OXIDATION–REDUCTION POLYMERS

I. SYNTHESIS OF MONOMERS[1]

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ABSTRACT

The preparation of two new monomers, 2,5-bis-(2-tetrahydropyranyloxy)-4′-vinyldiphenyl sulphone and 2-tetrahydropyranyl-4′-vinylphenyl thioether, for the synthesis of redox polymers is described.

The first systematic discussion of redox (electron exchange) polymers was presented by Cassidy (1). These polymers were divided into two classes: (i) those in which the active redox group formed a part of the backbone of the polymer chain and (ii) those in which the active group was a substituent on the polymeric chain. Examples of the first class are various condensation resins of hydroquinones, naphthaquinones, and anthraquinones with phenol and formaldehyde (2–6).

Polyvinylhydroquinone (7) is an example of the second class. Monomers such as vinylhydroquinone dibenzoate (8) and diacetate (8, 9) were produced, since it was soon realized that in order to obtain high molecular weight polymers, the hydroxyl groups in the monomer should be protected. Other vinyl monomers were synthesized, such as vinylhydroquinone bis-methoxymethyl ether (10), 1-vinyl-2,4,5-trimethyl-3,6-dihydroxybenzene (11), β-vinylanthraquinone (12, 13), and 2-methyl-3-vinyl-1,4-naphthaquinone (14). A polyhydroquinone was prepared from 3-(2,5-diacetoxyphenyl) propylene oxide (15).

Redox polymers of the second class have also been prepared by reactions with polymers. For example, polyaminostyrene was first diazotized and then reacted with an alcoholic solution of *p*-benzoquinone or 1,4-naphthaquinone (16, 17). Polyaminostyrene was also reacted directly with a naphthaquinone (16). Polyvinyl alcohol was reacted with β-formylanthraquinone (18).

Polymers of known and easily varied structure have obvious advantages in any systematic study of the properties of redox polymers. Our efforts have therefore been directed towards the synthesis of a vinyl monomer for which the oxidation potential could be varied in a simple manner. This was accomplished by joining a hydroquinone group through a stable sulphone bridge with another benzene ring containing —CH_2CH_2Br side chain. The latter can easily be dehydrobrominated to give a vinyl group. A simple hydroquinone could be replaced by a substituted hydroquinone or a naphthahydroquinone. In this way, different redox polymers could be prepared and their oxidation potentials measured and compared with simple homologues.

Vinyl monomers, reported so far, have generally one property in common: the vinyl group is attached directly to the same benzenoid ring which undergoes a redox cycle. It is possible that the interactions between adjacent redox residues will be different from those of a simple polyvinylhydroquinone (1, 7), since the redox group in the monomer reported here is further removed from the backbone chain.

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[1] *Manuscript received August 31, 1961.*
Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario. Taken from the theses submitted by J. Yannopoulos and W. Metanomski to the School of Graduate Studies, University of Toronto in partial fulfillment of the requirements for the degree of Master of Applied Science in May and January, 1960, respectively.

