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Chemical Faculty,
Lomonosov Moscow State University

U. D. C. 541.61

OXIDATION–REDUCTION POLYMERS

E. E. Ergozhin and F. T. Shostak

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1. INTRODUCTION†

Great interest has arisen in recent years in macromolecular compounds of a new type, oxidation–reduction polymers or, as they are still called, electron exchangers. The latter term has been coined by analogy with ion exchangers, but its choice is unfortunate, since the oxidation or reduction of a polymer does not involve the

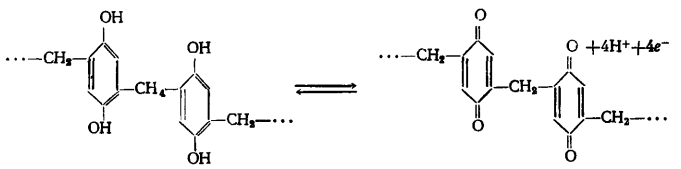
† Fresh results have been published since this paper was submitted for publication, and are collected together in the supplementary references[205-275].

exchange of electrons, as occurs with ions in the case of ion exchangers, but their absorption or donation. Nevertheless, the term has become widely used both in the Soviet and in the foreign literature. Several authors prefer the term "redox resins" or "redoxites".

The synthesis of ion-exchange resins was accomplished in 1936. It was established that the acidic or basic groups of the original monomers retain their properties in the polymeric compounds. The question naturally arose of the possibility of obtaining similar systems containing other functional groups. Much attention was paid to the synthesis of macromolecular compounds containing groups capable of reversible oxidation and reduction. Tsvet discussed the role of such a system as early as 1906 [1] in papers on the chromatographic method of investigation. Many workers have shown that redox groups maintain their oxidation–reduction functions in polymeric compounds. Numerous papers have been published on the synthesis and application of redox polymers, but they have usually been concerned with particular questions, and do not show the present-day position or the prospects for this class of compounds. The few papers and reviews [2-25,205-207] of general character do not give an all-round account of the subject. No systematic classification of redox polymers or rational nomenclature for them has yet appeared.

Redox polymers are macromolecular compounds showing limited swelling, of three-dimensional structure (sometimes linear), which differ in composition but contain groups capable of undergoing reversible oxidation–reduction reactions with substances which can undergo these reactions and are present in contact with the polymers. Their behaviour is similar to that of soluble redox systems, the main difference being that redox polymers are obtained in the form of insoluble granules, can therefore be readily separated from the solution with which they are in contact, and do not contaminate the reaction products.

The reaction resembles the redox process between quinol and quinone. The oxidation–reduction process of a redox polymer can be represented by the equation



Redox polymers are not in the nature of ion exchangers, since they do not contain fixed ions, and therefore undergo oxidation and reduction, not ion exchange, although the phenolic hydroxyls of some redox polymers behave in strongly alkaline medium as fixed ionogenic groups. Individual redox polymers obtained in recent years contain, in addition to the redox groups, fixed strongly acid groups (they are sometimes termed redox ion exchangers [25]).

Work on the synthesis of redox polymers began only comparatively recently. Prokhorov and Yankovskii [26] first obtained redox ion exchangers in the early 1940s by treating sulphonated coal with an iron(II) salt. Later Mills and Dickinson [27] prepared redox ion exchangers by treating anion exchangers with solutions of copper (or silver) salts. According to Sansoni [15] patent claims appeared in 1944 for the preparation of redox polymers by polycondensation methods.

At the end of the 1940s Cassidy and his coworkers [28,29] made extensive investigations on the synthesis and application of polymeric electron exchangers based on vinylquinol. Somewhat later Sansoni [30] published work on the preparation of redox ion exchangers based on monomeric redox systems sorbed on ion exchangers.

Manecke [31] synthesised polycondensation polymers based on benzenepolyols, and Soloway and Schwartz [32] those based on naphthaquinones. The work of Gregor and his coworkers [33,208], Overberger and Lebovits [34], Trostyanskaya [2], Berlin et al. [35-37], Davankov [38,39], Dalibor [40], etc. is also widely known.

2. SYNTHESIS OF REDOX POLYMERS BY POLYCONDENSATION

Attempts have been made to obtain redox polymers by the polycondensation of polyhydric phenols, aminophenols, and phenylenepolyamines with formaldehyde [15].

Redox polymers have been synthesised by the polycondensation of quinol or resorcinol with formaldehyde, and of quinol, pyrogallol, and catechol with phenol and formaldehyde [41,42]; and the synthesis and properties of monomolecular quinol–phenol–formaldehyde compounds have been described [43].

A method has been patented [44] for preparing a series of redox condensation polymers on the basis of pyrogallic acid, catechol, and resorcinol.

In order to improve the chemical stability, redox polymers have been synthesised [45,46] on the basis of polycyclic aromatic derivatives of juglone, 2-hydroxyanthraquinone, alizarin, anthrarufin, quinalizarin, chrysazin, and purpurin.

Redox polymers have been obtained also from quinol and formaldehyde, or quinol, phenol, and formaldehyde [19,47-49], or resorcinol, Methylene Blue, and formaldehyde [50], or resorcinol, various dyes, and formaldehyde [40].

Conditions for the production of resorcinol–quinol–formaldehyde polymers have been more closely specified [51].

Berlin and his coworkers [35-37,52,53] have synthesised a new class of macromolecular compounds, the polyaminoquinones, which are capable of oxidation–reduction, and have high thermal stability. These polymers have been obtained by the reaction of chloranil with benzidine (or hexamethylenediamine), quinone with diamines, and of *p*-benzoquinone with bisdiazotised *p*-phenylenediamine, benzidine, and benzidine-3,3′-dicarboxylic acid. Their enhanced thermal stability and their improved magnetic, electrical, and ion-exchange properties make them of great interest [54-56].

Polycondensation of the original monomer with formaldehyde has been used to obtain [57] redox polymers from *p*-nitrosophenol, *p*-nitrosoaniline, hydrazobenzene, arsenobenzene, indamines, indophenols, benzenepolyols, anthracenepolyols, naphthalenediols, phenanthrenepolyols, etc. [209]

A polymer possessing high redox capacity has been synthesised [32] from naphthazarin (5,8-dihydroxy-1,4-naphthaquinone) and formaldehyde.

A linear redox polymer has been obtained [58] by converting *N*-methoxymethyl-polyamides into the *N*-mercaptomethyl form, which in turn can probably be reversibly oxidised and reduced.

The polycondensation[59] of equimolecular quantities of *p*-dimethoxybenzene and 1,4-bischloromethyl-2,5-dimethoxybenzene gives poly-(2,5-dimethoxy-1,4-phenylenemethylene), which after demethylation and oxidation gives a polyquinone. Polymeric quinones are also obtained by oxidising the product of the polycondensation of quinol, phenol, and formaldehyde in the molecular proportions 1:1:3, etc.[210,211]

Polycondensation redox polymers have unsatisfactory kinetic properties[25]. This is one of the principal reasons for their limited use. The poor kinetic properties are to a considerable extent due to the low swellability of the polymers. The ability to diffuse[19,25,60,61], which in these cases determined the reaction velocity, was inadequate. The hydrocarbon skeleton of ion exchangers is hydrophobic, and only the introduction of polar groups into the skeleton confers hydrophilic properties — and hence the power of limited swelling — on the polymer. Although polar (phenolic) groups are present in the macromolecule of polycondensation redox polymers, they are little dissociated in aqueous solution, and therefore the swelling power of the polymer is low. On the other hand, redox reactions, unlike ion-exchange processes, are not ionic, and therefore occur slowly.

Redox processes in solution can be catalysed by certain substances[62,63]. The oxidation $Fe^{2+} \rightarrow Fe^{3+}$, for example, occurs more rapidly in the presence of chloride ions. It has been established[64], in an investigation of electron-exchangers, that chloride ions accelerate the reaction of cerium ions with the polymer. Manecke and his co-workers[46] did not observe this effect of chloride ions on their redox polymers, but they showed that, when monomeric quinones are added to the solution, the reaction between oxidant and polymer is more rapid and the potential of the polymer is established within a shorter time on titration (Fig. 1). The monomeric quinone is here acting as a catalyst. The quinone probably reacts with the quinol form of the polymer to form a semiquinone, the latter form of the polymer being oxidised more rapidly[46]. It is generally known[65,66] that under certain conditions a monomeric quinol can react with a monomeric quinone, and that intermediate products can be formed in the oxidation of quinol. Thus there are no grounds for completely excluding the possibility of such processes in polymeric compounds.

