inert insoluble polymeric particle, the complexation of a charged sensitizing species to a polyelectrolyte or the covalent attachment of photoreceptive molecules to a polymer backbone generally yield satisfactory macromolecular photosensitizers. In the first instance, polymeric sensitizers formed by adsorption of the dye onto a polymer, the state of adsorbed species can influence the effectiveness of the system as a whole. Dye molecules have long been known to undergo a self-association process in solution and this phenomenon can be either enhanced or completely suppressed once the dye is in the domain of the polymer [546,547]. The absorption spectra of dimeric or higher aggregated dyes shift to shorter wavelengths with respect to that observed for the monomeric dye species. The aggregation of chlorophyll in solution [548,549] and in thin solid films [550,551] of the pigment is a well established phenomenon. The way in which the fluorescence spectra of bacteriochlorophyll [552] and bacterioviridin

TABLE 17

Some photochemical reactions sensitized by polymer-bound species

Sensitizer	Polymeric matrix	Type	Sensitized reaction	Ref. [a]
Chlorophyll	Adsorption of dye to polycaprolactam	N	Photosensitized reduction of Methyl Red by ascorbic acid	1
as above	polyacrylonitrile	N	as above	2
as above	wool keratin	N	as above	3
Cu(II) and Mg(II) chlorophyllin	Polymerized chlorophyllin–styrene monomers	C	Photosensitized reduction of Fast Red A by ascorbic acid and quinone	4–6
Co(II), Fe(II) and Mg(II) complexes of photoporphyrin IX	Polymerized PPIX–styrene esters	C	as above	5
Free-base TTP and chlorophyll	Pearl-polymerized polymethacrylate particles	E	Photoreduction of Fast Red A and riboflavin. Oxidative quenching of sensitizer at high pH, reductive at low pH	7, 8
Anthracene, pyrene	Formaldehyde polymers	C	Photooxidation of leuco crystal violet	9
β-Carotene	Polyacrylonitrile	N	Reduction of thionine and Methyl Red by ascorbic acid	10
as above	Wool keratin	N	as above	3
Pheophytin-a	Polystyrene	N	Reduction of azo dyes by ascorbate and *N*′-alkyl-1,4-dihydronicotinamides	11
Chlorophyll	Polyvinylpyrrolidone	S	Photoreduction of the azo dye Fast Red S enhanced in the presence of the polymer	12, 13
Mn(III) tetrapyridylporphyrin	Benzoquinone polymer	N	Photoreduction of quinone to hydroquinone	14

Ru(II)(bipy)$_3$	Cellulose	N	Reduction of methylviologen in the solid phase using EDTA as the electron donor. Reaction retarded in the presence of water	15, 16
as above	Iminodiacetic acid type ion exchange resin	I	Photoreduction of methylviologen in water-swollen resin	17
as above	Dowex 50 W-X8, sulphonated polystyrene ion exchanger	I	Reduction of methylviologen by TEOA. Viologen radicals produce H_2O_2 via the superoxide ion from dissolved oxygen	18
Ferrocene	Vinylferrocene, styrene, maleic anhydride terpolymer	C	Photoreduction of Fast Red A with ascorbic acid	19
Viologen	Chloromethylated Polystyrene	C	Photooxidation of 2-propanol	20
Alloxan	Polymerized alloxan	C	Reduction of quinones, triphenyl tetrazolium chloride, viologens and the Tillman reagent	21
Triphenylmethane dyes	Polymethacrylic acid	I	Photoreduction of tetrazolium salts by dye only occurs in the presence of the polymer	22
Rose Bengal	Polyvinylpyrrolidone	I	Photoreduction of tetrazolium salts by dye only occurs in the presence of the polymer	23
Ru(II)(bipy)$_3$	PVA solution	N	Photoreduction of Ag^+ to Ag^0 enhanced by prevention of the back reaction by PVA. O_2 can also be liberated from H_2O in the presence of zeolite–RuO_2	24

TABLE 17 (continued)

Sensitizer	Polymeric matrix	Type	Sensitized reaction	Ref. [a]
Colloidal TiO_2/PVA	PVA solution	N	Laser-induced (347.1 nm) valence band holes of TiO_2 oxidize $2X^-$ to X_2^- ($X = Br, Cl, I$). The polymer stabilizes the colloid but retards the oxidation process	25

[a] See Table 1.

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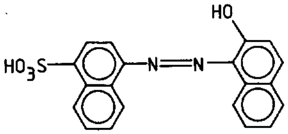
[553] alters with temperature are very similar for the porphyrins in vivo and in thin films. Such a parallel does not preclude pigment–pigment interactions in natural systems [554]. However, recent evidence suggests that monomeric chlorophyll units exist in a protein–chlorophyll complex in chloroplasts [555]. Chlorophyll and β-carotene can be deposited on polycaprolactam, polyethylene, polystyrene or zeolite particles; however these systems are much less effective than their homogeneous counterparts due to a high degree of aggregation of sensitizer molecules on the polymer phase [556–558]. Smaller aggregates, such as dimers, retain some vestige of sensitizing ability [556]. In other polymeric systems the formation of monomeric chlorophyll units can increase the efficiency of the photosensitization process 20-fold [559,560]. The judicious use of polymers or surfactants enables the creation of a hydrophobic environment where dissaggregation of a macrocyclic sensitizer is favored. For instance, various porphyrins [561,562], as well as zinc(II) tetrasulphophthalocyanine, can be efficient sensitizers [563,564] in a hydrogen generation system, but due to self-aggregation in solution their usefulness becomes limited [565]. The incorporation of these blue dyes into cationic micelles results in the dissaggregation of the chelate to monomeric photoactive units [566].

The photosensitizing behavior of free base tetraphenylporphyrins trapped within methacrylate polymers has been reported to be pH dependent, much like the free species in solution [567,568]. The reduction of Fast Red A (**51**) proceeded by photoxidation of the porphyrin in acidic media and photoreduction at alkaline pH. Chlorophyll in vivo behaves similarly [569], though there have been some assertions that the photoactive active center in chlorophyll-a assumes an oligomeric form [570,571]. Synthetic polymers carrying pendant chlorophyll-a dimers coupled by an ethylenebisamide bridge have been shown to be more effective sensitizers than mononuclear units attached to similar polymers [572]. Often, such comparisons seldom amount to very much as the inaccessibility of the photoreceptor to the donor and acceptor substrates can contribute to low overall activity of the sensitizer, which is highly dependent on the polymeric matrix employed [573].



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The tris(2,2′-bipyridyl) ruthenium(II) complex is currently receiving a lot of attention as a photocatalyst for decomposing water by solar radiation [532,574]. Since water is transparent to visible light, hydrogen and oxygen evolution systems require some sensitization to the visible output of the sun.

This sensitizer enjoys extensive popularity since the maximum absorption of the chelate is at 480 nm, which is the wavelength of maximum solar spectral intensity [575]. The photochemistry and quenching of the excited state of Ru(II)(bipy)$_3^{2+}$ complexes in solution [576,577], in phospholipid resides [578], in micellar [579] and polyelectrolyte [580] solutions, coordinated to poly(4-vinylpyridine) [581–584] and covalently bonded to polystyrene derivatives [585–588] and fluorosulphonate membranes [404,589,590] by various metal ions, has been examined. The behavior of [Ru(II)(bipy)$_2$]$^{2+}$ bound to PVP upon irradiation in methanol or aqueous acid solution is much like that of the unbound species [581–592]. At ambient temperature the macromolecular sensitizers are observed to luminesce weakly in methanol and acid solutions, and much more intensely from frozen methanol solutions or from films of the polymer at room temperature. The polymeric complexes can be highly cross-linked and become insoluble in most solvents, but well suited for film casting.

The reaction of Ru(II)(bipy)$_2$Cl$_2$ with PVP in refluxing methanol yields predominantly [Ru(bipy)$_2$(PVP′)Cl]$^+$, however at very low loading levels of the complex on the polymer, the disubstituted species, [Ru(bipy)$_2$(PVP′)$_2$]$^{2+}$, may be formed [581,582,584]. PVP′ represents one pyridine unit of the polymer PVP. Similarly, in the presence of pyridine, the species [Ru(II)(bipy)$_2$(PVP′)py]$^{2+}$ can be prepared [584]. The solubility characteristics of each mono- and di-substituted species are different.

