OXIDATION–REDUCTION POLYMERS

II. STANDARD OXIDATION POTENTIALS OF REDOX HOMOPOLYMERS AND THEIR MONOMERIC MODELS[1]

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ABSTRACT

A new monomer, 2,5-bis-(2-tetrahydropyranyloxy)-4-methyl-4′-vinyldiphenyl sulphone, has been prepared. The standard oxidation potentials of two linear redox homopolymers, derived from this monomer and the one previously reported (1), and of their intermediate and model compounds, have been measured using continuous and discontinuous titration techniques.

In Part I (1) we reviewed briefly the literature on redox monomers and polymers, especially those containing hydroquinone units. Since then further contributions in this field have been published.

Cassidy and co-workers (2, 3) have investigated the properties and reactions of methyl-substituted hydroquinones and vinylhydroquinones in their search for redox polymers of improved stability. Manecke and Storck (4) have reported the synthesis of 1- and 2-vinylanthraquinones.

Further condensation-type polymers have been prepared: hydroquinone–resorcinol–formaldehyde (5), pyrogallol–formaldehyde (6), dichlorohydroquinone–trioxane (7), and dimethylhydroquinone–formaldehyde (7). In order to study the redox behavior of these polymers, which in their idealized form would consist of repeating hydroquinone units linked by methylene bridges, model segmers have been synthesized (8, 9) and their standard oxidation potentials measured.

Izoret (10) continued his work on anthraquinone polymers. A new polymer containing hydroquinone units has been prepared by the reaction of a polymeric amine with 2,5-dihydroxyhydrocinnamic acid lactone (11). The reaction of diamines with *p*-benzoquinone led to the synthesis of various aminoquinones (12).

Practical applications of redox polymers in batteries and dielectric compositions have been reported (13–15).

We have continued our investigations of polymers containing repeating hydroquinone units joined through a sulphone bridge to a polystyrene chain. Monomers and model compounds of increased stability were sought.

The organic syntheses are shown schematically below. Isopropylbenzene was chlorosulphonated and then reduced by alkaline sodium sulphite to give *p*-isopropylbenzenesulphinic acid (II). The sulphinic acid was reacted with *p*-benzoquinone to give diphenyl sulphone III, which was used subsequently as a model segmer of polymer X.

A new monomer, 2,5-bis-(2-tetrahydropyranyloxy)-4-methyl-4′-vinyldiphenyl sulphone (VII) was synthesized. The structure of sulphone V has not been positively established regarding the relative position of the —SO_2Ar and —CH_3 groups on the hydroquinone

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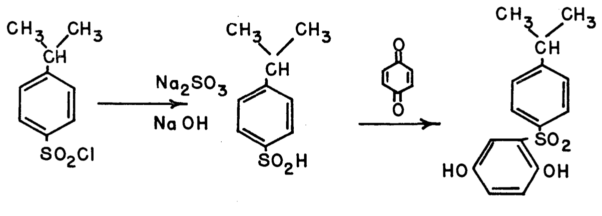
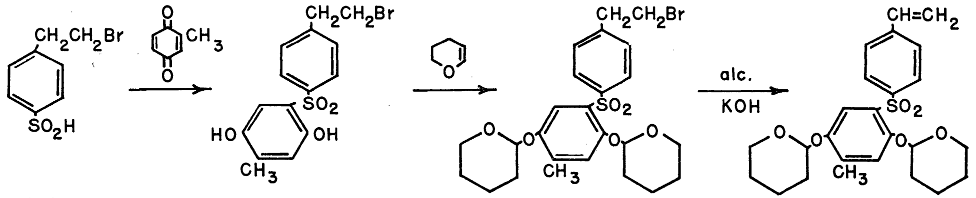
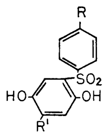


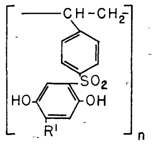
(I) (II) (III)



(IV) (V) (VI) (VII)



	R	R'
III	$CH(CH_3)_2$	H
V	CH_2CH_2Br	CH_3
VIII	CH_2CH_2Br	H
IX	CH_2CH_3	H



	R'
X	H
XI	CH_3

nucleus. The electron demand of the carbonyl oxygens and the low electron affinity of the —CH_3 group create a marked deficit at the carbon atom para to the —CH_3 group (16); therefore the 4-methyl isomer should be obtained in highest yield. If some 3-isomer is obtained, it should be difficult to pyranylate both phenolic groups since one of the phenolic groups would be sterically hindered. The product obtained experimentally consisted essentially of one isomer which could be fully pyranylated. A very small amount of another isomer which could not be fully pyranylated was also obtained. It is therefore suggested that the isomer used in this work is the 4-methyl isomer.