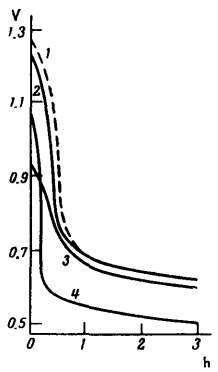


Fig. 1. Fall in potential with time during the reduction of a sulphuric-acid solution of Ce^{4+} on various redox polymers[46]: 1) redox polymer from quinol, phenol, and formaldehyde; 2) redox polymer from quinol, hydroxybenzenesulphonic acid, and formaldehyde; 3) as (2) in 1 *N* KCl solution; 4) as (2) with additions of a catalyst (dimethylbenzoquinone).

It has been proposed to introduce other polar groups, mainly sulpho-groups[46,212] (Fig. 1), to improve the hydrophilic and kinetic properties of redox polymers. However, they are found to diminish the stability of the polymer, and above all do not produce sufficient effect.

The addition of oxidation and reduction catalysts does not solve the kinetic problem. The decisive factor in the reaction velocity is the diffusion of reactants into the interior of the polymer. The low swelling power of the polymer does not provide sufficiently large intramolecular pores, commensurate with the radius of the reactant ions or molecules. Therefore reaction takes place only on the surface of the polymer grains, or else inside the grain but at an extremely low rate. There is no great value in accelerating the process on the surface of the grains, since the redox capacity is insignificant in such cases. The rate-determining factor is not the reaction itself but the diffusion process.

The authors consider that it is possible to accelerate redox processes by producing a polymer of definite structure, e.g. macroporous, which would ensure ready access of the reactants to all functional groups.

An extensive literature exists on the effect of structure on ion-exchange processes[213] and on the use of ion-exchange sieves[67-96]. The use of strongly swelling polymers, possessing great intramolecular porosity, is of decisive importance for the ion exchange of substances of high molecular weight[97,98]. The synthesis has recently been developed, and the industrial manufacture organised, of macroporous ion exchangers of low swelling power. Such resins have considerable advantages over the usual strongly swelling ion-exchange resins, being characterised by improved physicochemical properties[99,214-232].

A method has been proposed[100] for the synthesis of macroporous redox polymers which permits a considerable increase and control of their moisture content, and hence of the reaction velocity. It yields polymers of high and controllable porosity, this being achieved by adding to the reaction mass sufficient of an inert diluent, which is subsequently washed out of the final product. Compounds containing hydroxyl, carboxyl, or carbonyl groups, several inorganic salts, carbohydrates, and other substances can be mixed with the initial monomers for this purpose. Isopentyl alcohol and oleic acid are the most effective; pyridine, sodium chloride, glucose, etc. are less effective. The resulting redox polymers are characterised by increased moisture-absorption and redox capacity and improved kinetic properties (Fig. 2). The amount of additive used is of great significance here.

Methods for the synthesis of phenol–formaldehyde polymers have been worked out in some detail. However, the first attempts at preparing quinol–phenol–formaldehyde redox polymers showed little success. The polymers were obtained as a powdery mass, which was hydrophobic and of low redox capacity. It was later proposed[42] that ethanol and other organic substances should be used as solvents, and this permitted considerable improvement in the properties of the resulting electron exchangers.

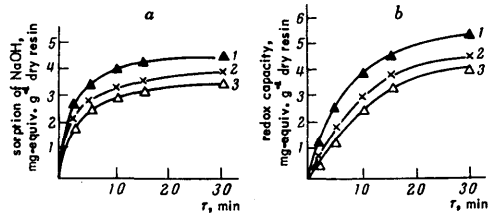


Fig. 2. Kinetic curves for macroporous redox polymers [100]: *a*) sorption of NaOH; *b*) the reduction $Fe^{3+} \rightarrow Fe^{2+}$; with the pores formed by different concentrations of isopentyl alcohol: 1) 0.55 M; 2) 0.92 M; 3) 0.

Phenol has also been used as third component in the synthesis of benzenepolyol–formaldehyde redox polymers, with the aim of (1) obtaining insoluble cross-linked polymers, and (2) avoiding the formation of semiquinones.

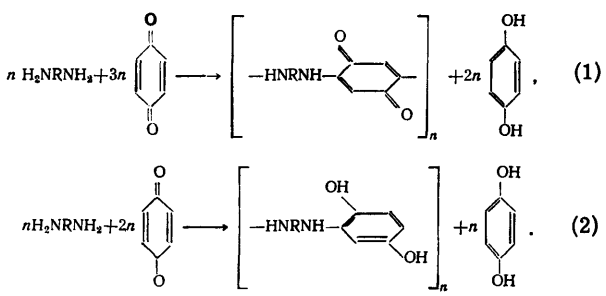
Little difference is found among methods suggested for the synthesis of this type of redox polymers. The preparation of quinol–formaldehyde polymers can be cited as a characteristic example [19,42,100]. A mixture of quinol and phenol was dissolved in ethanol, concentrated hydrochloric acid was added, and then a solution of formaldehyde was gradually introduced. The reaction mass was heated to about 60°, and maintained at this temperature first with stirring in the reaction vessel and then in a thermostat. The resulting polymer was ground up, and unchanged monomers were rinsed out and extracted with alcohol and water.

In order to obtain redox polymers based on mixtures of benzenepolyols, a solution of formaldehyde and quinol in methanol was added to the reaction vessel. After some time resorcinol and an acid catalyst were added at an elevated temperature, and an exothermic reaction began. The polymer was freed from unchanged impurities by steam-distilling off the latter [51].

Redox polymers were obtained based on resorcinol and Methylene Blue [50] and on resorcinol and various dyes [32,40].

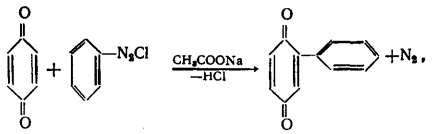
Polymers based on juglone, 2-hydroxyanthraquinone, alizarin, anthrarufin, chrysazin, quinalizarin, and purpurin have been obtained in the same way as quinol–phenol–formaldehyde polymers, in alcoholic medium but under more severe conditions, with precondensation at 100°, hardening, and aging of the gel at 100–150° for several hours. The more severe processing conditions have a deleterious effect on the redox properties of the resulting polymers [45,46].

Polyaminoquinones have been obtained by the interaction of various diamines with chloranil and *p*-benzoquinone in alcohol at elevated temperature [35,52]. The reaction of quinones with diamines can be represented by the scheme [52]



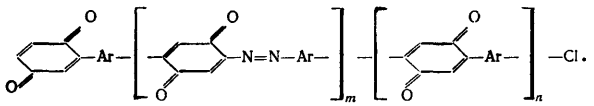
Increasing the quantity of diamine had no effect on the yield of polyaminoquinone.

The process of arylating quinones by the action of diazonium salts [101,102]

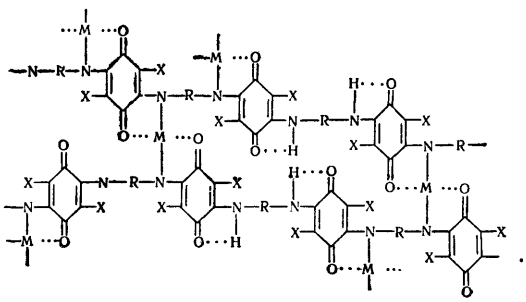


and the application of this method to the preparation of arylated quinones [103], as well as the synthesis of a diquinonylbenzene by the reaction of *p*-phenylenebisdiazonium salts with *p*-benzoquinone, have been described previously [104].

