

# Dihydroxybenzene/benzoquinone-containing polymers : organic redox polymers

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**Summary :** *Dihydroxybenzene/benzoquinone-containing polymers : organic redox polymers*

Polymers containing hydroquinone, catechol, or their corresponding benzoquinones are a special class of redox polymers. Three pathways of their syntheses are possible : condensation polymerization of suitable monomers, addition polymerization of vinyl monomers containing redox moiety, and chemical attachment of redox unit onto premade polymeric matrix. A range of functionalized matrices have been employed such as polyethers, polyesters, polycarbonates, polyurethanes, polyamides, and others. Protection of their phenolic functionality has conducted to chemically interesting redox polymer precursors. The presence of a redox moiety coupled with the extant functionalization of the polymer matrix makes the materials very valuable, of wide properties and consequently of vast applicability.

**Mots clés :** *Polymères redox, polyhydroquinone, polycatéchol, polybenzoquinone.*

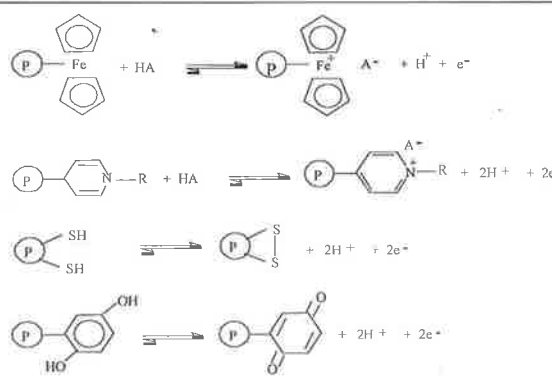
**Key-words :** *Redox polymers, polyhydroquinone, polycatechol, polybenzoquinone.*

At the close of 20<sup>th</sup> century, chemists would have held in hands a widespread and striking means for the synthesis facility as well as for an unraveling characterization of their new products, and this owes to the ahead-striding of science in general and technology. Certainly, one of the everlasting upheavals in chemistry field has been the solid-state peptide synthesis, ingeniously achieved by Robert Bruce Merrifield at Rockfell University (USA) in 1963 [1] and for which he was awarded the Nobel prize in chemistry in 1984. His success lies basically in the use of a polymeric support, namely the copolymer of styrene and divinylbenzene, which has been chemically modified for attachment and immobilizing one functionality of a starting amino acid. Since then, a deluge of scientific work has been devoted to chemical reactions on and of polymers, and consequently classes of polymers such as polymer-bound reagents and polymer-bound catalysts have been emerged. A careful examination of

redox resins containing dihydroxybenzene reveals their importance as they belong to the polymer reagents class, a class well summed up by G. Gelbard in « *L'Actualité Chimique* » [2]. The first transfer agent polymers reported in the literature were undoubtedly the redox polymers.

Polymer redox systems are known by the terms « *oxidation-reduction polymers* » and « *electron-transfer polymers* ». The name « *electron-exchange polymers* » was also assigned to these resins on the analogy of « *ion-exchange resins* », but Sansoni [3] pointed out that a transfer is occurring instead of exchange, thus this name has been dropped. These redox polymers

are high molecular-weight substances that can transfer electrons in contact with reactive ions or molecules. Therefore, polymers of this sort can be oxidized or reduced with appropriate oxidizing and reducing agents, respectively. These resins are usually loaded with functional groups of the redox-type. A variety of redox functionalities has been of great interest for polymer chemists. Among the most widely studied redox polymers are ferrocene, pyridinium, mercaptyl, and hydroquinone containing polymers. Oxidized and reduced forms of these polymers are compiled in *scheme 1* in which  $\textcircled{\text{P}}$  stands for a polymer matrix. Ferrocene-containing polymers are valuable elec-

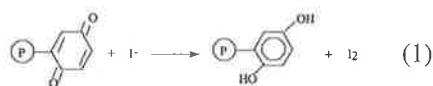


Scheme 1 - Examples of redox polymers.

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troactive materials. The ferrocene unit can be anchored onto a variety of polymer matrices. For example, Allock [4] reported a synthesis of polyphosphazene bearing ferrocene or ruthenocene, having molecular weight as high as  $2 \cdot 10^6$ . In Daly's laboratory [5] the ferrocene moiety was introduced on styrene-methyl methacrylate copolymer; this polymer-bound ferrocene exhibits a potential electroactivity as confirmed by cyclovoltametric measurements.

The first application of these resins was the oxidation of iodide to iodine as shown in (1) [6]. Some of the early examples are poly(vinylhydroquinones) and the condensation products of hydroquinone and formaldehyde. In this present account, some aspects of the synthesis of the poly(dihydroxybenzene) and related resins as well as some of their properties and of their applications are but not exhaustively outlined.



## Synthesis of redox polymers

Three main routes could be conceived as ways of preparation of redox polymers. They are : 1) condensation polymerization of suitable monomers, 2) attachment of redox groups onto preformed polymers, and 3) addition polymerization of vinyl monomers bearing redox units.

## Condensation polymers

The earliest redox polymers were by far the synthetic polymers derived from formaldehyde and hydroquinone. The condensation of these two substances yielded phenoplasts. Resorcinol and its derivatives are among those that are stable to oxidation and used in commercial phenoplast formulation. Catechol and hydroquinone, a 1,2 and 1,4-dihydroxybenzene respectively, are of interest because they are capable of forming quinoid systems. The naphthaquinone and anthraquinone derivatives are also examples of this category of oxidized polyphenols. The quinoid unit of catechol is unstable and most quinones are sensitive to light and oxidants. Condensation polymers may be classified into two categories : those which have the redox units as part of the backbone and

those which have them as pendent from the matrix.

## Redox units as part of backbone

(The different reactions illustrated in this part are gathered in *table I* and in *schemes 2* and *3*).

Although formaldehyde-hydroquinone polymers were prepared in the beginning of this century, it was only in 1949 that a description of these resins as electron-transfer polymers was given [7]. The condensation polymerization of hydroquinone and formaldehyde is a base or acid-catalyzed reaction (2) (*table I*).

Different products can be formed in three different stages of the reaction depending upon the initial hydroqui-

none-formaldehyde molar ratio and the reaction conditions. In the first stage, **A**-stage, the products exist as mono-, di-, and trinuclear methylolphenols which are soluble in acetone, ethylacetate, and dioxane. In the second stage, **B**-stage, as the condensation reaction continues, the products became oligomeric which reduces their solubility. These **B**-stage polymers are termed « *resoles* » which are highly branched structures with methylene bridges linking the benzene rings. In the third stage, **C**-stage, condensation resumes on heating the resole mixture to produce high molecular weight crosslinked polymers with defied insolubility and fusibility.

A change of formaldehyde-hydroquinone ratio results in a change of che-

**Table I** - Condensation polymers with redox units as part of backbone.

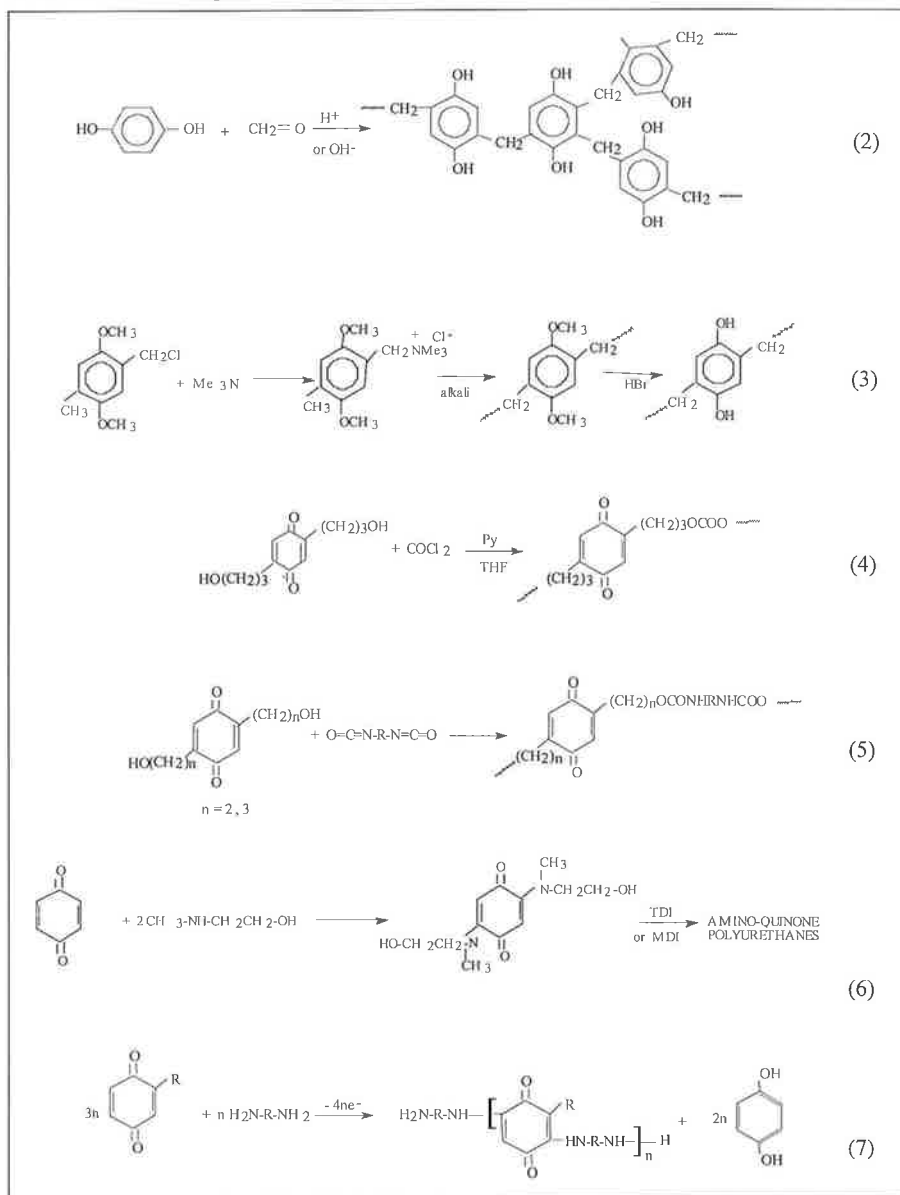
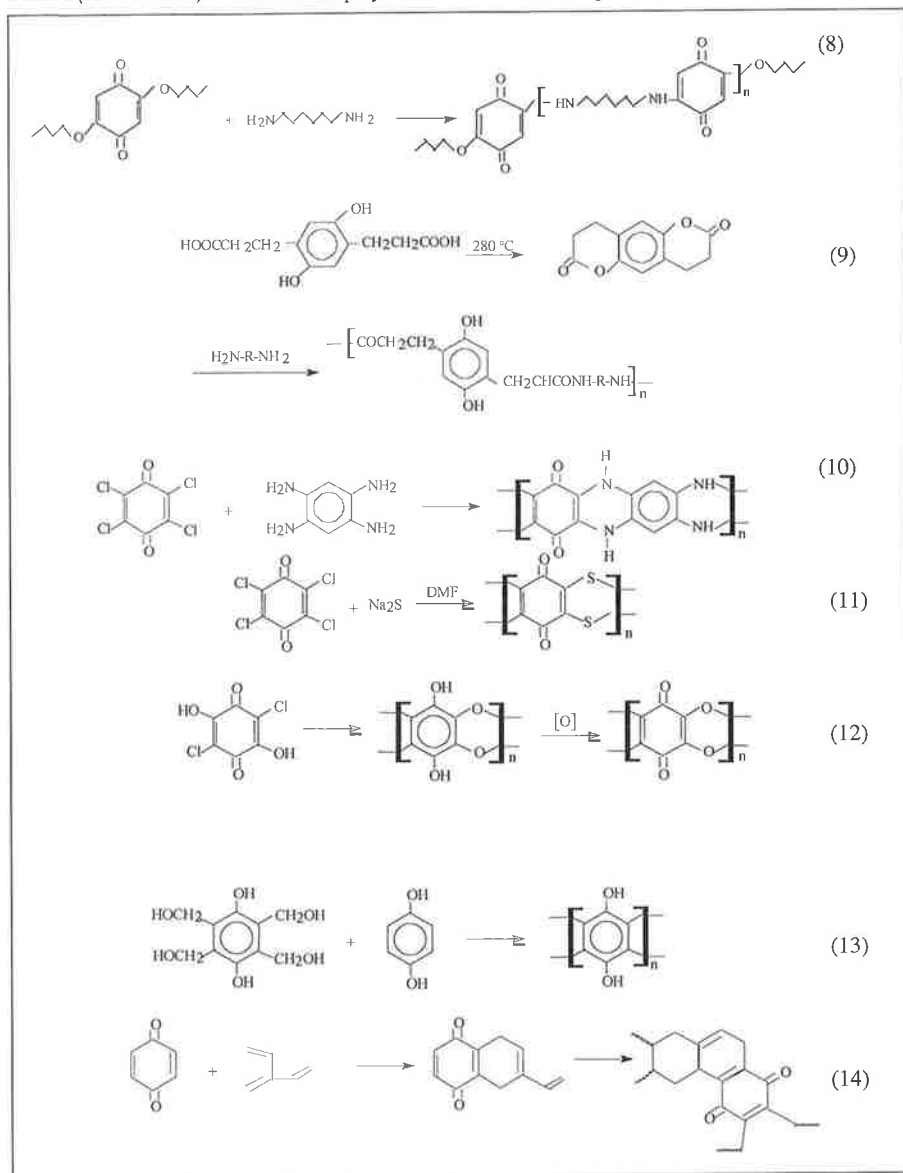


