p-Styrenesulfinic Acid and Its Polymer as Reactants

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The free-radical aqueous polymerizations of *p*-styrenesulfinates (Na, K, NH_4, $NHEt_3$-salts) provided water-soluble polymers with high molecular weights at low conversions. The polymers contained 62—84% of the sulfinate unit and indicated half-oxidation potentials ranging from 340 to 415 mV. The nucleophilic reactions of the sodium polysulfinate [poly(sulfinic acid)] prepared from cross-linked polystyrene are highly dependent upon the swelling nature of the solvent. The reactions consisting of (A) simple displacements with activated halomethyl groups, (B) reductive additions to quinonoid compounds such as TCNQ and alizarin, and (C) displacements of the activated aromatic nitro groups, *e.g.*, of 2,4,7-trinitrofluorenone have been investigated and the results compared with those of *p*-toluene and *p*-styrenesulfinates. The effect of the solvent on the reaction rate is in the order: DMSO>DMF> HMPA.

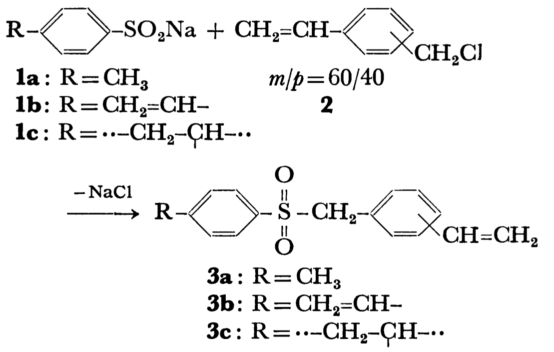
Arenesulfinic acids and their salts are of chemical interest since they are mild reductants and take the role of nucleophiles in many reactions.

From the standpoint of obtaining a novel and usefuel polymer reagent, *p*-styrenesulfinic acid and its salts have been synthesized and it has been shown that polymers of high-molecular weights are formed.[1]

This paper summarizes the results of the investigations conducted on the redox properties of the pendant polymers synthesized from *p*-styrenesulfinates by free-radical polymerizations as well as the nucleophilic reactions of the *p*-styrenesulfinate (sulfinic acid) polymers prepared from polystyrene by means of polymer reactions, together with those of *p*-toluenesulfinate and *p*-styrenesulfinates (sulfinic acids).

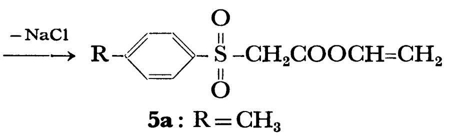
The following nucleophilic reactions were examined:

(1)



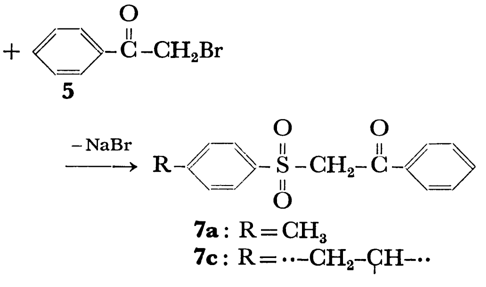
1a: R=CH_3 *m*/*p*=60/40 **2**
1b: R=CH_2=CH-
1c: R=…CH_2-CH-…
-NaCl
3a: R=CH_3
3b: R=CH_2=CH-
3c: R=…CH_2-CH-…

(2) **1a, c** + $ClCH_2COOCH=CH_2$ **4**



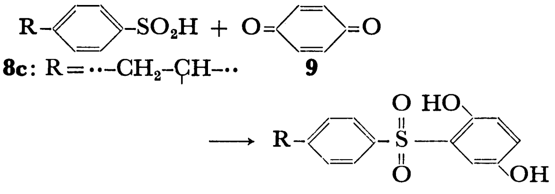
-NaCl
5a: R=CH_3
5c: R=…CH_2-CH-…

(3) **1a, c** +



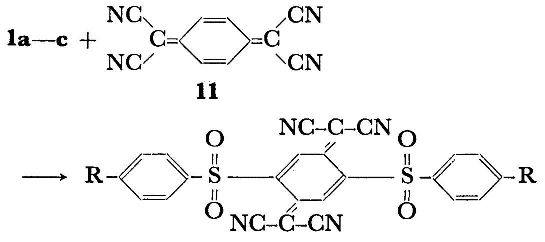
5
-NaBr
7a: R=CH_3
7c: R=…CH_2-CH-…

(4)



