

Polyradicals: Synthesis, Spectroscopy, and Catalysis

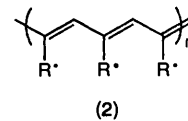
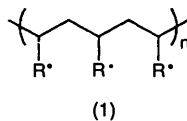
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1 Provenance of Polyradicals

Polymers have always been useful as chemically robust structural components and such applications are expected to continue for most bulk commodity polymers. Alongside these engineering materials, designed for their mechanical properties, specialized polymers have been developed in the past few decades which contain periodic functionality suiting them for specific physico-chemical tasks. Examples include electrode coatings, catalysts, photo-resists, and light-emitting polymers. Polyradicals combine together the high molecular weights and structural regularities of common solid-state polymers, with the unique characteristics associated with the unpaired electrons present in free radicals. In the production of virtually all polyradicals advantage is taken of the ease with which chains and networks can be built up by the stepwise repetition of sequences of reactions like addition, coupling, condensation *etc.* from the standard methods of polymer synthesis. The product polyradicals contain a succession of paramagnetic centres, usually stable free radicals or radical ions. These radical centres occur as repeating side chain units, or as repeating electronic structures within the polymer backbone, and they are ordered by the recurrent polymer structure.

Two major classes of polyradicals can be distinguished. First, those with unconjugated backbones to which stable radicals are attached as pendant groups, *i.e.* (1). The second class contains materials with conjugated backbones of the polyacetylene type, linked either to free-radical side-groups, *i.e.* (2), or incorporating repeating paramagnetic centres within the backbone. Technically, lightly doped poly(acetylenes), poly(thiophenes), polypyrroles) *etc.* belong to this second class, because in polypyrrole, for example, the doping process (oxidation) introduces



polarons (radical cations delocalized over *ca.* four monomer units) which are the major charge-carriers. However, conducting polymers have received excellent coverage elsewhere¹ and, with a few exceptions, are excluded from the present review.

Polyradicals contain ordered arrays of unpaired electrons and their most important chemical properties stem from this. Because the incorporated free radicals usually have accessible oxidation or reduction potentials, polyradicals can act as catalysts, or as full reactants, in a variety of electron transfer processes. Depending on the nature of the electron array, ferromagnetic, ferrimagnetic, or antiferromagnetic behaviour may be displayed. Polyradicals, in contrast with conducting polymers, may have appreciable conductivity *before* doping. It is also possible that, in conjugated polyradicals containing two different kinds of non-bonding electrons, enhanced conductivity could be produced and that pairwise mobility of the electrons could even give rise to superconductivity.

In this review we shall discuss the synthesis, characterization, and spectroscopy of polyradicals. We shall also survey the chemical reactivity, including the electrochemistry and catalysis of, for example, single electron transfer reactions. Physical properties will not be discussed in detail, except where it is relevant to the design of polyradical structures for the goals of ferromagnetic and superconducting materials.

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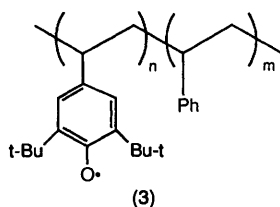
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Andrews. He has been a frequent Visiting Scientist at the National Research Council of Canada in Ottawa and, in collaboration with Keith Ingold, has examined the structural and kinetic behaviour of many free radical types. His current research interests include synthetic and mechanistic studies of reactive intermediates, organic and biochemical aspects of dioxygen and nitric oxide behaviour, and functionalized conducting polymers.



2 Synthetic Strategies

Four basic strategies have been utilized for the production of various types of polyradicals. (i) A monomer containing a vinyl, diacetylene, thiophene, pyrrole, *etc.* unit, to which is attached a stable free radical, is polymerized by free radical, anionic, topochemical photolytic, or electrochemical means, to give a polyradical directly. This approach is severely limited by the fact that the radical centre in the monomer often inhibits, prevents, or diverts the polymerization process. (ii) A similar monomer, but functionalized with a free radical precursor is polymerized. Subsequent treatment of the polymer, usually oxidation or reduction, converts the precursors into free radicals. For example, polymers containing hindered secondary amine groups may be oxidized to poly(nitroxides), polymers containing quinones may be reduced to poly(semiquinone radical anions), and polymers with diazo groups may be photolytically cleaved to give poly(triplet carbenes). (iii) Stable free radicals are chemically attached (grafted) to a preformed polymer. The advantage of this approach is the good control which can be exercised over the molecule weight by selection of an appropriate starting polymer such as a poly(butadiene) or a poly(acrylic acid). (iv) Free radical precursors are chemically attached to a preformed polymer which is subsequently oxidized, reduced, or otherwise chemically treated to give the polyradical. The main drawback to strategies (ii) and (iv), which give precursor polymers, is the difficulty of ensuring complete conversion of the precursor groups, particularly if, as often happens, the polymer is not very soluble in inert reaction solvents. For example, synthesis of copolymers, (3), which were prepared by irradiation of an oxallyl ester with an attached phenol, were recently reported.²