An additional model segmer (IX) with an ethyl group was synthesized by reducing the bromoethyl side chain of the sulphone VIII.

The intermediate and model compounds were characterized by analysis, infrared spectra, and their standard oxidation potentials.

The monomers were polymerized using α,α'-azodiisobutyronitrile as an initiator. After treatment with acid to expose the phenolic groups, the linear homopolymers (X and XI) were characterized by their standard oxidation potentials. Potentiometric techniques have been used with redox polymers by other investigators (5, 6, 17–19). The sulphur analyses on the polymers X and XI are lower than the theoretical and might suggest that depyranylation was incomplete. On the other hand, all phenolic groups would be exposed during titration in strong acids. Since the titration curves of the polymers were comparatively flat, any error in estimating E_0 through an incorrect assumption of the equivalent weight of the polymers would be within the experimental limits indicated in Table II.

A simplified form of the Nernst's equation was used to calculate the standard oxidation potential (E_0) for the quinone–hydroquinone redox systems:

$$E_{\mathrm{h}} = E_0 + \frac{RT}{2F} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} + \frac{RT}{F} \ln [\mathrm{H}^+]^*$$

where E_{h} is the cell potential referred to a standard hydrogen electrode. The difference between the cell potential at 50% and that at 25% oxidation, taken from the titration curve, is called the index potential (E_{i}) and is theoretically equal to 14.1 mv at 25° C for a simple bivalent redox reaction.

It was realized early in this work that all compounds containing the non-substituted quinone group were unstable under certain titration conditions. In cases where instability was encountered, a discontinuous titration method (20–22) was used. Briefly, predetermined amounts of the oxidant were added to known amounts of the samples to be oxidized and the change of potential with time was recorded. In all cases this change was linear and the cell potential at each stage of oxidation was obtained by extrapolation to zero time, as illustrated in Fig. 1. The value of E_0 reported for all titrations was obtained

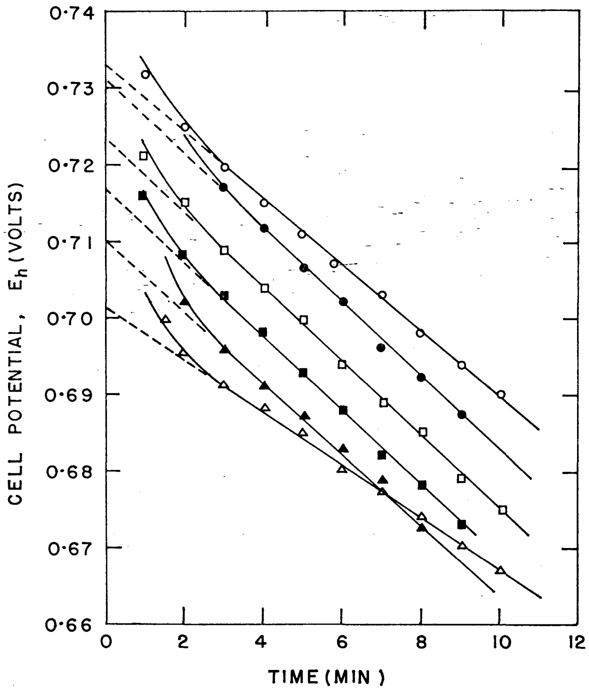


FIG. 1. Discontinuous titration of the sulphone VIII (No. 3, Table II): △ 12.2; ▲ 24.4; ■ 36.7; □ 49.0; ● 61.2; ○ 73.4% oxidation. Points were taken from recorder results.

**This simplified treatment makes the usual assumptions for a weak dibasic acid in strongly acid solution and neglects semiquinone formation, activity coefficients, and liquid junction potential. The term E_0 combines $(RT/2F) \ln K_1K_2$ with E^0, the conventional standard potential.*

by averaging the values calculated from each individual addition of oxidant as illustrated in Table I. The potential decay is a useful index of the instability of the oxidized form of the compound. A composite curve of the cell potential at zero time versus percentage oxidation leads to the familiar potentiometric titration curve illustrated in Fig. 2.

TABLE I

Discontinuous titration of sulphone VIII (No. 3, Table II), 112 mg (0.628 meq) in 250 ml acetic – sulphuric acid, pH 0.5, 24° C

0.0768 *N* $Ce(SO_4)_2$ (ml)	% oxidation	Initial potential E_h (v)	E_0 (v)	Potential decay (mv/min)
1.00	12.2	0.701	0.756	3.4
2.00	24.4	0.710	0.749	4.7
3.00	36.7	0.717	0.751	4.9
4.00	49.0	0.723	0.750	4.8
5.00	61.2	0.731	0.752	4.8
6.00	73.4	0.733	0.746	4.3
		Average	0.751 ±0.005	4.5±0.4