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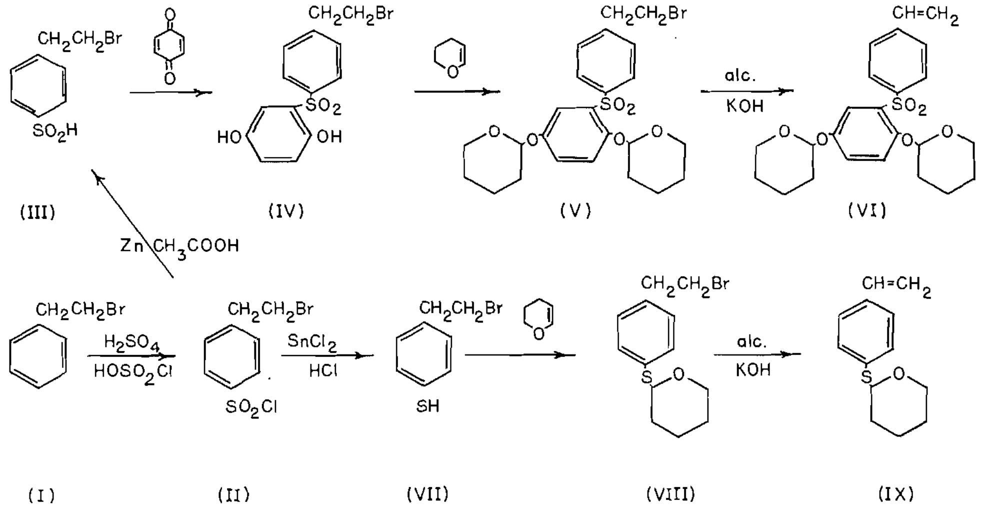
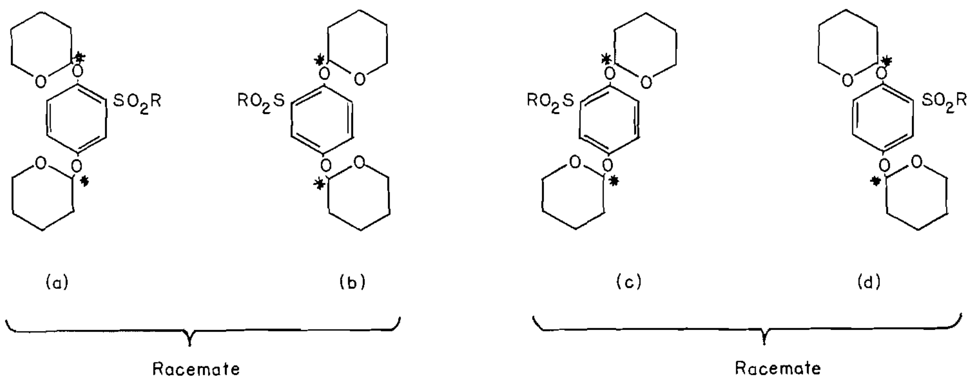
Can. J. Chem. Vol. 39 (1961)

The synthesis of a new monomer, 2,5-bis-(2-tetrahydropyranyloxy)-4′-vinyldiphenyl sulphone (VI) was achieved in five steps according to the scheme shown below.



β-Bromoethylbenzene (I) was chlorosulphonated and then reduced by zinc in acetic acid to *p*-(β-bromoethyl) benzenesulphinic acid (III). The sulphinic acid was reacted with *p*-benzoquinone to give a diphenyl sulphone IV. The hydroxyl groups were protected by making use of a reaction with 2,3-dihydropyran (19) to give a bis-tetrahydropyranyl ether V. Finally, the side chain was dehydrobrominated using an alcoholic solution of potassium hydroxide.

The possibility of the existence of two racemic diastereoisomers of V has not been overlooked. Stern, English, and Cassidy (20) isolated two isomers of bis-2-tetrahydropyranyl ether of hydroquinone, assigning to them the meso and racemic configurations. In our case none of the isomers has a plane of symmetry because of the presence of an additional substituent group —SO_2R, and therefore two racemic diastereoisomers are expected, as shown below.



R= $C_6H_4CH_2CH_2Br$

The hydroxyl groups could also be protected by acetylation or benzoylation, but the esters partially decomposed during dehydrobromination. Dehydrobromination of these esters using other bases, such as pyridine, lutidine, or triethanolamine, is being studied and shows some promise.

The acetal bond, on the other hand, is very stable under strong alkaline conditions. The tetrahydropyranyl groups can be removed from the polymers by an acid treatment, exposing free —OH groups.

Polymers with thiol groups are of interest as another type of redox resin and ion exchanger. Brubaker (21) has patented the synthesis of polyvinylthioacetate and pointed out the oxidation of polyvinylthiol to polyvinyldisulphide. Polythiolstyrene was prepared by Gregor, Dolar, and Hoeschele (22), and Seifert (23) by various reactions on the benzene ring of the polystyrene. Similarly, poly(vinylbenzylmercaptan) was prepared by Parrish (24), Okawara, Nakagawa, and Imoto (25), and Trostyanskaya and Tevlina (26). Hamamura, Tatsukawa, and Uno (27) produced polythiol resins by the condensation of various thiophenols with formaldehyde. Overberger and Lebovits (28) were the first to synthesize a monomer, *p*-vinylphenyl thioacetate, which was polymerized and saponified to give poly-*p*-thiolstyrene.

