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# Some New Nitrogen-Containing Redox Polymers

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# Some New Nitrogen-Containing Redox Polymers

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## ABSTRACT

Synthesis of some new N-substituted aziridinyl compounds by the addition of aziridine to monovinyl- and divinyl-substituted p-quinones is described. The redox potentials of the monomers, their polymerization behavior, and the properties of redox polymers derived from them were investigated.

Different polymerizable monosubstituted and disubstituted vinyl-4,7-indazolequinones were prepared by 1,3-dipolar addition of vinyldiazomethane to 1,4-benzoquinones. By copolymerization of 5,6-dichloro-3-vinyl-indazolehydroquinone triacetate with 5,6-dichloro-1,3-divinyl-indazolehydroquinone diacetate as a crosslinking agent, followed by hydrolysis and sulfalkylation of the resulting copolymer with propane sultone, chemically stable redox resins were obtained.

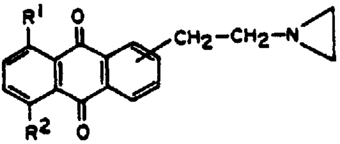
## INTRODUCTION

The quinone system inhibits the radical polymerization of some vinylquinones [1], so it is necessary to block the quinone group before preparing polymers from such monomers. For this reason we searched for another polymerizable group that could be used to incorporate the quinone moiety into polymeric structures. Monomers containing the cationically polymerizable aziridine group were therefore prepared by addition of aziridine to the vinyl groups of several vinylquinones and their polymerization behavior was investigated. Polymers obtained from these monomers were expected to swell in acid-aqueous solutions because of their content of tertiary amino groups. It seemed that the redox properties of such polymers could be studied without the necessity of introducing hydrophilic groups by further reaction, as is the case with most vinyl-type redox resins.

## RESULTS AND DISCUSSION

### Polymers from Monomers Containing Aziridine Groups

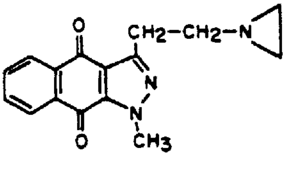
The addition of the aziridine group to vinylquinones [2, 3] depends on the activation of the vinyl group. Vinylquinones which do not have a completely substituted quinone nucleus can also add aziridine to the quinone by 1,4-addition [4]. To avoid this difficulty our initial studies were on the reaction of aziridine with completely substituted vinylquinones. By reacting different vinylanthraquinones with aziridine in sealed tubes, the following aziridinylquinones [5] were synthesized:



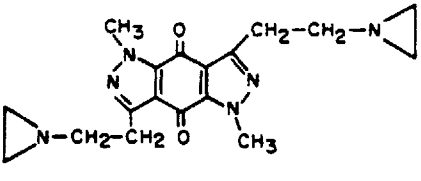
I

| | $R^1$ | $R^2$ | |
|---|---|---|---|
| Ia | H | H | $1\text{-}CH_2\text{-}CH_2\text{-}N\lhd$ |
| Ib | H | H | $2\text{-}CH_2\text{-}CH_2\text{-}N\lhd$ |
| Ic | H | $CH_2\text{-}CH_2\text{-}N\lhd$ | $1\text{-}CH_2\text{-}CH_2\text{-}N\lhd$ |
| Id | $CH_2\text{-}CH_2\text{-}N\lhd$ | H | $1\text{-}CH_2\text{-}CH_2\text{-}N\lhd$ |

Vinylated pyrazolequinones in this reaction gave the aziridinylquinones II and III [5]:

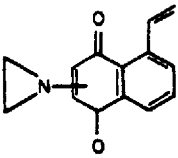


II

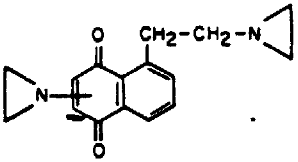


III

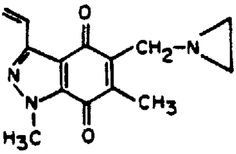
More complicated are the reactions of aziridine with other vinylquinones. Different side reactions and also uncontrolled polymerizations take place [5]. Some of the products isolated from such reactions are