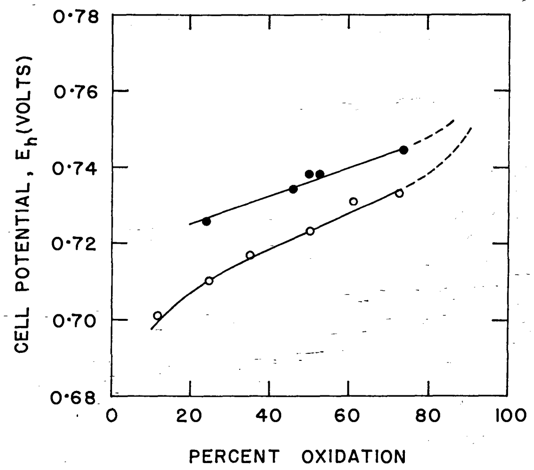


FIG. 2. Discontinuous titration (composite curve) of the sulphone VIII and polymer X (Nos. 3 and 11, Table II): ○ sulphone (pH 0.5); ● polymer (pH 0.3).

Representative examples of continuous and discontinuous titrations are shown in Table II. Hydroquinone and toluhydroquinone were titrated to check the apparatus and various techniques. The mean value of two platinum electrodes has been reported. These electrodes agreed within less than 1 mv for the model compounds and showed a maximum discrepancy of 7 mv for the polymers.

As previously mentioned the oxidized form of sulphone VIII was unstable. Therefore, a discontinuous titration was required for determination of the standard oxidation potential of this sulphone. Titration in various solvents, at different pH and using two oxidants, yielded the same values of E_0 within the experimental error. It was generally found that the decomposition of the oxidized form was much slower in solutions of lower water concentration and of lower acidity. In the case of bromine titrations it might be

TABLE II

Potentiometric titrations

No.	Compound	Solvent	Oxidant	pH	Temp. (° C)	E_0 (v)	E_i (mv)	Potential decay (mv/min)	Method
1	Hydroquinone	Acetic – sulphuric acid (*a*)	0.0764 N $Ce(SO_4)_2$	0.7	24	0.696±0.004 (*b*)	15	—	Continuous
2	Toluhydroquinone	50% acetic acid (*c*)	0.1060 N Br_2 in 50% acetic acid	1.2	22	0.639±0.004 (*d*)	14	—	Continuous
3	Sulphone VIII	Acetic – sulphuric acid (*a*)	0.0768 N $Ce(SO_4)_2$	0.5	24	0.751±0.005	12	4.5	Discontinuous
4	Sulphone VIII	50% acetic acid (*c*)	0.1060 N Br_2 in 50% acetic acid	1.4	22	0.756±0.009	10	5.1	Discontinuous
5	Sulphone VIII	50% acetic acid + Na acetate (*e*)	0.0772 N Br_2 in 50% acetic acid	3.7	22	0.753±0.005	20	0.7	Discontinuous
6	Sulphone VIII	80% acetic acid (*c*)	0.0482 N Br_2 in 80% acetic acid	0.3	25	0.748±0.004	13	1.3	Discontinuous
7	Sulphone III (isopropyl model)	Acetic – sulphuric acid (*a*)	0.0768 N $Ce(SO_4)_2$	0.6	22	0.740±0.003		5.9	Discontinuous
8	Sulphone IX (ethyl model)	50% acetic acid + Na acetate (*e*)	0.0772 N Br_2 in 50% acetic acid	3.6	22	0.762±0.005	20	1.1	Discontinuous
9	Sulphone V (methyl-substituted)	Acetic – sulphuric acid (*a*)	0.0775 N $Ce(SO_4)_2$	0.6	24	0.716±0.005	11	0.5	Discontinuous
10	Sulphone V (methyl-substituted)	80% acetic acid (*c*)	0.1400 N Br_2 in 80% acetic acid	0.25	23	0.727±0.005	15	—	Continuous
11	Polymer X	80% acetic acid (*c*)	0.0495 N Br_2 in 80% acetic acid	0.30	25	0.753±0.005	8	0.3	Discontinuous
12	Polymer XI (methyl-substituted)	80% acetic acid (*c*)	0.0390 N Br_2 in 80% acetic acid	0.30	25	0.721±0.005	12	Nil	Discontinuous
13	Polymer XI (methyl-substituted)	80% acetic acid (*c*)	0.0540 N Br_2 in 80% acetic acid	0.35	26	0.718±0.008	5	—	Continuous

NOTE: (*a*) Prepared by mixing equal volumes of 0.085 N sulphuric acid and glacial acetic acid.
(*b*) Literature value: 0.696 v at 25° C in 50% acetic acid (23).
(*c*) Percentage by volume.
(*d*) Literature value: 0.643 v at 25° C (24).
(*e*) 0.07 g of sodium acetate added per ml of solvent.

suspected that drifting potentials were due to bromination. However, this is not likely, since the redox groups are very sensitive to oxidation and the bromine concentration was less than 0.005 *N*. In any case, if bromination of the quinonoid ring did take place, the potential would have risen rather than fallen during the course of titration. It was also found that the potential decay was about the same for both ceric sulphate and bromine titrations. The secondary reaction of the quinone was first order with respect to the quinone and it is possible that an addition of water, similar to the formation of hydroxynaphthahydroquinone (21) or hydroxyhydroquinone (25), is involved.