Allowing for the co-radicals produced in the photochemical reaction, only about 25% of the theoretical concentration of polymer-bound spins was observed. The disruption of the radical array in incompletely converted polyradicals can have drastic effects on any desired cooperative activity of the final material, for example, the electrical conductivity or ferromagnetism. Consequently, optimization of the yield of radical centres is a major concern.

3 Specialized Methods of Characterization

3.1 EPR Spectroscopy of Polyradicals³

Spin-spin dipolar interactions in solid state polyradicals lead to a broadening of the EPR lines compared with solution spectra. In favourable cases the degree of broadening can be calculated from known or estimated spin densities and the distance the spins are apart. Dipolar interactions are typically on the order of 10^{-2} to 10^{-1} cm⁻¹ (10 to 100 mT). A biradical, for example, generally exhibits a six-line spectrum in frozen glasses; from this spectrum two parameters D and E may be extracted. The value of D is related to the distance the two spins are apart, and the degree of interaction of the spin-containing orbitals. A conjugated, or folded over, biradical has a D of *ca.* 0.06 cm⁻¹, while a non-conjugated biradical has a much lower value of D . On the other hand, exchange interactions (J) can be larger than the dipolar interaction by up to two orders of magnitude. They can bring about exchange-narrowing of linewidths to approach those of the monomer radicals in solution. If the observed linewidth of the solid polyradical is the same as that for the polymer in a dilute solution or in a dispersed solid, then it is reasonable to assume that the *intrachain* exchange interactions

dominate. If the observed linewidth is broader than in solution, then *interchain* exchange interactions are important. As the temperature is lowered the dipole-dipole linewidth increases, while the exchange-narrowed linewidth is unchanged.

The integrated signal intensity is proportional to the magnetic susceptibility, χ . This may be useful when the contributions of two different signals to the bulk magnetic susceptibility are under consideration.

3.2 Electrical Conductivity

Polymer conductivities span a wide range. For example, Teflon has a conductivity of $< 10^{-18}$ S/cm (Ω^{-1} cm⁻¹) and is an insulator whereas polythiophene, which has a conductivity of 10^2 S/cm in its oxidized ('doped') form, is a good conductor. These differences reflect the number and mobility of itinerant electrons or holes. The electrical conductivity of a polymer sample indicates whether the charge carriers are delocalized and mobile, giving rise to high conductivities, or localized and immobile, leading to low conductivities. Many novel electrically conducting polymers are prepared as powders, and must be pressed into pellets before the conductivity is measured, generally by attaching four fine gold wires or by pressing four graphite contacts onto the sample.¹ These contact methods prevent cracking of brittle pellets. Two of the contacts are used to pass a known current, the other two measure the voltage drop across the sample: this is called the four-point probe method, a procedure which eliminates the effect of contact resistance. A pressed powder sample, however, may have a lower conductivity than the intrinsic conductivity because of the resistance between the powder particles and the inherent defects in the polymer chains. Defect-free, oriented-chain doped-polyacetylene samples have been produced with conductivities of up to 10^5 S/cm, approaching those of metals.

Turning to polyradical samples, since they contain a large number of unpaired electrons which have singly-occupied (or vacant) orbitals in the adjacent radical centre to jump to, we should expect the conductivity to reflect the mobility of the electrons. A high conductivity for a polyradical indicates that the unpaired electrons are mobile and metallic; this will tend to cause the electrons to pair up. However, a low conductivity would indicate immobile, localized electrons and the possibility of unpaired spins.