The bis-bipyridyl ruthenium(II)–PVP complex can undergo both photosubstitution and photoanation reactions in various solvents, and consequently the spectral and sensitizing properties of the macromolecular species change. Though the emission lifetimes of the monomeric and macromolecular species are much the same, the maximum of the emission band of the polymeric Ru(II) complexes are red-shifted by about 10 nm [584], reflecting the different coordination properties of the two species. Polyelectrolytes such as polyvinylsulphate, on the other hand, have little or no effect on the absorption or luminescence properties of tris-bipyridyl ruthenium(II) complexes. Again, Ru(II)(bipy)$_3^{2+}$ complexes covalently bound to polystyrene do not show appreciable spectral differences from the homogeneous monomer [588]. Highly pH-sensitive polymeric sensitizers have been prepared [587]. The absorption and luminescence spectra of carboxylate derivatives of Ru(II)(bipy)$_3^{2+}$ attached to *p*-aminostyrene-*N*-vinylpyrrolidone copolymers are strongly influenced by pH. The acid dissociation of the $-$CO$_2$H group in the bipyridine ring at higher pH has been shown to greatly increase the luminescence of the polymeric complex. Some photochemical reactions sensitized by polymeric species are summarized in Table 17.

(iii) Photoenergy transfer in macromolecular systems

The transduction of light energy has been discussed by Howell and Vieth [592]. The purple membranes from such species as *Halobacterium holobium* on sulphonated polysulphone cation exchange films [592a] have also been observed to be photochemically active. Totally synthetic polymers have also been investigated as possible macromolecular donor or acceptor relays in light-harvesting assemblies [592b], imitating the natural photosynthetic membranes in plant chloroplasts. The photoenergy absorbed by antenna chlorophyll is transferred to a reaction center which drives the linked electron-transport system to couple the oxidation of water with concomitant reduction of NADP to NADPH [593]. Recent developments in the use of aromatic hydrocarbon sensitizers [594,595] have inspired the construction of polymers bearing anthracene, pyrene and perylene photoreceptors [596–599]. Providing excimer formation [598,600] and photodimerization are minimized, the polymer matrix enables long-range singlet energy migration to an active site where the sensitized reduction of oxygen by crystal violet can occur [596]. Similar energy-transfer phenomena have been observed for fluoranthene dispersions in polystyrene [601], and the photodimerization in various polymers of pendant thymine bases has been related to the degree of intramolecular self-association of the bases and singlet energy migration [602].

Surfactant derivatives of methylviologen can be used to solubilize zinc porphyrins and may engage in oxidative quenching of the porphyrin sensitizer with electron transfer through the viologen vesicle proceeding by a tunnelling mechanism to a suitable catalyst leading to the production of hydrogen from water [539]. The photosensitized electron transport in symmetrical and asymmetrical vesicles incorporating a surface-active chlorophyll [603] or a zinc porphyrin has also been described [604–606]. The electron transport from EDTA or ascorbic acid (within the vesicle) across membranes of dipalmityl-L-α-phosphatidylcholine to methylviologen outside the vesicle was sensitized by cationic zinc porphyrin derivatives, and mediated across the membrane by ubiquinone (UQ_{10}) or tetraphenylporphine. A new technology of polymerizing the surfactant units in micellar bilayers has emerged [607–610]. Surfactant viologen derivatives can be converted by a process of sonication, radical polymerization and chemical modification to yield a chemically stable disymmetrical polymerized surfactant vesicle which contains the viologen moiety within the vesicle. Photoexcitation of $Ru(bipy)_3^{2+}$ on the outside of the polymeric particle results in electron transfer from the sensitizer across the bilayer to yield a long-lived reduced form of methylviologen [607].

Polymeric viologens can function quite well as poly-acceptors in macromolecular electron relays in various light-driven water-splitting systems.

Progress has been made towards more efficient systems by preparing polymeric viologens which concentrate the photosensitizer and the multielectron redox catalyst in the domain of the electron mediator [611,612]. Work along similar lines has progressed with viologens possessing surfactant properties [612–615]. One group of workers [611] has shown that pendant viologens on a styrene–acrylamide copolymer are more effective as electron mediators during hydrogen production than their monomeric counterparts. However, this is only the case when reduced chemically, and not with sensitized photoreduction of the polymeric viologens. The latter phenomenon may be a result of a decreased probability of encounter between the photosensitizer and the acceptor molecules in the polymeric matrix. The chemical nature of the polymer can be critical to the efficiency of the electron transfer from the sensitizer in its excited state to viologen units. Polyvinylviologens, for example, were found to be less effective in quenching the photoexcited state of $\mathrm{Ru(II)(bipy)_3^{2+}}$ than hexadecylviologens coupled with polychloromethylstyrene [612]. An increased reverse electron transfer has been blamed as the cause of the relative inefficiency of electron transfer in the latter system. The transport of electrons through polymeric viologens involves the formation of radical dimers [612] and popular opinion claims the formation of these dimers is detrimental to the activity of hydrogen photoevolution assemblies [611].

Nishijima et al. [612] have studied electron migration in polymerized *N*-vinylbenzyl-*N′*-*n*-propyl-4,4′-bipyridium films. Upon photoreduction of the polymer with $\mathrm{Ru(bipy)_3^{2+}}$ in the presence of EDTA, the electronic absorption spectrum of the macromolecule coincides with that of viologen cation radical dimers even when the concentration of photoreduced viologen units is quite low. A similar phenomenon is evident upon irradiation of solid films where the molecular motions of the polymer chains are negligible. At very low viologen/polymer ratios, viologen cation radical monomers can be detected. ESR studies of the photoreduced polymer in solution reveal a broad singlet (width of about 2G) without the characteristic hyperfine structures indicative of viologen cation radicals. The component line width of about 2G is too broad for polymer radicals in solution and it is thought that this broadening is a result of an electron-exchange mechanism. From the electronic absorption results it appears that the electron migration proceeds along the polymer until trapped as radical dimers. More efficient photosensitized reduction is possible by the juxtaposition of attached $\mathrm{Ru(bipy)_3^{2+}}$ and viologen units on a common polymer chain [616].

Several determinations of the quenching rate, K_q, of $[\mathrm{Ru(bipy)_3^{2+}}]^*$ by viologen-type relays [574,617–619] of different redox potentials have tested current theoretical and semi empirical models proposed for electron-transfer quenching reactions [620–622]. The work of Amouyal et al. [622] indicates that for the same redox potential, the molecular structure of the quencher does affect the value of K_q nearly as much as its reduction potential, $E_{1/2}$. According to the Rehm–Weller treatment, which is based on the kinetic scheme

$$\begin{tikzcd} D^* + A \arrow[r, shift left, "k_{12}"] \arrow[d, "1/\tau_0"] & D^*\text{- - -}A \arrow[l, shift left, "k_{21}"] \arrow[r, shift left, "k_{23}"] & D^+\text{- - -}A^- \arrow[l, shift left, "k_{32}"] \arrow[d, "k_{30}"] \\ D & & D \end{tikzcd}$$

the observed quenching rate constant, K_q, is given by

$$K_q = k_{12}/\{1 + (k_{12}/K_{12}k_{30})[\exp(\Delta G^*/RT) + \exp(\Delta G/RT)]\}$$

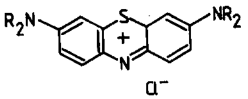
where ΔG is the free energy change in the electron-transfer step, ΔG^* the free energy of activation, and $K_{12} = k_{12}/k_{21}$. ΔG can also be related to the donor and acceptor potentials

$$\Delta G = E_{1/2}(D^+/D^*) - E_{1/2}(A/A^-) + w_p - w_r$$

where w_p and w_r represent the coulombic work required to bring the products and reactants together to form the ion pair and encounter complex, respectively. The latter terms can be neglected in media of high ionic strength. The free energy of activation for electron transfer, ΔG^*, can be related to the overall free energy change [620,623]

$$\Delta G^* = \tfrac{1}{2}\Delta G + \left[\left(\tfrac{1}{2}\Delta G\right)^2 + \Delta G^*(0)^2\right]^{1/2}$$

where $\Delta G^*(0)$ is the free energy of activation for $\Delta G = 0$. On the basis of these relationships it has been predicted [621] that K_q approaches the diffusion-controlled limit when ΔG is large and negative. With increasingly large values of ΔG, the magnitude of K_q should decrease and eventually become proportional to $\exp(-\Delta G/RT)$ when ΔG is large and positive. A comparison of K_q against ΔG for various $[\mathrm{Ru(bipy)}_3^{2+}]^*$/viologen couples strongly supports [622] the kinetic treatments proposed by Rehm and Weller [621]. Not all photoenergy transfer from the sensitizer to a polymeric electron relay is reversible. There is the occasional situation where even the polymeric donor or acceptor species is sacrificial and needs to be regenerated. For instance, Kaneko et al. [624,625] have shown that thionine dyes may induce a photopotential in solution, in the presence of certain sacrificial redox polymers. In the presence of the polymer PEI (polyethyleneimine) the photopotential of thionine (**52**) Methylene Blue or tolusafranine dyes are