A new monomer, 2-tetrahydropyranyl-4′-vinylphenyl thioether (IX) was prepared according to the scheme shown above. *p*-(β-Bromoethyl)benzenesulphonyl chloride (II) was reduced to *p*-(β-bromoethyl)thiophenol (VII). This reduction presented some difficulty since with reducing agents evolving hydrogen *in situ*, such as zinc in acidic medium, or lithium aluminum hydride (in the presence of sulphonyl group (29)), there was a simultaneous reduction of both $—SO_2Cl$ and $—CH_2CH_2Br$ groups. The final product of such a reduction was *p*-ethylthiophenol or a mixture of the sulphinic acid III and *p*-ethylthiophenol. The successful reduction of II to VII was achieved by using stannous chloride and hydrogen chloride in acetic acid, in which case no hydrogen was evolved. The thiol group can add across an olefinic bond (28) and therefore this group must be protected before dehydrobromination. Pyranylation with 2,3-dihydropyran has been used for this purpose. After the polymerization tetrahydropyranyl groups can be removed by acid treatment, exposing free —SH groups.

Both monomers were polymerized and copolymerized with other monomers. After acid treatment the polymers exhibited the expected redox properties and, in addition, the polymers with thiol groups had a high affinity for metal cations. A redox membrane was produced and preliminary experiments indicated the transfer of "oxidizing power" through the membrane with an apparent diffusion coefficient of about 5×10^{-7} cm^2/second. Investigation of the properties of these redox polymers in bead and membrane form is now in progress.

EXPERIMENTAL*

p-(β-Bromoethyl)benzenesulphonyl Chloride (II)

This compound has been previously prepared by Spinner, Ciric, and Graydon (30). The present procedure is based on the modifications introduced by Worsley (31).

A solution of β-bromoethylbenzene (I) (185 g, 1 mole) and acetonitrile (82 g, 2 moles) was added dropwise to 30% fuming sulphuric acid (265 g) at 20–30°. To the reaction mixture, chlorosulphonic acid (290 g, 2.5 mole) was added, the temperature being kept at 40–45°. Stirring was continued for 1 hour at the same temperature range. The mixture

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**Melting points are corrected. Microanalyses were done by Micro-Tech Laboratories, Skokie, Illinois, and Galbraith Laboratories, Inc., Knoxville, Tenn.*

was poured onto crushed ice and allowed to stand in a refrigerator for 30 minutes. The precipitate was filtered and recrystallized from petroleum ether (boiling range 80–100°), yielding 220 g (78%), m.p. 54–54.5° (previously reported 54–55° (30)).

Infrared spectrum: 1179 (s) and 1383 (s) (—SO_2—) cm^{-1} (32).

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

The sulphonyl chloride II (50 g, 0.177 mole) was dissolved in glacial acetic acid (250 ml) at room temperature and zinc dust (15 g, 0.23 mole) was added in small portions with constant stirring. The temperature was kept at 25–35°. After 1 hour of additional stirring at 30–35°, concentrated hydrochloric acid (150 ml) and then distilled water (125 ml) were added slowly. The reaction mixture was heated to 80°. On cooling of the mixture in an ice bath a white precipitate formed which, recrystallized from hot water, gave 32.5 g (74%) of a product melting at 95–95.5°. The compound changed rapidly on drying (over 1 hour) (33), on standing, and on further recrystallization, as was evidenced by widely varying melting points. Thus, all attempts to provide a sample suitable for analysis failed.

Reduction of the sulphinic acid III with stannous chloride in glacial acetic acid saturated with hydrogen chloride gave *p*-(β-bromoethyl)thiophenol (VII), a product identical with that produced by a direct reduction of the sulphonyl chloride II, as reported below. B.p. 92.5–93°/1.2 mm. Anal. Calc. for C_8H_9BrS (217.13): C, 44.25; H, 4.18; Br, 36.80; S, 14.76. Found: C, 45.05; H, 4.72; Br, 36.28; S, 14.43%.

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

This reaction is based on 1,4 addition of an aromatic sulphinic acid to a quinone, first reported by Hinsberg (34).