Table I (continuation) - Condensation polymers with redox units as part of backbone.

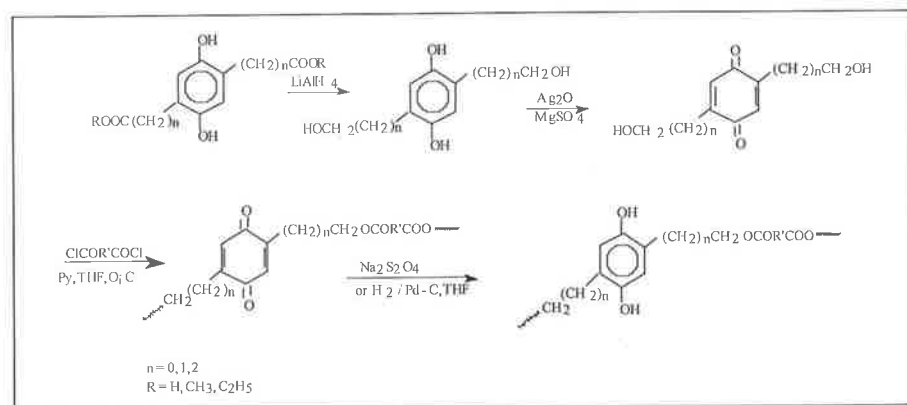


mical and physical properties. For example, the redox capacity increases as the formaldehyde concentration increases. Formaldehyde can be substituted by other aldehydes such as acetaldehyde, benzaldehyde, furfural, glyoxal, and paraformaldehyde. This latter which is a polymeric form of formaldehyde, in conjunction with hexamethylenetriamine, releases formaldehyde upon hydrolysis as reported by Kopra and Welcher [8].

Poly(2,5-dimethoxy-*p*-xylene) was made by reaction of 2,5-dimethoxy-4-methylbenzyltrimethyl ammonium chloride with alkali as illustrated in (3). The quaternary ammonium salt was obtained by treating 2,5-dimethoxy-4-methylbenzyltrimethyl chloride with trimethylamine. Demethylation of the

polymer with hydrobromic acid gave poly(2,5-dihydroxy-*p*-xylene) [9].

The hydroquinone diesters in *scheme 2*, are readily reduced in good yields to the hydroquinone diols with lithium aluminum hydride. The hydroquinone moiety is easily oxidized



Scheme 2 - Synthesis of poly(hydroquinone-esters).

almost quantitatively by stirring a tetrahydrofuran solution with a silver oxide and anhydrous magnesium sulfate to give the corresponding quinone [10]. The reaction of these quinoid dialcohols with a diacyl chloride in THF in the presence of pyridine yields polymer with a quinone unit as redox group. These polymers are easily reduced to hydroquinone polyesters with sodium dithionite or hydrogen and palladium-charcoal at ordinary temperature.

Cassidy [11], an authority in this field, prepared hydroquinone polycarbonate in quantitative yield by polymerizing 2,5-bis(3'-hydroxypropyl)-1,4-benzoquinone upon reacting with phosgene in THF medium containing pyridine (4). This polymer is soluble in organic media, such as acetone, chloroform, THF, and DMF, and can be readily reduced to the hydroquinone form by one of the reducing agents mentioned above.

Cassidy [12] also synthesized the hydroquinone polyurethane analogue. 2,5-Bis(3'-hydroxyalkyl)-1,4-benzoquinone can react with a diisocyanate at room temperature in the presence of triethylamine or dibutyltin diacetate as catalyst to lead to the corresponding quinoid polyurethane that precipitates from THF in *n*-hexane as yellow flakes (5). The reduction of quinoid polymer to the corresponding hydroquinoid form is achieved with no detection of a cleavage of the urethane-containing backbone.

Nikels and coworkers [13] recently condensed 2,5-bis(N-2-hydroxyethyl-N-methylamino)-1,4-benzoquinone which can be prepared as shown in (6), with a number of diisocyanate monomers such as MDI (diphenylmethane-4,4'-diisocyanate), TDI (tolylene-2,4-diiso-

cyanate), to produce amine-quinone polymers.

Quinone polyamines may be made by condensation of a diamine with a quinone as shown in (7). Among the diamines employed in the condensation with benzoquinone are *p*-phenylenediamine, benzidine, and hexamethylenediamine. A 1:3 ratio of diamine-benzoquinone is required to produce poly(aminoquinone). One feature of these reactions is that they occur spontaneously under oxidizing agent (calcium hypochlorite), lower temperature (sometimes at 0 °C), and 3-4 hour-time period. Erhan and coworkers [14-18] have vastly worked on the synthesis of this type of polymers employing substituted quinone arguing that the electron-donating substituent on quinone moiety will enhance the redox property of the polymer by lowering its redox potential,  $E_m$  or  $E_{1/2}$ ; thus, these polymers could be conceived as efficient oxidizing agents.

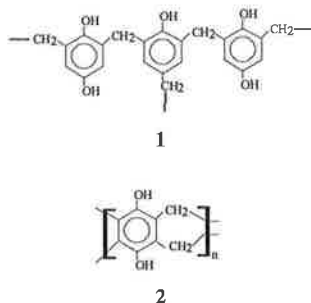
Colletti and coworkers [19] used instead a dialkoxyated quinone, (8), to come up with more tractable and reproducible poly(aminoquinones) than Erhan's. Yet, a degree of polymerization of these polymers is not high, ranging from 5 to 30.

Suzuki and Tazuke [20] explored the Mannich conditions to prepare 2,5-bis(dimethylaminomethyl)hydroquinone (HQMe), and 3,6-bis(dimethylaminomethyl)catechol (CAME) by reacting hydroquinone or catechol with aqueous dimethylamine and formaldehyde as given *scheme 3*. Dimethylaminomethyl hydroquinone and the catechol analogue are used as monomers in the formation of polyionenes as outlined in this scheme. The redox properties of these polyionenes were examined. They can be oxidized with

molecular oxygen in 1.5 % sodium carbonate solution. The precipitated brown powders showed an absorption band at  $1\ 630\ \text{cm}^{-1}$  in the infrared, indicating that hydroquinones (or catechol) of the polymers were oxidized to benzoquinone units.

Redox polyamides were developed by Iwakura [21] by condensing dilactones with diamine compounds. For example, in (9) the dilactone obtained by heating the corresponding diacid at 280 °C condensed with the diamine in dimethylacetamide (DMAc) upon warming the mixture for several hours. The hydroquinone polymer was obtained in 75 % yield and could be oxidized to quinoid polymer with ceric ammonium nitrate in DMAc.

In general, hydroquinone-formaldehyde based polymers are slow to react. To enhance their chemical reactivity, Manecke [22] designed a synthesis of redox polymers with appreciable redox capacity (6.4 meq/g) and high reactivity by combining hydroquinone, phenol, and formaldehyde. A polymer of type 1 was obtained.



In the previously discussed hydroquinone-bearing resins, the hydroquinone or quinone units are linked by single methylene bridges. In 1985, Dallah and co-workers [23] reported the synthesis of poly(bismethylenehydroquinone), **2**, where hydroquinone moie-

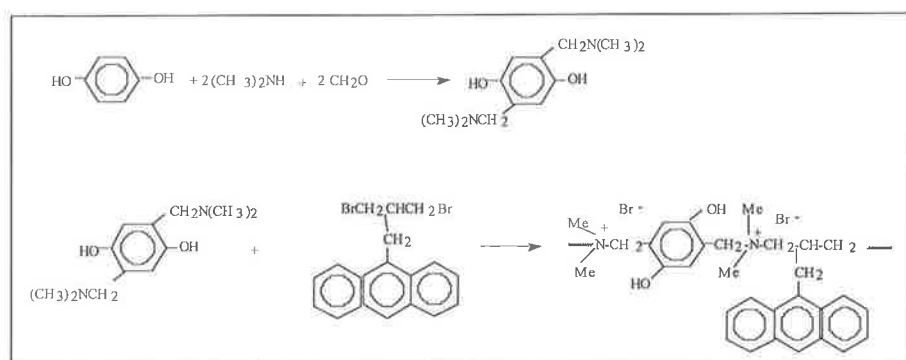
ties are held together by two methylene adjacent bridges in a ladder structure. This material was prepared by mixing trioxane and excess of hydroquinone in sulfolane and water in the presence of a catalytic amount of toluenesulfonic acid (TsOH). This air-oxidized redox polymer can be chemically oxidized with bromine-potassium hydroxide reagent. Both reduced and oxidized forms were fully characterized by a combination of FT-IR, elemental analysis, and  $^{13}\text{C}$  solid-state CP/MAS NMR. To recall, ladder polymers termed also « *double strand polymers* » are polymers with repeating units linked to each other at two connecting points.

