

# OXIDATION-REDUCTION POLYMERS

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## ABSTRACT

This review summarizes our work on the synthesis and redox properties of polymers with various quinone-hydroquinone systems. Information is given on our attempts to increase the chemical stability of the redox resins by suitable substitution and by other methods.

The redox properties were thoroughly investigated (e.g. redox potentials, redox capacity, rate of the redox reaction). A theoretical treatment is given for the redox behaviour of tetra- and hexa-valent redox systems.

Redox resins can be used as insoluble, regenerable oxidants or reductants. By means of these resins some organic substrates could be dehydrogenated and several metal ions could be reduced or deposited.

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For several years we have synthesized polymer redox systems and have investigated their electrochemical properties. Polymer redox systems are known by the names oxidation-reduction polymers, redox polymers, redox resins and electron-transfer polymers. Water-swellaible polymers which can reversibly be oxidized or reduced are usually named redox resins. The redox components of these polymers can be links of the polymer chains or they can be substituents of the chains. The chemical structure of the redox systems can be varied widely. There exist several reviews<sup>1-3</sup> on this subject: those of Cassidy can be especially recommended. This paper is a selective review of investigations of redox resins containing hydroquinone-quinone redox systems which have been performed in our laboratories.

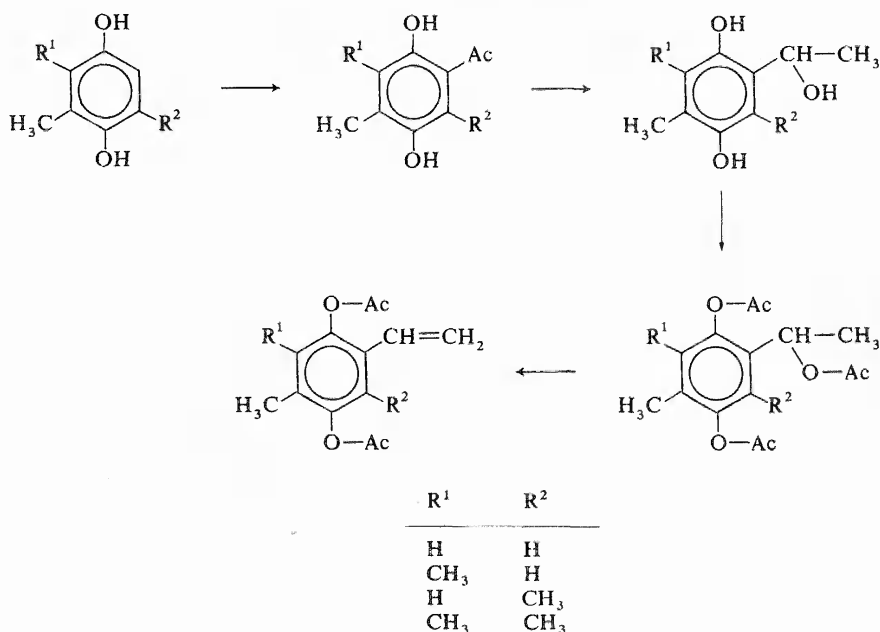
## SYNTHESIS OF REDOX RESINS

Redox polymers may be addition polymers synthesized by polymerizing hydroquinone-quinone derivatives which contain vinyl groups, or condensation polymers prepared by polycondensation of suitable compounds. They can also be prepared by polymer analogous reactions on preformed polymers.

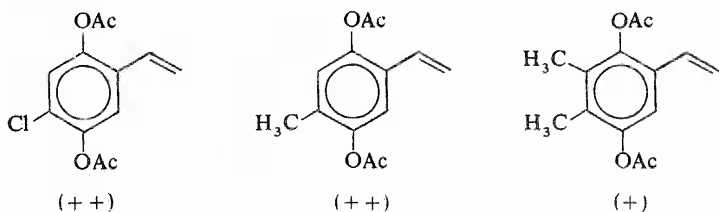
Examples of addition polymers are the redox resins which were investigated by Cassidy and his co-workers<sup>4</sup>. They were prepared on the basis of vinylhydroquinone. As the hydroquinone-quinone system inhibits polymerization, protecting groups (e.g. ether, acetate, benzoate) are usually introduced, which can be quantitatively removed after polymerization. A

copolymer can be obtained from vinyl hydroquinones, protected by acetylating the hydroxy groups, with divinylbenzene (DVB) as crosslinking agent and styrene as an additional comonomer. After sulphonation and regeneration of the redox system by splitting off the protecting groups a redox resin is synthesized which is swellable in water. This is a classical method of preparing redox resins by addition reaction. However, it was soon observed that to a certain extent irreversible oxidation of the polymer also takes place. That means the redox polymer is partially destroyed. This was believed to be caused by radical attack on the hydrogen atoms of the unsubstituted ring of the hydroquinone-quinone system during oxidation.

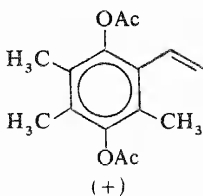
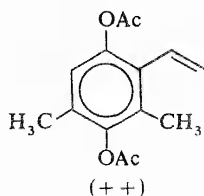
The hydroquinone-quinone systems can be stabilized by substituting the ring hydrogens with methyl groups<sup>5,6</sup>. So, we have synthesized several methylated vinylhydroquinone acetates and investigated their polymerizability. The synthesis is shown in the following scheme.