The interaction of bisdiazotised *p*-phenylenediamine, benzidine, and benzidine-3,3′-dicarboxylic acid with quinone has been used [53] to obtain hitherto undescribed polymeric azophenylenequinones of general formula



The polymers possess electron-exchange properties and appreciable electronic conductivity, are fairly thermostable, and gave narrow electron spin resonance signals having an integral intensity of the order of 10^{18}–10^{20} paramagnetic particles per gramme [53]. Polymeric aminoquinones are also able to form with metal salts insoluble and infusible complexes having roughly the structure [35]



The electron-exchange properties, reaction velocity, chemical stability, redox potential, and several other properties have been examined with many types of redox polymers. In the investigation of oxidation–reduction processes, oxidised polymers can be reduced with various reducing agents — ammoniacal sodium dithionite (10% solution in 1 *N* ammonia), a sulphuric-acid solution of titanous chloride (10% solution in 1 *N* sulphuric acid) — rate of oxidation usually being expressed by the change in potential of the polymer with time. The potentiometric titration curves obtained show that condensation products of quinol react more slowly than polymers of pyrogallol and catechol, a gradual slowing down in the redox process being observed with all specimens [31].

Polymers based on pyrogallol with a high phenol content reacted more rapidly (Fig. 3) and had lower chemical stability [31] (Table 2). The rate of oxidation of naphthaquinone (juglone) polymers was higher than that of polymers of the anthraquinone (quinalizarin) series, but lower than that of quinol polymers [45,46] (Fig. 4).

The redox capacity was most frequently determined from the number of milliequivalents of tervalent iron which could be reduced by one gramme of polymer (based on the

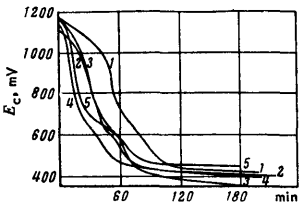


Fig. 3. Fall in potential with time in the oxidation of various redox polymers by the same quantity of oxidant[31]:
1) quinol–phenol–formaldehyde (1 : 1 : 2);
2) pyrogallol–phenol–formaldehyde (1 : 1 : 3);
3) pyrogallol–phenol–formaldehyde (1 : 0.5 : 2);
4) catechol–phenol–formaldehyde (1 : 2 : 4);
5) catechol–phenol–formaldehyde (1 : 1 : 2).

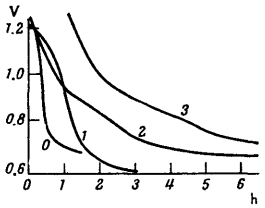


Fig. 4. Fall in potential with time in the reduction of a sulphuric-acid solution of Ce^{4+} on various redox polymers[46]:
0) quinol–phenol–formaldehyde (1 : 1 : 3);
1) juglone–phenol–formaldehyde (1 : 1 : 3);
2) quinalizarin–phenol–formaldehyde (1 : 1 : 4);
3) quinalizarin–phenol–formaldehyde (1 : 2 : 3).

TABLE 1. Redox capacity of naphthaquinone and anthraquinone polymers[46].

Component reactants	Molecular proportions	Redox capacity, mg-equiv. g^{-1}
Juglone–phenol–formaldehyde	1:1:3	4.5
2-Hydroxyanthraquinone–phenol–formaldehyde	1:1:2	1.1
Alizarin–phenol–formaldehyde	1:1:3	0.5
Anthrarufin–phenol–formaldehyde	1:1:2	1.4
Ditto	1:1:3	1.3
»	1:1:4	2.1
»	1:2:3	1.1
Chrysazin–phenol–formaldehyde	1:1:2	1.5
Ditto	1:1:3	1.5
»	1:1:4	2.5
»	1:2:3	1.5
Purpurin–phenol–formaldehyde	1:1:3	0.7
Quinalizarin–phenol–formaldehyde	1:1:2	1.7
Ditto	1:1:3	1.7
»	1:1:4	2.5
»	1:2:3	1.4

TABLE 2. Fall in redox capacity of certain polymers[31].

Component reactants	Molecular proportions	Redox capacity, mg-equiv. g^{-1}		Fall in capacity, %
		1st determination	2nd determination	
Quinol–phenol–formaldehyde	1:1:2	6.4	6.4	0.0
Ditto	1:1:2.5	7.0	6.9	1.4
»	1:1:3	6.8	6.7	1.5
»	1:0.5:2	9.9	9.2	7.1
»	1:0:1	14.7	12.6	14.3
Pyrogallol–phenol–formaldehyde	1:1:2	5.9	5.3	10.2
Ditto	1:1:3	5.5	5.1	7.3
»	1:1:4	5.3	4.6	13.2
»	1:1:2.5	3.9	3.3	15.4
»	1:2:3	4.2	3.6	14.3
»	1:2:4	4.0	3.6	10.0
»	1:0.5:1.5	7.5	6.3	16.0
»	1:0.5:2	7.7	6.5	15.6
»	1:0.5:2.5	7.7	6.5	15.6
Catechol–phenol–formaldehyde	1:1:2	7.3	5.8	20.6
Ditto	1:1:3	7.1	5.7	19.7
»	1:0.5:1.5	9.1	7.5	17.6
»	1:0.5:2	9.5	7.4	22.1

dry material) under equilibrium conditions[233]. Values representing the redox capacity of several polymers are given in Tables 1 and 2.

Chemical stability has usually been determined by repeating oxidation–reduction cycles, the redox capacity being determined after each cycle and the stability of the polymer being assessed from the change therein. Polymer samples obtained from dihydric phenols showed inadequate stability: their capacity fell somewhat after many alternations of oxidation–reduction cycles (Table 2)[19,31]. The stability fell also under the action of solutions of oxidising agents and of alkalis. Polymers obtained by treating sulphonated phenol-formaldehyde resins with potassium hydrogen fluoride or with diazotised sulphanilic acid and then reducing with sodium dithionite solution were also unstable[47].

The fall in redox capacity might be a consequence of — (1) gradual elution of components of low molecular weight containing active groups, (2) irreversible oxidation of hydroxybenzenes in the polymer to quinone methides[31,105], and (3) degradative processes.

Polymers based on chloranil and benzidine were black in colour, did not melt, and did not dissolve in the usual organic solvents, being soluble only in concentrated sulphuric acid and partly in formic acid and dimethylformamide; whereas polymers of chloranil and hexamethylenediamine were infusible pinkish grey powders, insoluble in the usual organic solvents but soluble in concentrated sulphuric acid[35,37]. Their disadvantage is the difficulty of quantitative reduction of active groups. Polyaminoquinones are more difficult to reduce[52] than polyvinylquinols[28,29], being similar in this respect to aromatic polyquinones[106] containing systems of conjugated bonds.

The ability of polyquinones in oxidised and reduced states to swell has been examined[107,234]. The infrared spectra have shown that, after a few oxidation and reduction cycles, polyquinones acquire a very small number of carboxy-groups.

The physical and mechanical properties, the chemical stability, and the static and dynamic redox capacity of resorcinol–quinol–formaldehyde polymers have been examined[51] as functions of the hydrogen-ion concentration, the rate of filtration, and the concentration of reducible iron ion; the reproducibility of the static redox capacity has also been determined. After seven oxidation–reduction cycles, the capacity has fallen from 4.4. to 3.6 mg-equiv. × × g^{-1}, the mean decrease per cycle being 2.6% (Fig. 5). The apparent redox potential was determined by potentiometric titration, and a technique worked out for regenerating the oxidised polymer. Tin(II) chloride, sodium sulphite, sodium dithionite, hydroxylamine, and other substances were used as reductants, the most successful reducing agent for this polymer being sodium dithionite. The physical and mechanical properties and the chemical stability of the resulting polymers are listed in Table 3.

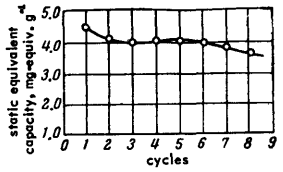


Fig. 5. Reproducibility of static redox capacity of resorcinol–quinol–formaldehyde polymer with respect to the iron ion [51].

TABLE 3. Physical and mechanical properties and chemical stability of quinol–resorcinol–formaldehyde polymers [51] (determined by methods described in monograph [108]).