Earlier in 1965, Naarman [24-25] patented for the BASF company his findings on the preparation of ladder-architected polymers containing quinone units, equations (10) and (11). Chloranil was the starting monomer in most cases. The oligomers produced in (11) are featured with its dithiane functionality in a ladder skeleton.

A highly oxygenated aromatic ladder polymer is the one reported by Kim in 1982 [26] as outlined in (12). A self-condensation of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone gave straightforwardly the intermediate hydroquinone-containing resin which is prone to oxidation.

Also, the ladder-structured polymer having a quinone unit can be formed by the condensation of tetramethylolated hydroquinone with unsubstituted hydroquinone (13) [27]. The polymer thus obtained was water soluble.

Exploring the dienophilic character of the quinone molecule, Bailey and Economy [28-29] were able to perform a polymerization via a Diels-Alder reaction between quinone and 2-vinylbutadiene as a diene. In (14) the Diels-Alder adduct acquires the two characters, dienophile and diene, and thus can react in both sides to propagate affording a polymer. The crystalline polymer obtained had a molecular weight of about 700 and showed solubility only in hexafluoropropanol. This peculiar solubilization of such polymers only in fluorinated solvents may make them promising materials, usable in some future industry.



*Scheme 3* - Polyionenes containing hydroquinone.

### Pendent redox groups from backbone

(The different reactions of this part can be found in *table II*).

The redox units such as hydroquinone and catechol may be pendent from the polymer matrix which could not be affected by the oxidation-reduction phenomenon. Indeed, poly(2,5-dihydroxyphenylalanine) and poly(3,4-dihydroxyphenylalanine), a poly(DOPA), were synthesized by attaching hydroquinone and catechol units, respectively, on polypeptide matrices [30]. For instance, 3,4-diacetoxyphenylalanine hydrochloride was prepared by treatment of 3,4-dihydroxyphenylalanine with acetyl chloride. Reaction of 3,4-diacetoxyphenylalanine with phosgene afforded N-carboxyanhydride which polymerized via a ring opening polymerization with a trace of sodium hydroxide in dioxane. Acidification followed by cleavage of the acetyl groups yielded poly(3,4-dihydroxyphenylalanine) (15).

A pendent redox unit from a polyurethane matrix was also made [31]. As shown in (16), the quinoid diol derivative reacted with a diisocyanate to give the monomer **3** which upon condensation with glycol led to the corresponding polyurethane in which quinone diol alternates with quinone glycol.

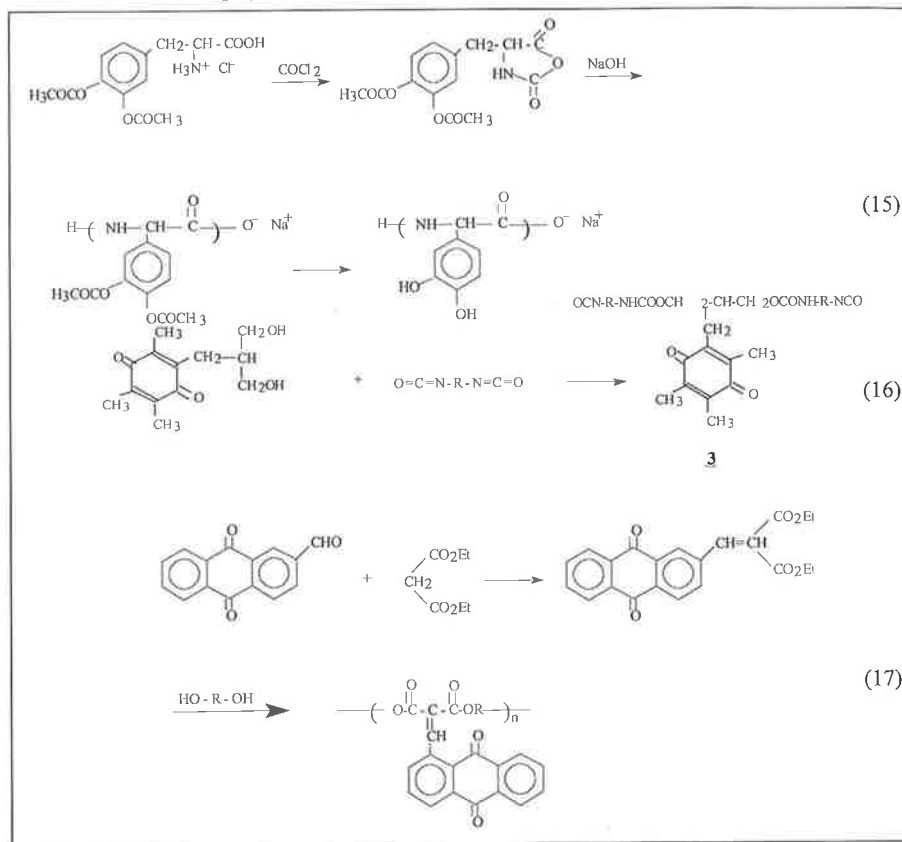
Izoret [32] successfully synthesized a redox polymer with an anthraquinone as redox unit pendent from polyester chain. Reaction of diethyl malonate with 2-formylanthraquinone under « malonic ester » synthetic conditions provided the vinylanthraquinone derivative (17). This latter compound could be condensed with a derivative using sulfuric acid as catalyst to give the poly(anthraquinone) derivatives. 1,4-Dihydroxybutane, diethyleneglycol, and glycerol were among the polyalcohols used in this type of condensation.

### Attachment of redox units onto premade polymers

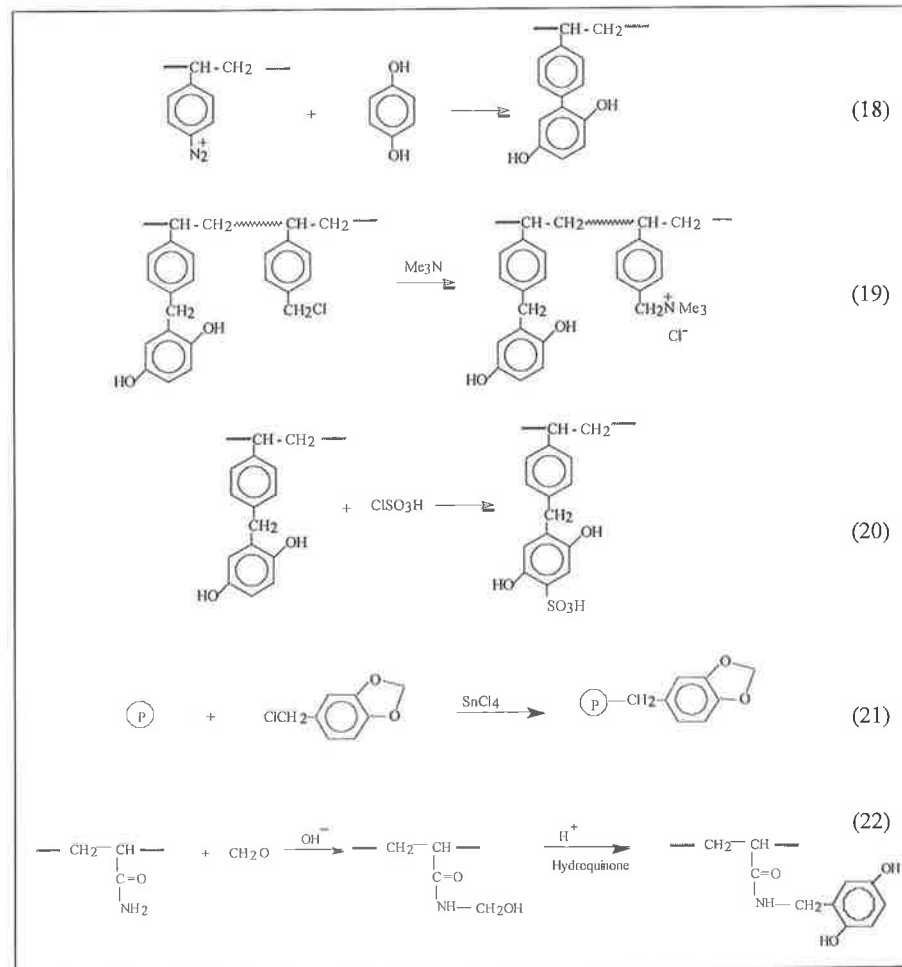
(The different reactions of this part are compiled in *table III* and *schemes 4* and *5*).

Electron-transfer polymer may be prepared by attachment of a redox unit onto a preformed polymer. This attachment can be realized by chemical sub-

**Table II** - Condensation polymers with pendent redox units from backbone.



**Table III** - Attachment of redox units onto premade polymers.



stitution, displacement, or other kinds of reactions on functional groups already existing on the polymer matrix. For example, as early as 1957, Sansoni [3] prepared redox polymer by reacting hydroquinone with poly(styrene-diazonium salts) (18) (table III). This functionalized polymer was made by nitration of polystyrene followed by reduction of the nitro group to an amino group and subsequent treatment with nitrous acid. As expected, the diazonium salts generated crosslinking between the polymeric chains. The same author placed a ferrocene moiety on a polystyrene backbone employing a similar procedure.

As described by Kun [33], hydroquinone-quinone redox polymers may be readily made using either quinone or hydroquinone in protected or unprotected form in a Friedel-Crafts reaction with halomethylated styrene-divinylbenzene copolymer. As outlined in

scheme 4, Friedel-Crafts reaction of the chloromethylated poly(styrene-divinylbenzene) with hydroquinone, benzoquinone, 1,4-dimethoxybenzene, and 1,4-diacetoxybenzene in the presence of a Lewis acid such as  $\text{SnCl}_4$  gave the polymeric vinylbenzylhydroquinone after removal of the protecting groups. The poly(vinylbenzylhydroquinone) may be oxidized to poly(vinylbenzylbenzoquinone) which, in turn, may be reduced to the hydroquinone again.