We found that monomers with methyl groups at position 5 (*meta* to the vinyl group) polymerize badly<sup>7</sup>. The polymerization was initiated by radicals from benzoyl peroxide or  $\alpha, \alpha'$ -azo-bis-isobutyronitrile in *n*-butanol.



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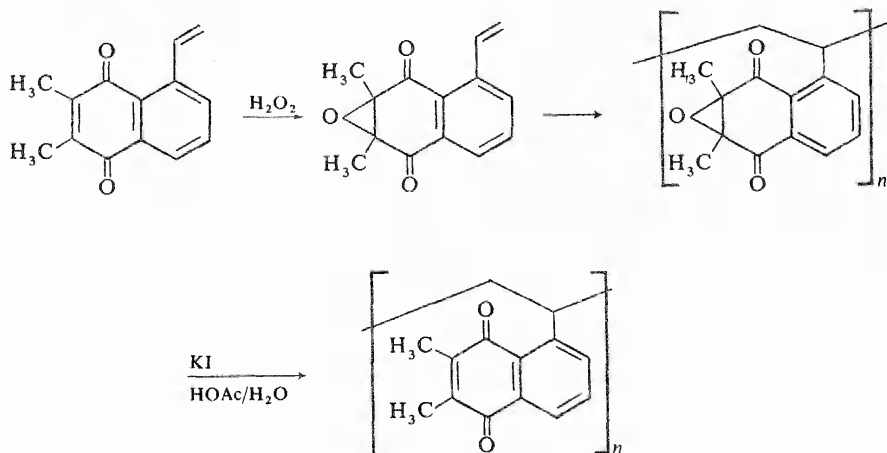


(+ +) = good polymerizability (80–90% yield)

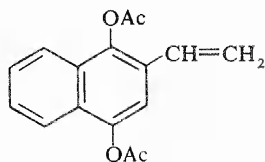
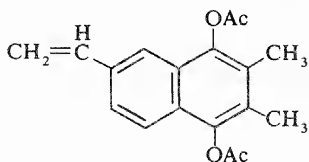
(+) = poor polymerizability (ca. 20% yield)

Redox resins produced from 1-vinyl-2,4-dimethyl-3,6-diacetoxybenzene by the usual procedure had good chemical resistance<sup>7</sup>. Their redox capacity was ca. 2.1 meq g<sup>-1</sup>, i.e. 1 g of dry resin reduces 2.1 mmol of Fe<sup>3+</sup> to Fe<sup>2+</sup>. As the resin contains SO<sub>3</sub>H groups, the redox resin showed an ion-exchange capacity of 3.5 meq g<sup>-1</sup>. By incorporating methyl substituents as electron-donating groups into the hydroquinone–quinone system the redox potential decreases. Therefore, depending on the substitution, redox resins can be produced with different redox potentials.

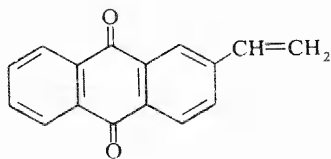
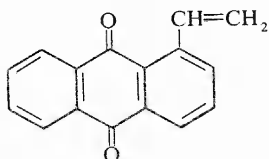
The hydroquinone–quinone redox systems can be stabilized by anellation of the quinone system with aromatic rings. 2-Methyl-3-vinylnaphthoquinone<sup>8</sup> was synthesized, which polymerized badly as hydroquinone diacetate. Therefore, the 2,3-dimethyl-5-vinylnaphthoquinone<sup>9</sup> was prepared. Unfortunately this monomer and its hydroquinone derivatives were not polymerizable. It was found, however, that epoxidation of the quinone yielded a compound which could easily be copolymerized. The polymer quinone epoxide was converted into the corresponding poly(vinylnaphthoquinone) by using KI in aqueous acetic acid.



The following polymerizable vinylnaphthoquinone diacetates were also synthesized<sup>10, 11</sup>.

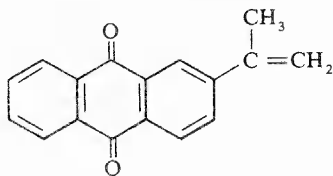


By annelating both sides of the benzoquinone the very stable anthraquinone system is obtained. Both vinylanthraquinone isomers were synthesized<sup>12</sup>.



The 1-vinylanthraquinone polymerized very badly. The 2-vinylanthraquinone could be polymerized and copolymerized with styrene and DVB<sup>13</sup>. The copolymerization had to be performed in dimethylsulphoxide by thermal initiation, because the monomer is only slightly soluble. After sulphonation resins were obtained with redox capacities up to 4.76 meq g<sup>-1</sup> and ion exchange capacities from 2.0 to 4.5 meq g<sup>-1</sup>. The midpoint redox potential of this redox resin was *ca.* 127 mV (pH 1.09). Also macroreticular resins could be prepared with this monomer. Although the anthraquinone redox resin had a relatively good chemical resistance, it was noticed that hydrogen peroxide attacks the resin and decreases the crosslinking.

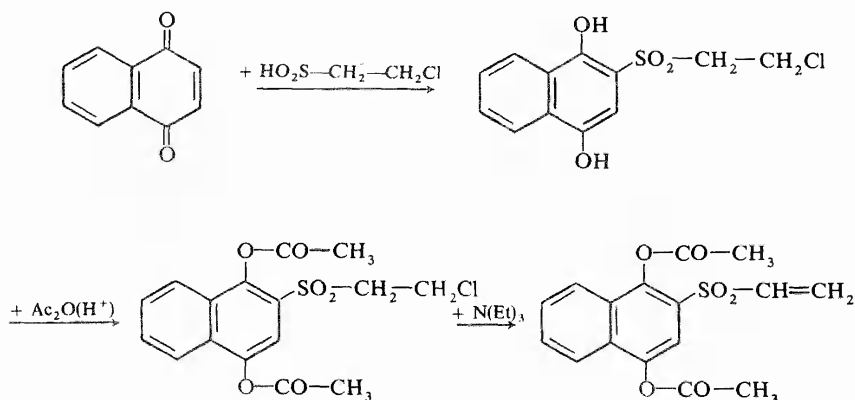
To improve the oxidation resistance of the polymer chain 2-isopropenylanthraquinone<sup>14</sup> was synthesized.