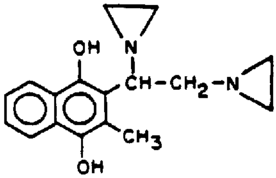
IV



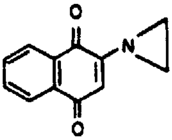
V



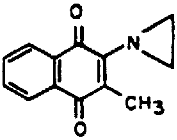
VI



VII



VIII



IX

The aziridinylquinones in which the aziridine groups was linked by an alkyl bridge with the quinone nucleus were polymerized cationically by use of diethylsulfate (DES) as initiator in dioxane or benzene with good yields. The IR spectra of the aziridinylquinone homopolymers show no absorption band for piperazine rings at 930 $cm^{-1}$ [6, 7]. A weak band at 3070 $cm^{-1}$, typical for the aziridine ring CH-valence frequency, was observed, indicating aziridine rings as end groups of the polymer.

Monomers IV, VIII, and IX did not polymerize and Compound V gave no cross-linked polymers. It is evident that mesomeric interaction of the free electron pair of the aziridine nitrogen with the quinone nucleus so lowers the basicity of the nitrogen that cationic initiation by quaternatization of the aziridine nitrogen is not possible.

Copolymers of the aziridinylquinones Ia and Ib with various amounts of the cross-linking agent 1,4-bis-[2-(1-aziridinylethyl]-benzene (X) were prepared (Table 1) by polymerization in benzene or dioxane solution at 70°, using diethylsulfate as initiator, In order to obtain polymers with good mechanical properties, large amounts of cross-linking agent had to be used. This was detrimental to the swelling properties of the products. By synthesizing a terpolymer of Ia and X with [2-(1-aziridinyl)-ethyl]benzene (XI), a polymer with both good strength and good swelling characteristics could be obtained, however (Table 2). A similar cross-linked redox polymer was also synthesized from X, XI, and II (Table 2).

TABLE 1. Copolymerization of Monomers Ia and Ib with Cross-Linking Agent X

| Resin No. | Mole ratio Ia/X | Mole ratio Ib/X | Properties of the resins | Redox capacity (meq/g) Calc[a] | Redox capacity (meq/g) Detr[b] | Redox capacity (meq/g) Detr[c] |
|---|---|---|---|---|---|---|
| 1 | 10/1 | - | Soft, inhomog | - | - | - |
| 2 | 7/1 | - | Soft, inhomog | - | - | - |
| 3 | 4/1 | - | Hard | 6.04 | 5.79 | 5.31 |
| 4 | 2/1 | - | Hard, brittle | 5.19 | 5.04 | 4.32 |
| 5 | - | 5/1 | Soft | - | - | - |
| 6 | - | 3/1 | Hard | 5.72 | 5.48 | 5.12 |

[a] Calculated from the ratio of monomers in the polymerization mixture.

[b] Determined by means of quantitative IR analysis (see Experimental).

[c] Determined by oxidation (50 days at 40°C) with periodically renewed 0.1 M $(NH_4)Fe(SO_4)_2$ in 2 N $H_2SO_4$ and titration of $Fe^{2+}$ with 0.02 N $KMnO_4$.

The yields of Resins 3, 4, 6, 7, and 8 were about 70-80%. It was therefore possible that the compositions of the copolymers were different from those of polymerization mixtures. The quinone contents of the polymers were therefore determined by quantitative IR

TABLE 2. Copolymerization of Monomers Ia and II with Monomer XI and Cross-Linking Agent X

| Resin No. | Mole ratio Ia/XI/X | Mole ratio II/XI/X | Properties of the resins | Redox capacity (meq/g) Calc[a] | Redox capacity (meq/g) Detr[b] | Redox capacity (meq/g) Detr[c] |
|---|---|---|---|---|---|---|
| 7 | 3/3/1 | - | Hard | 4.03 | 3.97 | 3.61 |
| 8 | - | 3.5/2.5/1 | Hard | 4.46 | 4.38 | 4.10 |

[a] Calculated from the ratio of monomers in the polymerization mixture.

[b] Determined by means of quantitative IR analysis (see Experimental).

[c] Determined by oxidation (50 days at 40°C) with periodically renewed 0.1 M $(NH_4)Fe(SO_4)_2$ in 2 N $H_2SO_4$ and titration of $Fe^{2+}$ with 0.02 N $KMnO_4$.

analysis [8, 9]. As can be seen in Tables 1 and 2, the quinone contents (meq/g) of the polymers, as calculated from the compositions of the polymerization mixtures or as determined by IR analysis or by titration, are not appreciably different.