Because of the low reactivity of the chloromethyl group, Russian investigators [34] developed a synthesis of bromomethylated copolymer by reacting the chloromethylated resin with lithium bromide in a mixture of boiling dioxane and acetone for 20 hours. They carried out the Friedel-Crafts reaction on bromomethylated copolymer with quinone, anthraquinone, and dialkylether of hydroquinone. Dioxane and dichloro-

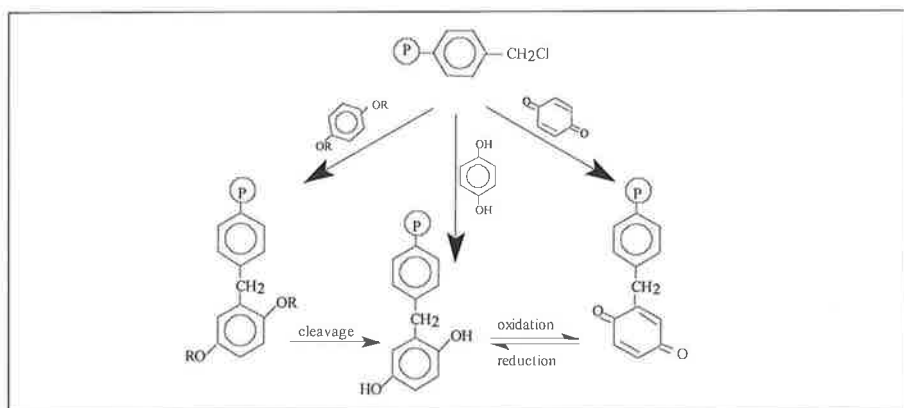
ethane proved to be the best swelling media for this special case.

The hydrophilicity of these redox polymers can be improved by the incorporation of an ion-exchange group. By limiting the concentration of redox units added to the polymer matrix, a significant number of halomethyl groups is available for subsequent chemical modification. For example, reaction of the remaining chloromethyl groups with triethylamine (19), yielded hydrophilic redox polymers containing anion exchange groups. While maintaining a maximum number of redox units available, enhanced hydrophilicity of the resins may be achieved by reacting the hydroquinone units of the resin with chlorosulfonic acid as illustrated in (20). The sulfonated redox polymers could be employed as cation exchange resins [35].

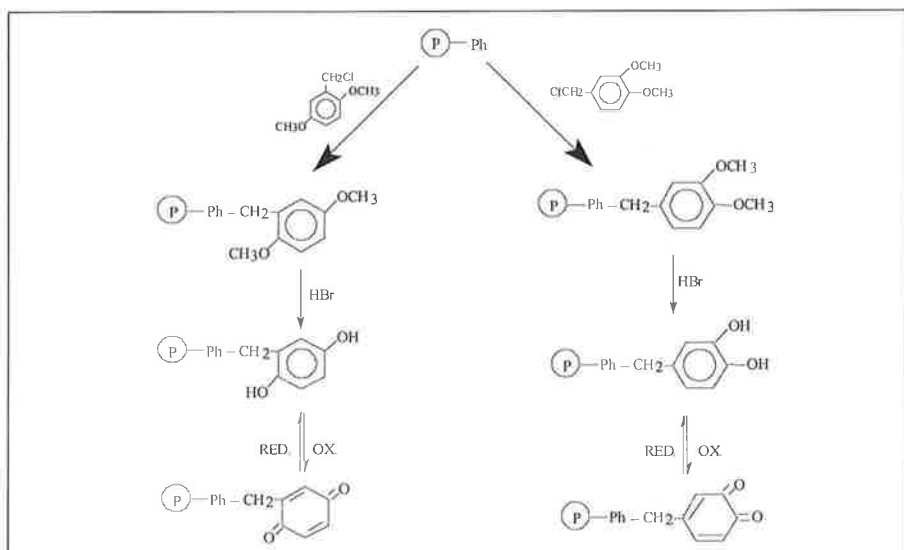
Kun [36] also worked on the attachment of anthraquinone and its derivatives such as 2-methylantraquinone and 2-ethylantraquinone onto styrene-divinylbenzene copolymer via Friedel-Crafts reaction described above. By the same procedure, Warshawsky [37] treated the above-cited chloromethylated copolymer with catechol to produce polymeric catechol. This latter resin, however, was destined to make polymer crown ethers.

Generally, in such alkylation reactions, the remaining unreacted chloromethyl groups of the supporting resin can induce side reactions and other some effects. To avoid such unwanted reactions, Iwabuchi [38] introduced hydroquinone or catechol units on the same support by Friedel-Crafts alkylation of styrene-divinylbenzene resin with 2,5- and 3,4-dimethoxybenzyl chloride, followed by demethylation with hydrobromic acid as given in scheme 5. In this fashion, a high content of redox units on the resin could be accomplished.

In Daly's laboratory [39], 1,3-benzodioxole, a valuable redox group precursor, was introduced into a variety of polymer matrices. The polymeric supports were several condensation polymers, such as poly(2,6-dimethyl-1,4-phenylene oxide), poly(phenylene ether sulfone), and phenoxy resins. To achieve a high degree of incorporation of catechol synthons, piperonyl chlo-



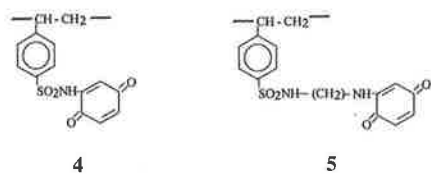
Scheme 4 - Friedel-Crafts reaction of chloromethylated poly(styrene-co-divinylbenzene) with redox units.



Scheme 5 - Friedel-Crafts alkylation of styrene-divinylbenzene copolymer, P-Ph, with 2,5- and 3,4-dimethoxybenzyl chloride.

ride was reacted with the above-chosen carriers under the standard Friedel-Crafts alkylation conditions (21), then the methylenedioxy group was subjected to cleavage to end up with polymeric catechols.

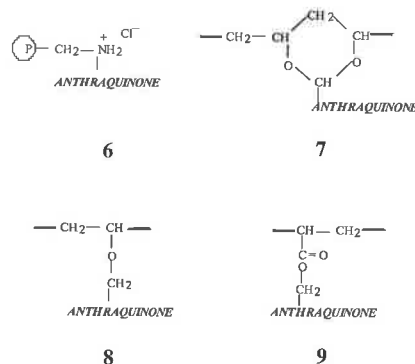
Manecke [40], a well-versed worker in this area, converted poly(styrene sulfonic acid) crosslinked with 10 % divinylbenzene to poly(styrene-4-sulfonyl chloride) which is designed as starting material for different polymers containing *p*-benzoquinone. For example, reaction of poly(styrene-4-sulfonyl chloride) with 2-aminohydroquinone-4-benzoate and subsequent debenzooylation followed by oxidation of the hydroquinone group yielded the redox polymer 4. Another polymer carrier can be obtained by reacting one amino group of a diamine compound, such as ethylenediamine and hexamethylenediamine, with sulfonyl chloride functionality of the polymer and the other with benzoquinone to give a polymer of type 5. Poly(vinyl alcohol) crosslinked with 1 % terephthalaldehyde was also employed as benzoquinone carrier. These benzoquinone-carriers, reported by Manecke, exhibited a great efficiency in immobilizing enzymes, *e.g.*, chymotrypsin.



Kamogawa [41] attached hydroquinone moiety onto a polyacrylamide matrix with no major difficulty. The homopolymer or copolymer of acrylamide can be methylolated with an equivalent of formalin or paraformaldehyde under basic conditions (22). Treatment of methylolated polyacrylamide with hydroquinone under acidic conditions affords the redox polyacrylamide.

As stated earlier, the anthraquinone group can be introduced into a variety of polymer matrices. For example, the reaction of 2-aminoanthraquinone with chloromethylated polystyrene crosslinked with divinylbenzene gave the hydrophilic redox polymer 6. Izoret [42] reported the incorporation of anthraquinone on the polymer backbone via an acetal linkage. He treated

2-formylanthraquinone with poly(vinyl alcohol) to produce the polymer 7 which is highly stable under alkali conditions. He also described a synthesis of anthraquinone polymer by reacting poly(vinyl alcohol) with 2-chloromethylanthraquinone to give 8 where the redox unit is linked across an ether bridge. The same author prepared polymer 9 by treating poly(acrylic acid) with 2-hydroxymethylanthraquinone.



## Vinyl polymers

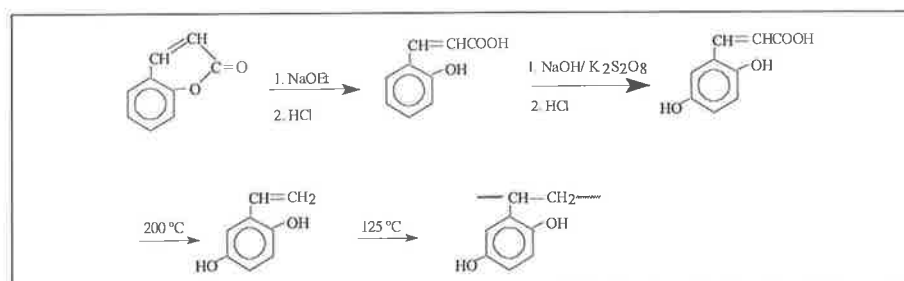
(The different reactions of this part can be found in *table IV* and *schemes 6, 7, 8, 9, 10, 11* and *12*).

Despite the sparse difficulties in the preparation, coupled with the overall low yields, synthesis of specific monomers for specific redox polymers has the advantages that the composition and the structure of the resulting polymers are known with increased certainty and well characterized by analytical techniques. These synthetic difficulties are encountered when one has to apply acid-base or redox reactions to the preparation of materials, themselves highly sensitive to acids, bases, or radicals.

Addition polymerization of a vinyl monomer bearing a redox unit remains the privileged pathway inasmuch as high redox units content can be fulfilled with a better solubility than the condensation polymers.

Poly(vinyldihydroxybenzene), namely poly(vinylhydroquinone) and poly(vinylcatechol), are not straightforwardly prepared owing to the intrinsic properties of the phenolic functionality present in the monomer, that is : 1) it inhibits powerfully radical polymerization, 2) a concomitant reaction would result with an organometallic reagent in anionic polymerization and, 3) lastly, the bidentate complexation with a Lewis acid in cationic polymerization would unavoidably ensue. Therefore, it is imperative to mask the phenolic functionality by means of a protecting group which can be easily removed under mild conditions. Yet, few attempts to conduct the polymerization of naked monomers can be found in the literature. A half century ago, Cassidy [43] succeeded in preparing vinylhydroquinone but in a multi-step synthesis ; as outlined in *scheme 6*, coumarin can be converted to *o*-coumaric acid with potassium persulfate to give 2,5-dihydroxycinnamic acid which can be decarboxylated at 200 °C to afford vinylhydroquinone. The polymerization of this monomer in the absence of a catalyst proceeded at 125 °C to produce only oligomers, indicating the inhibiting ability of the free hydroxy group of the ring.