By copolymerizing this monomer with styrene and DVB or acrylic or methacrylic acid, stable resins<sup>15</sup> were obtained. They could be prepared in bead-form and also with a macroreticular structure. This could be done because the monomer had a good solubility. These redox resins are now commercially available<sup>16</sup>.

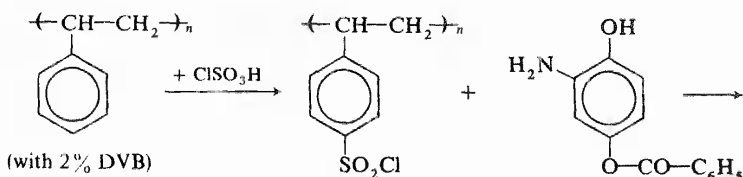
Many model compounds in which hydroquinone groups and derivatives are linked by the sulphone function have been prepared in our laboratory<sup>17-22</sup>.

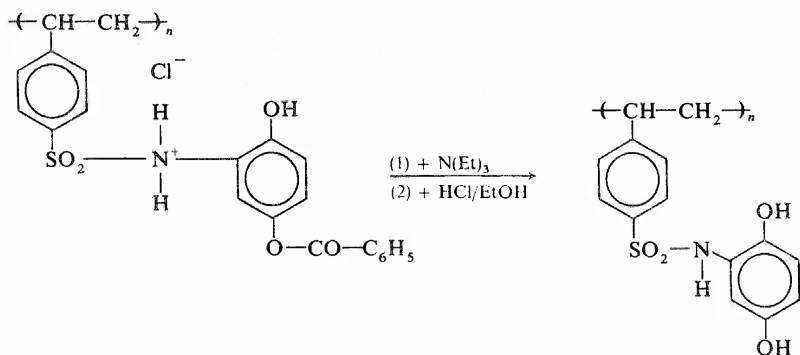
The quinoid forms of many hydroquinone sulphones are unstable in aqueous media. Therefore, we had to use a special titration procedure<sup>19, 23</sup>. Protecting the quinone nucleus by permethylation or anellation with aromatic rings resulted in compounds which were sufficiently stable to be potentiometrically measured in the acetic acid-water (1:1) system<sup>24</sup>.



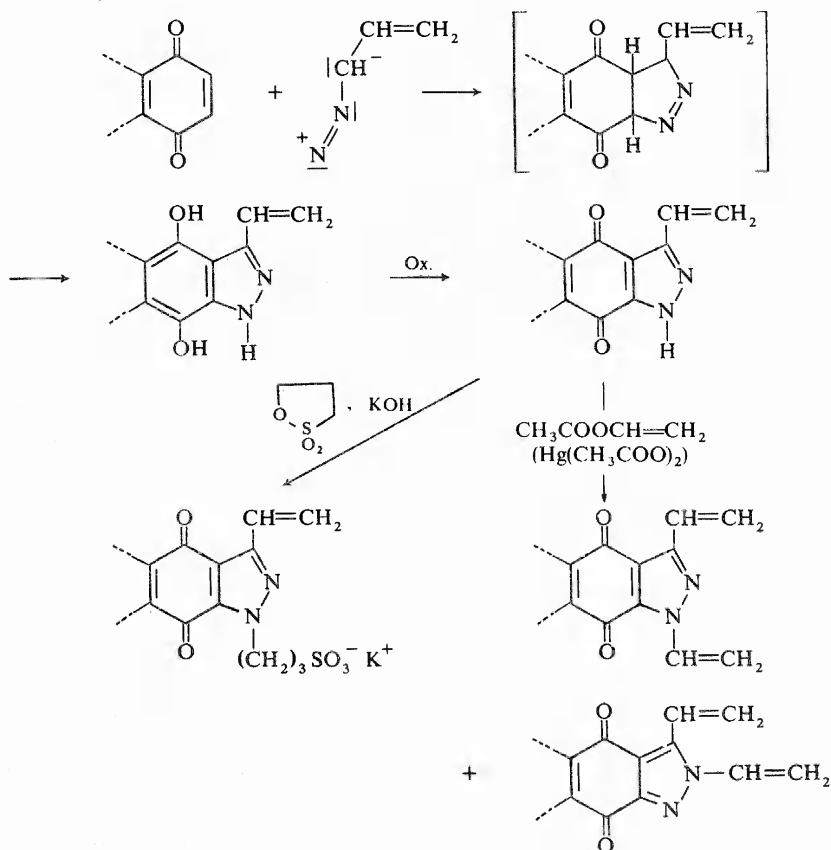
1,4-Diacetoxy-2-vinylsulphonylnaphthalene<sup>22</sup> was synthesized. This compound yielded no homopolymer by thermal or free-radical initiation, yet we were able to produce copolymers with either styrene or styrene-DVB. In order to improve swellability by means of introducing hydrophilic groups the preswollen copolymers were chlorosulphonated. The subsequent hydrolysis to sulphonic groups resulted in splitting off the protecting acetyl groups at the same time. The crosslinked copolymer had good mechanical properties and pretty good chemical stability. The redox capacity of  $3.2 \text{ meq g}^{-1}$  and the exchange capacity of  $3.26 \text{ meq g}^{-1}$  coincided with the calculated values.