For the application and investigation of redox polymers, it is important that their reactions occur at reasonable rates. Since the rates of redox resin reactions depend on the rate of diffusion of substrates in the polymers, such rates depend on the swellability of the resins. As can be seen in Fig. 1, the redox polymers swelled in acid-aqueous solution. Thus a further introduction of hydrophilic groups into these redox polymers was not necessary. As would be expected, the higher cross-linked redox polymers swelled to lower extents than did the lower cross-linked polymers (compare the swelling characteristics of Resins 3, 4, and 7, which contained the same quinone systems, in Fig. 1).

For practical applications it is important that the resins have chemical stability and a high redox capacity in addition to good swelling and mechanical properties. The redox capacities of the above-mentioned redox polymers were obtained by first reducing the polymers with $NaBH_4$ in alkaline solution and then oxidizing the reduced polymers with 0.1 M $Fe^{3+}$ solution in 2 N $H_2SO_4$.

At room temperature the oxidations proceeded very slowly, but reaction rates at 40°C were sufficient to enable 60-70% of the expected oxidation to occur in 2-3 hr. The total redox capacity (approx 90%) could be reached after much longer times (see Tables 1 and 2). The good reproducibility of the redox capacity and the fact that only small

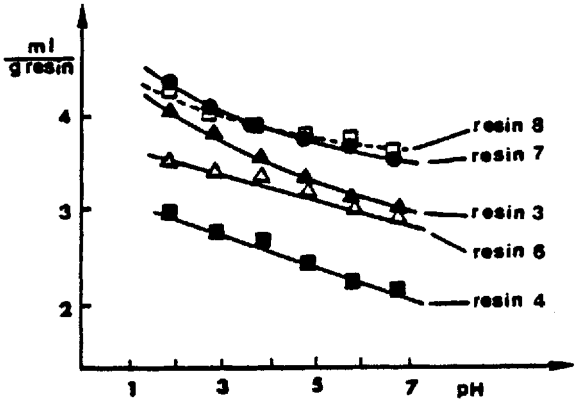


FIG. 1. Dependence of resin swelling (vol/g resin) in citric acid-phosphate buffers ($\mu = \Sigma c_i z_i = 0.5$) on pH.

loss of the redox capacity (approximately 3%) was noted after 3 redox cycles show that the resins have good chemical stability. They were also mechanically stable.

Another important characteristic of redox polymers is their oxidation potential. By measuring potentials after exactly half-oxidation of the polymers with 0.1 N $Ce^{4+}$-solution in 1 N $H_2SO_4$ at 40° C, determing the pH values of the solutions after a constant equilibrium potential was reached, the apparent standard oxidation potentials for pH = 0 were calculated. The values of the oxidation potentials of the polymers, together with their carbonyl stretching frequencies, can be seen in Fig. 2. Also the midpoint redox potentials of the monomers were determined potentiometrically by titration with $TiCl_3$ solution in an acetic acid/water (1:1, v/v) mixture. Their values are 100-150 mV. They also varied linearly with carbonyl stretching frequencies of the compounds (Fig. 3). It was interesting to note that the C=O valence frequencies and the redox potentials of the redox polymers varied with their redox capacities. The lower the content of redox groups on the polymer, the lower was the C=O band frequency and the lower was the oxidation potential. Thus, Homopolymer Ia absorbed at 1671 $cm^{-1}$ whereas Polymer 3 absorbed at 1667 $cm^{-1}$ and its oxidation potential was 142.1 mV. Similarly, Copolymer 7 absorbed at 1665 $cm^{-1}$ and its oxidation potential was 131.0 mV.

## Polymers from Vinylated Pyrazolequinones

We continued our work on nitrogen-containing redox polymers by synthesizing several new substituted vinyl-4,7-indazolquinones [10-12].