Later, Iwabuchi [44-47] found that tributylborane (TBB) was capable of initiating the copolymerization of some unprotected vinylhydroquinone derivatives with some common comonomers ; copolymerization in the presence of TBB of 2-vinyl-1,4-hydroquinone and 2-methyl-5-vinyl-1,4-hydroquinone, with methyl methacrylate, styrene, acrylonitrile, acrylamide, and 4-vinylpyridine was successful in each case. It was therefore concluded that vinylhydroquinone behaves like styrene in the copolymerization reaction initiated by TBB. However, the homopolymerization of unprotected vinylhydroquinone



*Scheme 6 - Synthesis and polymerization of vinylhydroquinone.*

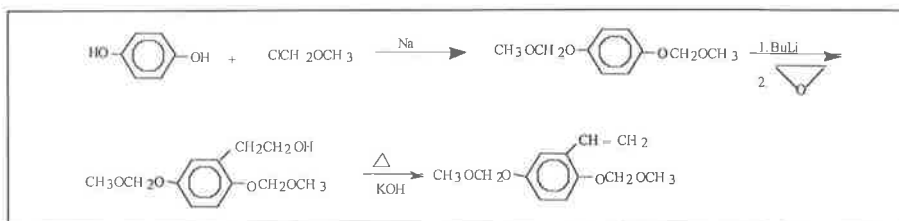
with the same catalyst failed to produce polymer under identical conditions.

An interesting exception was the polymerization of 4-vinyl-2-methoxyphenol (4-vinylguaiacol); this monomer yielded a low conversion (12.5 %) of moderately high molecular weight product but after a polymerization time of 200 hours [47].

Esters, ethers, and acetals have been elected as blocking groups by many investigators in this field. Cassidy [48] selected bis(methoxymethyl) ether as protecting group in the synthesis of poly(vinylhydroquinone) and poly(3-vinylcatechol). Both catechol and hydroquinone were treated with sodium metal in methyl alcohol to produce the monosodium salt of hydroquinone or catechol, the chloromethyl methyl ether was added to react with the mixture to give the hydroquinone or catechol bis(methoxymethyl) ether as depicted in *scheme 7*. When this latter compound was metalated by reaction with butyllithium and subsequently treated with ethylene oxide,  $\beta$ -hydroxyethyl-hydroquinone bis(methoxymethyl) ether or catechol analogue was obtained in quantitative yield. Dehydration of this alcohol over potassium hydroxide afforded vinylhydroquinone bis(methoxymethyl) ether (or catechol analogue) in high yield. Polymerization of these monomers followed by hydrolysis in methanolic hydrochloric acid produced the desirable polymers.

The chief drawback of the use of bis(methoxymethyl) ether is that it releases free formaldehyde upon hydrolysis of the polymer. The formaldehyde can produce the crosslinking in the presence of acid and hydroquinone. The use of its analogue, bis(ethoxyethyl) ether, however, generates acetaldehyde which is less reactive than formaldehyde [49]. But with either blocking group, crosslinking may be ensued during the deblocking process; the extent differs only with the carbonyl condensation.

Iwabuchi [50] prepared 2-methyl-5-vinyl-*o*-*o*'-bis(1'-ethoxyethyl) hydroquinone in 14 % yield from 2-methylhydroquinone using the method of Cassidy. He observed that when the corresponding alcohol was heated at elevated temperature, e.g., 240 °C, the protecting groups were displaced



*Scheme 7 - Synthesis of protected vinylhydroquinone and vinylcatechol.*

without the dehydration of the alcohol. Further, when the blocked alcohol was heated over acidic alumina at 200-220 °C, the major product was a cyclic ether, a coumarin derivative.

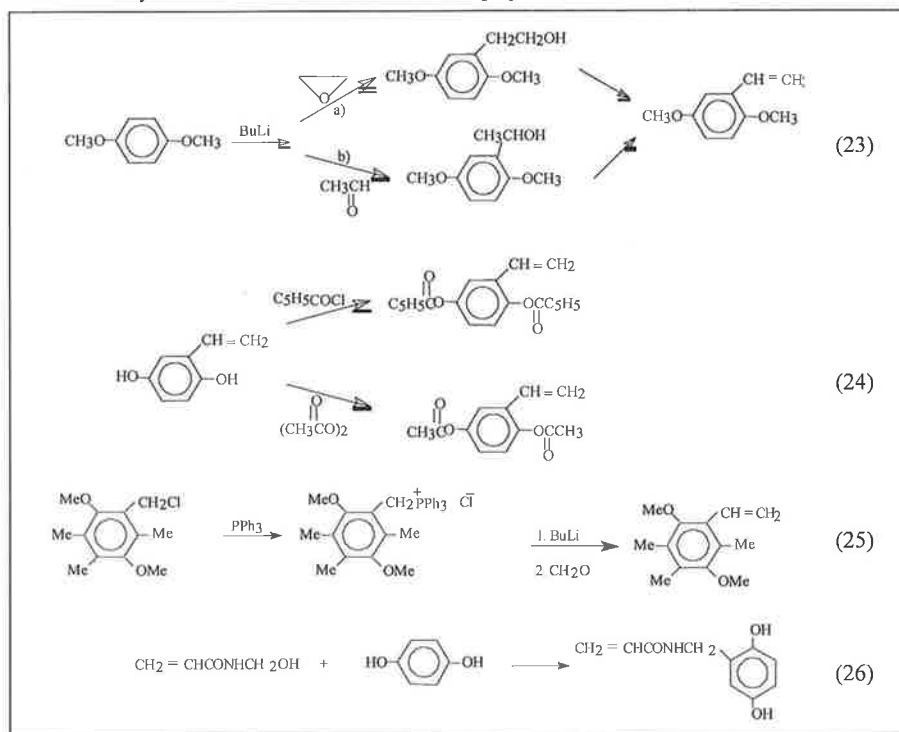
A very clean method to produce a protected hydroquinone monomer is the reaction of 1,4-dimethoxybenzene with butyllithium followed by reaction with ethylene dioxide to give the  $\beta$ -hydroxyethyl-1,4-dimethoxybenzene (23a) (*table IV*). Dehydration of the alcohol by heating it over fused potassium hydroxide provided 2,5-dimethoxystyrene [51]. Acetaldehyde can be substituted for ethylene oxide leading to  $\alpha$ -hydroxyethyl analogue, (23b), which, upon acid-catalyzed dehydration, yields the vinyl monomer. The polymerization of this monomer in the presence of benzoyl peroxide (BPO) proceeded without complication [52].

Although the application of esters as blocking groups proved to be limited because they react with organometallic

reagents, 2-vinyl-1,4-hydroquinone diacetate monomers were prepared [53]. The synthesis involved the reaction of vinylhydroquinone with acetic acid or benzoyl chloride as traced in (24). The high polymers obtained were deprotected via saponification to yield poly(vinylhydroquinone).

It was noted that some hydroquinone-containing polymers oxidize irreversibly. The intermediate semiquinone radical appears to add 1,4 to an unsubstituted ring of a quinone system. Hence, polysubstitution of the aromatic ring with appropriate groups, *i.e.*, methyl, would stabilize the hydroquinone-quinone system. Cassidy and Kun [54] reported the synthesis of poly(1-vinyl-3,6-dimethyl-2,5-hydroquinone) and poly((1-vinyl-3,4,6-trimethyl-2,5-hydroquinone) employing the decarboxylation of the corresponding cinnamic acid. The diacetates of these polymers were made by Manecke [55]. 2,5-Dimethoxy-3,4,6-trimethylstyrene

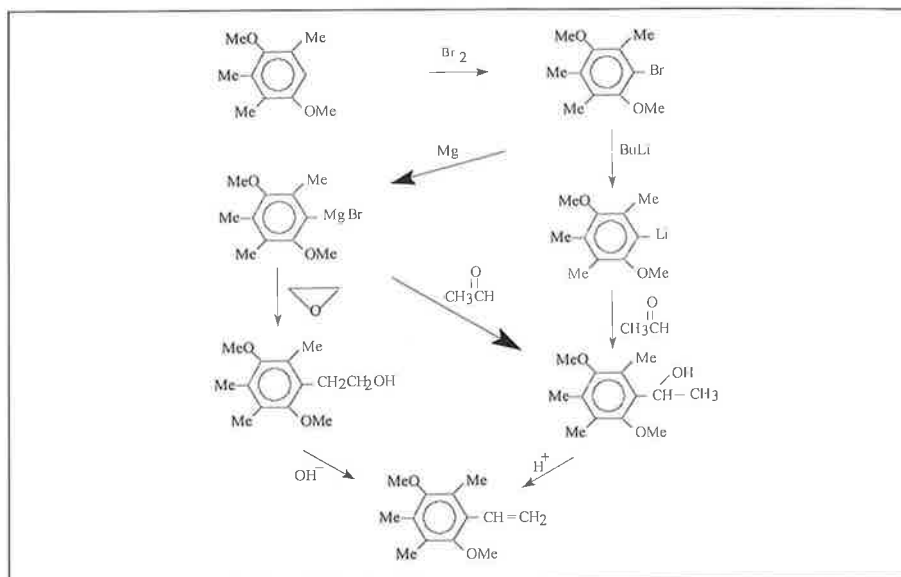
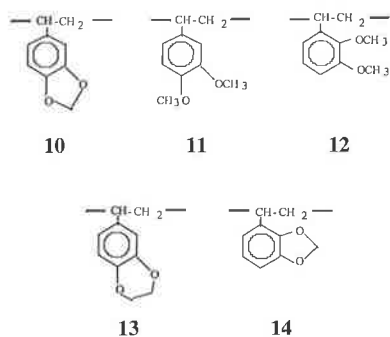
**Table IV - Vinyl monomers with redox units and their polymers.**





was prepared by three routes [53, 56] as shown in *scheme 8*. The first path involves bromination of 1,4-dimethoxy-2,3,5-trimethylbenzene followed by formation of a Grignard intermediate which gave  $\beta$ -hydroxyethylbenzene derivative upon treatment with ethylene oxide; dehydration of this alcohol over potassium hydroxide afforded the tri-substituted vinyl monomer. The second route consisted of acetaldehyde reaction with either the Grignard intermediate or the lithiated dimethoxybenzene to produce the corresponding  $\alpha$ -hydroxyethylbenzene derivative. The lithiation step took place with butyllithium via a bromine-lithium exchange; vinyl monomer was obtained by dehydration of the resulting alcohol in the presence of an acid.

Grignard and Wittig reactions were also applied by Daly and Moulay [57] to evaluate formal linkage, dimethoxyl, and dioxanyl as blocking groups. In fact, they reported five fully characterized poly(vinylcatechol) precursors: poly(5-vinyl-1,3-benzodioxole) (**10**), poly(3,4-dimethoxystyrene) (**11**), poly(2,3-dimethoxystyrene) (**12**), poly(6-vinyl-1,4-benzodioxane) (**13**), and poly(3-vinyl-1,3-benzodioxole) (**14**). The deblocking process with hydrobromic acid or boron trichloride has been sometimes accompanied with instability of the generated polydihydroxybenzene resins to air and became insoluble with the exception of poly(3-vinylcatechol), the deprotected form of **12**.