Hydroquinonesulphonamides were also included in our investigations. We prepared a lot of model substances which were potentiometrically measured<sup>23, 25</sup>. An increase in the hydrolysis stability was observed by substituting hydroquinone with the  $-\text{NH}-\text{SO}_2-\text{R}$  group instead of  $-\text{SO}_2-\text{R}$  ( $\text{R} = \text{phenyl}$  or  $\text{NH-phenyl}$ ). Amongst other polymers we prepared a polymer hydroquinonesulphonamide by a polymer analogous reaction. It was stable and had good redox properties ( $4.7 \text{ meq g}^{-1}$ )<sup>26</sup>.



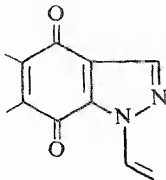
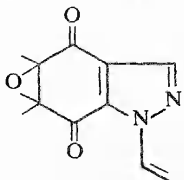
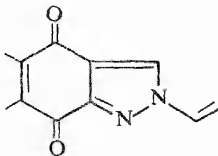
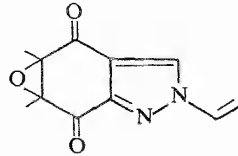
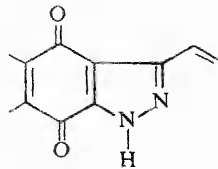
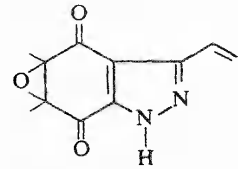


Most of the redox systems containing sulphone and sulphonamide groups did not have perfect properties. Our investigations have shown that substituted pyrazoloquinones yield very stable redox polymers<sup>27-30</sup>. Vinyl pyrazoloquinones can be prepared by 1,3-dipolar cycloaddition of diazo-propen-2 to suitable quinones. Because of their acid N—H pyrazole function these compounds can be sulphalkylated with excellent yields or *N*-vinylated with vinyl acetate.



It is interesting to notice that most of the *N*-vinylated pyrazoloquinones cannot be polymerized by radicals unless an epoxy group is introduced into the quinone moiety. This epoxy group can be reduced later with KI in acetic acid.

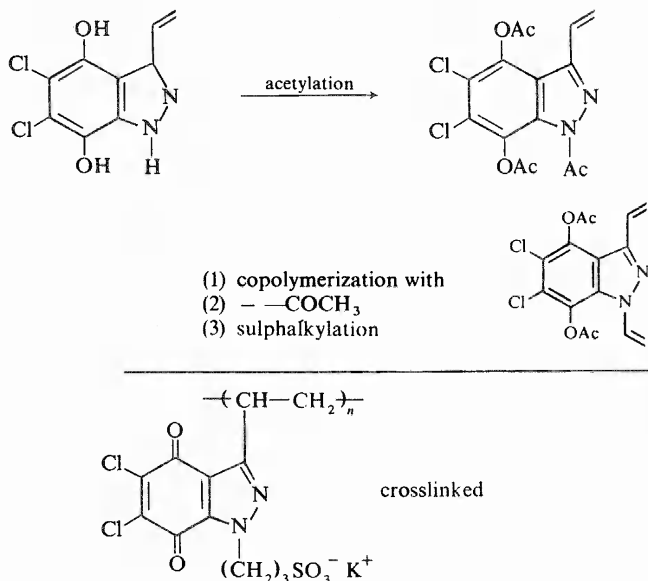
Table 1. *N*-vinylpyrazoloquinone derivates and their polymerizability\*

	
(-)	(++)
	
(-)	(++)
	
(+)	(++)

\* as indicated in brackets

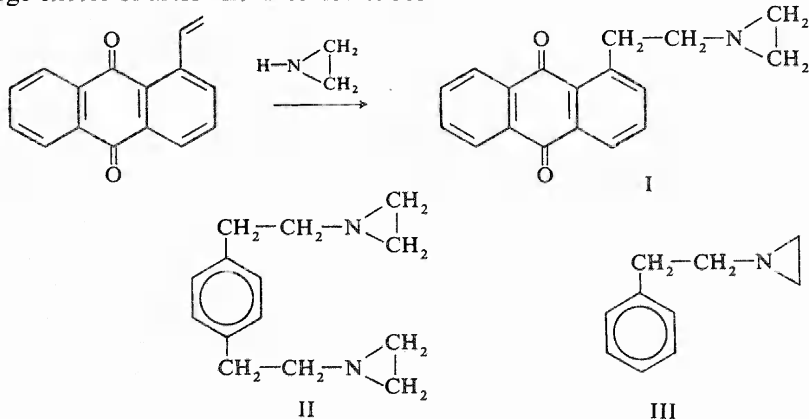
3-Vinyl-1H-benzo[*f*]indazole-4,9-dione and the crosslinking agent<sup>30</sup> 3,7-divinyl-1H,5H-pyrazolo[5,4-*f*]indazole-4,8-dione were copolymerized after being sulphalkylated. The swellability of the resulting product was too high, leading to poor mechanical stability. Resins with much better mechanical stability were obtained from these monomers performing the sulphalkylation *after* the copolymerization. (Redox capacity  $5.0 \text{ meq g}^{-1}$ , ion exchange capacity  $2.68 \text{ meq g}^{-1}$ , polarographic half-wave potential of the monomers *ca.* 130 mV).