3.3 Electrochemistry

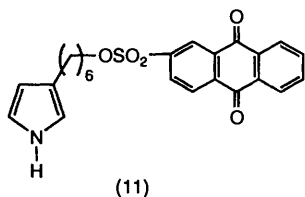
Many radical groups are redox-active, and hence electrochemical measurements can confirm that the redox potential of the polyradical is similar to that of the monoradical redox unit; a broad redox couple indicates extensive hydrophobic or electrostatic interactions between groups. The percentage redox activity (charge associated with each monomer unit) of a sample indicates whether the radical groups are accessible to the electrode and whether fast electron transfer between redox groups is possible. Immobilization of the polymer onto the electrode surface is very convenient for making these measurements, as well as measuring D_{ct} , the diffusion coefficient of charge transport within the polymer, which is a sensitive function of polymer solvation, flexibility, and structure. There is also a great deal of interest in measuring the rate of redox reactions mediated by the polymer interior and outer surfaces. In many cases electrochemical oxidation is a convenient way to synthesize conjugated polyradicals, or to generate *in situ* radical groups from non-radical precursors.

4 Unconjugated Polyradicals

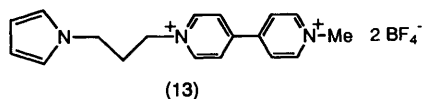
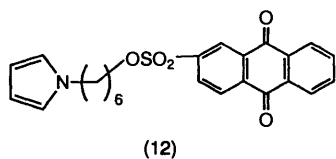
The first rather ill-defined polyradicals were prepared in the mid '50s by incorporating DPPH (diphenyl picryl hydrazyl), triarylmethyl, or verdazyl radicals into poly(styrene) by irradiating with γ -rays and subsequently oxidizing the polymers.⁴ Subsequently, the most popular unconjugated polyradicals have

electrodes made in this way can be activated by applying the appropriate potential, and used for the catalysis of electron transfer initiated chemical transformations.

The polymerization process links pyrrole nuclei *via* their 2- and 5-positions so that any functional groups must be attached at the pyrrole nitrogen atom (1-position) or the 3-position of the pyrrole nucleus. The latter derivatives are quite difficult to prepare so that only a few such polymers have been studied. These include poly(11) which was readily formed by electrochemical oxidation; films were highly electroactive.⁸

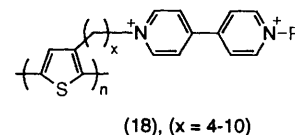
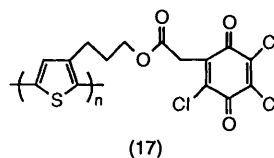
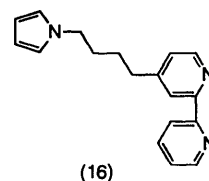
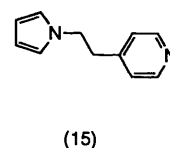
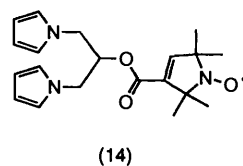


Many different polyradicals have been made from N-substituted pyrroles. A thorough exposition of this area has been given in recent interesting reviews.⁹ The chain linking the substituent to the pyrrole nitrogen must be at least two methylene units long for electrochemical polymerization to be successful. Polypyrroles with reducible substituents include the quinone-containing poly(12), which catalysed the reduction of oxygen, and viologen containing-poly(13).¹⁰ Platinum electrodes coated with viologen-containing poly(pyrroles) were shown to catalyse the reduction of organo-halogen compounds.¹¹



For pyrroles linked to oxidizable substituents the potential needed to cause polymerization may be greater than that required to oxidize the substituent. Regardless of this, several such monomers have successfully been polymerized by cyclic voltammetry, provided that the potential is swept sufficiently positive for initiation of the oxidative pyrrole coupling process – as we have shown for a pyrrole monomer linked to a TEMPO group.¹² Electrodes coated with poly(14) exhibited a reversible couple due to oxidation of nitroxide to oxoammonium cation. In the presence of an added alcohol the oxoammonium ions were reduced to the hydroxylamine and the alcohol was oxidized to aldehyde or ketone. Then, reoxidation of the electrode-bound hydroxylamine to oxoammonium cations prepared the system for another catalytic cycle.¹³ Although this system successfully converted alcohols into aldehydes/ketones on an analytical scale, problems with the electrode coating stability were encountered on scaling up the process. Ruthenium complexes made from pyrroles N-functionalized with pyridine and bipyridine ligands such as poly(15) and poly(16) were found to be better electrocatalysts for alcohol oxidation.¹⁴ Many other poly(pyrroles) with attached metal complexes of pyridines, porphyrins, and cyclams have been investigated.⁹

Thiophenes functionalized at the 3-position can be polymerized by controlled potential oxidation only if electron withdrawing groups are remote from the thiophene. Usually the redox functional group must be separated from the thiophene by a methylene chain of at least two units. Poly(thiophenes) with quinone side chains such as (17)¹⁵ and viologen side chains such

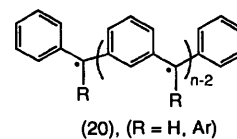
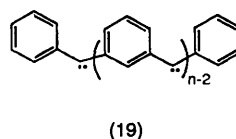


as (18)¹⁶ have been made and studied electrochemically. Electronic conductivities up to 6 S/cm have been recorded and these materials are being tested for electrochromic devices and as microelectrochemical transistors.