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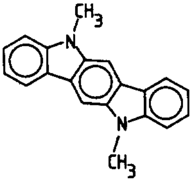
significantly higher than that of the dye/monoamine couple [625]. In the case of thionine, the triplet state of the dye is reduced to the semithionine or to the leucothionine by the monoprotonated amine units in the polyamine. The exact nature of the oxidized form of the polymer remains undecided, though analogous studies with monomonic amines suggest amine oxides as the final product [626]. Similar results were obtained with photoredox polymers derived from the coupling of thionine dyes with PAA [624]. These polymeric systems can be used to power photovoltaic cells.

(iv) Photoreduction of metal ions in organized systems

The photoreduction of ferric salts and bichromates by ultraviolet light has been known for more than a century [627]. Ultraviolet photoreductions involve the direct excitation of a metal ion complex and reduction is believed to proceed by an electron transfer from the photoexcited metal to its ligand [628]. These phenomena are particularly interesting in view of the fact that photolysis of transition metal ions in their CTTS (charge transfer to solvent bands) in acidic media can lead to the evolution of hydrogen from water [532]. In many cases the reduction of the metal ion is assisted by a sensitizing dye. Many mild reducing agents can serve as an electron donor, however it is often difficult to avoid the direct reduction of the metal center. This problem can be overcome by employing chelating agents for the metal ion which also serve as electron donors for the excited dyes.

For instance, the photoreduction of various metal ions (Fe^{3+}, Ti^{4+}, CrO_4^-, Cu^{2+}, Ag^+, MoO_4^-, Hg^{2+}) can be achieved using Methylene Blue as a sensitizer and EDTA as both the chelating agent and the sacrificial donor [629]. Such light-driven reduction systems can be affected by the presence of a polymer or they in turn may influence the dynamic properties of a polymer solution. The dye-sensitized degelling of a polyacrylamide gel complexed with mercuric ions was found to be a result of the reduction of Hg(II) to Hg(I), the latter being unable to participate in interchain cross-linking. Similarly, the insolubilization of gelatin has been observed with dye-sensitized photoreduction of the chromate ion [629]. Surfactants [542] and polyelectrolytes [580], which are known to affect the photoinduced electron transfer from $Ru(bipy)_3^{2+}$ to Cu^{2+}, have been reported recently. In both the polyelectrolyte and micellar systems the rate of quenching of the lowest charge transfer state of $Ru(bipy)_3^{2+}$ by Cu^{2+} is significantly enhanced, however in the former system a reversal of the quenching phenomenon was observed at higher concentrations of Cu^{2+} ions. An enhancement of the back reaction meant that no net electron transfer to the copper(II) ions was observed. Cu^{2+} ions have also been found to participate in efficient oxidative quenching of DI (*N*,*N'*-dimethyl-5,11-dihydroindolo-[3,2,6]-carbazole) (**53**) in micelles of sodiumlaurylsulphate [539,630,631]. The introduction of Cu^{2+}, as a counter-ion atmosphere, to a solution of DI in anionic micelles induces a 300-fold decrease in the fluorescence yield and lifetime of DI. In this case intramicellar electron transfer from DI* in the micelle to Cu^{2+} in solution is rapid and the back reaction is prevented by an even more rapid replacement of Cu^{+} by Cu^{2+} in the Gouy–Chapman layer (Fig. 20). Once in the aqueous phase, Cu^{+} can be used for a second redox process, namely the reduction of $Fe(CN)_6^{3-}$, which in the reduced state is negatively charged and because of coulombic repulsion can no longer approach the micelle. As a result, the system achieves electron/hole separation since the oxidized sensitizer (S^{+}) remains in the micellar aggregate.



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The quenching of uranyl ion fluorescence by Fe^{2+} is accelerated in the presence of polyvinylsulphate (PVS) [632]. The polyelectrolyte serves to concentrate ionic species of similar charge polarity, but opposite to that of itself, in the potential field of the macromolecule. Predictably, the effect of PVS on the photoinitiated electron transfer from the lowest charge-transfer

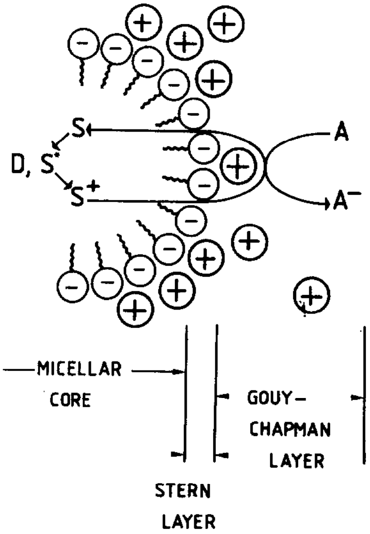
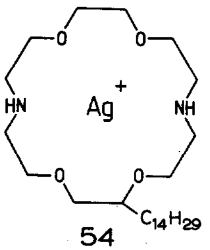


Fig. 20. Photoionization processes in a micelle [642].

state of Ru(bipy)$_3^{2+*}$ to Fe(III) was to increase the electron-transfer process [633]. However, at high coverage of polymer by Fe(III) the rate constant diminished, probably due to configurational changes of the polymer caused by the Fe(III) cations.

Crown ether surfactant derivatives have been developed recently and they serve to concentrate both the sensitizer and metal ion in the micelle [634]. The crown 5-*n*-tetradecyl-1,1,10-diaza-4,7,13,16-tetraoxi-cyclooctadecane, for instance, strongly binds Ag$^+$ ions into large micellar aggregates (**54**). Sensitizers as the cyanine dye (**55**) were shown to be oxidatively bleached with



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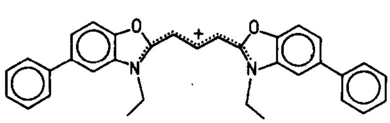

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simultaneous formation of Ag^0. Reduction of the silver(I) ion to silver(0) in the crown ether cavity prevents nucleation of silver atoms, and the monomeric state of the metal atom is thus maintained [532].

O. PHOTOINDUCED HYDROGEN AND OXYGEN EVOLUTION

(i) Macromolecular water-splitting assemblies

The production of hydrogen by photoirradiated chloroplast–bacterial hydrogen assemblies [635–638] and semi-synthetic biophotolytic membranes [592] are currently under investigation as model systems for the photoproduction of hydrogen by unicellular algae and photosynthetic electron transport. The electron-transport process between photosystems II and I in synthetic chloroplast-hydrogenase systems can be bypassed using exogeneous electron donors such as ferrodoxin [638], methylviologen [639,640] or even polymeric viologens [617,641]. Such discoveries led to the development of semi-synthetic biopolymeric systems for the photoproduction of hydrogen (Table 18), and similar totally synthetic polymeric systems for the conversion of solar energy were developed as a matter of course (Table 19). The general features of such photoredox catalysts in colloidal and microheterogeneous systems have been reviewed recently [532,575,642–647].