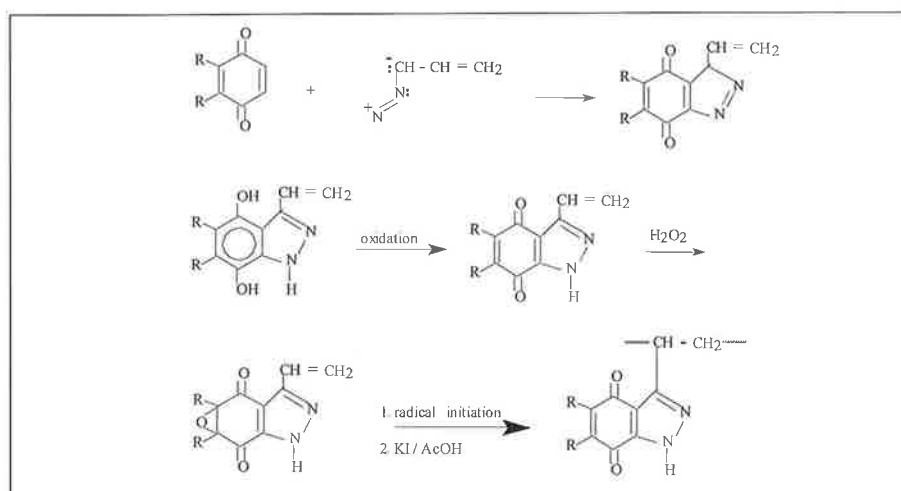
*Scheme 8* - Preparation of 2,5-dimethoxy-3,4,6-trimethylstyrene.

It is worthy to recall that catechol functionality and the alkoxyated derivatives such as those in **10**, **11** are abundantly spread in naturally occurring alkaloids; yet, their specific contribution to the global activity of the alkaloid molecule is still not elucidated.

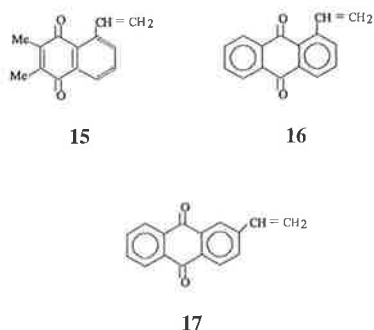
Manecke and coworkers [58] reported the preparation of 3-vinylpyrazoloquinone and its derivatives. Their polymers showed high stability and resistance to degradation reactions. For example, 3-vinyl-pyrazoloquinone can be prepared by 1,3-dipolar cycloaddition of diazopropen-2 to the substituted quinone as illustrated in *scheme 9*. It is interesting to notice that N-pyrazoloquinones cannot undergo polymerization by radical initiators unless an epoxy group is introduced into the quinone side. The epoxy group may be

removed at the end of the reaction with potassium iodide in acetic acid.

The hydroquinone-quinone redox systems can be stabilized also by annellation of the quinone with aromatic rings. Thus, poly(vinylnaphthaquinone) and poly(vinylanthraquinone) derivatives were prepared [59]. 2,3-Dimethyl-5-vinylnaphthaquinone, **15**, and both vinylanthraquinone isomers, **16** and **17**, were made by dehydration of the hydroxyethylnaphthaquinone and anthraquinone analogue. Amazingly, the monomer **16** polymerized only when an epoxy group was introduced into the quinone unit as required for the polymerization of 3-vinylpyrazoloquinone. However, the 2-vinylanthraquinone could be cleanly homopolymerized and copolymerized with styrene and divinylbenzene, while the 1-vinyl isomer did not polymerize readily.



*Scheme 9* - Synthesis of poly(3-vinylpyrazoloquinone).



Pyraniloxy groups also proved to be effective as blocking groups. Spinner and coworkers [60] designed a synthesis of poly(2,5-dihydroxy-4'-vinyl-diphenyl sulfone) from the corresponding monomer when the hydroxyl functionalities of the hydroquinone units were protected by pyraniloxy groups. Reaction of *p*-( $\beta$ -bromoethyl)benzene sulfonic acid, prepared from  $\beta$ -bromoethylbenzene, with quinone led to the corresponding hydroquinone sulfone as shown in *scheme 10*. Treatment of this sulfone with 2,3-dihydroxy-pyran gave the protected hydroquinone sulfone. Dehydrobromination with alcoholic potassium

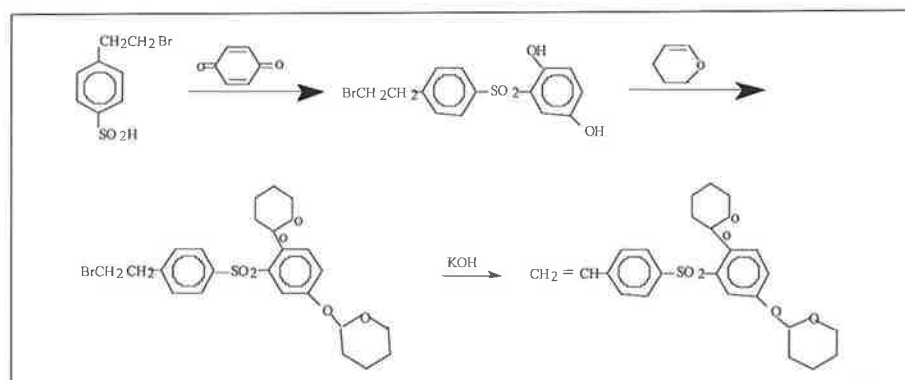
hydroxide yielded the corresponding vinyl monomer. The same investigators [61] reported the preparation of poly(2,5-dihydroxy-4-methyl-4'-vinyl-phenyl sulfone) employing a similar procedure.

Komogawa [62] succeeded in attaching hydroquinone to *N*-hydroxyethyl methyl acrylamide prepared by alkaline methylation of acrylamide with formaldehyde at room temperature as given in (26). The hydroquinone-containing monomer was readily polymerized to afford redox acrylamide resin.

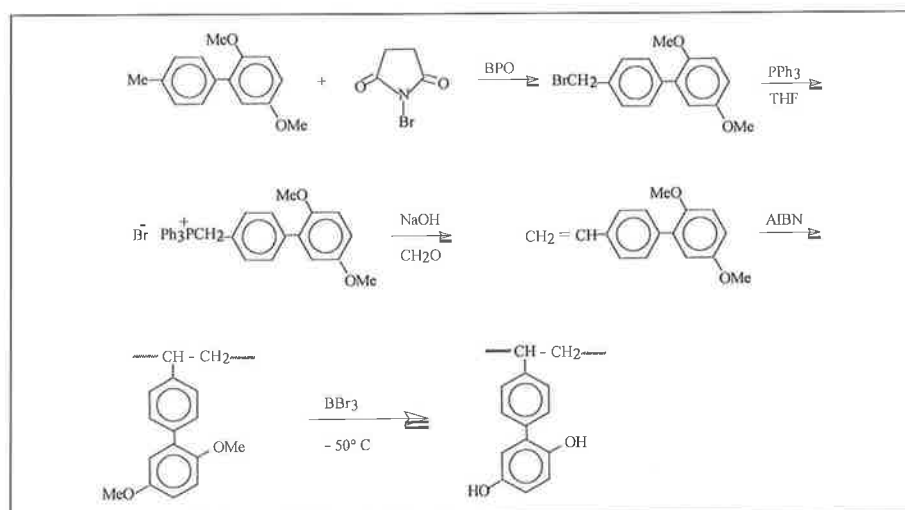
Mehta [63] prepared poly(4'-vinyl-2,5-dihydroxy-1,1'-biphenyl), poly(4'-vinyl-2,3-dihydroxy-1,1'-biphenyl), poly(4'-vinyl-3,4-dihydroxy-1,1'-biphenyl) by polymerizing the corresponding monomers obtained via Wittig reaction. For example, bromination of 4'-methyl-2,5-dimethoxy-1,1'-biphenyl with *N*-bromosuccinimide in the presence of benzoyl peroxide gave 4'-bromomethyl-2,5-dimethoxy-1,1'-biphenyl as illustrated in *scheme 11*. The treatment of this bromomethyl compound

with triphenylphosphine yielded 4'-(triphenylphosphonium) methyl-2,5-dimethoxy-1,1'-biphenyl bromide. The mixture of this phosphonium bromide salt and 50 % aqueous sodium hydroxide and 37 % formalin provided 4'-vinyl-2,5-dimethoxy-1,1'-biphenyl which polymerized cleanly in the presence of AIBN. Demethylation was induced by boron tribromide.

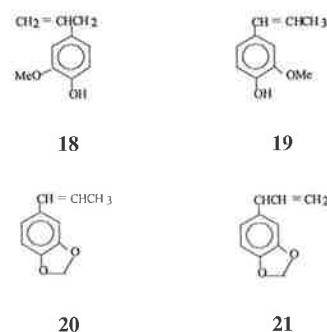
Iwabuchi and coworkers [64-65] tackled the copolymerization of some naturally occurring vinylcatechol precursors with some common comonomers. The copolymerization reaction of 4-propenylpyrocatechol derivatives, such as eugenol, **18**, isoeugenol, **19**, isosafrole, **20**, and safrole, **21**, with acrylonitrile, maleic anhydride, and methyl methacrylate, were investigated employing TBB as initiator. It was found that only homopolymerization occurred when they were reacted with methyl methacrylate under the same conditions. Later, the same investigators [66] developed a synthesis of a vinyl monomer containing 1,3-benzodioxole and methyl methacrylate units. As described in *scheme 12*, 3,4-methylenedioxybenzyl methacrylate was prepared from 3,4-methylenedioxybenzyl alcohol and methacryloyl chloride. The monomer was radically polymerized in the presence of TBB. Treatment of the resulting polymer with phosphorus pentachloride gave the corresponding carbonate which upon hydrolysis yielded the poly(3,4-dihydroxybenzylmethacrylate).



*Scheme 10* - Pyraniloxy as protecting group.



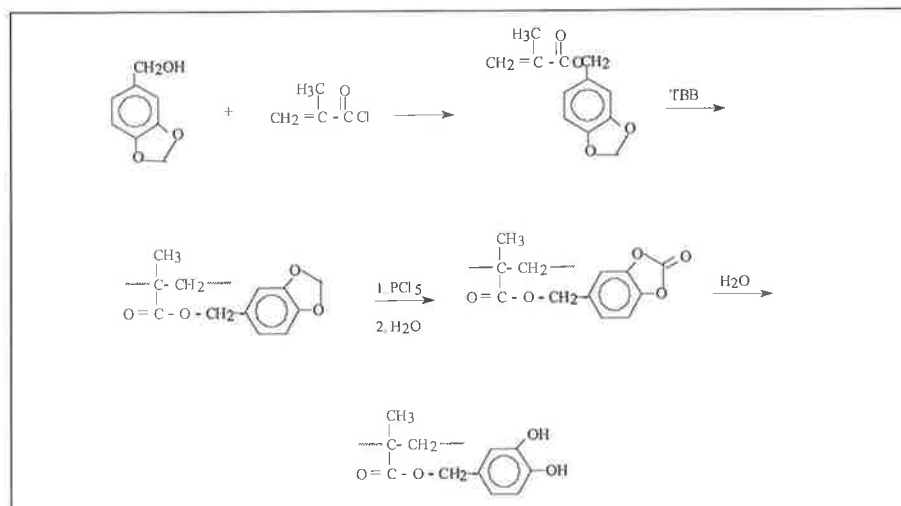
*Scheme 11* - Synthesis of poly(4'-vinyl-2,5-dihydroxy-1,1'-biphenyl).