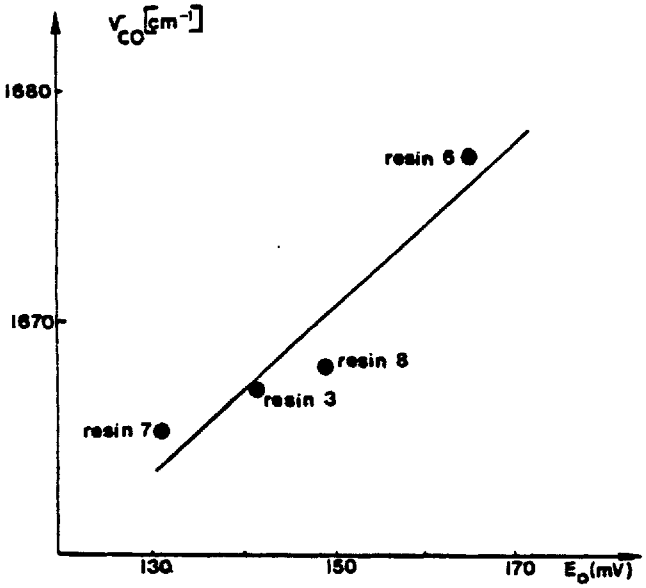
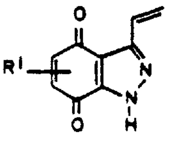
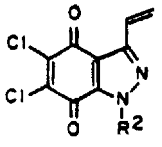


FIG. 2. Correlation of the apparent standard oxidation potentials of resins derived from aziridinylquinones with their carbonyl stretching frequencies.

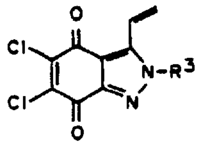
These were synthesized with the objective of obtaining monomers and polymers with high redox potentials. The vinylindazolequinones were prepared by 1,3-dipolar addition of diazo-(2)-propene to p-benzoquinone or its monosubstituted or disubstituted derivatives or by addition of diazomethane to p-benzoquinones, followed by vinylation with vinyl acetate. It proved possible to add diazomethane or vinyldiazomethane to only one side of p-benzoquinone [11]. The following monomers (XII-XIV) with redox potentials of 340-460 mV were prepared:



XII



XIII



XIV

$R^1 = \frac{H}{\text{XIIa}}\ \frac{Cl}{\text{XIIb}}\ \frac{CH_3}{\text{XIIc}}\ \frac{OCH_3}{\text{XIId}}$ $R^2 = \frac{H}{\text{XIIIa}}\ \frac{CH_3}{\text{XIIIb}}\ \frac{CH{=}CH_2}{\text{XIIIc}}$

$R^3 = \frac{CH_3}{\text{XIVa}}\ \frac{CH{=}CH_2}{\text{XIVb}}$

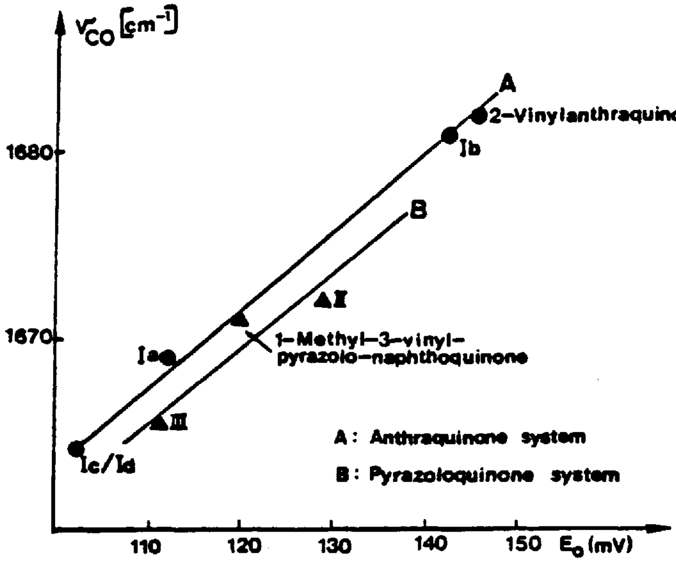


FIG. 3. Correlation of the carbonyl stretching frequencies of aziridinylquinones with their oxidation potentials as measured in 1:1 (v/v) acetic acid/water mixtures.

The redox potentials of the chlorine substituted vinyl-indazolequinones are higher than those of vinylindazolequinones which were previously synthesized in our group. We also found a linear relation between the carbonyl stretching frequencies of these monomers and their standard oxidation potentials (Fig. 4). The polymerization behavior of the vinyl-4,7-indazolequinones and of the corresponding vinylindazolehydroquinone diacetates and triacetates in dioxane or dimethylformamide solution was investigated. The results are summarized in Tables 3 and 4.

All acylated vinylindazolehydroquinones could be polymerized, but the N-vinylated compounds showed a lower tendency to polymerize.