Previously prepared polymers of this type had low redox potentials. Therefore, we tried to synthesize polymers with higher potentials<sup>27, 31</sup>. For example 5,6-dichloro-3-vinyl-1H-indazole-4,7-dione could easily be polymerized after being reduced and acetylated to 5,6-dichloro-3-vinyl-indazolehydroquinone-1,4,7-triacetate. Redox polymers were obtained by copolymerization of this monomer with the crosslinking agent 5,6-dichloro-1,3-divinyl-indazolehydroquinone-4,7-diacetate. To improve swellability the polymer was sulphalkylated.



The swelling curve indicates that the swelling volume of the redox resin changes only slightly within a broad pH range. This is very favourable for column application. The redox capacity was  $4.25 \text{ meq g}^{-1}$  and the ion exchange capacity was  $2.27 \text{ meq g}^{-1}$ . The apparent standard redox potential  $E_0$  was determined to be  $476 \text{ mV}$  ( $20^\circ\text{C}$ ).

Good results are achieved with some new nitrogen-containing redox polymers<sup>27</sup>. The quinone system inhibits the radical polymerization of some vinyl quinones. Introducing the aziridinyl group into certain vinylated quinones by adding aziridine to the vinyl group, monomers could be obtained which can easily be polymerized by cations. Vinyl quinones not having a completely substituted quinone nucleus can also add aziridine to the quinone nucleus by 1,4-addition<sup>27, 32</sup>. Homogeneous products were obtained by reacting some vinylanthraquinones and vinylpyrazoloquinones with a large excess of aziridine in sealed tubes.





1-[2(1-Aziridinyl)ethyl]-anthraquinone (I) obtained from 1-vinylanthraquinone could be copolymerized with various amounts of the crosslinking agent 1,4-bis[2-(1-aziridinyl)-ethyl]-benzene (II) but the product was too soft. In order to obtain polymers with good mechanical properties, large amounts of crosslinking agent had to be used. This deteriorated the swelling properties of the products. By synthesizing a terpolymer with [2-(1-aziridinyl)-ethyl]-benzene (III), a polymer with both good strength and good swelling characteristics could be obtained<sup>33</sup>.

Additional introduction of hydrophilic groups into these redox polymers was not necessary because of their content of tertiary amino groups. For practical applications it is important that these resins have good chemical stability and a high redox capacity (3.6–5.3 meq g<sup>-1</sup>) in addition to good swelling and mechanical properties in acid solutions.

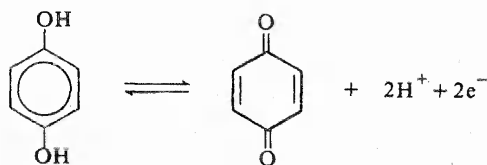
Redox resins are easily accessible by condensing formaldehyde with phenol and di- or tri-hydroxybenzenes<sup>34, 35</sup>. We have investigated with special accuracy the polycondensates of phenol-formaldehyde-hydroquinone which yielded rather stable spongy redox resins with good redox characteristics (redox capacity: 4.5–6.0 meq g<sup>-1</sup>). Also polycondensates with hydroxylated naphthoquinones and anthraquinones were prepared<sup>36, 37</sup>.

We also succeeded in synthesizing redox resins by a polymeranalogous reaction: Poly( $\alpha$ -methylstyrene) was reacted with phthalic acid anhydride under Friedel-Crafts conditions. By cyclization with polyphosphoric acid we obtained a polymer containing 8 mol % 2-isopropenylantraquinone units<sup>38</sup>.

### THE REDOX BEHAVIOUR OF THE REDOX RESINS

For the characterization of redox resins their redox capacities and their redox potentials are the main data. Besides these, the velocity of their redox reactions is an important factor for their practical use. The redox capacities depend on the composition of the polymers and are measured in meq g<sup>-1</sup> resin. For estimates of their possible application in oxidation-reduction reactions it is important to know their redox potentials. The potentiometric titration of redox systems is a convenient method to determine their redox potentials.

The redox process of the hydroquinone-quinone system can be described by the following equation:



For better clearness we shall use this equation in the following abbreviated form:



The potentiometric titration curve of this system can be described by the simple Nernst equation for processes consisting of a two-electron step.

$$E = E'_m + \frac{RT}{2F} \ln \frac{[Q]}{[H]}$$

$E'_m$  is the pH-dependent midpoint potential which is measured at 50 per cent oxidation ( $E'_m = E_0 - 0.059 \text{ pH}$ ).

The shape of the titration curve can be characterized by the index potential  $E_i$ , the difference of the potentials at 50 and 25 per cent oxidation or 75 and 50 per cent oxidation<sup>39</sup>. A deviation of the limiting value of the index potential ( $E_i = 14.1 \text{ mV}$  at 25°C) indicates the presence of redox species other than H and Q, e.g. of semiquinones.

The redox potential of a reversible redox system in solution can be measured at an inert electrode against the usual reference electrodes. If the redox system is insoluble, a direct determination of the redox potential is impossible. Therefore, it is convenient in most cases to add small amounts of a soluble redox system (called a mediator) with a standard potential similar to the polymer. The mediator should reach equilibrium with the redox resin. In this case the determined redox potential of the dissolved system equals the redox potential of the polymer. Since the equilibration process within the redox resin usually takes a long time, it is difficult to determine whether equilibrium is reached or not.