The photosensitized generation of hydrogen from water requires a photosensitizer, an electron donor, an electron mediator and a multielectron redox catalyst as depicted in Fig. 21. The sensitizer (S) in its photoexcited state

TABLE 18

Some biopolymeric systems for photo-production of hydrogen

Sensitizer	Electron donor	Electron mediator	Redox catalyst	Ref. [a]
Chloroplast films	Ascorbic acid and 2,6-dichlorophenolindophenol	Methyl viologen	Hydrogenase (*Desulfovibrio vulgaris*)	1
Ru(II)TPP·(CO) solubilized in non-ionic detergent	Mercaptoethanol or triethanolamine (TEOA)	Methyl viologen	Hydrogenase (*D. vulgaris*)	2
	$Na_2S_2O_4$	Methyl viologen	Hydrogenase (*D. vulgaris*)	3, 4
Triphenylamine	Triphenylamine	Methyl viologen	Hydrogenase (*D. vulgaris*)	5
Chloroplasts	Ascorbic and NADPH	Methyl viologen	Hydrogenase (*Clostridium butyricum*)	6
Thylakoids immobilized in a foam support	H_2O		Hydrogenases	7
Zn(II) tetraphenylporphyrin solubilized by non-ionic detergent	TEOA or β-mercaptoethanol	Methyl viologen	Hydrogenase (*D. vulgaris*)	8
$Ru(bipy)_3^{2+}$	TEOA or EDTA	Methyl viologen	Hydrogenase (*D. vulgaris*)	9
Cd-Tetraphenylporphyrin trisulphonic acid	TEOA or β-mercaptoethanol	Methyl viologen	Hydrogenase (*D. vulgaris*)	10

[a] See Table 1.

1 T. Yagi and H. Ochiai, Adv. Hydrogen. Energy, 1 (1979) 1293.
2 I. Okura and N.K. Thuan, J. Chem. Soc., Chem. Commun. (1980) 84.
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10 I. Okura, S. Aono, M. Takeuchi and S. Kusunoki, Nouv. J. Chim., 6 (1982) 221.

TABLE 19

Some polymeric assemblies for the photo-production of hydrogen

Sensitizer	Electron donor	Electron mediator	Redox catalyst	Ref.[a]
Ru(II)(bipy)$_3^{2+}$ in solution	EDTA	Methyl viologen	Colloidal Pt in a polyvinylalcohol (PVA) matrix	1, 2
Ru(II)(bipy)$_3^{2+}$ in solution	TEOA or $Na_2S_2O_4$	Methyl viologen and benzyl viologen coupled to a styrene/acrylamide copolymer	Colloidal Pt–PVA	3
Ru(bipy)$_3^{2+}$ in solution	EDTA	Poly(*N*-vinylbenzyl-*N*′-*n*-propyl-4,4′-bipyridium bromide) chloride	Colloidal Pt stabilized by polyvinylpyrrolidone and the viologen polymer	4
Ru(bipy)$_3^{2+}$ covalently attached to polystyrene (solid phase)	TEOA or EDTA in solid form	Methyl viologen	Platinum black in HCl sol/methanol phase	5

$Ru(II)(bipy)_3^{2+}$ covalently attached to polystyrene (solid phase)	TEOA or EDTA	Methyl viologen	Colloidal Pt–PVA in an acidic alcohol solution	6
Zn TPP solubilized in a solution of nm ionic detergent	TEOA or β-mercaptoethanol	Methyl viologen	Detergent stabilized colloidal platinum	7
$Ru(III)(bipy)_3$	EDTA, TEOA	Methyl viologen	Rh, Ru, Pt–polyvinylalcohol colloids	8
as above	EDTA	Methyl viologen	Pt–Polyvinylalcohol colloid	9

[a] See Table 1.

1 J. Kiwi and M. Grätzel, Nature (London), 281 (1979) 656.
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8 J.M. Lehn, J.P. Sauvage and R. Zeissel, Nouv. J. Chim., 5 (1981) 291.
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reduces the electron mediator (D) which in turn transports the electron to the redox catalyst. The presence of an electron donor is necessary to keep the sensitizer in the reduced state as discussed earlier.

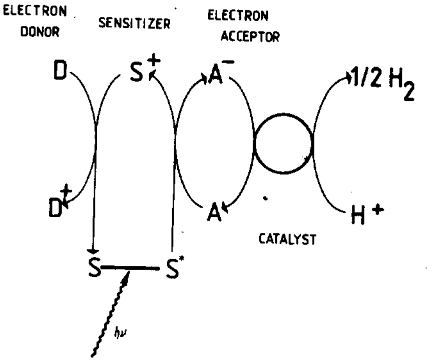

Fig. 21. Catalyzed photoevolution of hydrogen from water [611].

Table 18 summarizes the recent interest in using extracts of hydrogenase from various sources as hydrogen evolution catalysts in synthetic ternary D/S/A light-harvesting systems. That hydrogenase (H_2:ferricytochrome C_3 oxidoreductase, EC 1.12.12.1) is an iron–sulphur protein similar to ferrodoxins is concluded from the presence of an intense electronic absorption at ~ 400 nm which is characteristic of iron–sulphur centers, and the reduced form of the enzyme has an ESR spectrum at reduced temperature [648]. The hydrogenases from *Clostridium pasterianum* [649], *Desulforibrio vulgaris* [650] and *Chromatium* [651] contain 12Fe–12S, 8Fe–8S and 4Fe–4S atoms per molecule of enzyme, respectively. It is quite probable that these iron–sulphur units are arranged as Fe_4S_4 clusters [648]. The role of cytochrome C_3 remains uncertain, as its presence is not necessary for hydrogen evolution [652]. Methylviologen is almost always the electron mediator used to relay electrons from some reducing agent to the enzyme. Early studies have shown the necessity for two molecules of methylviologen for each molecule of H_2 produced, since MV^+ is only a one-electron transfer agent [648,652,653]. The electronic mechanism of hydrogen evolution still remains undisclosed and any rationale of the mechanism has so far been limited to a kinetic treatment of the process. In an elementary hydrogen evolution mechanism it is assumed that the equilibrium constants of the binding of the first and second electron relays molecules are equivalent

$$E + S^- \overset{K}{\rightleftharpoons} ES^-$$

$$ES^- + S^- \overset{K}{\rightleftharpoons} ES_2^{2-}$$

$$ES_2^{2-} + 2H^+ \overset{k}{\rightleftharpoons} E + 2S + H_2$$

where E represents hydrogenase and S methylviologen (MV^{2+}). The rate of hydrogen evolution is then expressed as

$$V = \frac{kK^2[S^-]^2}{(1 + K[S^-])^2}$$

Apart from various hydrogenase extracts from bacteria and plants, noble metals are known to act as redox catalysts in the production of hydrogen from water. In fact, it was recognized some decades ago that colloidal Pt catalyzed water reduction by agents such as Cr^{2+}, V^{2+} [654] and methylviologen [655,656]. Ultrafine Au [657], Ag or Pt dispersions in a stabilizing polymer or polyelectrolyte are used in many assemblies that function like artificial chloroplasts, where the role of the catalyst particle is to couple the anodic oxidation of the reduced relay, A^-, with H_2 generation from water. Metal oxides such as the "Adams" catalyst (PtO_2) and IrO_2 have also been tried [532].

Reducing agents such as sodium dithionite [611,648,658], tertiary amines such as triethanolamine [585,586,611] or triphenylamine [659], thiols [660,661] and EDTA [585,586,612,622–664] are commonly used, depending upon the particular sensitizer employed. It must be emphasized that the electron donor is a sacrificial component of the macromolecular hydrogen evolution apparatus and is not usually regenerated. The chloroplast of the green plant can split water to its constituent elements by coupling the photoevolution of oxygen with the photoproduction of hydrogen by a series of electron mediators as depicted by the Z-scheme [592,643,665]. Recent attempts have been made to imitate this behavior, dispensing with expensive sacrificial electron donors altogether and using water as the ultimate electron source. The marriage of both H_2 and O_2 photoproduction in polymer-stabilized assemblies is a rapidly developing field of chemical research. The reviews by Calvin [643], Kiwi [532,575], Grätzel [532,642,644] and others [645] clarify both the state-of-the-art and problems associated with photochemical water-splitting systems.

The success of chloroplasts in this respect hinges upon the intermediary role played by manganese–protein complexes which function within the framework of the Z-scheme. The accumulation of four redox equivalents leads to the oxidation of water by a water-splitting enzyme which involves at least two manganese atoms per molecule of enzyme. During the four-electron oxidation of water, ESR and proton relaxation evidence suggest the two manganese atoms undergo a redox cycle between Mn(II) and Mn(III) [665].

In several model systems RuO_2 [666–670], IrO_2 [671,672] and MnO_2 [672] have recently proven themselves to be efficient oxygen-generation catalysts in sacrificial photochemical half-cells. Other transition metal oxides such as those of cobalt or nickel may also promote O_2 evolution in the presence of a suitable oxidizing agent, but the yields of oxygen are less than stoichiometric [673] and the process is less efficient than that using RuO_2 [668], where the oxidation of water proceeds by a four-electron process without the intermediate formation of hydrogen peroxide [667].