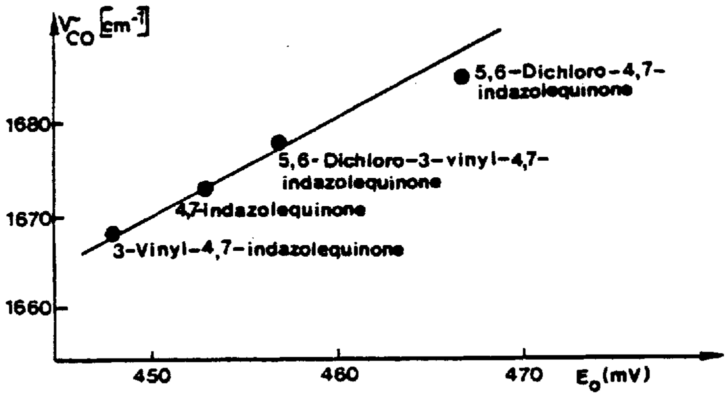


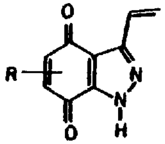
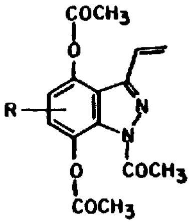
FIG. 4. Correlation of the carbonyl stretching frequencies of 4,7-indazolequinones with their oxidation potentials as measured in 1:1 (v/v) acetic acid/water mixtures.

With the exception of 5,6-dichloro-1,3-divinyl-4,7-indazolequinone, the chlorine-substituted indazolequinones did not polymerize. The reason for the different polymerization behavior of the various monomers is not known.

The 5,6-dichloro-substituted vinylindazolequinones [12] possess the best properties for the synthesis of stable redox polymers. A resin was prepared by copolymerization of a mixture of 5,6-dichloro-3-vinylindazolehydroquinone-1,4,7-triacetate (90 mole %) and of 5,6-dichloro-1,3-divinyl-4,7-indazolehydroquinone diacetate (10 mole %), followed by hydrolysis of the acetyl groups with 1 $\underline{N}$ KOH. After oxidation of the copolymer to the quinone form with air, the product was sulfalkylated with propanesultone. The S-content of this product (Resin 9) was 6.0 ± 0.2%. The theoretical S-content of a quantitatively copolymerized product would be 8.12%, so that 75% of the theoretical amount of substitution was obtained. The ion exchange capacity determined for the resin was 2.27 meq/g (81% of the theoretical value of 2.81 meq/g). The maximal obtained redox capacity was 4.25 meq/g (70% of the theoretical value of 5.8 meq/g). This redox capacity was achieved at 20° C after 60 days exposure of the resin to a periodically renewed solution of 0.1 $\underline{M}$ $Fe^{3+}$ in 2 $\underline{N}$ $H_2SO_4$. Fifty percent of this capacity can be reached after approximately 8 hr exposure of the resin to 0.1 $\underline{M}$ $Fe^{3+}$ in 2 $\underline{N}$ $H_2SO_4$. The apparent standard redox potential $E_0$ determined for the resin was 476 mV (20° C). The resin was swellable in water (see Fig. 5).

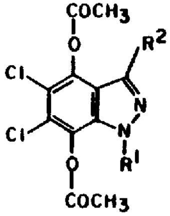
From the swelling curve one can see that the swelling volume of

TABLE 3. Homopolymerization of Monosubstituted 3-Vinyl-4,7-indazolequinones and of Monosubstituted 3-Vinylindazolehydroquinone Triacetates

| | | —R | Mp of monomers, (°C) | Yield of monomers, (%) | $E_0$ of monomers (mV) | Yield of homopolymers[a] (%) |
|---|---|---|---|---|---|---|
|  | XIIa | —H | 175-178 | 25 | 448 | 70 |
| | XIIb | —Cl | 188-191 | 39 | 459 | - |
| | XIIc | —$CH_3$ | 230-233 | 33 | 387 | 44 |
| | XIId | —$OCH_3$ | 268-272 | 25 | 341 | 58 |
|  | XVa | —H | 123-124 | 37 | | 76 |
| | XVb | —Cl | 139-140 | 58 | | 40 |
| | XVc | —$CH_3$ | 135 | 70 | | 9 |
| | XVd | —$OCH_3$ | 125-126 | 62 | | 31 |

[a] Compound XII polymerized in dioxane (1.0 wt% AIBN, 48 hr at 60°C), Compound XV polymerized in dimethylformamide (1.0 wt% AIBN, 48 hr at 60°C).