Conditions	Solvent	Loss in wt., %
Thermal stability 150°	Methanol	20.45
Comminution 93.2%	Ethanol	17.4
Grinding 102.7%	Acetone	19.7
Bulk density of air-dry polymer 0.686 t m^{-3}	Benzene	2.5
Bulk density of moist polymer 0.588 t m^{-3}	Hydrogenated kerosene	2.0
Swellability, 11.66%	3.5 *N* nitric acid	4.2
	3.5 *N* hydrochloric acid	0.2
	6.0 *N* sulphuric acid	1.5
	2.5 *N* caustic soda	6.1

It was concluded from an analysis of the potentiometric titration curves that a semiquinone is formed during the redox titration of a polymer based on quinol, resorcinol, and formaldehyde, or on quinol, phenol, and formaldehyde [41,109]. An equation suggested earlier [110] was used to calculate the equilibrium constant for oxidised and reduced forms of the condensation products, which in the second case (molecular proportions 1 : 1 : 2) was 43. [41]

The standard redox potential E_0 of these polymers has been determined. For the first group of polymers E_0 = = 0.68 V, [51] whereas the values for the second group are 0.605 V at pH 1.67, [41] and 0.70 V at pH 0.2. [31]

Measurement of the redox potential of an electron--exchange polymer by potentiometric titration consists in mixing the insoluble polymer with a soluble compound possessing a redox function, in which it is easy to measure the redox potential [23,41,111]. When equilibrium is established, the redox potential of the polymer E_{pol} is equal to the potential of the solution E_{soln}. By means of the auxiliary system in solution, therefore, the equilibrium potential of the solid redox polymer can be measured at the same time.

If the concentration of oxidised substances is represented [23] by [Ox], and that of reduced substances by [Red], we obtain for the solution

$$E_{soln} = E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}}, \quad (1)$$

and for the polymer

$$E_{pol} = E_{0\,pol} + \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}, \quad (2)$$

where E_0 is the standard redox potential (in V), n the number of electrons involved in the reaction, F Faraday's constant (96 500 C), R the gas constant (8.31 J deg^{-1} $mole^{-1}$), and T the absolute temperature (°K). When equilibrium is established, we have

$$E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}} = E_{0\,pol} + \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}, \quad (3)$$

which can be written

$$E_{0\,pol} = E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}} - \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}. \quad (4)$$

Substitution for the difference in potential from Eqn. (1) in Eqn. (4) yields for the redox potential of the polymer finally

$$E_{0\,pol} = E_{soln} - \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}. \quad (5)$$

If $[Ox]_{pol}/[Red]_{pol}$ is known, $E_{0\,pol}$ can be calculated. When 50% of the reactive groups in the polymer have been oxidised, we obtain

$$\frac{[Ox]_{pol}}{[Red]_{pol}} = 1 \quad \text{and} \quad \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}} = 0, \quad (6)$$

i.e.

$$E_{0\,pol} = E_{soln}. \quad (7)$$

The equilibrium constant can be calculated in the way described by Manecke [112]. Reaction of the redox polymer in the reduced form H_2R with oxygen, for example, can be represented schematically by the equation

$$2H_2R + O_2 \rightleftarrows 2R + 2H_2O.$$

The equilibrium constant k for this reaction is computed from the difference between the potential of oxygen $E_{0\,O_2}$ and that of the polymer $E_{0\,pol}$:

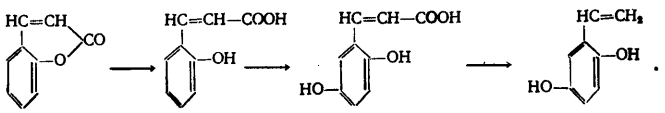
$$E_{0\,O_2} - E_{0\,pol} = \frac{RT}{4F} \ln \frac{a_R^2 \, a_{H_2O}^2}{a_{H_2R}^2 \, P_{O_2}} = \frac{RT}{4F} \ln k, \quad (8)$$

$$\ln k = \frac{4R}{RT} (E_{0O_2} - E_{0\,pol}). \quad (9)$$

Putting $E_{0\,O_2}$ = 1.23 V and $E_{0\,pol}$ = 0.7 V, [31,41,42] we obtain $k = 3 \times 10^{36}$.

3. SYNTHESIS OF REDOX POLYMERS BY POLYMERISATION

In 1949 macromolecular compounds capable of oxidation and reduction were obtained by the polymerisation of vinylquinol [28,29]. The vinylquinol starting material was prepared by the scheme [28,29,113,114]

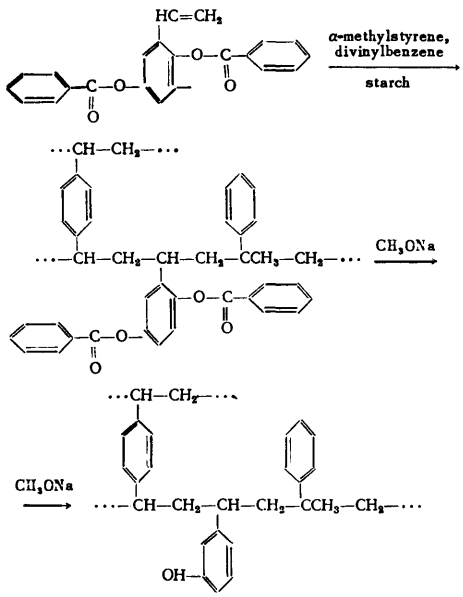


It can also be prepared by another method [115,116], which consists of several stages and its very laborious. The final yield of vinylquinol is low as in the previous case.

The polymerisation of vinylquinol was conducted, without a catalyst, in sealed tubes at 125°. After cooling, the polymer was extracted with hot benzene to remove unchanged monomer. The polymer was a brittle solid mass, pale amber in colour, soluble in polar organic solvents but insoluble in benzene. In the presence of water the polymer became soft and tacky. It was not a success: although all the active groups were reduced, the polymer gradually lost its activity with repeated oxidation–reduction cycles [28,29].

It was established later[117,118] that these polymers consisted predominantly of dimers and trimers of vinylquinol. It is difficult to obtain macromolecular compounds because quinol itself inhibits polymerisation[119].

When the hydroxy-groups in vinylquinol were protected by conversion into dibenzoates or diacetates, polymers could be obtained of molecular weight of the order of 70 000.[117,121] The dibenzoate or the diacetate was copolymerised also with styrene, α-methylstyrene, vinylpyridine, methyl methacrylate, methyl acrylate, or divinylbenzene in the presence of an initiator (benzoyl peroxide, azoisobutyronitrile) and a protective colloid (starch) at an elevated temperature (58–90°) in sealed tubes which had first been evacuated and then filled with nitrogen. The polymerisation was conducted in toluene (styrene and α-methylstyrene), chloroform (4-vinylpyridine), or benzene (methyl methacrylate and methyl acrylate). The duration of polymerisation was 30 minutes, and the degree of conversion <10%.[121-125]



The linear polymers were precipitated with hexane[124]. Linear benzoylated polymers dissolved better in toluene than in acetic acid; whereas the solubility of acetylated polymers was greater in acetic acid.

Polymers of different composition were obtained[126] by copolymerising vinylquinol with acrylic or maleic acid.

In order to improve the kinetic properties[64,122-123,127], cross-linked polymers and copolymers of the above dibenzoates or diacetates were sulphonated, and the ion-exchange and electron-exchange properties investigated. Oxidation and reduction of the sulphonated polymers were extremely slow, but completely reversible over the range $8.5 > pH > 4.7$. Outside these pH limits, partial decomposition of the polymers and irreversible oxidation were observed, and under certain conditions the cation-exchange capacity decreased. The stability of the polymers could be increased by replacing vinylquinol by its methylated derivatives, and divinylbenzene by other cross-linking agents. The polymerisation of 2,5-dimethoxy-3,4,6-trimethylstyrene and 2,5-dimethoxy-3,6-dimethylstyrene gave[128] new methylated vinylquinol polymers — polyvinyl-3,4,6-trimethylquinol and polyvinyl-3,6-dimethylquinol — possessing redox properties. Polymerisation was conducted in the presence of the boron trifluoride–ether complex at a low temperature (-20°) for 36 h. The resulting polymer was treated with hydrobromic acid in glacial acetic acid. The former dissolved in organic solvents, whereas the latter was an insoluble rubberlike substance.

The chemical shifts in the nuclear magnetic resonance signals of several methylated quinols and their derivatives have been measured[129], and the behaviour of dimethyl ethers of quinol and that of methylated quinols on oxidation, etc. have been studied[120,130,235,236].

It has been proposed[127] to obtain redox polymers also by the copolymerisation of vinylquinol with monomers of general formula $CH_2 : CAlkAr$, where the alkyl group contains 1–8 C atoms, and Ar represents phenyl, biphenylyl, naphthyl, or their derivatives. Sometimes other components have been added to the initial reaction mixture.