The technology of both hydrogen and oxygen photoevolution is now fairly well advanced, but the science of coupling these two photochemical half cells (Fig. 22) to yield a true water-splitting system is still in an early stage of development. Grätzel [644] has described three fundamental types of light-harvesting systems employed in photocleavage of water

$$2H_2O \xrightarrow[\text{catalyst}]{h\nu} 2H_2 + O_2$$

The first type contains a sensitizer and an electron relay (donor or acceptor molecule) which upon photoinduced electron transfer drives O_2 and H_2 evolution at separate catalytic sites as depicted in Fig. 22. Instead of using two separate catalysts, one for O_2 and the other for H_2 evolution, the possibility of promoting both reactions on the same catalytic surface has been realized with RuO_2 [674].

In the second type of system, the sensitizer is adsorbed onto a colloidal

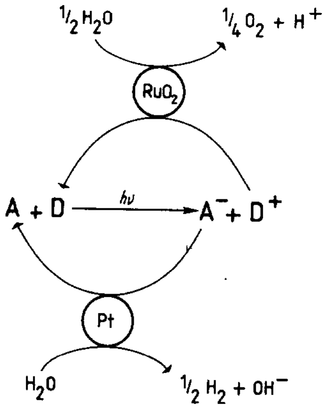

Fig. 22. Schematic representation of a coupled water-splitting system [680].

semiconductor particle and no electron relay is required because electrons are injected from the excited state of the sensitizer into the conduction band of the semiconductor (TiO_2 or RuO_2) and channeled to Pt deposited on the semiconductor particle with subsequent H_2 production. A second catalytic site, which may or may not be codeposited on the semiconductor particle, mediates O_2 generation from S^+ and H_2O.

In the third type of light-harvesting system the colloidal semiconductor itself absorbs visible light and an electron–hole pair is formed through band-gap excitation. The electron gives rise to H_2 formation whilst the latter affords oxygen generation from water, both processes being mediated by suitable catalytic sites deposited on the semiconductor surface [644]. The application of these photophysical phenomena to the development of alternate energy sources is quite topical in itself, but here we will pursue the role of the macromolecule in artificial hydrophotolytic systems.

(ii) The role of the polymer

It is widely known that for hydrogen evolution catalysts (HEC), such as platinum metal, the catalytic activity increases as the size of the noble metal particle decreases [575,642,675–678]. The participation of polymers in promoting redox reactions in microheterogeneous assemblies is well documented for both hydrogen and oxygen evolution systems [575]. Though the art of preparing ultrafine monodispersed colloids is well advanced [679] dramatic increases in H_2 yields can be obtained when noble metal oxide HEC macrodispersions are replaced by polymer-stabilized noble metal colloids. For example, PtO_2 particles of approximately 5×10^4 nm diameter have largely been abandoned in favor of colloidal Pt, Pd or Ru of some 50 nm diameter [666]. A decrease in the radius of a Pt–PVA HEC from 50 to 10 nm can result in a six-fold increase of the hydrogen evolution rate in a given system [680]. Similarly, the addition of PVA to a powdered RuO_2 oxygen evolution catalyst (OEC) [680] results in a more complete dispersion of the catalyst and the rate of H_2 production increases five fold with respect to the system without the polymer [666].

The dispersion of the catalyst is thus seen as an important factor in controlling the catalytic activity. Each catalyst particle behaves as a microelectrode, and a smaller electrode size is advantageous (with regard to the mass transport of the electroactive species from the catalytic site), as well as the surface area per unit weight of catalyst employed. The use of a stabilizing polymer is mandatory if one wishes to prevent agglomeration of the catalyst microspheres. Despite the advantages of polymer-stabilized systems, aggregation [681,682] of polymer-coated particles and setting-out of the protective polymer by electrolytes [683] are unacceptable. The polymers used to stabilize the microheterogeneous particles must therefore be resistant to such phenomena. Several articles concerning the stabilization of the macromolecules themselves to those effects, and their adsorption to microheterogeneous particles, treat this subject more fully [532,684–686].

Typical examples of the polymers employed in such assemblies are polyvinylalcohol (PVA) (a copolymer of vinylacetate and vinylalcohol), which is most commonly used, polyvinylpyrrolidone (PVPr), polyacrylamide (PAA) and polyoxyethylene (POE). PVA has currently been finding wide application in the stabilization of HEC, OEC and bifunctional photocatalytic particles, as Table 19 clearly shows. Kiwi et al. [532] have claimed that a good stabilizer for RuO_2 microspheres is a polymeric system containing sodium dodecylsulphate with PVP, whereas styrene–maleic anhydride copolymers [687] can interfere with the catalytic process. Henglein [688,689] and Meisel and co-workers [690,691] have recently prepared stable colloidal particles of Ag and Au protected by sodiumdodecylsulphate and polyvinylsulphate, respectively. Other assemblies contain cationic polysoaps such as C_{16}–PVP to stabilize 3.2 nm Pt particles [532].

The preparation of polymer-stabilized colloids is by no means a recent innovation. Pt–PVA colloids date from the early 1940s [678,692], and recent methods involve the reduction of H_2PtCl_6 with citric acid in the presence of a suitable polymer, until Pt^0 crystallites appear [693]. This method has proven successful with Carbowax 20-M (a block copolymer of two polyethyleneglycol (MW8000) units linked by a short chain). The structure of the polymer–Pt colloid is not unique and can depend upon such factors as the method of manufacture and pH. In older preparative methods [678,692] of Pt–PVA particles, centrifugation techniques enabled the isolation of supernatant fractions containing Pt–PVA particles of ~ 10 nm diameter.

(iii) Catalytic selectivity

For coupled OEC/HEC water-splitting systems, the rates of catalytic activity have to be sufficiently fast to intercept kinetically the back reactions, and selective interaction between catalyst and the respective cathodic or anodic electron mediator is mandatory, otherwise a shortcircuiting of the back transfer in each case may result. In an $RuO_2/Ru(bipy)_3^{2+}/MV^+/Pt$ system, this would be equivalent to a reduction of $Ru(bipy)_3^{3+}$ by the charged platinum particle instead of H_2 production.

The nature of the polymer surrounding the catalyst particle decides to what extent the catalysts are selective. In several Pt/RuO_2 systems using $MV^{2+}/Ru(bipy)_3^{2+}$ relays it has already been shown that the colloidal Pt particles can interact almost exclusively, whilst little or no reaction with the oxidized sensitizer, $Ru(bipy)_3^{3+}$, takes place [694]. An understanding of the underlying factors affecting catalytic selectivity is necessary if interception of

$$MV^+ + O_2 \rightarrow MV^{2+} + O_2^-$$

the thermally induced back reaction and oxygen reduction are to be successful.

Copolymers of maleic anhydride and styrene, having pronounced hydrophobic character, have been used in the past to endow the Pt microelectrode with some measure of protection. The electron relay, MV^+, is relatively hydrophobic and manages to penetrate the polymeric sheath of the colloid Pt particle, whereas $Ru(bipy)_3^{3+}$ is prone to interact more strongly with hydrophilic or negatively charged surfaces such as RuO_2 [687].

From a selection of gelatin, polyvinylpyrrolidone (PVPr), polyacrylicacidhydrazide and polyvinylalcohol (PVA), other workers have found that only the latter type polymers can form highly active Pt–colloid dispersions [680]. This may be related to the selective migration of electron relays to and from the catalyst surface. Individually protecting both the PtHEC and RuO_2 OEC with a styrene–maleic anhydride copolymer resulted in an overall poor quantum yield due to poor selectivity [687]. The cationic polysoap PVP–C_{16} (polyvinylpyridine with a pendant 16-carbon aliphatic chain) is an excellent stabilizing agent for 320 nm Pt particles [675] prepared by the reduction of hexachloroplatinate by citrate [693]. The pronounced hydrophilic nature of $C_{14}MV^{2+}$ (**56**) is completely changed upon reduction to $C_{14}MV^+$, the monoreduced species being strongly hydrophobic in character and is readily solubilized by surfactant assemblies [614]. This effect has been exploited to achieve charge separation in the photoinduced redox reaction between $Ru(bipy)_3^{2+}$ and $C_{14}MV^{2+}$ with a severe retardation of the back reaction [613]. It is understandable that the use of $C_{14}MV^{2+}$ as an electron mediator in conjunction with a PVP–C_{16}/Pt HEC has produced a highly successful H_2 photoevolution half-cell in which the back reaction is minimized and selectivity is optimized [675].