As was shown above the redox process also involves protons, leading to a pH-dependence of the redox potential. Because most of the redox resins contain ionogenic groups as hydrophilic parts ( $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$ , etc.) the distribution of the protons between the outer solution and the resin will be ruled by the Donnan equilibrium. This affects the potential of the resin in a complicated way, so that the  $E'_m$  of the redox resins are usually measured at definite conditions.

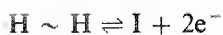
Potentiometric titration curves of the redox resins generally show higher midpoint potentials ( $E'_m$ ) than the corresponding monomer units. The slopes of the curves show a steeper increase and sometimes the curves are unsymmetrical. As there are many possible explanations for this behaviour, soluble model compounds of definite structure were synthesized and their redox behaviour was investigated.

Tetravalent redox systems with the following structures have been synthesized and measured potentiometrically (cf. Table 2).

A tetravalent system may be described by the following abbreviation



For a four-electron step the titration curve would be very flat according to the Nernst equation with an  $E_i$  of 7.1 mV at 25°C. Actually the measurements always result in an  $E_i \geq 14.1 \text{ mV}$  (25°C). So it can be assumed that the redox reaction consists of two divalent steps, inserting an intermediate I<sup>4,2a, b</sup>.



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 Table 2 Potentiometric data of some tetravalent redox systems  
 (acetic acid-water = 1:1, v/v; 25.0°C;  $K_2Cr_2O_7$ )<sup>40</sup>

System	$E'_{mh}$ mV	$E'_1$ mV	$E'_2 - E'_1$ mV	$K$
	587.2	21.3	39.6	21.9
	574.3	18.5	32.6	13.2 <sup>41</sup>
	568.2	16.8	(17.8)	(4.0)
	575.3	15.2	21.9	5.5
	569.7	14.5	18.7	4.3
	621.3	14.2	—	—

From the Nernst equations at constant pH

$$E = E'_1 + \frac{RT}{2F} \ln \frac{[I]}{[H \sim H]} \quad (1)$$

$$E = E'_2 + \frac{RT}{2F} \ln \frac{[Q \sim Q]}{[I]} \quad (2)$$

$$E = \frac{E'_1 + E'_2}{2} + \frac{RT}{4F} \ln \frac{[Q \sim Q]}{[H \sim H]} \quad (3)$$

and the redistribution reaction



$$\frac{[I]^2}{[H \sim H][Q \sim Q]} = K \quad (4)$$

results equation 5.

$$E'_2 - E'_1 = \frac{RT}{2F} \ln K \quad (5)$$

The difference in the redox potential of the individual divalent steps is connected with the equilibrium constant  $K$ .

$E'_1$  and  $E'_2$  are the pH-dependent midpoint potentials of both divalent oxidation steps.

$E'_m = (E'_1 + E'_2)/2$  is the pH-dependent measured midpoint potential of the redox system.

The constant  $K$  can be obtained from the titration curves by means of the index potential.

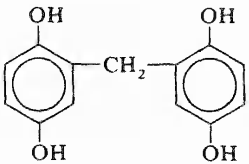
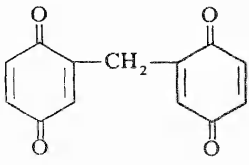
$$E_i = \frac{RT}{2F} \ln \left[ \frac{1}{2}K^{\frac{1}{2}} + \frac{1}{2}(K + 12)^{\frac{1}{2}} \right]$$

The maximal content of the intermediate I is given by

$$\left( \frac{[I]}{[H \sim H] + [I] + [Q \sim Q]} \right)_{\max} = \frac{K^{\frac{1}{2}}}{2 + K^{\frac{1}{2}}}$$

The limiting value for  $K$  is 4. This follows from considerations similar to those used for deriving the ratio of the first and second dissociation constants of dibasic acids which should be at least  $4^{4.3}$ . This means that according to a statistical point of view the difference  $E'_2 - E'_1$  should not be less than 18 mV(20°C). This limiting value will be obtained only if no interactions exist between the redox groups.

We were able to elucidate the constitution of the intermediate I using n.m.r. spectroscopy<sup>40</sup>. The compounds IV and V and their equimolecular mixture show in tetradeuterioacetic acid at 100°C the following peaks (solvent peak 2.04 p.p.m. as reference).

		chemical shift for the methyl group $\delta$ (p.p.m.)
	IV	3.83 (s)
	V	3.61 (m)
equimolar mixture of IV and V		3.70 (m)
		and peaks at 3.83 and 3.61 (according to IV and V having much less in- tensities)

These n.m.r. spectra show that a new peak is produced in the mixture. This signal is situated nearly half-way between the former peaks and gives evidence for a new compound VI.

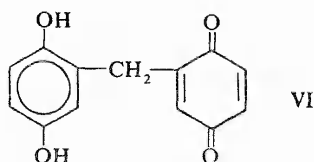


Table 2 shows that the elongation of the connecting chain between the redox systems results in a decrease of the index potential close to the limiting value of 14.1 mV. This value is not completely reached because there are other factors influencing the index potential. In addition to the inductive effect intramolecular complexes (quinhydrone) can also be formed to a certain extent.

Table 3 illustrates the results of our calculations of existing complexes in tetravalent redox systems at 50 per cent oxidation. The explanation of this procedure would be too extensive.

The longer the intramolecular distance the less is the complexing. Compounds with sterically favoured complex formation also show higher amounts of the quinhydrone.