The oxidized form of the methyl-substituted sulphone V decomposed very slowly in 50% acetic acid and was completely stable in 80% acetic acid so that redox titration of this compound and its analogous polymer could also be carried out by the continuous method (Fig. 3). The observation that the methyl-substituted polymer was more stable than the unsubstituted polymer agreed with the results of Kun and Cassidy (2).

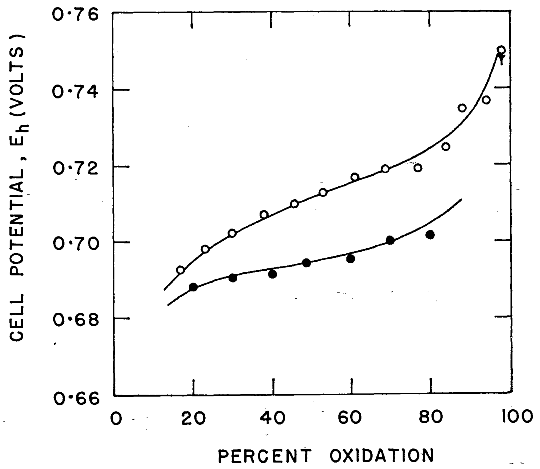


FIG. 3. Continuous titration of the methyl-substituted sulphone V and polymer XI (Nos. 10 and 13, Table II): ○ sulphone (pH 0.25); ● polymer (pH 0.35).

In addition to the instability mentioned above, all compounds and polymers could not be accurately titrated past about 90% oxidation because of a downward drifting potential.

TABLE III
Standard oxidation potentials

Compound	E_0 (v)	ΔE_0* (mv)
Hydroquinone	0.696	
Sulphone VIII	0.748–0.756	52–60
Sulphone III	0.740	44
Sulphone IX	0.762	66
Polymer X	0.753	57
Toluhydroquinone	0.639	
Sulphone V	0.716–0.727	77–88
Polymer XI	0.718–0.721	79–82

*The difference between E_0 of the compound and that of the parent hydroquinone.

Table III shows that the group R on the non-oxidizable benzenoid ring did not appear to influence the E_0 of the compound to any great extent. However, the nature of the substituent R′ on the quinonoid ring influences the oxidation potential of the compound. Carter in an unpublished contribution quoted by Evans and De Heer (26) stated that there is a linear relationship between the E_0 of many substituted quinones and Hammett's substituent constant (σ_p). We have examined the literature on this point and found such a relationship exists. Data on the derivatives reported here and on other derivatives being examined indicate that a similar relationship may apply for substituted 2,5-dihydroxydiphenyl sulphones.

The addition of the —$SO_2C_6H_4R$ group to the quinones caused an increase in potential over the parent quinone in all cases. This increase ranged from 44 to 66 mv for the hydroquinone derivatives and from 77 to 88 mv for the toluhydroquinone derivatives. The increase in potential is in agreement with the expected effect of the strongly electron withdrawing —SO_2Ar group. Fieser and Fieser (27) reported an increase of 121 mv for 1,4-naphthaquinone with a —$SO_2C_6H_4CH_3$ substituent. The above data and information on other derivatives now being examined indicate that there may be a linear relation between the change in E_0 (after addition of the —$SO_2C_6H_4R$ group) and Hammett's σ_p constant for the original substituent on the quinonoid nucleus.

The polymers were titrated in 80% acetic acid only, because of their limited solubility in other solvents. The oxidized polymer precipitated with the first addition of the oxidant, but seemed to remain well dispersed. The manner in which the measurements on the polymers were taken is illustrated in Fig. 4 and 5. The non-substituted polymer X (Fig. 4) appeared to be considerably more stable than its monomeric analogues (0.3 mv/minute potential decay, as compared to 1.3 mv/minute). The hydroquinone groups seemed to