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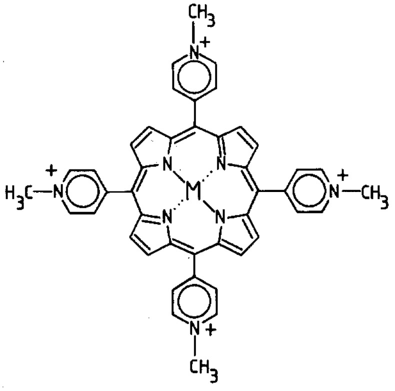
The selectivity effect of the polymer surrounding the redox catalyst has not just been effective in preventing the interaction between the oxidized sensitizer $Ru(bipy)_3^{3+}$ and the Pt HEC, but also other sensitizers such as $ZnTMPyP^{4+}$ (zinc(III) meso-tetra(*N*-methylpyridinium)porphyrin) (**57**) behave similarly. This selectivity is lost, however, when PVP–C_{16} is replaced by Carbowax-20M. Pt and RuO_2 catalysts protected by this polymer fail to split water even under the best conditions. The lack of specificity of Carbowax-20M protected particles can be attributed to the hydrophilic nature of this polymer which allows the access of oxidized sensitizer species to the catalytic surface. Uncharged hydrophilic polymers seem to be unsuited for selective protection of redox catalysts in coupled water-splitting systems.



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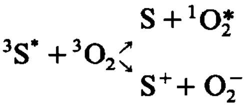
In systems where Pt is deposited onto a TiO_2 matrix, polymeric coatings are still required to aid dispersion of the microheterogeneous catalysts. As discussed earlier, the TiO_2 supporting matrix can themselves act as a secondary electron-acceptor relay. In the case of TiO_2 particles at low pH, the surface of the particle is positively charged ($\xi = 28$ mV) [532] and the access of oxidized sensitizers to the catalyst surface is impaired by electrostatic forces and thus specialized polymeric blankets are not required for selectivity purposes in such a case.

The preparation of bifunctional catalysts [695] containing both Pt and RuO_2 on the same TiO_2 particle has enabled the construction of water-decomposition systems requiring only the catalyst and a sensitizer [695,696]. In this type of assembly cross reaction between the two electrodes on the TiO_2 particle are minimal, and as there is only one homogeneous component in the system no polymer selectivity phenomena need be considered.

P. PHOTODYNAMIC MACROMOLECULAR SYSTEMS

The observation that electronically excited singlet oxygen (${}^1\Delta_g O_2$) molecules participate as reactive intermediates in dye-sensitized photooxygenation reactions was first suggested by Kautsky more than 40 years ago [697]. Molecular oxygen in its triplet ground state (${}^3\Sigma_g O_2$) is able to quench the triplet photoexcited state of dyes to yield singlet oxygen [698,699] (Fig. 23) or the superoxide anion [698,700] by competitive mechanisms.



$$ {}^{3}\mathrm{S}^{*} + {}^{3}\mathrm{O}_2 \begin{array}{l} \nearrow \mathrm{S} + {}^{1}\mathrm{O}_2^{*} \\ \searrow \mathrm{S}^{+} + \mathrm{O}_2^{-} \end{array} $$

Sensitizers for which both reactions may occur include several free-base porphyrins, metalloporphyrins and ruthenium(II) bipyridyl complexes. Even when superoxide formation predominates, "chemical luminescence" to yield singlet oxygen may still occur.

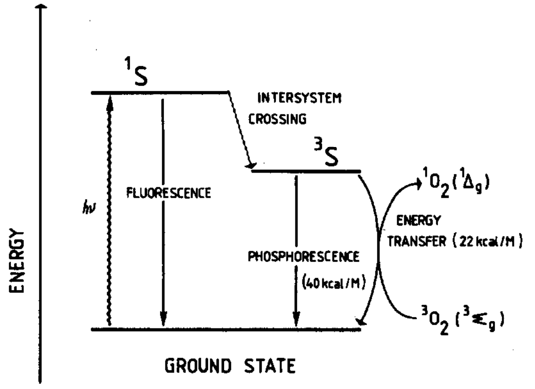


Fig. 23. Energy states and transitions of sensitizing dyes [698].

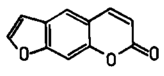
$$O_2^- + S^+ \rightarrow S + {}^1O_2^*$$

Compounds that sensitize the formation of singlet oxygen are known as photodynamic substances and more than 400 dyes are known to possess this ability [701,702], among them being natural and synthetic porphyrins, phthalocyanine and porphyrazine porphyrin analogues [703] and many histochemical stains [704,705].

According to Fowlks [706] a definite order exists describing the effectiveness of photodynamic sensitizers. For anthracene-like compounds with two meso atoms, as indicated, the series

C,C < C,O ≤ N,N, < N,O ⩽ C,N < N,S

is apparent. With psoralens (**58**) substitution of nitro or amino groups at the



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5-position results in a loss of its tanning activity [707]. Replacement of the ring nitrogen of Methylene Blue (**52**) by carbon gives thiopyronin. The latter is an even more potent sensitizer. Pyronin, whose structure can be derived from thiopyronin by exchange of sulphur for an oxygen atom, exhibits much less photodynamic ability than Methylene Blue [702].

Photodynamic substances are well known for their role as mutagens in the

TABLE 20
Photodynamic macromolecular systems

Sensitizer	Polymeric system	Type	Photooxidation reaction	Ref. [a]
Rose Bengal	Covalent attachment of the dye to a chloromethylated styrene–divinyl copolymer. Heterogeneous system	C	Reaction of singler molecular oxygen with olefinic and other substrates	1–3
Hematoporphyrin chlorophyllin	Covalent attachment of sensitizer to polystyrene in a heterogeneous system	C	Photooxidation of 2,3-diphenyl-*p*-dioxene	2
Triphenylmethane dyes	Complexation to methacrylic acid polymers	I	Para-toluenediamine and tetrahymena oxidation	4–6
Rose Bengal	Complexation to polyvinylpyrrolidone	N	Enhancement of photodynamic hemolysis. Degradation of histidine	6–8
Methylene Blue	Complexation in polymethacrylic acid	I	Degradation of histidine	8
Rose Bengal	Complexation of the anionic dye to a strongly basic anion exchange resin. Amberlite IRA 400	I	Photooxygenation of olefinic hydrocarbons by the heterogeneous catalyst	9
Methylene Blue	Complexation of the cationic dye to a strongly acidic cation exchange resin. Amberlite IRC 200. Heterogeneous system	I	Oxidation of 2-methyl-2-butene and anthracene with O_2, to the respective hydroperoxides	9
Methylene Blue Rose Bengal Malachite Green Acridine Orange	Complexation of the dye to various ion-exchange resins	I	Photooxidation of *p*-cresol and phenol as a model for aerobic photooxidation of industrial wastes	10

Furocoumarins	Covalent coupling or complexation with DNA	C	Photooxidation of dopa, to demonstrate photomutagenicity of DNA–dye complexes	11
Acridine Orange Methylene Blue Proflavine	Complexation with DNA	I	Photodynamic degradation of DNA *in vitro* and *in vivo*	12
Eosin	Dye complexation to eggwhite lysozome at pH 4–12	I, N	Degradation of lysozome by oxidation of tyrosine and tryptophan residues	13
Rose Bengal	Polystyrene matrix	C	Photooxygenation of triphenylphosphine selenide yielding the phosphine oxide	14

[a] See Table 1.

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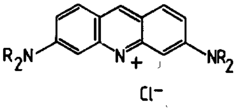
degradation of proteins [708], nucleotides [709] and nucleic acids [710], both in vitro [703,711] and in vivo [712]. Singlet oxygen has also been successfully harnessed in the various endeavors of chemical synthesis [698,713–715].