5.2 Co-operative Magnetic Interactions in Conjugated Polyradicals¹⁷

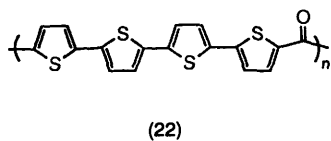
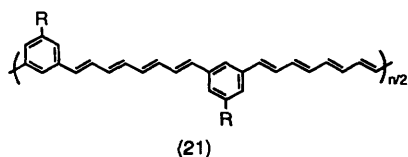
For solids composed of ordered arrays of atoms or molecules, each containing one or more unpaired electrons, there are several possibilities for intermolecular cooperative behaviour amongst the spins. Most commonly, the exchange interaction between the unpaired electrons is negative so that antiparallel coupling occurs and results in overall antiferromagnetic behaviour. To achieve macroscopic ferromagnetism the exchange interaction must be positive so that parallel alignment of spins is obtained over extended regions of the solid. The goal of creating an organic ferromagnet has stimulated a lot of attention from innovative scientists. Indeed it seems to exercise the same attraction as the proverbial lodestone. Several ways whereby ferromagnetism might be achieved have been suggested by theoreticians. Of the three main models, the Topological Model, has provided greater inspiration in the design of polyradical magnets than the well known McConnell (I) and McConnell (II) mechanisms.¹⁶

In the Topological Model ferromagnetic coupling (strictly, intramolecular high spin states arising from Hund's rule), occurs in very large organic species which contain bands of degenerate, or nearly degenerate, orbitals as a consequence of their molecular topology.¹⁸ For example, in polymeric triplet carbenes (19), or radicals (20) (R = H, Ar), in which the aromatic substitution is *meta*, the frontier π -orbitals constitute three distinct bands. In polymeric species this topological arrangement leads to the formation of a band of non-bonding MOs (NBMOs) in addition to the full or valence band and the vacant or conduction band. The poly(phenylcarbenes)(19) have additional σ -non-bonding MOs which are of similar energy to the π -non-bonding MOs and contribute to the NBMO. If the energies of the non-bonding orbitals are all the same, or nearly so, they constitute a family of superdegenerate orbitals in which all the unpaired electrons will have parallel spin. Polyradicals of this type have the potential to



behave as linear ferromagnets. Magnetic resonance and magnetic susceptibility measurements on several oligomeric carbenes of type (19) in the solid state showed that they do indeed exhibit the predicted high spin multiplicities.¹⁹ For example, the pentacarbene, (19)($n = 6$) was found to have an undecet electronic configuration. However, these oligocarbenes were only stable at cryogenic temperatures and so far there has been no success in making polymeric analogues.

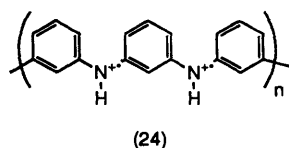
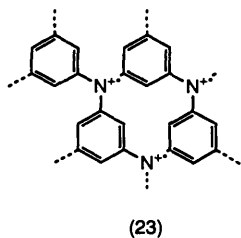
Building on this same basic concept, Fukutome and co-workers mapped out the design of 'polaronic ferromagnets' which consist of lengths of conjugated polyene (polyacetylene) chain connected by π -systems with an odd number of sp^2 -carbons.²⁰ Unpaired electrons are then created by doping the conjugated blocks. The linking odd π -systems, e.g. *meta*-substituted aromatic rings, build in the correct topology to induce ferromagnetic coupling of the spins. For example, oxidation of (21) should create polarons in the tetraene blocks which will be separated by *meta*-substituted aromatic rings. The latter introduce three (or five) sp^2 -carbon atoms into the π -system so that the polymer will possess a band of non-bonding superdegenerate orbitals which will constrain all the polaron spins to be parallel. Similarly, if blocks of thiophenes of sufficient length to support polarons were linked by carbonyl groups, which introduce one sp^2 -carbon into the chain (22), they should ferromagnetically couple the induced polarons.