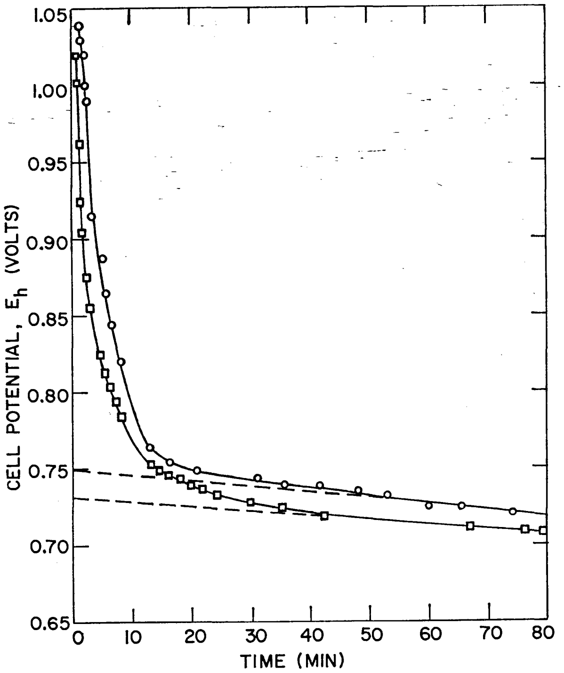


FIG. 4. Discontinuous titration of the polymer X (No. 11, Table II): □ 58.7; ○ 70.6% oxidation.

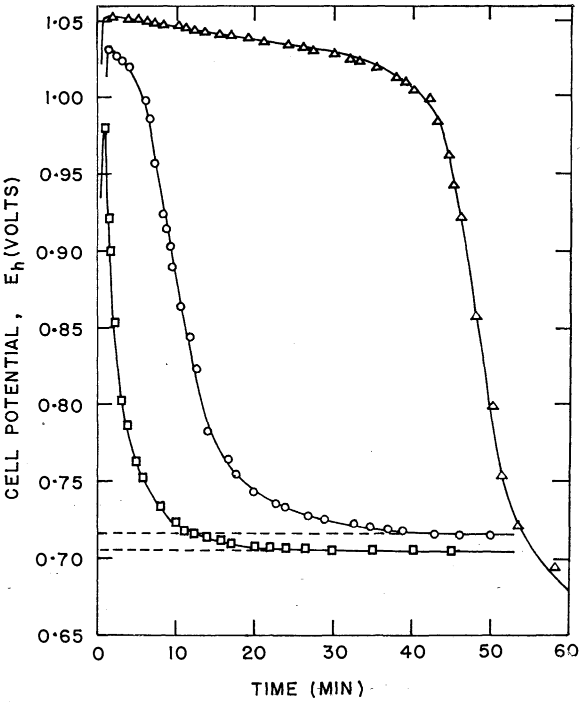


FIG. 5. Discontinuous titration of the polymer XI (No. 12, Table II): □ 51.5; ○ 77.3; △ 109.9% oxidation.

be readily accessible to oxidant, although equilibrium was attained slowly (Fig. 5), as has been noted by other investigators (18, 19). Stable equilibrium potentials were obtained for methyl-substituted polymer XI up to 80% oxidation. A downward drift of potential was obtained at higher percentage oxidation. Figure 5 also illustrates the instability of these materials when an excess of oxidant is used.

A suspension of polymer XI (80% oxidized) was reduced with hydrogen in the presence of a Pd catalyst. This stable polymer could not be completely reduced, probably because of the insoluble nature of the oxidized form. The partially reduced polymer was reoxidized and for the same degree of oxidation the titration curve compared well with the original titration curve.

It was found that the difference between the E_0's of the polymers and those of the corresponding intermediate and model compounds was small (-13 to $+9$ mv). These results are to be contrasted with those of Robinson, Fernandez-Refojo, and Cassidy (18) and Manecke (19), who reported E_0 values for polymers up to 100 mv higher than those of the model segmers. It is probable that our results are different, because the "substitution" due to polymer growth is far removed from the redox centers. However, the possible influence of polymeric structure on E_0 cannot be overlooked.

Robinson *et al.* (18) have stated that the variation of E_0 with the ratio of the oxidized to reduced form* of their polymers was due to nearest neighbor interactions. Manecke (19) made a similar statement with regard to his data on condensation redox polymers. It

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**From the experimental point of view this can be alternatively considered as a deviation of the index potential (E_i) from that expected for the simple bivalent redox reaction.*

should be pointed out that, if titrations are carried out in extremely dilute solutions, these interactions would be mainly between groups on the same chain. Examination of our results indicate that the index potentials of our polymers are closer to the theoretical value for a simple bivalent redox reaction than those of other investigators (18, 19). It thus appears that separation of the redox groups from the backbone chain by the benzene ring has considerably decreased the interaction of adjacent redox groups, as was suggested in Part I (1).

Investigation of more stable monomers and polymers is now in progress.

EXPERIMENTAL*

p-Isopropylbenzenesulphonyl Chloride (I)

This compound has been previously prepared (28, 29), but it was not isolated in a pure form.