Reaction with carbonyl chloride of a suspension of 2,5-diacetoxyphenylalanine hydrochloride[131] in dioxan gave 4-(2,5-diacetoxybenzyl)-2,5-dioxooxazolidine, polymerisation of which in dioxan in the presence of alcoholic alkali yielded poly-β-(2,5-diacetoxyphenyl)-DL-alanine of molecular weight 11 000, which could be hydrolysed by alkali and by concentrated hydrochloric acid to poly-β-(2,5-dihydroxyphenyl)-DL-alanine. These methods can be used to obtain new redox polymers of polypeptide character.

A general method has been worked out[132] for obtaining hydroxylated polystyrenes possessing electron-exchange properties and high redox potentials, and methods have been improved for the synthesis of polyvinylquinol. Poly-3-vinylcatechol and poly-3-vinylbiphenyl-4,4′-diol have been prepared from the bismethoxymethyl ethers of the 3-vinyl derivatives of respectively quinol, catechol, and biphenyl-4,4′-diol. The structure of the ethers was established by hydrolysis and reduction to ethyl derivatives of phenols, and also by infrared and ultraviolet spectroscopy. Polymerisation of the resulting monomers was conducted in toluene in the presence of benzoyl peroxide.

Sulphonated derivatives of dicyclopentadienyliron (ferrocene) have also been obtained[133], but were unstable to oxidants. They deposited iron. Potentiometric titration of ferrocene and several of its derivatives has been undertaken. Titration of the diammonium disulphonate gave no positive results, since the reversible transition of iron from the ferrous to the ferric form was accompanied by side-reactions.

Redox potentials have been determined[64,134], ultraviolet spectra of polymers and copolymers of vinylquinol have been recorded, and the effects of pH, salt concentration, and sulphonation on the absorption spectra have been studied. The apparent standard redox potential has been found to depend on the degree of reduction and to be independent of molecular weight when the latter is large. The polymers proved to have higher potentials than the monomers. The potential of a polymer is established slowly on titration at a platinum electrode.

Methods have been described[135] for obtaining 2-vinylanthraquinone from 2-methylanthraquinone. Macromolecular compounds having electron-exchange properties have been prepared by the polymerisation of 2-vinylanthraquinone or by its copolymerisation with styrene, α-methylstyrene, or maleic anhydride in the presence of azoisobutyronitrile, benzoyl peroxide, titanous chloride, or metallic sodium.

Anthraquinone redox polymers have been obtained[136] by the polymerisation of 2-vinylanthraquinone, the reaction of anthraquinone-2-aldehyde and anthraquinon-2--ylmethyl toluene-*p*-sulphonate with poly(vinyl aclohol), and also the polycondensation of ethyl anthraquinon-2--ylmethylenemalonate with ethylene glycol, butane-1,4--diol, diethylene glycol, glycerol, etc.[237].

2,3,5-Trimethyl-6-vinylbenzene-1,4-diol[137], 2-methyl--3-vinyl-1,4-naphthaquinone[138], 1(and 2)-vinylanthraquinone[139], 2,3-dimethyl-5-vinyl-1,4-phenylene diacetate, and 2,3,5-trimethyl-6-vinyl-1,4-phenylene diacetate[140] have been synthesised, among other monomers[238-248], for the preparation of redox polymers.

Soluble and cross-linked poly-*m*-aminostyrene has formed the basis[141,142] for the synthesis of poly-6-vinylisatin, poly-6-vinylindirubin, and poly-6-vinylindol-3-benzothien-2′-ylindigo, and the redox capacity, apparent standard redox potential, and other properties have been examined. Porous indigoid resins have been obtained from porous poly-*m*-aminostyrene.

2-Methyl-3-vinyl-1,4-naphthaquinone and 2-vinylanthraquinone have been used to obtain redox polymers of more ordered structure[143,144,249] and improve chemical properties. Naphthaquinone derivatives did not polymerise, and their diacetates polymerised with great difficulty. Therefore only copolymers of 2-vinylanthraquinone with styrene and with divinylbenzene possessing redox properties were obtained. The copolymerisation was conducted in dimethyl sulphoxide at 140°. Replacement of part of the latter by n-butyl acetate and lowering the temperature of copolymerisation to 100° yielded redox polymers of spongy structure. The copolymer was sulphonated to improve its kinetic properties. The rate of the redox reaction was sufficiently high if not more than 70–80% of the total redox capacity was used. Other parameters are given in Table 4.

2,5-Bistetrahydropyran-2′-yloxyphenyl *p*-vinylphenyl sulphone, 2-tetrahydropyranyl *p*-vinylphenyl sulphide, and 4-methyl-2,5-bistetrahydropyran-2′-yloxyphenyl *p*-vinylphenyl sulphone have been synthesised[145,146,250], and converted into redox polymers. Continuous titration and a method of periodic titration with bromine in 80% acetic acid gave the standard redox potentials E_0 of the linear redox polymers as 0.753 ± 0.005 V for poly-*p*-vinylphenylsulphonylquinol, 0.718–0.721 V for poly-2-methyl-5-*p*--vinylphenylsulphonylquinol, and also other values for intermediate and model compounds. It was established that substituents in an unoxidised benzenoid ring have no significant influence of E_0, whereas the value of the latter is appreciably affected by the nature of a substituent in a quinonoid ring. Addition of an $RC_6H_4SO_2$ group to quinones increased E_0 by 44–66 mV in the case of quinol derivatives, and by 77–88 mV in the case of methylquinol.

Macromolecular redox systems can be obtained which are based on compounds of the polyvinylformal type[147].

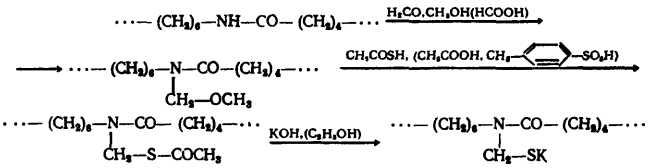
TABLE 4. Composition, ion-exchange capacity, and redox capacity of sulphonated 2-vinylanthraquinone polymers[144].

Specimen	Molar ratio of 2-vinylanthraquinone to sum of comonomers	Divinylbenzene in polymer, mole %	Ion-exchange capacity, mg-equiv. g^{-1}	Redox capacity, mg-equiv. g^{-1}
1	1:10 spongy	12.5	4.375	1.26
2	1:10	12.5	4.491	1.01
3	1:3	6.0	3.563	2.60
4	1:2	6.0	3.080	3.24
5	1:1	8.0	2.021	4.76
6	1:1	6.0	2.042	4.61
7	1:1	4.0	2.084	4.46

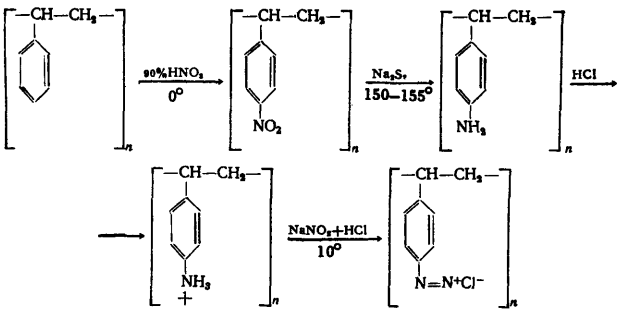
4. SYNTHESIS OF REDOX POLYMERS BY THE INTRODUCTION OF REACTIVE GROUPS INTO AN INERT POLYMER

Inert macromolecular compounds, containing no redox groups, have been used to obtain redox polymers.

The introduction of mercapto-groups into polyamides (nylon) yields electron-exchange polymers[25]:



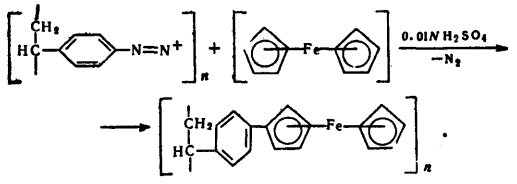
Sansoni[15] nitrated[148] cross-linked polystyrene, reduced the resulting poly-*p*-nitrostyrene to poly-*p*-aminostyrene, and diazotised the product:



He obtained[15,21] the redox polymers KVPAS, MVPAS, PFPAS, WBPAS, MBPAS, and CHPAS by coupling the diazotised poly-*p*-aminostyrene with Crystal Violet, Methyl Violet, Parafuchsine, tetramethyl-*p*-phenylenediamine, Methylene Blue, and *p*-benzoquinone respectively. These polymers showed different colours in oxidised and reduced forms. The most successful product was obtained by coupling with Methylene Blue.