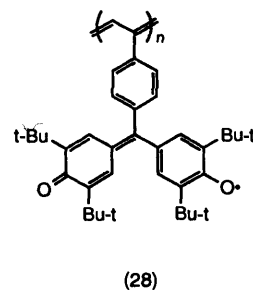
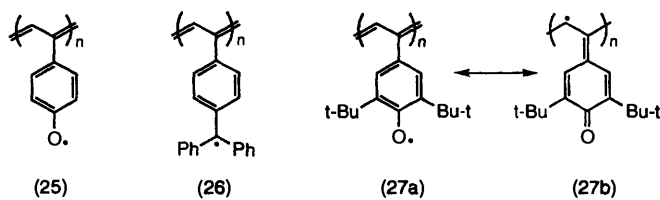
A polymer of type (21), with octadecyloxy substituents ($R = OC_{18}H_{37}$) to promote solubility, was made by Dougherty and co-workers.²¹ This material, when oxidatively doped with AsF_5 , showed weak ferromagnetic coupling. The small magnitude of the ferromagnetism was accounted for by intermolecular antiferromagnetic coupling between segments of the chain situated close together in the solid. Moreover, the doping was inhomogeneous so that the number of spins introduced was too small for uniform interaction to develop. Further design is needed—for example, more controlled doping could be achieved by electrochemical methods—but this is obviously a promising strategy in the search for organic ferromagnets.

A further attempt to arrange the radical units in accord with the topological model was based on the oxidative coupling of 1,3,5-triaminobenzenes to provide polymers conjugated in two dimensions. Polymer (23), for which ferromagnetic interactions have been claimed, was prepared as a precipitate from a solution of triaminobenzene in acetic acid.²² A one-dimensional version of this polymer, *i.e.* (24), was prepared by the Ullmann coupling of *m*-bromoaniline. However, doping of this material led to a spin concentration of only 1 in 60 monomer units.²³

Ovchinnikov showed that alternant hydrocarbons (and

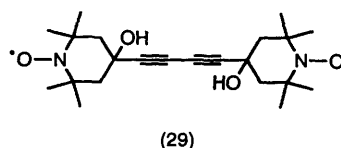


heteroatomic analogues), for which the number of atoms in the two sets was unequal, would have a finite spin multiplicity. He identified several series of molecules, with members increasing by a regular repeating unit, for which the resultant spin would be proportional to the size.²⁴ Other theoretical studies have shown, however, that pendant radical groups may interact with each other *via* a conjugated backbone.²⁵ These examples included hypothetical polyacetylenes and polyacenes as well as conjugated polyradicals such as (25) in which the unpaired electron would be conjugated with the backbone π -system. Several polyradicals of this general type, e.g. (26)²⁶ and (27)²⁷ and the galvinoxyl derivative (28)²⁸, have been prepared, but the solids did not display bulk ferromagnetism; probably because pairing of adjacent spins took place. The surprisingly stable (27) with up to 38% of the theoretical spins was prepared from the parent phenol by oxidation with either PbO_2 or alkaline ferricyanide; addition of base produced the polyanion. The visible spectrum of (27) indicated a fairly long π -system, and the EPR spectrum of the polyradical in solution implied coupling to the backbone protons. This suggested that spin was delocalized onto the chain and a quinone group was formed (27b). The reversible decrease in the EPR signal at $T < 50$ K indicated an antiferromagnetic interaction.



Polyradical (28) was prepared in a similar way, giving up to 80% of the theoretical number of unpaired spins. The EPR spectrum in solution showed evidence for *intrachain* dipolar interactions. In the solid state the EPR linewidth of the 77% spin polymer indicated both *intrachain* exchange and *interchain* dipolar interactions. There was no evidence, however, for ferromagnetic spin ordering in this sample. It is interesting to contrast the essentially *localized* spins of (28) with the chain-delocalized spins of (27), which unfortunately couple antiferromagnetically. Other polyradicals with polyacetylene and polyimine backbones containing nitroxide, nitronyl nitroxide, and verdazyl units have been examined but without finding evidence of ferromagnetic behaviour.

Perhaps the system to attract most attention has been that based on 4,4'-(butadiene-1,4-diyl)-bis(TEMPOL) (29). Following the original work with (29), numerous attempts have been made to prepare ferromagnetic polymers from diacetylenes substituted with nitroxides, or other stable free radicals, either by topochemical photolysis, pyrolysis, or mechanical means. This research has been critically reviewed recently.²⁹ Although



claims of ferromagnetic behaviour have been made, the reported saturation magnetizations have been very low, and the polymers have been chemically ill-defined. It seems probable that in most, if not all cases, the magnetism is due to trace amounts of iron-containing impurities.