Isopropylbenzene (cumene) (50 g, 0.416 mole) was added dropwise to chlorosulphonic acid (447 g, 3.83 mole), the temperature being maintained below 5°. The reaction mixture was poured onto crushed ice and an oil settled. This oil was separated, washed with water, and dried over anhydrous sodium sulphate. Distillation under reduced pressure gave 60 g (66%) of a colorless oil, b.p. 142–143°/12 mm, d_4^{25} 1.225, n_D^{25} 1.5350. Anal. Calc. for $C_9H_{11}ClO_2S$ (218.70): C, 49.42; H, 5.07; Cl, 16.22; S, 14.66. Found: C, 49.44; H, 5.45; Cl, 16.04; S, 14.79%. —SO_2Cl: Calc. 45.5. Found by the method of Barker *et al.* (30) 45.9%.

A derivative, *p*-isopropylbenzenesulphonamide, was prepared by reacting the sulphonyl chloride I with concentrated ammonium hydroxide. Crystallization from 60% ethanol gave white plates melting at 107–107.5° (previously reported 107–108° (31)). Anal. Calc. for $C_9H_{13}NO_2S$ (199.27): C, 54.24; H, 6.58; N, 7.03; S, 16.09. Found: C, 54.27; H, 6.60; N, 6.93; S, 15.94%.

p-Isopropylbenzenesulphinic Acid (II)

The sodium salt of this acid has been prepared by Gilman and Cason (32), but free sulphinic acid has not been reported.

The sulphonyl chloride I (20 g, 0.091 mole) was suspended in a solution of 150 g of sodium sulphite and 10 g of sodium hydroxide in 500 ml of water. The mixture was heated to 70°, stirred for 1 hour, allowed to cool to room temperature, and acidified with concentrated hydrochloric acid. A yellowish oil separated overnight. It was dissolved in 150 ml of diethyl ether and washed repeatedly with water. Evaporation of the solvent left 6.7 g (40%) of a yellowish viscous oil. The crude material gave a strong positive Smiles' test for aromatic sulphinic acids (33). It was used without further purification for the next step.

2,5-Dihydroxy-4′-isopropyldiphenyl Sulphone (III)

A suspension of *p*-benzoquinone (3.9 g, 0.036 mole) in 20% ethanol (150 ml) was added slowly to a suspension of the sulphinic acid II (6.7 g, 0.036 mole) in 20% ethanol (500 ml). The product settled overnight and crystallization from 25% ethanol gave fine, sandy crystals (4.4 g, 42%) melting at 147.5–148°. Anal. Calc. for $C_{15}H_{16}O_4S$ (292.34): C, 61.62; H, 5.52; S, 10.97. Found: C, 61.30; H, 5.66; S, 11.06%. Infrared spectrum: 1156 (s) and 1307 (s) (—SO_2—) (34), 3390 (s) (—OH) (1) cm^{-1}.

A derivative, 2,5-diacetoxy-4′-isopropyldiphenyl sulphone, was prepared by reacting the dihydroxy sulphone III with acetic anhydride and a drop of concentrated sulphuric acid as a catalyst. Crystallization from 30% ethanol gave white plates melting at 139.5–140°. Anal. Calc. for $C_{19}H_{20}O_6S$ (376.41): C, 60.62; H, 5.36; S, 8.52. Found: C, 60.53; H, 5.22; S, 8.43%.

p-(β-Bromoethyl)benzenesulphinic Acid (IV)

The preparation of this compound has been reported in Part I (1). The reduction of the corresponding sulphonyl chloride was carried out in an acid medium, instead of a more conventional reduction by alkaline sodium sulphite, because of the instability of the bromoethyl side chain in alkaline medium. Therefore in every run a large quantity (15–20%) of a by-product, *p*-(β-bromoethyl)phenyl *p*-(β-bromoethyl)benzenethiosulphonate, resulting from the disproportionation of the sulphinic acid, was obtained. This by-product was recrystallized once from 50% ethanol, and then twice from *n*-hexane, yielding white crystals, m.p. 78.5–79°. Anal. Calc. for $C_{16}H_{16}Br_2O_2S_2$ (464.24): C, 41.39; H, 3.47; Br, 34.43; S, 13.82. Found: C, 41.29; H, 3.73; Br, 34.61; S, 13.61%.

The same thiosulphonate was obtained by refluxing freshly recrystallized sulphinic acid IV for 2.5 hours in glacial acetic acid containing 4% of 1:1 sulphuric acid. The reaction mixture was diluted with water and cooled. The precipitate was filtered and recrystallized once from 50% ethanol and twice from *n*-hexane, yielding white crystals, m.p. 78.5–79°. This product gave no depression in mixed melting point with the analyzed sample.