## Properties of redox polymers

### Condensation polymers

Among the condensation polymers studied, those derived from formaldehyde-phenol were given the most attention. These crosslinked resins with phe-



Scheme 12 - Synthesis of poly(3,4-dihydroxybenzylmethacrylate).

Table V - Redox properties of some polycondensates of phenol-formaldehyde with redox units [67, 68, 69].

Redox Unit	Formula	Redox Cap. (meq/g)	$E_m^m$ (V) (pH = 7)
Alizarin		0.5	-
Anthrarufin		1.1-2.1	-
Chrysazin		1.5-2.5	-
Hydroquinone		7	0.22
2-Hydroxy-anthraquinone		1.1	0.19
Juglone		4.5	0.12
Quinalizarin		1.4-2/5	-
Purpurin		0.7	-

nol or resorcinol moieties condensed with a variety of redox units including hydroquinone or quinone exhibit a wide range of properties. Table V compiles the redox properties of some polycondensates of phenol-formaldehyde with various redox units. Some of these resins are quite stable, others degraded and decomposed in contact with strong oxidants.

As noted earlier, the change in concentration of one component of the reaction mixture results in change in physical and chemical properties of the resin. In fact, the redox capacity (the amount of redox equivalent per gram of redox resin) of the resin increases with an increase in ratio of formaldehyde. The phenol-formaldehyde-hydroquinone polymers generally show decreased

chemical stability as the phenol content is lowered ; however, the content of formaldehyde seems to have slight effect on its chemical stability. Kruglikova and Pashkov [70-71] prepared the sulfonic acid derivatives of pyrocatechol and hydroquinone by polycondensation with formaldehyde and phenol. They found that the chemical stability and the swelling properties of such polymers increased with the ratio of phenol, but their redox capacities decreased.

Anthraquinone-containing resins are found to react more slowly with redox agents than those having hydroquinone units. Rendering the resin hydrophilic by replacement of phenol with phenol-sulfonic acid failed to increase the redox reactivity.

Redox polyamides [21], equation (9), in reduced form are white to light brown powder flakes, soluble in DMAc, DMF, and formic acid. The oxidized forms of these polymers are yellow solids, soluble in the same solvents. Unfortunately, the redox properties of these polyamides were not studied.

Hydroquinone polycarbonates [11], (4), have molecular weights ranging between 380 and 20,000. While the reduced forms exist as colorless waxes or oils, the oxidized forms are yellow or brownish-yellow solids. The viscosities of the reduced resins are found to be higher than those of the oxidized materials. The midpoint potentials,  $E_m^m$ 's, were generally around 0.64 V.

Hydroquinone polyurethanes [12], (5), were generally soluble in THF and DMF. The reduced polymers were white powders but their oxidized polymers were bright yellow solids. The viscosities of the reduced forms were larger than those of oxidized forms. The redox potentials were in the range of 0.25 - 0.29 V.

Ladder amino-quinone polyurethanes, owing to their double strand structure, are insoluble in common solvents with the exception of some polymers mentioned earlier. This defied insolubility hampers their full characterization.

Marine organisms such as mussels, barnacles, and the tube worms are known to stick tightly to substrates of different kinds ; this fact will bring

about a detrimental effect to ship hull as well as a slowdown speed of a ship, and for this purpose antifouling paints have been formulated. It has been found the stickiness is due to a polypeptide-nature adhesive, secreted by them. This latter functions in very striking conditions : a wide range of temperature and salinity of the medium, and strong shear stress. This naturally occurring polypeptide is composed of a high content of amino acid 3,4-dihydroxyphenyl-*L*-alanine, commonly called DOPA. Lately and for a better understanding this phenomenon, Yu and Deming [72] were able to bring forth a synthetic polypeptide analogue through a ring-opening polymerization of *N*-carboxyanhydride monomers (NCA), a similar reaction to (15). Upon oxidation of DOPA, they noticed a gel-like product, a cross-linked network with strong and moisture-resistant adhesive bonds to aluminum, steel or glass and to a lower degree to plastics. It is worthwhile to recall that *L*-DOPA is biologically active and used as a drug in treatment of Parkinson's disease.

## Vinyl polymers

In general, polymers in which hydroxyl functionalities are masked by protecting groups such as benzoyl, methyl, bis(methoxymethyl), and bis(ethoxyethyl), are readily soluble in halogenated and aromatic solvents from which they can be precipitated into alcoholic solvents (methanol and ethanol). On the other hand, the free HO-polymers once produced are no longer soluble in the above-mentioned solvents, but are soluble in polar and protic solvents (methanol, dioxane, THF, and DMF). The free hydroquinone polymers are not very soluble in glacial acetic acid, but if little of water is added they dissolve readily, suggesting that intermolecular interactions of the polar groups may crosslink the chain but the weak association is readily replaced by interaction with water molecules.

These polymers are white in color when initially isolated. As opposed to their precursors, they become unstable to air and turn pink especially when moisture is present. The fully oxidized polymers are yellow and exhibit lower solubility than the reduced resins, but

they can be dissolved in THF, DMF, and dioxane. The partially oxidized polymers show also decreased solubility in organic solvents. Astonishingly and as mentioned earlier, poly(3-vinylcatechol) prepared from **12** withstood air-sensitivity for long period of time under aerobic conditions (several months) and the white-colored polymer started to turn pink only after this period, yet its solubility in glacial acetic acid - water system was unchanged [57].

These polymers can be made water-soluble if a sulfonic acid group is introduced. For example, Cassidy [52, 73] reported the sulfonation of poly(vinylhydroquinone dibenzoate) with concentrated sulfuric acid. The resulting sulfonated polymer, with the ester group cleaved *in situ*, is quite soluble in water. Another method of producing water-soluble resins is to copolymerize redox monomer with hydrophilic comonomer such as acrylic acid, ester, and amide.

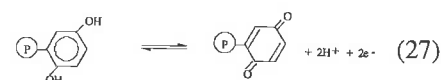
One of the outstanding properties of the poly(vinylcatechol) is that their precursors are quite chemically reactive owing to the electron-donating nature of the blocking groups, that is, the alkoxy functionality. To mention but a few, chloromethylation, lithiation, bromination, sulfonation, and aminomethylation reactions were successfully applied to these polymeric catechol precursors (**10**, **11**, **12**, **13**, **14**) and have shown some interesting chemistry [74-77]. A careful mastering of the experiment conditions must be taken because of the highly reactive dialkoxy-substituted benzene rings leading to some side reactions such as crosslinking.

Crosslinked polymers can be swollen in some media. For example, the copolymer of vinylhydroquinone dibenzoate with divinylbenzene was obtained as hard, white, opaque beads that swelled in toluene and benzene. Upon saponification, these beads swelled in *t*-butyl alcohol and became transparent [53]. A terpolymer of vinylhydroquinone,  $\alpha$ -methylstyrene, and 5 % divinylbenzene behaved in the same way as the copolymer. The sulfonation of this resin yielded a product in the form of beads which were highly swollen in water, and could be readily oxidized and then reduced. Degradation of the

polymer was detected after prolonged contact with strong oxidizing agents such as ceric sulfate or bromine-water. The sulfonated polymer behaved as redox resin and cation exchange resin as well. The redox capacity was evaluated to be 5.7 meq/g, and the cation-exchange capacity was found to be 3.9 meq/g [78].

## Potentiometric titration of redox polymers

For the characterization of the redox polymers, the redox capacities and the redox potentials are the definitive properties. The redox capacities are measured in meq/g of resin. The measurement of their redox potentials estimates their applicability as oxidant-reductant reagents. The equation below (27) describes the redox process hydroquinone ( $H_2Q$ ) - quinone (Q) as an example :



The Nernst equation for this redox system is shown in (28) where  $E_n$  represents the potential of the system against the hydrogen electrode measured in volts ;  $E_m$  stands for the midpotential, that is the potential at 50 % oxidation.

$$E_h = E_m + \frac{RT}{2F} \ln \frac{[Q]}{[H_2Q]} \quad (28)$$

In a potentiometric titration of a redox substance in solution, for each addition of titrant, the observed potential is allowed to reach a value constant with time. This is assumed to represent an equilibrium state. In ordinary potentiometry with simple redox substances, the indicator electrode responds very rapidly to the addition of the titrant. However, the response of the electrode is rather slow with redox polymer solutions [57, 73].

In dealing with the measurement of the potentials, several factors seem always to be the sources of the difficulties in measuring the redox properties of polymers. A major factor is the presence of oxygen which can be titrated with titanium chloride. Solubility and wettability of the resins contribute to the complications. While solubility problems may arise with linear polymer, the wettability may affect the properties of the crosslinked polymers. A

third source of difficulty is the slowness of reaching the equilibrium value with redox polymers due to the redistribution of the oxidized sites. When the redox polymer is titrated, the reaction with the titrant is usually fast in respect to the redox functionality of the polymer [78]. However, it might take minutes to hours for potentiometric equilibrium to be attained. The reason is that equilibrium is reached only after an interchange process in which the oxidized groups are distributed to equilibrium along the chain, and thus the process is slow.

Potentiometric titration curves of the redox resins generally show higher midpotentials,  $E_m$ , than the corresponding monomer units (about 35 mV higher). This is a general observation of many investigators [31, 79] and can be explained by « *polymeric effect* » ; that is, the oxidized form of the redox resin

tends to adhere to the indicator electrode, therefore the potential will raise. The slopes of the curves show a steeper increase and sometimes the curves are unsymmetrical. This behavior can be explained in terms of influence of the inductive effect, the complexation, and the steric effect of neighbouring redox system (hydroquinone-quinone) on the potentials. A color change during the titration operation can be noted, that is, the initially colorless solution of poly(vinylhydroquinone) starts to turn pink as the titrant is added and this becomes intense in the midpoint neighbouring, and finally to orange - bright yellow of a poly(vinylbenzoquinone) ; the pink color has been allotted to the presence of a quinohydrone intermediate. Some examples of redox polymers with redox potentials are listed in *table VI*. From this latter, it appears clearly that redox potentials are well

dependent on the nature of the polymer carrier.