Generation of $'O_2$ [698,716] may be achieved by the reaction of potassium superoxide with water [717] or sodium hypochlorite with hydrogen peroxide [718], the decomposition of potassium tetraperoxochromate [719] and from the microwave discharge through gaseous oxygen [720]. Natural sources include the adrenodoxin reductase enzyme system [721], xanthine oxidase [722] rat liver microsomes [723] and human polymorphonuclear leukocytes upon phagocytosis [724]. However, the photosensitized formation of singlet oxygen using various dyestuffs remains the method of choice for most synthetic and mechanistic evaluations. The in situ photogeneration of $'O_2$ by heterogeneous polymeric sensitizers offers a clean, recoverable system well suited to photodynamic endeavors.

A number of such heterogeneous sensitizers have been reported recently and these are summarized in Table 20. These systems are comprised of a photosensitizing dye either adsorbed or covalently attached to a preformed polymeric matrix. Inorganic supporting matrices have also been investigated as these are less susceptible to degradation by $'O_2$ [725,726].

The penetration of the sensitizing dye into biopolymers augments its photodynamic behavior. The degree of aggregation of the dye in the polymer phase plays a large part in determining the effectiveness of the macromolecular complex as a whole [709]. The binding of Methylene Blue to an ion-exchange resin results in a loss in the sensitizing ability of the polymer-complexed dye [727,728]. The complexation of Acridine Orange or proflavin (**59**) with DNA results in the intercalation of the dye molecules between base pairs of the DNA at low dye concentrations [729–732], whereas at much higher dye concentrations the electrostatic fixation of the dyes cations to the phosphate groups of the DNA outside the double helix predominates [729]. In the latter instance intermolecular association of the dyes is believed to be responsible for a marked decrease in the photodynamic activity of the complexed dye [710,732]. Similar results have been obtained for the Acridine Orange–tobacco mosaic virus (TMV) RNA complex [733], in which case only the polymer dye complex formed at very low concentrations of the dye are photodynamically active [734].



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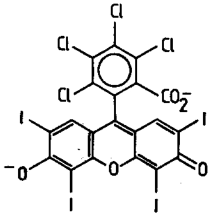
Fluorescence measurement techniques can be a powerful tool for ascertaining whether small differences in dye structure significantly alter its photodynamic capability in the bound state [735]. *N*-methyl proflavine and *N*-propyl Acridine Orange display differing fluorescence behavior when complexed with calf thymus DNA. The fluorescence intensity of the former polymer–dye complex decreased with increasingly large DNA/dye ratios, whereas that of the latter increased under similar circumstances. It is not yet clear whether the fluorescence quenching occurs through dye–DNA interactions or, more likely, through polymer-influenced dye–dye association into aggregates.

The fluorescence intensity of the polymer–dye complex is a good indicator of its photodynamic activity when the system is exposed to molecular oxygen. The fluorescence intensity of proflavine dyes is quenced by DNA and that of Acridine Orange increased [735]. Similarly, proflavine is an active photosensitizer in solution, but seems rather ineffective in the bound state [736], whereas Acridine Orange behaves conversely. Some authors [737,738] are of the opinion that proflavin and its derivatives are more readily intercalated between the base pairs of DNA, whereas Acridine Orange and its derivatives undergo mostly external binding.

Thus, the photodynamic activity of DNA–dye complexes at low loading levels of the dye are strongly dependent on the state of the sensitizer. Dimers and higher aggregates of the sensitizer [704,732,739,740] are seen to retard the photodynamic activity by a process of self quenching [705]. Other factors can also have a profound influence on dye-sensitized photooxidations [741]. The binding of Methylene Blue to polymethacrylic acid decreases the quantum efficiency of the dye, but the relative decrease in efficiency does not parallel the degree of binding. The binding of Rose Bengal (**60**) to polyvinylpyrrolidone results in a decreasing quantum efficiency of the dye–polymer complex, but when ~ 75% of the dye molecules are bound the photodynamic efficiency begins to rise [742]. The lifetimes of the excited species, Dye$^+$ and $'O_2$, do not increase on binding, and it is thought that the observed decrease in photoactivity on binding most probably results from increased microscopic viscosity of polymeric solutions. Metastable dye species formed by flash irradiation of bound triphenylmethane dyes are not appreciably quenched by oxygen [743], and oxygen quenching of eosin triplets is



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strongly suppressed upon binding to albumin [744]. In such systems the bound dye molecules seem to be protected from interaction with oxygen by the enfolding polymer chain.

The coordination of furocoumarins to DNA results in a highly altered UV absorption spectrum of the sensitizer [745], either due to complexation or perhaps to dissaggregation of the dye complex. Whichever the case, complexed or the covalently bound heterocyclic compound psoralen (**58**) generates $'O_2$ more actively than the free furocoumarin in solution. A suspension of Rose Bengal in a polar solvent is a relatively ineffective photosensitizer for the generation of $'O_2$ due to self-quenching phenomena. The covalent attachment of the dye to chloromethylated styrene–divinylbenzene beads results in an efficient heterogeneous photosensitizer [716] containing monomeric dye units.

However, some workers claim that high concentrations of sensitizer solutions are required to form biopolymer–sensitizer complexes with pronounced photodynamic activity [702,746]. Under such conditions the dye would be in a highly aggregated state, though such effects probably arise from concentration-dependent dye binding [709] to specific sites in the macromolecule. The complexation of Methylene Blue to commercially available ion-exchange resins seriously reduces its effectiveness as a sensitizer for the aerobic photooxidation of cresol [728,741]. No systematic variation of photoactivity with various loading levels of the dye on Duolite C-20X4 resin was observed. Different polymeric matrices augment or retard the operation of the sensitizer in ways that are not yet understood.

Q. PHOTOVOLTAIC DEVICES FROM POLYMERS

(i) Types of photogalvanic cells

Electrodes coated with polycrystalline chlorophyll-a or related molecules can be used to induce a photocurrent under certain conditions [747] and, similarly, light-driven electric cells have been constructed from chloroplast membranes [748,749] and PS-I particles [750]. More recently, Ochiai et al. [751,752] reported the construction of chloroplast electrodes prepared by the deposition of type C chloroplasts onto an SnO_2 optically transparent electrode using PVA and bovine serum albumin as immobilizing supports. On illumination these electrodes generate an anodic current when coupled with a saturated calomel electrode.

The development of purely synthetic photogalvanic cells is now being vigorously pursued [753,754]. According to Albery [754] there are two basic types of photogalvanic cells (Fig. 24):

(1) the electrolyte between an optically transparent and a dark electrode

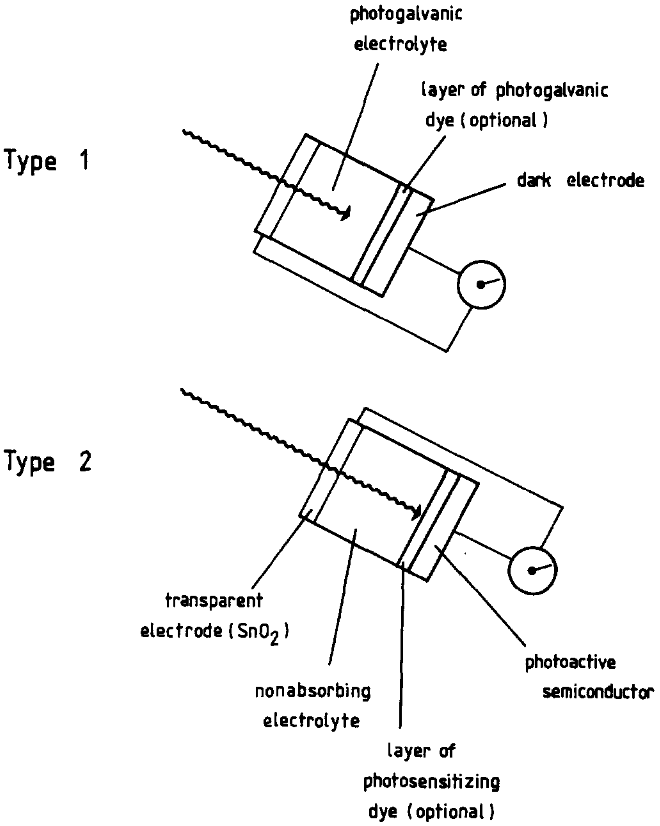


Fig. 24. Photogalvanic electrode systems.

absorbs light and generates an electric current via a donor/acceptor redox couple; and

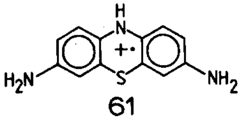
(2) the electrolyte is not photoactive, but merely serves to separate and transport holes/electrons generated at the semiconductor–electrolyte interface.