**Melting points are corrected. All ethanol solutions are reported on a percentage by volume basis. Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.*

2,5-Dihydroxy-4-methyl-4′-(β-bromoethyl)diphenyl Sulphone (V)

A solution of toluquinone (12.7 g, 0.104 mole) in absolute ethanol (125 ml) was added dropwise to a suspension of the sulphinic acid IV (26 g, 0.104 mole) in 30% ethanol (1 liter). Stirring was continued for 1 hour, the mixture was diluted with 1125 ml of water and chilled for several hours in an ice bath. The precipitate was recrystallized from 25% ethanol, yielding 21 g (55%) of a white product melting at 121–122°. Anal. Calc. for $C_{15}H_{15}BrO_4S$ (371.25): C, 48.53; H, 4.07; Br, 21.53; S, 8.63. Found: C, 48.73; H, 4.14; Br, 21.51; S, 8.74%. Infrared spectrum: 1142 (s) and 1308 (s) ($-SO_2-$) (34), 3390 (s) ($-OH$) (1) cm^{-1}.

A derivative, 2,5-diacetoxy-4-methyl-4′-(β-bromoethyl)diphenyl sulphone, was prepared. Crystallization from 25% ethanol gave a white product melting at 59–60°. Anal. Calc. for $C_{19}H_{19}BrO_6S$ (455.33): C, 50.10; H, 4.20; Br, 17.55; S, 7.04. Found: C, 50.16; H, 4.26; Br, 17.46; S, 7.23%.

In certain runs, small amounts of a material of much higher melting point, having all the characteristics of a dihydroxydiphenyl sulphone, were isolated. This was probably 2,5-dihydroxy-3-methyl-4′-(β-bromoethyl)diphenyl sulphone. Repeated recrystallizations from 20% ethanol and mixtures of benzene and petroleum ether yielded a white product melting at 146–147°. Anal. Calc. for $C_{15}H_{15}BrO_4S$ (371.25): C, 48.53; H, 4.07; Br, 21.53; S, 8.63. Found: C, 48.88; H, 4.20; Br, 23.46; S, 9.15%. Infrared spectrum: 1147 (s) and 1302 (s) ($-SO_2-$) (34), 3390 (s) ($-OH$) (1) cm^{-1}.

Attempts to pyranylate this material fully under a variety of conditions failed. Only a monopyranylated derivative, 2-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-4′-(β-bromoethyl)diphenyl sulphone, melting at 112–113°, was obtained. Anal. Calc. for $C_{20}H_{23}BrO_5S$ (455.39): C, 52.75; H, 5.09; Br, 17.55; S, 7.04. Found: C, 52.86; H, 5.05; Br, 17.29; S, 7.03%.

The monopyranylated sulphone was easily decomposed by treatment with hydrochloric acid, yielding the dihydroxy sulphone (3-methyl isomer).

2,5-Bis-(2-tetrahydropyranyloxy)-4-methyl-4′-(β-bromoethyl)diphenyl Sulphone (VI)

This preparation was similar to that previously reported for a non-substituted hydroquinone derivative (1). One modification included the precipitation of the final product from an absolute ethanol solution of the crude product by *n*-hexane. The pale yellow solid obtained (4.5 g, 77%) melted at 51–53°. Anal. Calc. for $C_{25}H_{31}BrO_6S$ (539.48): C, 55.65; H, 5.79; Br, 14.81; S, 5.94. Found: C, 55.37; H, 5.50; Br, 14.61; S, 6.29%.

Repeated recrystallizations did not improve the melting point range. This product is believed to be a mixture of stereoisomers of the type discussed previously (1).

2,5-Bis-(2-tetrahydropyranyloxy)-4-methyl-4′-vinyldiphenyl Sulphone (VII)

The procedure was similar to that previously reported for a non-substituted monomer (1). Potassium bromide precipitated during the course of the reaction. A pale yellow liquid (4.1 g, 87%), which gave a negative test for halogen, was obtained. It was insoluble in dilute sodium hydroxide solution, which indicated that the hydroxy groups remained protected. Attempts to purify the monomer VII by distillation were unsuccessful because of its high boiling point and instability at high temperatures.

2,5-Dihydroxy-4′-ethyldiphenyl Sulphone (IX)

2,5-Dihydroxy-4′-(β-bromoethyl)diphenyl sulphone (VIII) (1) (8.5 g, 0.024 mole) was dissolved in a hot solution of 300 ml of water, 70 ml of concentrated sulphuric acid, and 120 ml of glacial acetic acid, to which 0.5 g of zinc had been added. The solution was refluxed for 7 hours during which an additional 4.5 g of zinc was added in small portions. When the solution was diluted with 200 ml of water and cooled, a fluffy white precipitate settled. The crude product was purified by dissolution in 5% sodium hydroxide solution containing a trace of sodium hydrosulphite and precipitation with 25% acetic acid. A white product (3.8 g, 58%) melted at 181.5–182°. Anal. Calc. for $C_{14}H_{14}O_4S$ (278.31): C, 60.42; H, 5.07; S, 11.52. Found: C, 60.15; H, 5.30; S, 11.29%.