TABLE 4. Homopolymerization of Acylated Mono- and Divinyl-5,6-dichloroindazolehydroquinones

| | | $R^1$ | $R^2$ | Mp of monomers (°C) | Yield of homopolymers[a] (%) |
|---|---|---|---|---|---|
|  | XVIa | $-CH{=}CH_2$ | $-H$ | 162 | 23 |
| | XVIb | $-CH{=}CH_2$ | $-CH{=}CH_2$ | 190-192 | 97 |
| | XVIc | $-CO{-}CH_3$ | $-CH{=}CH_2$ | 170 | 81 |
| | XVId | $-CH_3$ | $-CH{=}CH_2$ | 168-169 | 91 |

[a] Polymerization in dimethylformamide (1.5 wt% AIBN, 48 hr at 60°C).

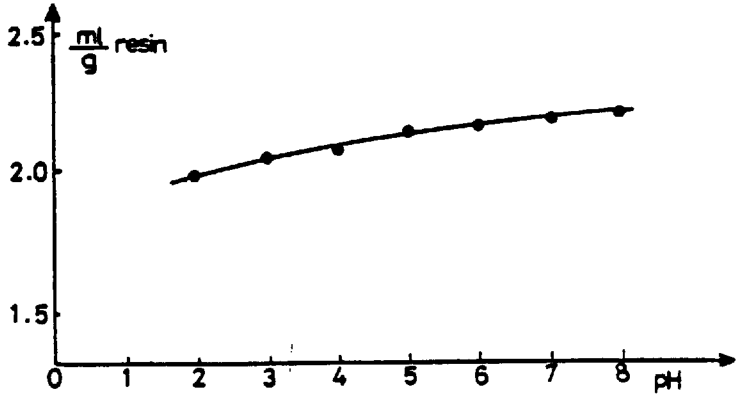


FIG. 5. Dependence of resin swelling (vol/g of dry Resin 9) in citric acid-phosphate buffers ($\mu = \Sigma c_i z_i = 0.5$) on pH.

the redox resin changes very little over a broad pH range. This is very favorable for column applications. The properties of the resin did not change after being submitted to several redox cycles. This indicates that the resin has good chemical and mechanical stability.

## EXPERIMENTAL

### Monomers

The aziridinylquinones Ia-d, II, and III were obtained by reacting the corresponding vinylquinones with aziridine in sealed tubes at 80° C. The aziridine was dried with $CaH_2$ prior to use. Monomers IV-IX were obtained under normal pressure [5, 13].

3-Vinyl-4,7-indazolequinone (XIIa) [11] and the monosubstituted and disubstituted-3-vinyl-4,7-indazolequinones XIIb-d [10] and XIIIa [12] were synthesized by 1,3-dipolar addition of vinyldiazomethane to substituted p-benzoquinones in benzene or ether solution. Methylation of XIIa with dimethylsulfate in aqueous KOH gave the isomers XIIIb and XIVa in high yields. The N-vinyl-derivatives XIIIc and XIVb were obtained by vinylation of XIIIa with vinyl acetate in the presence of Hg(II) acetate and catalytic quantities of conc $H_2SO_4$ [10, 14]. The vinylhydroquinone acetates, XV and XVI, were synthesized by reductive acetylation of the substituted vinyl-4,7-indazolequinones with acetic anhydride and zinc and catalytic quantities of $H_2SO_4$ [10, 15].

## Homopolymerization Procedures

With the exception of IV, VIII, and IX, the aziridinylquinones were polymerized cationically in solution. The monomers were dissolved in benzene or dioxane (30-40% solution) and 2-4 wt% of DES as catalyst was added at 70-80° C. After 2-3 hr the red solution was poured into methanol/ether and the homopolymers precipitated. They were reprecipitated several times (dioxane/methanol).

The 3-vinyl-4,7-indazolequinones and their corresponding hydroquinone acetates were homopolymerized in dioxane or dimethylformamide (DMF) solution in sealed tubes. AIBN (1 wt%) was used as a catalyst and the reactions were conducted for 48 hr at 60°. Generally, 100 mg quantities of the monomers were dissolved in just enough solvent to obtain a homogeneous solution. The tubes were flushed with nitrogen prior to sealing to remove oxygen. The homopolymers were precipitated out of the solution into methanol. They were reprecipitated several times, and then dried. The yields obtained are provided in Tables 3 and 4.