The coupling of diazotised poly-*p*-aminostyrene[251] with *p*-benzoquinone, 1,4-naphthaquinone, naphthaquinone oxide, anthraquinone, and 1-chloroanthraquinone gives polymers having electron-exchange properties[33]. When quinol is used, polymers of the polyphenylbenzoquinone type are obtained[149].

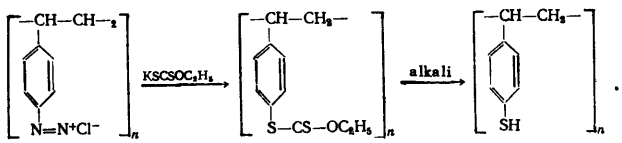
Polyferrocenestyrene redox resins have been obtained from diazotised poly-*p*-aminostyrene and ferrocene[150,207]:



Their apparent redox potentials (415 ± 10 mV) and their redox capacity with respect to the Fe^{3+} ion (5.4 mg-equiv.g^{-1}) were determined. After twelve oxidation–reduction cycles the redox capacity had fallen from 5.4 to 2.4 mg-equiv. g^{-1}.

A similar method for obtaining redox polymers has been described by other authors[151,152,252].

Redox polymers of benzenethiol type have been obtained in a similar way[33,153]. Diazotised polyaminostyrene was converted by the action of potassium xanthate into poly-(vinylphenyl xanthate), which was hydrolysed to the corresponding thiol:

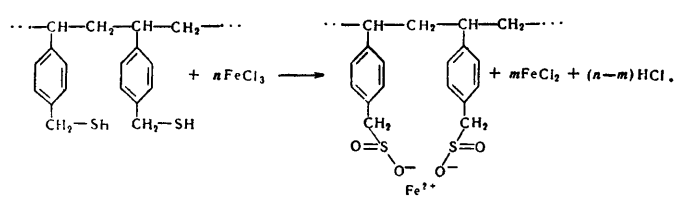


The redox capacity of the resulting polymer was 6.6 mg-equiv. g^{-1}. The same polymer has been synthesised from *p*-aminoacetophenone[34].

It has been proposed[154] to obtain redox polymers by introducing mercapto-groups and others[253,254] into copolymers of styrene and divinylbenzene.

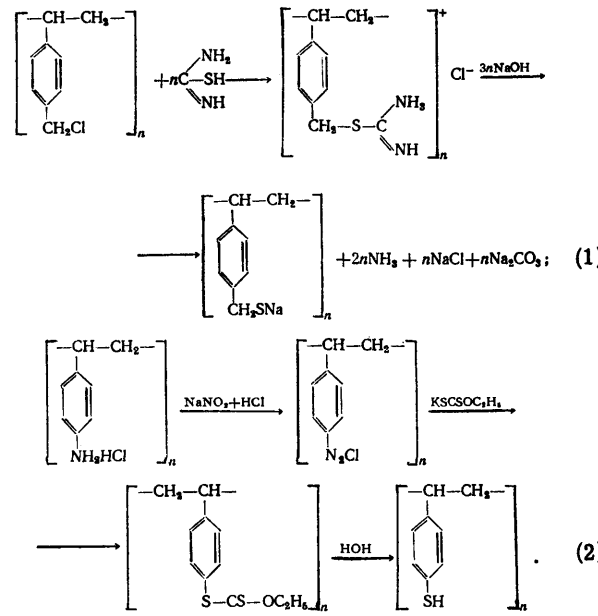
Trostyanskaya and Tevlina[155] tested methods for preparing styrene–divinylbenzene copolymers containing mercapto-groups, and found the optimum conditions for the synthesis. Copolymers of styrene with divinylbenzene or diallyl maleate, obtained by copolymerisation in suspension, were chloromethylated by the action of paraformaldehyde and hydrogen chloride in the presence of zinc chloride[156]. The chlorine atoms in the copolymers were replaced by mercapto-groups by the action of sodium sulphide or thiourea followed by hydrolysis.

The thio-copolymers showed high redox power, which remained unchanged during 8–10 cycles. The exchange capacity for the sodium ion was 2.9 mg-equiv. g^{-1} at pH > 10, and 1.9 mg-equiv. g^{-1} at pH 7, while the electron-exchange capacity with respect to the Fe^{3+} ion was 0.4 mg-equiv. g^{-1}. It was pointed out that most of the mercapto-groups could be oxidised to the sulphinic acid, and take part in ion-exchange with reduced iron cations:



Mercapto-copolymers of styrene and divinylbenzene have been used for the reduction of bivalent copper ions from $CuCl_2$ solution to univalent copper, and of silver ions to metallic silver.

The synthesis[38] and properties have been described of polymers of two types containing thiol groups, a chloromethylated styrene-divinylbenzene copolymer being treated with a solution of thiourea (scheme 1) or an aminated copolymer being diazotised, xanthated, and hydrolysed (scheme 2):



The polymers possessed both electron-exchange and ion-exchange properties. The dynamic exchange capacity with respect to the Ag^+ ion from 0.1 *N* silver nitrate solution was 2.7–2.8 and 2.13 mg-equiv. g^{-1} for (1) and (2) respectively.

A simplified method has been developed[157–159] for obtaining electron-exchange polymers of thiol type based on styrene–divinylbenzene copolymers, by treating the swollen copolymer with a solution of elementary sulphur in carbon tetrachloride in the presence of aluminium chloride with heating. The duration of the reaction at 75–78° was 8–9 h. The redox capacity of such a polymer is lower than 1.6 mg-equiv. g^{-1}.

Conditions have been studied[160,161] for the interaction of sulphur and polystyrene in dichloroethane and nitrobenzene in the presence of Friedel–Crafts catalysts. The products possessed little redox ability.

Redox polymers have been prepared by the reaction of anthraquinone-2-aldehyde with poly(vinyl acetate) and poly-(vinyl alcohol)[162,255], the reduction of sulphonyl chlorides of styrene-divinylbenzene copolymer with polysulphides[163], and the treatment of polymers of 2-vinylpyridine with chloromethane or bromomethane[164] or of polymers and copolymers of vinyl monochloroacetate with alkali or alkaline-earth metal hydrosulphides[165], etc.[166] Treatment of poly(vinyl chloride) with hydrogen sulphide under pressure gives polychloroethylenethiol[167]. Poly(methyl α-mercaptoacrylate) has been obtained by the reaction of poly-(methyl α-bromoacrylate) with potassium hydrosulphide.

Reaction of a solution of poly(vinyl alcohol) with thiourea in the presence of hydrogen bromide gives a thiouronium salt[168–179], which is hydrolysed by alkali to polyethylenethiol.

Macromolecular compounds possessing redox properties have been obtained by the reaction[171] of styrene–maleic anhydride copolymers with 1-aminoanthraquinone,

7-amino-3-oxophenothiazine, and *p*-amino-*p'p"*-bisdimethylaminotriphenylmethane.

It has been claimed[172] that thermostable polymers having electron-exchange properties can be obtained by adding an alcoholic solution of a diamine and/or a polyamine rapidly with stirring to a hot alcoholic solution of *p*-benzoquinone. The mixture is boiled for about 40 minutes, and the polymer separated after a few hours.

Redox polymers have been obtained by using the reaction of a polymeric primary or secondary amine with the lactone of β-2,5-dihydroxyphenylpropionic acid[173].

Electron-exchange polymers have been obtained by treating polychlorotrifluoroethylene (Kel-F) powder with a solution of tetrachloroquinol in ether[174]. The redox capacity was 1.6 mg-equiv. g^{-1} based on the dry polymer. These redox polymers were unstable: after a few oxidation-reduction cycles, a fall was observed in the already low redox capacity (perhaps owing to the elution of active components of low molecular weight).

5. REDOX ION EXCHANGERS

Ion-exchange materials, which form the framework, can be used as starting materials for the preparation of redox ion exchangers. Additional functional groups are attached to them by subsequent treatment with monomeric compounds possessing redox properties. These monomers either react with the resin or are adsorbed on it.

Prokhorov and Yankovskii[26] suggested a method for removing dissolved oxygen from water by passing the latter through a layer of sulphonated coal previously treated with a solution of a ferrous salt. This for the first time opened up a path to the preparation of redox ion exchangers.