(ii) Type 1 photogalvanic cells

Photogalvanic cells of this type do not differ substantially from the D/S/A couples mentioned earlier. The separation of the energetic species, D^+ and A^-, in solution, and their selective discharge at the appropriate electrode, is the basic mechanism by which the cell operates. Considering the plethora of D/S/A photoactive systems that are known to exist, the varieties of photogalvanic cells that can be constructed are almost endless.

One of the most promising photogalvanic electrolytes is the iron–thionine

(**52**) system, which has been discussed in detail by Albery [754]. Other thiazine dyes that have been investigated for their photogalvanic properties are Methylene Blue (**52**) and various disulphonated thionines [755]. The $Fe^{III/II}$–$Ru^{II/III}$ bipy system is also under the scrutiny of many photochemists [754,756]. Polymeric dye-electrolytes are also finding application in this area. Shigehara et al. [757] have examined thionine/Fe(II) and polymer-attached thionine/Fe(II) systems in photogalvanic cells and postulate a catalytic cycle involving a one-electron reduction of thionine (**61**). We hasten to add that this mechanism differs from that of Albery et al. [755] who visualized the photoreduction process proceeding through a doubly reduced leucothionine (**62**) molecule. Shigehara et al. [757] found that the presence of polymers such as polyvinylalcohol or sucrose increased the photopotential, ΔE, and the photocurrent, I, of their monomeric thionine/Fe(II) cell by enhancing the electron exchange between Fe(II) and Fe(III). Even greater values of ΔE and I were obtained with polymeric thionines (**63**). The excellent ability of the polymeric thionines to generate photo-induced electricity was attributed to the strong electrostatic repulsion between Fe(III) and the semi-reduced species bound to the cationic polymers, as this repulsion diminished the short circuiting reaction or the bulk back reaction with Fe(III). A similar observation on polymeric thionines has been reported previously [758].



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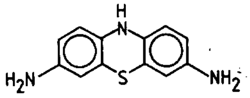

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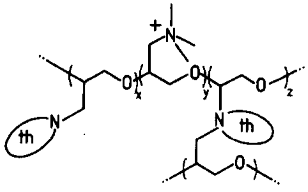

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Other authors have also reported on photogalvanic systems derived from polymeric azine and thiazine dyes [624,625,759]. The thermal back reaction was again prevented by electrostatic repulsion between Fe(III) ions and pyridinium moieties in a polyvinylpyridine–pendant thionine matrix. The back reaction was prevented to a much greater extent than in the monomeric system, enabling longer photopotentials and currents to be attained. One drawback of thionine-type monomeric or polymeric photogalvanic electrolytes is the degradation of the excited state thionines in the presence of oxygen [759]. More recently, photocurrents have been generated by incorporating $Ru(bipy)_3^{2+}$ and methylviologen into polysulphonate (Nafion) films on graphite electrodes. The response of the electrode could be switched to register cathodic and anodic photocurrents by controlling the applied electrode potential [759a].

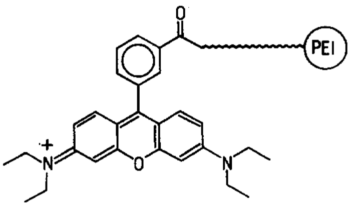
(iii) Type 2 photogalvanic cells

The key problem in many electrochemical solar cells is photodissolution of the narrow bandgap semiconductor anode material. To date, the best stability in such cells has been attained with *n*-type cadmium chalcogenides (CdX, X = S, Se or Te) and *n*-type GaAs electrodes stabilized by chalcogenide/polychalcogenide redox couples. The stabilization of *n*-CdSe photoanodes has also been achieved with non-aqueous solutions of redox electrolytes such as $Fe(CN)_6^{3-/4-}$ [760]; the mechanisms of hole and electron transfer has been discussed elsewhere [753,761]. Solid polymer electrolytes, although not photoconducting, have been used to aid the charge separation at the semiconductor/electrolyte interface. Solid solutions of alkali metal salts and polyethyleneoxide (PEO) have recently been suggested as electrolytes for high energy density batteries [762–764] and also in semiconductor-type photoelectrochemical cells [758,765]. PEO/KI solid solutions have a conductivity of $\sim 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and optoelectric cells require sandwich films of 100 nm or less [766].

However, even in the presence of redox electrolytes, small bandgaps semiconductors are still susceptible to photoanodic and photocathodic degradation [767]. The photoanodic degradation of *n*-Type Si has been greatly suppressed by the electrodeposition of a highly conductive polymer such as polypyrrole on the surface of a photoelectrode [766–770] and the polymeric film mediated hole transfer to an $Fe^{II/III}$ electrolyte [768]. Polyaniline films have also been investigated [768a]. Polypyrrole films can have conductivities up to $100\ \Omega^{-1}\ cm^{-1}$ [769]. Previous work on *n*-type GaAs coated with polypyrrole also showed stabilization of the semiconductor against photocorrosion, however the polymer exhibited poor surface adhesion in the presence of aqueous electrolytes [771]. Modification of a semiconductor surface (*n*-Si) with 0.5 nm Pt films enabled improved adhesion and stability of the polypyrrole (100 nm) coated photoelectrode system [770]. Similar results were achieved with *n*-Si/gold/polypyrrole wafer electrodes, where the gold/polypyrrole layers mediated photogenerated holes. These holes were relayed to the electrode–solution interface where oxidation of an Fe(II) electrolyte took place [772]. Block [420] has reviewed the conductive and photoconductive properties of various organic and organometallic polymers. There are several highly conductive polymeric systems that may, in the near future, find application alongside the polypyrroles.

The protection of photoanodes by organometallic species such as ferrocene [773] has also proven successful. Such redox systems remove photogenerated holes from the semiconductor–electrode surface and pass them to the redox species in the electrolyte, thereby keeping the hole concentration at the electrode surface below the critical value for photodecomposition. Haas et al. [774] have gone one step further and applied electroactive polymers to *n*-$MoSe_2$ and *n*-WSe_2 electrodes. It was shown that under illumination, transfer of a hole from the valence band of the semiconductor to an Fe(II/III) electrolyte was catalyzed by a layer of Ru(bipy)$_2$Cl complexed to poly(4-vinylpyridine) attached to the electrode surface. The oxidized polymer could also inject holes into the valence band of the semiconductor. Photosubstitution reactions of the polymeric coating, however, prevented prolonged use of the coating.

Adsorbed polymeric species can also be used to sensitize semiconductor electrode processes. Dye sensitization of wide band gap semiconductors in photoelectrochemical cells has been dealt with elsewhere [775–777]. Metal-free phthalocyanines [778] and films of the surfactant, Ru(bipy)$_2$(bipy-$C_{19}H_{39}$)(ClO_4)$_2$ [779], the dyes rhodamine B [775] and merocyanine [780] and other dyes [781] have also been studied in this regard. Morashima et al. [782,783] have recently supported rhodamine B (**64**) and merocyanine (**65**) on polyethyleneimine and polyvinylalcohol for use as sensitizers of photoelectrode processes. In the presence of hydroquinone solutions, a SnO_2 optically transparent electrode coated with a rhodamine B–PEI film exhibited a spectrally sensitized photocurrent. Pt electrodes coated with PVA–merocyanine and PEI–merocyanine films also displayed photocathodic currents. Similar results have been achieved with vinyl derivatives of Ru(phen)$_3^{2+}$ electropolymerized on a TiO_2 electrode [376].



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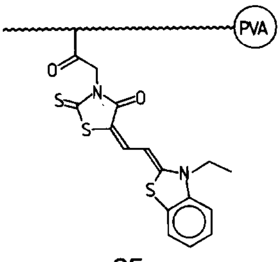

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It is generally held that only dye molecules directly adsorbed onto the semiconductor surface are responsible for the photocurrent [778]. Hence the application of insoluble dye multilayers on the electrode has often been unsuccessful mostly because of the high ohmic resistance and increased self-quenching phenomena [775]. In the case of these polymers however, the dye-sensitized photocurrent at the SnO_2 electrode far exceeded that of monomeric dyes species in solution and a very efficient mechanism for excited state migration to the semiconductor surface must operate.

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