A derivative, 2,5-diacetoxy-4′-ethyldiphenyl sulphone, was prepared. Crystallization from 25% ethanol gave white plates melting at 144–144.5°. Anal. Calc. for $C_{18}H_{18}O_6S$ (362.39): C, 59.65; H, 5.01; S, 8.85. Found: C, 59.32; H, 4.81; S, 8.78%.

Poly(2,5-dihydroxy-4′-vinyldiphenyl Sulphone) (X)

2,5-Bis-(2-tetrahydropyranyloxy)-4′-vinyldiphenyl sulphone (1) (3.006 g, 0.0068 mole) and α,α'-azodiisobutyronitrile (30 mg) were dissolved in 15 ml of toluene and heated in a sealed tube at 95–96° for 72 hours. Precipitation with methanol and reprecipitation with petroleum ether (80–100°) from a toluene solution yielded a white fluffy product (1.91 g, 63%), insoluble in 5% sodium hydroxide solution, with a softening range of 165–185°. Anal. Calc. for $(C_{24}H_{28}O_6S)_n$ (444.52): S, 7.21. Found: S, 6.85%.

The polymer was treated with 50% hot acetic acid to remove the tetrahydropyranyl groups, dissolved in dioxane, and precipitated by petroleum ether. A light tan product, soluble in 5% sodium hydroxide (yellow solution), softened at 200–210°. Anal. Calc. for $(C_{14}H_{12}O_4S)_n$ (276.30): S, 11.60. Found: S, 9.79%.

Poly(2,5-dihydroxy-4-methyl-4′-vinyldiphenyl Sulphone) (XI)

The crude monomer VII (2.298, 0.0050 mole) and α,α'-azodiisobutyronitrile (28.3 mg) were heated in a sealed tube at 95° for 24 hours. The very viscous pale amber polymerization product was dissolved in 15 ml of chloroform and precipitation by petroleum ether (80–120°) yielded a white product (1.36 g, 55%), insoluble in absolute ethanol and 5% sodium hydroxide solution, sparingly soluble in benzene and toluene, with a softening range of 170–185°. Anal. Calc. for $(C_{25}H_{30}O_6S)_n$ (458.56): S, 6.99. Found: S, 8.66%.

Treatment with 50% acetic acid and precipitation from dioxane solution by petroleum ether gave a white product, soluble in 5% sodium hydroxide solution (yellow solution), with a softening range of 175–185°. Anal. Calc. for $(C_{15}H_{14}O_4S)_n$ (290.33): S, 11.05. Found: S, 10.01%.

Potentiometric Titrations

(a) Apparatus

The assembly consisted of a saturated calomel electrode connected by a saturated potassium chloride bridge* to the titration vessel equipped with two bright platinum electrodes, a glass electrode, and a magnetic stirrer. The cell potentials were measured using a precision differential d-c. voltmeter (Model 801H, John Fluke Mfg. Co.). The change of potential with time was measured using a potential recorder (Model A-70, John Fluke Mfg. Co.). Nitrogen was purified by passage through Fieser's solution (36) and lead acetate solution.

(b) Continuous Titration

These titrations were performed in a conventional manner (35). Some of the experimental runs are listed in Table II. Between 0.685 and 1.01 meq of the compound to be titrated in 80 ml of solvent was used in each titration.

(c) Discontinuous Titration

A typical titration (No. 3 in Table II) is described. A stock solution of the sulphone VIII (equiv. wt. 178.61), containing 2.8010 g (0.0157 equiv.) in 250 ml of 90% acetic acid, was prepared. Ten milliliters of this solution (112.0 mg, 0.628 meq) was added to 240 ml of the acetic–sulphuric acid in the titration vessel. Nitrogen was bubbled through the solution and the solution stirred for 1/2 hour. One milliliter of the oxidizing agent, 0.0768 N ceric sulphate (corresponding to 12.2% oxidation), was added rapidly and the cell potential recorded using a potential recorder. The potential at zero time was obtained by extrapolation of the potential–time curve (Fig. 1). The same procedure was repeated by taking another 10 ml of the stock solution, adding 2.0 ml of the oxidant (corresponding to 24.4% oxidation), and recording the change of potential with time again. A third curve was obtained when 3.0 ml of the oxidant (36.7% oxidation) was added to another 10 ml sample, and so on. A composite titration curve was then constructed from the initial (zero time) potentials (Fig. 2). The standard oxidation potential (E_0) was calculated, as shown in Table I.

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**Before titration the saturated* KCl *bridge was conditioned several hours in the solvent to be used to ensure stability of junction potential (35).*

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