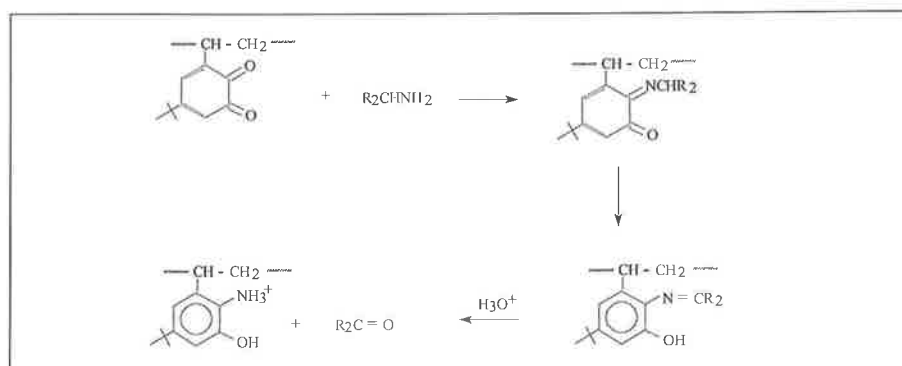
A variety of oxidants and reductants are employed in oxidation-reduction reactions of the redox resins [35]. Bromine, iodine, cerium (IV), iron (III), and hydrogen peroxide are considered the most efficient oxidants, thus useful titrants in potentiometric titration of soluble redox polymers. Reduction of the oxidized form may proceed with sodium dithionite, titanium (III), potassium iodide, and sodium sulfite and bisulfite.

The titration of insoluble redox resins in a heterogeneous medium requires the presence of a soluble mediator. This latter must be added in a small amount and should have a standard potential similar to the polymer in concern. Theoretically, the redox potential of the mediator and that of the polymer in study would be equal when equilibrium is established between them. Hydrazobenzene was employed for this matter by Manecke [83] and Iwabuchi [38].

Table VI - Examples of redox polymers and their redox potentials.

Polymer Support	Redox Unit	$E_m$ (V)	Ref.
Poly(N-hydroxymethylmethacrylate)	Hydroquinone	0.64	62
Poly(vinylhydroquinone)	Hydroquinone	0.45	49
Cellulose	Hydroquinone	0.695	80
Poly(vinyl alcohol)	Hydroquinone	0.706	81
Poly(vinylhydroquinone-co-maleic anhydride)	Hydroquinone	0.752	79
Poly(4-vinylcatechol)	Catechol	0.693	47
Poly[2-( <i>o</i> -methyl)-4-vinylcatechol]	Catechol	0.724	47
Poly(3-vinylcatechol)	Catechol	0.764 <sup>a</sup> 0.432 <sup>b</sup> 0.870 <sup>b</sup>	57
Poly(styrene-co-divinylbenzene)	Anthraquinone	0.15	36
Poly(styrene-co-divinylbenzene)	1-Amino-anthraquinone	0.52	82

<sup>a</sup>: Temperature, 23 °C ; <sup>b</sup>: Temperature, 35 °C, two midpotentials were detected in this condition.



Scheme 13 - Oxidation of primary amines by poly(benzoquinone).

## Applications

Specifically targeted applications make the redox polymers distinctly valuable and versatile resins. Among their manifold applications, the best one is their use as insoluble and recoverable oxidizing and reducing agents in chemical reactions. In this case, the facet of their use is the easy separation from the substrate solution by simple filtration, thereby phasing out the purification work-up and possible contaminants. This was the case when Daly and Kaufmann [84] demonstrated the great effectiveness of the poly(styrene-co-3-vinyl-5-*t*-butyl-1,2-benzoquinone) in the oxidation of primary amines to ketones by *t*-butyl-*o*-benzoquinone moiety as shown in *scheme 13*. This oxidation using this redox polymer prevailed over the similar low molecular weight reaction reported by Corey [85].

Moreover, Manecke [86] oxidized numerous organic compounds by passing them through a resin bed made up of hydroquinone-phenol-formaldehyde condensation resin, or by mixing the resin with the substrate solutions. In this way, Haas and Schuler [87] were able to dehydrogenate tetralin to yield

naphthalene. Also, Cassidy [88] elucidated the oxidation of hydrazobenzene to azobenzene employing the same technique. Manecke [67, 89] further reported the oxidation of cysteine to cystine and ascorbic acid to dehydroascorbic acid.

Iodide could be oxidized to iodine using redox polymer in its reduced form as mentioned in the introduction (1).

The coplanar bidentate complexing property through the catechol unit has been employed to generate phosphorous and boron polymeric reagents. For instance, in Daly's laboratory [39], the catechol-borane polymer was prepared and showed a reduction selectivity of primary alcohols amid a reducible mixture of organic compounds.

The chelating ability to heavy metallic ions through the catechol entities is another facet of the polymeric catechols and this property is *in vivo* applied in the fascinating mechanism of iron transport by a siderophore called *Enterobactin* (molecular formula  $C_{30}H_{27}O_{15}N_3$  with three catechol units) into a plant cell [90]. Mimicking the nature, two American biochemists devised *in vitro* molecules of *Enterobactin* size employing catechol or substituted catechol as active part in sequestering metallic ions [91].

Redox polymers in their reduced forms were used for the reduction of ions and for depositing metals from their solutions. For example, Manecke [92] employed poly(vinylhydroquinone) resin to deposit several metals from their ion solutions by a batch process. In this manner, silver was deposited from  $AgNO_3$  solution, and selenium from sulfuric acid-selenate solution. The deposited metals could be dissolved without affecting the redox resins. Iwabuchi [38] studied the adsorption of metallic ions onto resins having hydroquinone and catechol moieties. In this investigation, resins with catechol units adsorbed nearly ten times more mercuric ions ( $Hg^{2+}$ ) than other metallic ions studied, *i.e.* copper ( $Cu^{2+}$ ), aluminum ( $Al^{3+}$ ), cobalt ( $Co^{3+}$ ), and lead ( $Pb^{2+}$ ). Under the same conditions as the catechol experiments, the adsorption of metallic ions by resins with hydroquinone group failed in all cases.

All Ebran's poly(aminoquinones) (7) shared one peculiar characteristic : the

unusual affinity toward all metals and alloys, namely iron-made devices. These polymers possess the capacity of displacing water and machine oils from wet, dirty, rusty metal surfaces. Furthermore, the cured resins (with one of the following hardeners : diisocyanates, diepoxides, polyaziridines, etc.) applied as metallic surface coatings manifested a strong anticorrosion activity.

Removal of oxygen from water is desirable because the corrosion of iron and steel in contact with water is thought in part to be related to the dissolved oxygen in water. Manecke [89] reported that condensation polymers of hydroquinone-phenol-formaldehyde removed oxygen from water very efficiently without the addition of salts or other additives. The course of this removal apparently involved the oxidation of the reduced form of the resin with oxygen to quinone while the resulting hydrogen peroxide reacted with another hydroquinone group to give quinone and water. The deoxygenation by this method was found to be more efficient and faster than the conventional technique using nitrogen as vehicle. The resin showed great potency in converting dissolved oxygen to hydrogen peroxide in the presence of stabilizers ; the yield was between 80 and 100 %. It was also suggested that the above redox resins may be used as antioxidants because of their great reactivity with oxygen.

The antioxidant properties of these polymers have been claimed in lowering the deterioration of some substances susceptible to oxidation such as unsaturated fatty acids, rubbers, paints, and in accelerating the drying process of some alkyd-based paints. Chakraborti and Nandi [93] have conducted research work in view of demonstrating the potent antioxidation of poly(hydric benzene). They have shown the antioxidant superiority of polyresorcinol and polyphenol over their monomeric analogues, by performing kinetic studies on AIBN-induced oxidation with molecular oxygen of a number of mono-unsaturated simple compounds such as tetralin, cumene, and cyclohexene. The inhibition rates of the respective oxidations of these compounds by polymeric resorcinol and polymeric phenol were much lower

than those with resorcinol and phenol. The polyresorcinol and polyphenol in this study were prepared by reaction of resorcinol and phenol respectively with anhydrous ferric chloride according to the procedure of Ehlers [94]. These actual results indicate clearly the inhibition propensity of the polymeric resorcinol in radical reactions, namely radical polymerization.

Interesting is the on-going application of the amino-quinone polyurethanes in the metal particle (MP) tape. These polymeric materials are of a paramount importance and thus were intentionally designed for the remedy of the inevitable corrosion of the iron pigment used in metal particle tape for high density mass-data storage systems. In short, this inherent application is intended to enhance the MP archivability. Nikels and coworkers have tested successfully these polymers for this purpose [95]. In addition, the amino-quinone polyurethanes were employed as wetting binders in the coating formulations containing iron pigments.

Oxidation-reduction polymers containing hydroquinone-quinone systems may be used to maintain a given redox potential and the reducing conditions in biological systems [96]. This is called « *poising* » in which a specific redox potential in a given medium may be held, to parallel the buffering phenomenon in acid-base chemistry. In fact, reduced cytochrome *c* was prepared using redox polymers [97] ; the activity of this enzyme was retained after the treatment with the polymer. The advantages of this method over the conventional way of reducing cytochrome *c* (with dithionite and hydrogenation using a platinum or palladium catalyst) are freedom from ionic contaminants and no need for metal catalyst. Another biochemical application is the dehydrogenation of NADH to  $NAD^+$  by the use of the quinone form of the condensed redox polymer [86, 98].

In the oilfield, some polymers such as carboxymethylcellulose (CMC) are often applied as to bring about a viscosity improvement and therefore to facilitate the oil drilling. In this regard, Patel [99] evaluated sulfoalkylated polymeric catechols, namely sulfomethylated and sulfoethylated resins. Indeed, polymeric catechols chemically

modified as such exhibited a marked ability to control the viscosity, the gel strength, as well as the filtrate loss of aqueous oil drilling fluids.

Polymers containing hydroquinone are claimed to act as a polymeric catalyst in flame-retardant intumescent system used as coating [100-101]. They are employed as carbonific materials to induce a char formation as carbonaceous layer and hence this latter layer will act as a barrier to heat transfer from the flame and to mass transfer of the oxidant and the fuel.

Other applications of redox polymers include photographic and electrical uses. It was found that hydroquinone redox polymers could be employed as non-diffusing reducing agents to photographic color emulsions [102]. Redox polymers were also applied in depolarization mass for primary and secondary cells [103]. Batteries using redox polymeric materials are claimed to eliminate possible deterioration due to the corrosion of the lead or iron accumulators caused by liquid electrolytes.

## Conclusion

While the synthesis of some redox polymer bearing hydroquinone, catechol, or benzoquinone, is somewhat straightforward, that of others proved to be painstaking task in that it requires a multistep way linked with specific conditions. Protection of some chemically sensitive functionalities in polymerization of vinyl monomers followed by subsequent deprotection add to the tediousness of the work-up. A broad spectrum of properties and of applications is inherently linked to the presence of the redox moiety bound to a polymer matrix. With the advanced organic synthesis of a targeted active molecule such as the so-called « *combinatorial chemistry* » [104-105] coupled with the new technique of « *mix and split* » [106], one can project in future further applications of polymer-bound redox units.

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