Redox ion-exchange resins have been obtained also by treating anion exchangers with solutions of copper or silver salts[27], which formed complex compounds with the amino-groups of the anion-exchange resin:

$$4R{-}NH_2 + CuSO_4 \longrightarrow [Cu\,(R{-}NH_2)_4]SO_4.$$

Reducing properties were conferred on them by subsequent treatment with alkaline sodium dithionite solution. This reduced the copper (or silver) to a finely divided metallic state, in which the corresponding oxidation readily occurred, and the reaction products could again be reduced. The cycle could be repeated many times. On passage of water through a layer of such an ion exchanger, however, small amounts of copper (or silver) ions passed into the filtrate as a result of dissociation of the complex compounds on the surface of the anion-exchange resin. In order to retain the ions, it was proposed to use a cation-exchange resin in the sodium form, or an anion-exchange resin in the hydroxide form.

Redox ion exchangers have been obtained[15,30,175] by treating the water-swollen cation-exchange resins Wofatit F, Amberlite IR 120, and Dowex 50 with solutions of salts of iron, tin, cerium, titanium, Fuchsine, Methyl Violet, Crystal Violet, Tolusafranine, Rosinduline, Capri Blue, or Methylene Blue; and the anion-exchange resins Wofatit M and Amberlite IRA 400 with solutions of quinol, anthraquinol, tetrachloroquinol, and dihydroindigodisulphonic acid.

In the same way[175-178] strongly basic anion-exchange resins have been used as the basis for the preparation of redox ion-exchangers with inorganic anions — $H_3PO_2^-$, $S_2O_3^{2-}$, SO_3^{2-}, $S_2O_4^{2-}$, $NH_2NHCSO_2^-$, and BH_4^- — their redox capacities and redox potentials being given in Table 5.

Redox ion-exchange resins (Table 6) have been obtained also by treating the strongly basic anion-exchange resin Dowex 2 with solutions of Alizarin, thymolphthalein, indigotetrasulphonate, indigodisulphonate, or Thymol Blue; the weakly basic anion-exchange resin Dowex 3 with a solution of thymolphthalein; or the cation-exchange resins Dowex 50 and Amberlite IRC 50 with solutions of Methylene Blue or Crystal Violet[180] (see also Ref. 256).

Redox ion-exchangers have been prepared in an analogous manner using Fuchsine and other active substances[19,257,258].

Dalibor[40,259] prepared redox ion exchangers by treating the strongly acidic KPS and the weakly acidic CP cation-exchange resins with solutions of dyes (Capri Blue, Thionine, Methylene Blue, Nile Blue, Neutral Red, etc.) and inorganic salts ($TiCl_3$, $CrCl_2$, $CuCl_2$, $Na_2S_2O_4$), and also by saturating the anion-exchange resin L 150 with solutions of mercaptoacetic or α-mercaptopropionic acid. This resulted in ionogenic bonding of the dye or inorganic salt with the resin. The interaction of Methylene Blue and of titanous chloride with the cation-exchange resin can be represented by the schemes

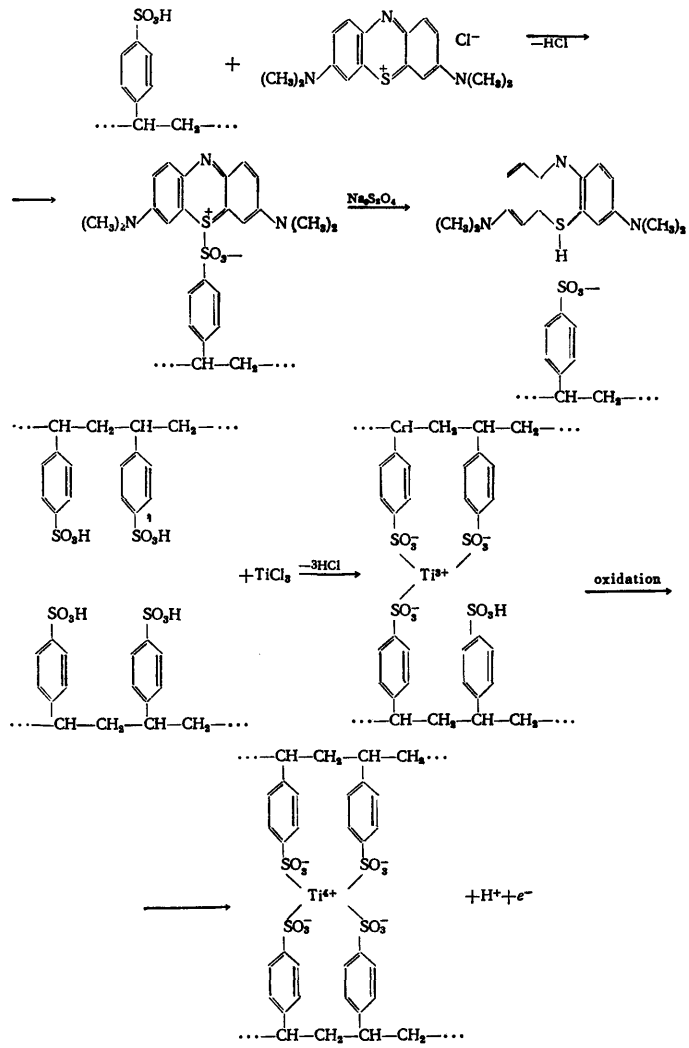


TABLE 5. Properties of some redox ion exchangers [176].

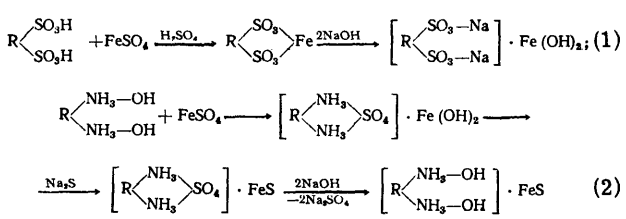
Bound anion	Redox capacity, mg-equiv. g^{-1}	time, min, to reach 50%	time, min, to reach 100%	Standard redox potential of free anion (Ref. 179)
SO_3^{2-}	0.83	5.0	20	−0.17
$S_2O_3^{2-}$	2.14	8.7	35	−0.08
$H_2PO_2^-$	0.37	8.3	30	+0.50
$S_2O_4^{2-}$	1.99	3.3	25	+1.12
$NH_2NHCSO_2^-$	2.13	5.4	60	
BH_4^-	8.4	—	—	

TABLE 6. Quantities of dyes adsorbed in various ion exchangers [180].

Dye	Ion-exchanger	Bound dye, mg/2 g ion-exchanger
Thymol Blue	Dowex 2 (strongly basic)	58.0
Indigodisulphonate	ditto	100.0
Indigotetrasulphonate	»	100.0
Thymolphthalein	»	40.0
Alizarin	»	99.8
Thymol Blue	Dowex 3 (weakly basic)	8.0
Thymolphthalein	ditto	10.0
Methylene Blue	Dowex 50 (strongly acidic)	98.2
Crystal Violet	ditto	99.2
Crystal Violet	Amberlite IRC 50 (weakly acidic)	99.4

The quantity of dye which is bonded, but not of titanium, depends on the degree of cross-linking and the porosity of the ion-exchanger (Table 7). This can be explained by the fact that the pores in the cation-exchange resin are smaller than the radius of the dye molecule but comparable with the radius of the titanium ion.

Vol'f and his coworkers [181-184] obtained redox ion exchangers by successively treating (1) cation exchangers and (2) anion exchangers with solutions of iron(II) sulphate, alkali, and sodium sulphide (see also Refs. 260 and 261):



Redox ion-exchange resins have been obtained also by saturating a weakly basic anion-exchange resin with $CuSO_4$ solution and then reducing with alkaline sodium dithionite solution, a strongly basic anion-exchange resin with sodium sulphite solution, and a polystyrene cation-exchange resin with iron(II) sulphate solution [49].

According to available information, the Chemical Process Co. of California has placed on the market in the U.S.A. the redox ion exchanger Dualite S-10, obtained by treating the anion-exchange resin Dualite A-3 with a solution of a copper salt [16,19,22,185].