Steric effects arising from hindered free rotation of the connected redox systems have an obvious influence on the midpoint potential. This is shown

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 Table 3. Species present at 50% oxidation in solutions of some tetravalent systems (acetic acid-water 1:1, v/v; 25.0°C; total concentration  $ca. 5 \times 10^{-4}$  mol/l.)<sup>40</sup>

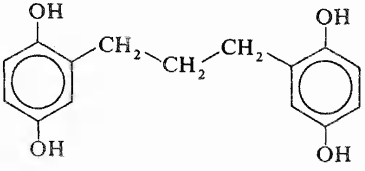
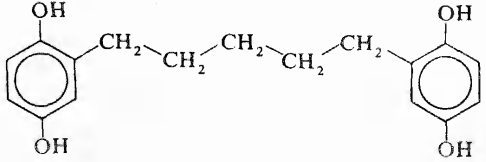
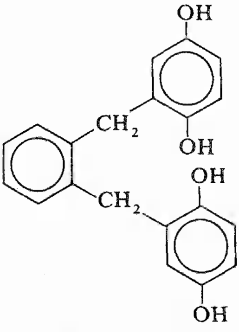
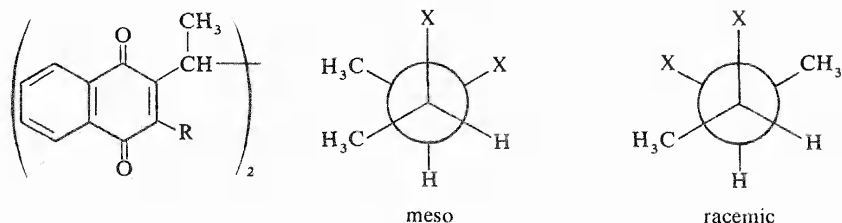
System	$E_i$ mV	H ~ H %	H ~ Q %	(H ~ Q) complex %	Q ~ Q %
	16.8	19.1	38.1	23.1	19.1
	15.0	23.4	46.7	6.6	23.4
	24.7	11.9	30.3	45.9	11.9

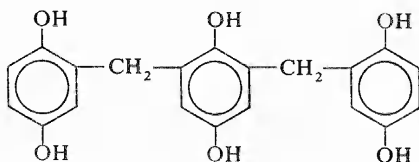
Table 4. Potentiometric data of tetravalent naphthoquinones (acetic acid-water = 4:1, v/v; 25°C; potassium dichromate)



Constitution	R	$E'_{mh}$ mV	$E_i$ mV	colour at 50% oxidation
meso	H	383.4	17.9	brownish
racemic	H	383.3	21.0	reddish
meso	CH <sub>3</sub>	299.6	17.5	brownish
racemic	CH <sub>3</sub>	286.3	18.5	reddish
benzoquinone	—	670.2	14.4	—

by some tetravalent naphthoquinone derivatives<sup>44</sup> which can be obtained in meso and racemic forms. A methyl group in the quinone nuclei changes distinctly the midpoint potential, due to hindered rotation. The index potential for racemic forms are always higher because they can exist in a conformation in which complex formation is favoured. (see *Table 4*).

Hexavalent redox systems have been synthesized either with a symmetric structure<sup>45</sup> (see *Table 5* below) or a reduced symmetric structure<sup>42a, 46</sup>.



During oxidation the symmetric hexavalent systems produce in each bivalent redox step only one intermediate.

In abbreviated form:



Compounds with reduced symmetry give two different intermediate compounds in each step. The analytical treatment of the potentiometric titration curves of the symmetric compounds is similar to that of the symmetric tetravalent systems<sup>45, 47</sup>. The results are:

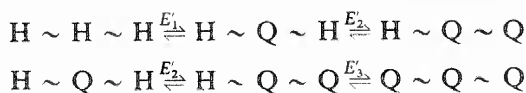
(i) The titration curves are symmetrical to the midpoint.

(ii) The formation constant  $K$  for the intermediate is equal by definition for the first and second redox step. This is concluded from the symmetry of the molecule.

(iii)  $K$  has a limiting value of 3. In the ideal case ( $K = 3$ ) the titration curve shows an index potential of 14.1 mV (25°C) because there exists no interaction between the redox systems. The differences of the midpoint potentials  $E'_2 - E'_1$  and  $E'_3 - E'_2$  are equal and have the same limiting value of 14.1 mV (25°C).

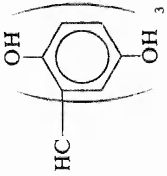
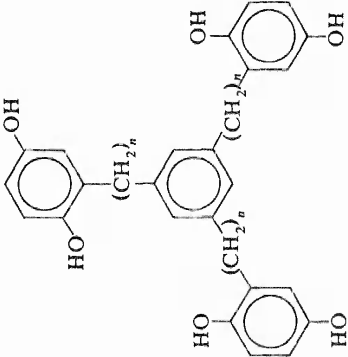
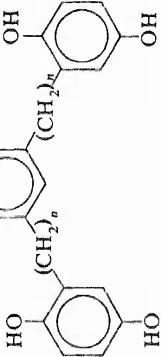
(iv) The equilibrium constant  $K$  for the intermediate can be determined using the index potentials. The results of the potentiometric titration of some compounds are shown in *Table 5*. They confirm our analytical approach.

The titration curve of hexavalent systems with reduced symmetry<sup>46</sup> can be analysed only by making several assumptions. The redox curve can approximately be considered to result from two tetravalent steps overlapping each other.