After many trials with solutions in various solvents, the following procedure, which yielded best results, was adopted. A suspension of *p*-benzoquinone (13.5 g, 0.125 mole) in water (500 ml) was added slowly to a suspension of the sulphinic acid III (31 g, 0.125 mole) in water (1 liter) at room temperature. A gradual change in the consistency of the suspended solid took place, the final product being very fluffy. The typical yellow color of quinone disappeared. Crystallization from 25% (by volume) ethanol gave a light sandy powder (36 g, 81%) melting at 130–130.5°. Anal. Calc. for $C_{14}H_{13}BrO_4S$ (357.22): C, 47.07; H, 3.67; Br, 22.37; S, 8.97. Found: C, 47.26; H, 3.81; Br, 22.61; S, 9.01%. Infrared spectrum: 1152 (s) and 1302 (s) (—SO_2—) (32), 3390 (s) (—OH) cm^{-1}.

A derivative, 2,5-diacetoxy-4′-(β-bromoethyl)diphenyl sulphone, was prepared by reacting the dihydroxysulphone IV with acetic anhydride and a drop of concentrated sulphuric acid as a catalyst. Crystallization from 50% (by volume) ethanol gave a white product melting at 110–110.5°. Anal. Calc. for $C_{18}H_{17}BrO_6S$ (441.30): C, 48.99; H, 3.88; Br, 18.11; S, 7.27. Found: C, 49.33; H, 3.96; Br, 18.25; S, 7.31%. Infrared spectrum: 1153 (s) and 1324 (s) (—SO_2—) (32), —OH band absent.

Another derivative, 2,5-benzoquinone-4′-(β-bromoethyl)phenyl sulphone, was prepared by oxidizing the dihydroxysulphone IV with silver oxide. Orange needles precipitated by high boiling point petroleum ether from a diethyl ether solution melted at 104–104.5°. Anal. Calc. for $C_{14}H_{11}BrO_4S$ (355.21): C, 47.33; H, 3.12; Br, 22.50; S, 9.03. Found: C, 47.10; H, 3.15; Br, 22.94; S, 9.20%.

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

The dihydroxysulphone IV (10 g, 0.028 mole) was dissolved in 2,3-dihydropyran (15 g, 0.178 mole) containing a few milligrams of *p*-toluenesulphonic acid as a catalyst. The solution was stirred at room temperature for 2 hours and left at the same temperature overnight. The volatile materials were then removed under vacuum, and the solid residue taken up in chloroform – diethyl ether (5:2) mixture (150 ml). The solution was shaken with several portions of 5% sodium hydroxide solution to remove the unreacted IV, washed with water, dried over anhydrous sodium sulphate, and concentrated. The precipitate formed was filtered and crystallization from 70% (by volume) ethanol gave 9.8 g (67%) of white crystals melting at 133–134°. Anal. Calc. for $C_{24}H_{29}BrO_6S$ (525.45): C, 54.86; H, 5.56; Br, 15.21; S, 6.10. Found: C, 55.05; H, 5.68; Br, 14.98; S, 5.97%.

This solid is one of the two racemates mentioned in the earlier discussion. Attempts to recover a presumably lower melting and more soluble racemate from the chloroform–ether mother liquor were not successful.

The pyranylated sulphone V decomposed on treatment with hydrochloric acid, giving the dihydroxysulphone IV, melting at 130–131°. This product gave no depression in mixed melting point with the original IV. The other decomposition product was 5-hydroxypentanal, identified by its 2,4-dinitrophenylhydrazone melting at 108.5–109° (reported m.p. 109° (35)).

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

A 10% alcoholic solution of potassium hydroxide (1.6 g KOH, 0.028 mole) was added dropwise to a boiling solution of the diphenyl sulphone V (12 g, 0.023 mole) in benzene (150 ml). The mixture was refluxed on a steam bath for 30 minutes. The precipitated potassium bromide was removed by filtration and the filtrate evaporated to dryness *in vacuo* at room temperature. The residue after a thorough washing with water was crystallized from 50% (by volume) ethanol. The white crystals obtained (6.5 g, 64%) melted at 126.5–127°. Anal. Calc. for $C_{24}H_{28}O_6S$ (444.52): C, 64.84; H, 6.35; S, 7.21. Found: C, 64.67; H, 6.43; S, 7.25; C, 64.60; H, 6.44; S, 7.35%.

p-(β-Bromoethyl)thiophenol (VII)

p-(β-Bromoethyl)benzenesulphonyl chloride (II) was reduced to VII with stannous chloride and hydrogen chloride (36, 37).