## Preparation of Redox Resins

The aziridinylquinones Ia, Ib, and II were copolymerized with various amounts of the cross-linking agent 1,4-bis-[2-(1-aziridinyl)-ethyl]benzene (X) at 60-80° C in 30-50% solution in dioxane or benzene with 2-4 wt% DES under stirring. In some instances [2-(1-aziridinyl)-ethyl]benzene (XI) was also present in the polymerization mixture (see Tables 1 and 2). The reddish brown copolymers were ground and extracted with benzene (2 hr) and methanol (2 hr). They were dried in vacuum and were fractionated by sieving.

Copolymerization of the vinylindazolehydroquinone acetates XVIa and XVIb (in the ratio of 90 mole % of XVIa and 10 mole % of XVIb) in DMF solution, using 1 wt% AIBN as initiator, was conducted in evacuated sealed tubes under exclusion of oxygen at 60° C (2.5 g XVIa, 0.3 g XVIb, 0.045 g AIBN in 20 ml DMF for 72 hr). The yield of the copolymer was 2.53 g. The copolymer was ground, extracted with benzene (6 hr), dried in a vacuum, and fractionated by sieving. The fraction ranging from 0.05-0.2 mm in particle size was stirred with 50 ml of 1 $\underline{N}$ KOH at room temperature for 48 hr to remove acetyl groups. This saponified copolymer was subsequently sulfalkylated by treatment with 4 g propanesultone in 10 ml 1 $\underline{N}$ KOH for 36 hr at room temperature. The product was washed with water and KCl solution. It was dried and stored in the K-form.

## Characterization of the Redox Resins

For the characterization of the redox resins, the sieve fraction of particle size 0.1-0.2 mm was taken. They were submitted to three redox cycles: reduction with 1% sodium dithionite solution in 2 N KOH, acidification with 2 N $H_2SO_4$, and oxidation with 0.1 M $Fe^{3+}$ solution in 2 N $H_2SO_4$.

## Quantitative IR Analyses (Determination of the Quinone Content)

The quinone contents of Copolymers 3, 4, 6, 7, and 8 were determined from their IR spectra. The spectra were recorded from polymers dispersed in KBr pellets. KSCN was used as an internal standard [8, 9]. The relative intensities of the carbonyl stretching band and the absorption of KSCN at 2100 $cm^{-1}$ were compared for the analysis. For calibration various amounts of a monomer (0.04-0.2 wt%) were mixed with KBr containing 0.2 wt% KSCN. The quotient $E_{C=O}/E_{KSCN}$ was plotted against wt% quinone.

## Swelling Behavior

Air-dried copolymers (500 mg) were swollen in McIlvaine buffers [16] of ionic strength $\mu = 0.5$ in the pH range 2-7. Degrees of swelling were determined according to the procedure of Manecke and Heller [17].

## Ion Exchange Capacity

Sulfonic acid groups present in Resin 9 were determined by displacement of hydrogen ions with potassion ions by treatment with 2 N KCl solution [18], followed by titration of the HCl liberated. The results obtained are presented below. Theoretical values are based on the assumption that sulfalkylation was quantitative and that the copolymer composition could be calculated from the relative amounts of monomers used to prepare the copolymer.

| | | |
|---|---|---|
| Ion exchange capacity | calc (max): | 2.81 (meq/g) |
| | found: | 2.27 (meq/g) (81% of calc) |
| S-content | calc (max): | 8.12% |
| | found: | 6.00% (75% of calc) |

## Redox Capacity

The redox capacities of the resins were determined according to the procedure of Manecke and Storck [18].

## Potentiometric Titration

The redox potentials of the aziridinylquinones and of the vinylindazolequinones were determined potentiometrically by reductive titration with 0.04 N $Ti^{3+}$ solution in acetic acid/water (1:1, v/v).

Potentiometric titration of the redox resins was performed according to the procedure of Manecke and Storck [18]. The resins were reduced with $NaBH_4$ and were then titrated with 0.1 M $Ce^{4+}$ solution at a pH of approximately 1.0. The midpoint potentials were determined by half-oxidation of the redox resins followed by measurement of the redox potential of the equilibrated solutions. The half-oxidation was calculated from the quinone content of the resin, as determined by IR analysis.

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