The potentiometric titration of polymer redox systems is characterized by a very slow establishment of a stable potential after each addition of titrant. This is attributed to a slow establishment of the redox equilibrium within

Table 5. Potentiometric data of symmetrical hexavalent systems (acetic acid-water 1:1, v/v; 25°C; potassium dichromate)<sup>4,5</sup>

System	$E'_{\text{mh}}$ mV	$E'_1$ mV	$K$	$E'_1$ mV	$E'_2$ mV	$E'_3$ mV
	584.4	25.7	13.1	551.3	584.4	617.5
	$n = 1$ 575.8	16.1	4.03	557.9	575.8	593.7
	$n = 2$ 568.6	15.2	3.54	552.4	568.6	584.8
Benzoquinone	621.3	14.2	—	—	—	—



the polymer and/or between mediators and the oxidant or reductant and the polymer.

The diffusion of the reactants in the redox resin is the rate-determining step. Therefore, the swellability of the resins is an important factor. Excessive swelling leads to mechanically unstable particles. For practical applications a compromise must usually be found by experiments. The titration curves of the redox resins deviate in shape and energy (e.g. position of the midpoint potentials) from those of the corresponding monomer redox systems. This is illustrated by the anthraquinone redox resins<sup>48</sup>. Polymers with a high content of anthraquinone (50 mol %) gave a midpoint potential (at pH = 1.17) of 122 mV and an index potential of 19 mV. Diminishing the redox content in the redox resin to 9 mol %, the titration gave a midpoint (at the same pH 1.18) of 108 mV and an  $E_i$  of 14.5 mV. The titration curve of the redox resin with the low content of anthraquinone had the same shape as the normal monomer anthraquinone system. This resin shows a ratio of *ca.* 8 styrenesulphonic groups per quinone unit. In the former resin the ratio is 0.9:1. It means that in both resins the redox units are in different environments. It is known e.g. that a change of the titration medium from water to ethanol raises the midpoint potential of benzoquinone by 13 mV. Another reason for the different potentials can be found in the shape of the titration curves of the polymers due to the nonuniformity of the redox systems and their immediate vicinity. The polymer redox systems show the same behaviour as the corresponding soluble monomers if the redox capacity is low and the micro-environment is similar to that in solution. This was confirmed by Cassidy and his co-workers with soluble oxidation-reduction polymers<sup>49, 50</sup>.

### APPLICATIONS OF REDOX RESINS

Redox resins are insoluble but swellable macromolecular compounds with reversible redox systems, which can exchange electrons and protons with the ambient medium. They can be used as regenerable insoluble oxidizing or reducing agents which can easily be separated by filtration from the substrate solution. That means the solution which has to be oxidized or reduced is not contaminated by the oxidizing or reducing agent. This is the great advantage of these substances compared with the usual soluble oxidants or reductants. There have been many proposals for the application of redox resins. In this paper only some examples of their applications which have been studied in our laboratories can be mentioned<sup>51, 52</sup>. Redox resins in the reduced form (hydroquinone form) have been used for the reduction of ions and for depositing metals. Using a poly(vinyl anthraquinone) resin<sup>51</sup> the following metals could be deposited by a batch process: silver from neutral  $\text{AgNO}_3$  solutions, copper from 2N sulphuric acid- $\text{Cu}^{2+}$  solutions, Te from neutral tellurite solutions, and red Se from 2N sulphuric acid-selenite solutions. The deposited metals could be dissolved without affecting the redox resin.  $\text{Fe}^{3+}$  could be reduced to  $\text{Fe}^{2+}$ ,  $\text{UO}_2^{2+}$  to  $\text{U}^{4+}$ , and  $\text{VO}_2^+$  to  $\text{V}^{3+}$  via  $\text{VO}^{2+}$ .

Redox resins in the reduced form can remove oxygen from solutions<sup>53, 54</sup>. In the presence of stabilizers they can reduce oxygen to hydrogen peroxide<sup>37, 55-57</sup> and hydrogen peroxide solutions can be produced<sup>51</sup>. We

applied the anthraquinone-containing resin in its reduced form in a column for the reducing of *p*-benzoquinone. Further we applied the condensation redox resin prepared from hydroquinone, phenol and formaldehyde in the quinone form for the dehydrogenation of various organic compounds<sup>52, 56</sup>. Cycloheptatriene can be dehydrogenated to the tropylium cation, 1,4-dihydronaphthalene to naphthalene, 9,10-dihydroanthracene to anthracene. 1,4-Dihydrocarbazole and 1,2,3,4-tetrahydrocarbazole could be dehydrogenated to carbazole, while the hexa- and dodeca-hydrocarbazole could not be dehydrogenated. Hydrazobenzene could be dehydrogenated to azobenzene, cystein to cystine, ascorbic acid to dehydroascorbic acid.

The possible applications of the redox resins in biochemistry and pharmacy are of great interest. For instance we were successful in dehydrogenating NADH to NAD<sup>+</sup> with a hydroquinone redox resin in the oxidized form. The redox resin in the quinone form also performed the Strecker degradation of alanine to acetaldehyde and also of other  $\alpha$ -amino acids<sup>52</sup>. Redox resins in the reduced form (hydroquinone form) were used successfully as anti-oxidants. Many other applications have been reported<sup>3</sup>.

With this selective and by no means complete review we intended to show that there are many possibilities of synthesizing redox polymers with various redox potentials. Many interesting electrochemical investigations have been carried out. There is a great field for physical chemists to extend the theoretical knowledge. Further applications seem to be promising. In conclusion the author wishes to underline the statement of Cassidy<sup>3</sup>: 'The whole field is ripe for exploitation'.

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