Dry hydrogen chloride was bubbled into a suspension of stannous chloride dihydrate (203.5 g, 0.9 mole) in glacial acetic acid (800 ml) at room temperature until the suspension became clear and homogeneous; 71.5 g (1.96 mole) of hydrogen chloride was required. *p*-(β-Bromoethyl)benzenesulphonyl chloride (II) (42.5 g, 0.15 mole) was added and the mixture was shaken for 15 minutes. Evolution of heat was observed during the reaction. On shaking of the mixture with 1:1 hydrochloric acid, a yellowish oil settled. This oil was separated and washed with concentrated hydrochloric acid and then water. Distillation under reduced pressure gave 26.4 g (81%) of a colorless oil* (b.p. 92.5–93°/ 1.2 mm). Anal. Calc. for C_8H_9BrS (217.13): C, 44.25; H, 4.18; Br, 36.80; S, 14.76. Found: C, 44.53; H, 4.36; Br, 36.76; S, 14.91%.

A derivative, mercuric mercaptide of *p*-(β-bromoethyl)thiophenol, was prepared by adding an excess of 20% mercuric acetate solution in dilute acetic acid to the thiophenol VII. Crystallization from benzene gave snow white crystals melting at 115.5–116.5°. Anal. Calc. for $C_{16}H_{16}Br_2HgS_2$ (632.86): C, 30.36; H, 2.55; Br, 25.26; Hg, 31.70; S, 10.13. Found: C, 30.63; H, 2.67; Br, 25.37; Hg, 31.25; S, 10.33%.

Another derivative, *p*-(β-bromoethyl)phenyl thiobenzoate was prepared by reacting the thiophenol VII with benzoyl chloride dissolved in benzene in the presence of pyridine. Crystallization from ethanol gave white needles, m.p. 49–49.5°. Anal. Calc. for

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**This thiophenol (as well as p-ethylthiophenol) was found to be a very strong skin irritant, a well-known property of thiophenols (38).*

$C_{15}H_{13}BrOS$ (321.23): C, 56.08; H, 4.08; Br, 24.88; S, 9.98. Found: C, 56.29; H, 4.70; Br, 24.90; S, 9.74%.

2-Tetrahydropyranyl-4′-(β-bromoethyl)phenyl Thioether (VIII)

The procedure is based on a method of Parham and DeLaitsch (19).

The thiophenol VII (26.3 g, 0.12 mole) was mixed with a 65% excess of 2,3-dihydropyran (27 g, 0.32 mole), 1 ml of ethereal solution of HCl (0.002 mole) was added, and the mixture refluxed for 48 hours at 30°. The mixture was shaken with three portions of 5% sodium hydroxide solution and washed with water. The excess of dihydropyran was removed by evaporation under reduced pressure. Attempts to purify the thioether VIII by distillation were unsuccessful because of its high boiling point and the instability of the brominated side chain at high temperatures.

2-Tetrahydropyranyl-4′-vinylphenyl Thioether (IX)

Approximately 30% excess of 10% alcoholic solution of potassium hydroxide was added to the crude thioether VIII. The mixture was refluxed for 30 minutes. The precipitated potassium bromide was removed by filtration, the filtrate was washed with water, dried over anhydrous sodium sulphate, and distilled under reduced pressure. Traces of *p-tert*-butylcatechol were added as a polymerization inhibitor prior to drying and distillation. The product was a colorless viscous oil (b.p. 134–135°/1.35 mm). Bromination calculated for 1.000 double bond; found 0.998. Anal. Calc. for $C_{13}H_{16}OS$ (220.33): C, 70.86; H, 7.32; S, 14.56. Found: C, 70.86; H, 7.52; S, 13.51; C, 71.72; H, 7.70; S, 15.02%.

ACKNOWLEDGMENTS

The authors wish to thank Mr. Z. May for his helpful suggestions. The financial assistance of the School of Engineering Research of the University of Toronto (to J. Y. and W. M.) and of Ontario Research Foundation (to W. M.) is gratefully acknowledged.

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