A redox anion exchanger has been obtained by saturating [186] an anion-exchange resin containing strongly and feebly basic functional groups (in the proportions 1 : 1) with an ammoniacal solution of sodium dithionite, and has been used to remove dissolved oxygen from desalinated water.

TABLE 7. Quantities of dye or titanium bound on cation exchanger [40].

Dye or titanium	Cation-exchanger and its degree of cross-linking, %		Bound dye or Ti, mg
Methylene Blue	KPS (strongly acidic)	3	557
Ditto	ditto	6	204
»	»	8	292
»	CP (weakly acidic)	3	162
»	ditto	5	144
Neutral Red	KPS (strongly acidic)	3	276
Ditto	ditto	6	176
»	»	8	200
»	CP (weakly acidic)	3	201
»	ditto	5	137
Janus Green	KPS (strongly acidic)	3	332
Ditto	ditto	6	80
»	»	8	112
»	CP (weakly acidic)	3	156
»	ditto	5	98
Capri Blue	KPS (strongly acidic)	3	540
Ditto	ditto	6	318
»	»	8	403
»	CP (weakly acidic)	3	22
»	ditto	5	28
Titanium	KPS (strongly acidic)	3	51.0
»	ditto	6	49.8
»	»	8	48.0

The anion-exchange resin used was a product of the condensation of phenoxyethyl chloride with tetraethylenepentamine.

The method of preparing redox ion exchangers is fairly simple. The water-swollen cation-exchange resin in the hydrogen form, or the anion-exchange resin in the hydroxide form, is stirred for a definite time in a solution of the appropriate dye or inorganic salt, and then carefully washed with water and alcohol to remove unchanged dye or salt. The compounds mentioned above are used as reducing agents.

Redox ion exchangers have not yet found wide practical application. As already mentioned, this is due mainly to their instability, low redox capacity and gradual decrease therein, and sometimes to unsatisfactory kinetic properties. Redox ion exchangers are therefore less promising than redox polymers.

Another class of compounds containing metals of variable valency must be mentioned, in particular derivatives of chlorophyll and haemin, which possess redox functions [187]. They are of no practical value owing to their insignificant redox capacity, but they are of some interest as models of enzymes [187-193]. Natural compounds of this type play an important part in biological processes [187].

6. INORGANIC ELECTRON EXCHANGERS

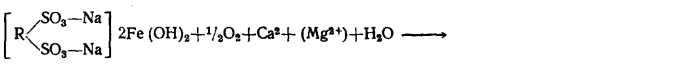
Several inorganic redox electron exchangers are known. The redox capacity of the mineral nontronite is 0.16 mg-equiv. g^{-1}, which corresponds to one-third of the total iron content [194]. The exchange capacity of the reduced form is aproximately 0.005 and 0.085 mg-equiv. g^{-1} with respect to the Cl^- and the $^{60}Co^{2+}$ ion respectively. Other inorganic electron exchangers — sodium polyvanadate, hydroxyphenyl silicate, etc. — also exist. The advantages of inorganic electron exchangers over redox polymers are absence of irreversible oxidation, relatively high rate of oxidation, and great stability to high temperatures and radiation; their disadvantages are very low capacity and instability in strongly acid and strongly alkaline media.

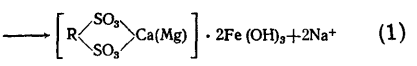
7. APPLICATIONS OF REDOX POLYMERS

Redox polymers can be used to reduce the ions Fe^{3+}, Cr^{6+}, V^{5+}, Ce^{4+}, Ti^{4+}, Ag^{+}, Pu^{2+}, etc.[2,48,100,174,175,195]; to separate cations by selective reduction[15]; for the selective reduction of aldehydes to alcohols[164]; for the oxidation of copper, tin, chromium, bromide, and iodide ions[100,155]; for the oxidation of aldehydes to acids[164]; for the dehydrogenation of hydrazobenzene, cysteine, ascorbic acid, tetrahydronaphthalene, etc.[112,196]; and also for the preparation of hydrogen peroxide[17,19,100,197,198]. They can be employed to remove peroxides or readily reducible substances from lubricating and transformer oils, to remove sulphur from refined petroleum fractions[164], and to free acetylene from oxygen[19] (see also Refs. 261-265).

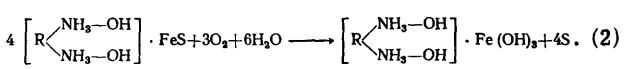
By means of redox polymers it is also possible to remove dissolved oxygen from water, which is very important in the struggle against corrosion[17,19,42,186,199,261,266-269].

Redox ion exchangers can be employed for the simultaneous deoxygenation and softening of water[183,184]:



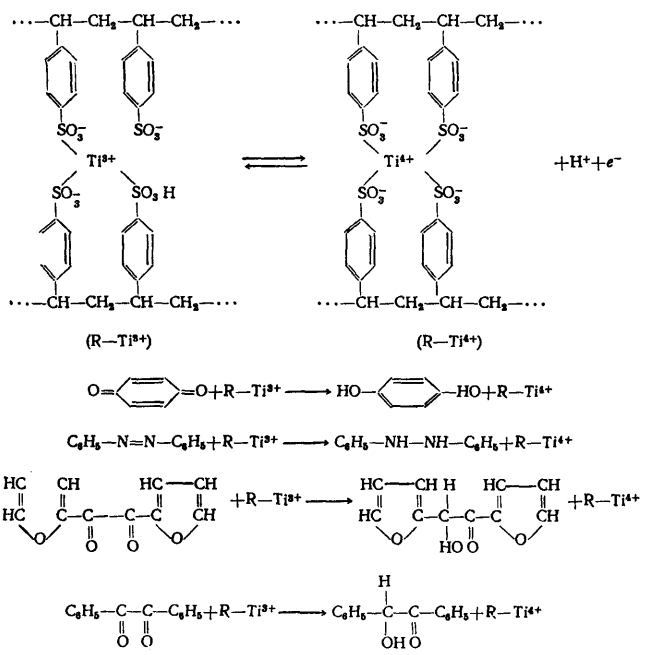


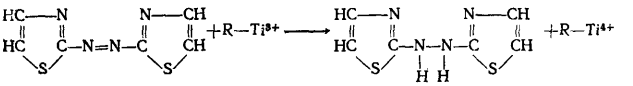
(1)



(2)

Redox ion exchangers based on Methylene Blue, Thionine, Capri Blue, Nile Blue, Neutral Red, and some other compounds have been used for the reduction of indigotetrasulphonate, indigodisulphonate, and Rosinduline GG. Redox ion exchangers prepared with Ti^{3+} and Cr^{2+} are employed for the reduction of *p*-benzoquinone, 1,4-naphthaquinone, benzil, furil, azobenzene, 2,2'-azothiazole, ammonium metavanadate, etc.[40]:





Redox ion-exchangers prepared by treating the anion-exchange resin L 150 with sodium dithionite solution have been used for the reduction of triphenyltetrazolium chloride and some other substances. The reduction of sodium tellurite and 2,2'-*p*-(di-*o*-methoxy)diphenylene-3,3',5,5'-tetraphenylditetrazole bromide by the anion-exchanger L 150 on which mercaptoacetic or α-mercaptopropionic acid has been adsorbed was accelerated by light[40].

Paper impregnated with a solution — or coated with an insoluble powder — of a redox polymer can be used in radial chromatography[121] and as an indicator for the detection of small traces of oxygen, chlorine, and other oxidising agents[50,201].

Redox polymers can be employed as electrodes for the measurement of solution pH[202] and as catalysts for oxidation or reduction[17,19,100,164] and other reactions[203].

The application of redox polymers in medicine for therapeutic purposes[163], mainly for protection from radiation[204], will evidently acquire great importance[270-275].

Redox polymers have not hitherto become widespread in industry. The reasons are the unsatisfactory kinetic properties, the instability of the capacity values, and the high cost of the initial components.

The immediate task is to develop methods for the synthesis of redox polymers which will ensure a high reaction velocity and chemical stability of the polymers.

The kinetics of redox processes can be improved by producing redox polymers of macroporous structure. The chemical stability can probably be increased by using very pure vinyl monomers and producing polymers of more regular structure.

The development of effective methods, involving few stages, of the synthesis of the initial monomers may appreciably lower the cost of redox polymers.

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Institute of Chemical Sciences,
Kazakh SSR Academy of Sciences,
Alma-Ata