5.3 Polyradicals: Electronic Conductivity and Superconductivity

According to the classic BCS theory, superconductivity is maintained by mobile pairs of non-spin-paired electrons (Cooper pairs) in which the electrons are coupled to each other *via* phonons, *i.e.* vibrational modes of the lattice material. Even for crystalline solids, theories explaining how Cooper pair formation is related to short and long range molecular and crystal structure are rudimentary, and theoretical guide-lines of this type are non-existent for organic or organometallic materials. It has been pointed out that the doubly charged bipolaron, thought to be present in doped conjugated polymers, is related to the Cooper pair, but so far no reports of superconductivity have been published. Data from the new Cu-oxide and related high T_c superconductors indicate that although the charge carriers *are* electron pairs, the force that keeps them together is not always phonon-coupling.³⁰ Conjugated polyradicals typically contain two types of unpaired electron which could, depending on the details of the structure, move in concert over long distances through the infrastructure. Poly(sulfur nitride), (SN)_n, which possesses one unpaired electron in each SN unit, becomes superconducting below 0.3 K.³¹

The doped polynitroxide (30) potentially has mobile polarons in the delocalized backbone in addition to the unpaired electrons of the nitroxide groups. Experimental investigation³² showed that (30) has low electronic conductivity probably because electron pairing *via* species such as (30b) is important. In addition, oxidation of the poly(*N*-hydroxypyrrrole) precursors was accompanied by significant disruption of the chains. More promising candidates appear to be poly(thiophenes) or poly(pyrroles) like (31), or more generally (32), where L are non-conjugated linkages and R• are stable free radicals. Polarons created in the conjugated backbone may be able to form Cooper pairs with unpaired electrons of the nitroxide groups. Transfer of the nitroxide electron to an adjacent oxoammonium site will convert the donor nitroxide into oxoammonium, and the acceptor oxoammonium into nitroxide. Potentially this could occur in response to the passage of a polaron along the backbone, depending on the nature of the linkage L, and hence electron-pair mobility along the chain would be actuated. Polyradicals of this type with nitroxide, quinone, viologen, and complexed transition metal side-chains are being studied.

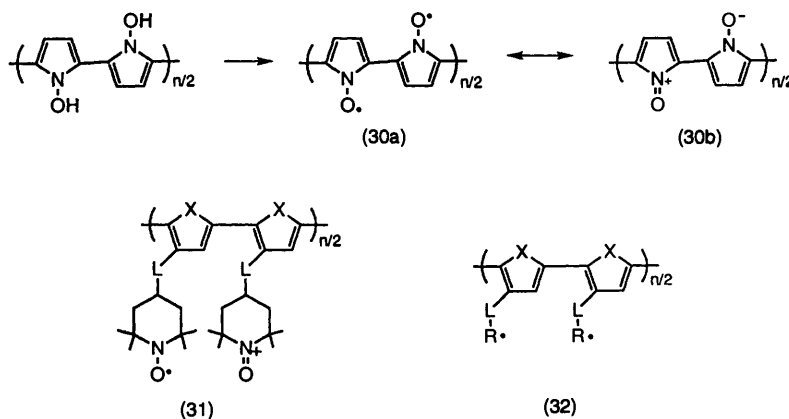
6 Future Developments

Electrodes coated with polyradicals containing nitroxides show good promise as catalysts for the electrochemical oxidation of

amines, alcohols, and other organic substrates. Similarly, it is likely that polyradicals functionalized with quinones or viologens will be developed for the electrochemical reduction of a range of substrates. There is a need for better methods of permanently attaching the polyradical films to the metal surfaces so that more robust electrodes with longer active lifetimes can be produced. Modified electrodes of this type will find use as probe elements in sensors. The polaronic magnets are obviously one of the most fascinating emergent concepts. A wide range of structural types have still to be investigated. There is a conspicuous need to improve chemical stability, perhaps by using oligothiophene rather than polyene blocks for housing the polarons. To prevent the *interchain* interactions which antiferromagnetically couple spins, structures with two- or three-dimensional regularities need to be designed and synthesized. There seems to be no limit to the functional groups which can be incorporated into polymers, or to the physical and chemical behaviour that such materials can mimic.

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