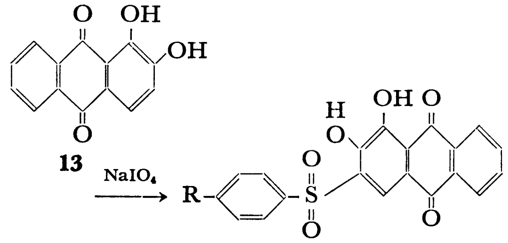
8c: R=…CH_2-CH-… **9**
10c: R=…CH_2-CH-…

(5) **1a—c** +



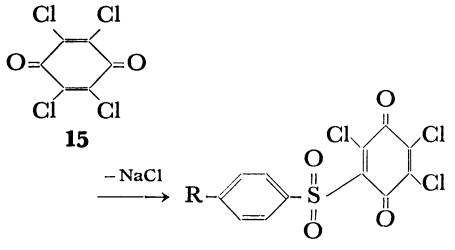
11
12a: R=CH_3
12b: R=CH_2=CH-
12c: R=…CH_2-CH-…

(6) **1c** +



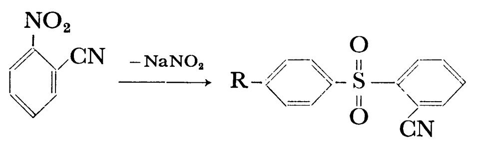
13 $NaIO_4$
14c: R=…CH_2-CH-…

(7) **1a, c** +



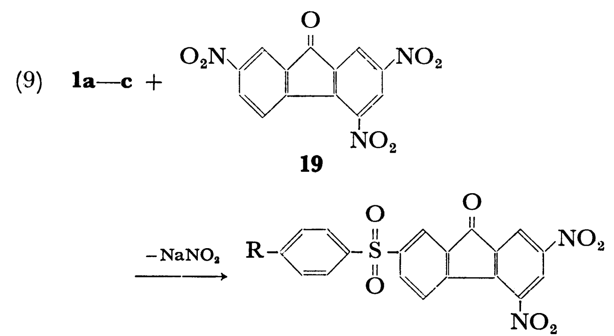
15
-NaCl
16a: R=CH_3
16c: R=…CH_2-CH-…

(8) **1c** +



$-NaNO_2$
17 **18c**: R=…CH_2-CH-…

(9) **1a—c** +



20a: $R=CH_3$
20b: $R=CH_2=CH-$
20c: $R=\cdots CH_2-CH-\cdots$

(10) **1c** +

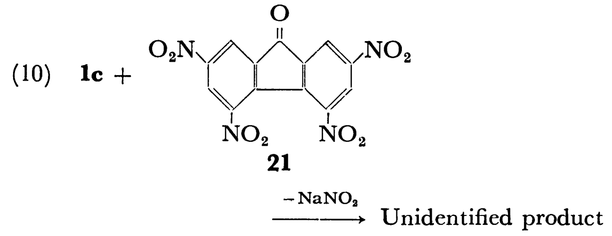
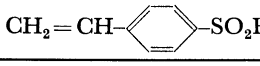


Table 1. Polymerization behavior of



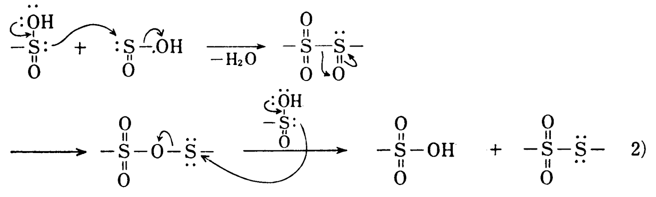
$CH_2=CH-C_6H_4-SO_2R$[a)]

R	Conversion/%	Precipitant	$[\eta]$ b) / dl g⁻¹	Sulfinate c) content/%	E_0 d) / mV
Na	29.7	MeOH	6.9	78	410
K	24.2	DMF	5.5	63	370
NH_4	31.0	EtOH	7.9	62	415
$NHEt_3$	45.6	*t*-BuOH	9.3	84	340

a) Aqueous solution with 10% monomer and 0.1% KPS. 70 °C×24 h. b) In water at 30 °C. c) By oxidative titration with bromine–water. d) Half-oxidation potential against a saturated calomel electrode at 20 °C.

Results and Discussion

The free-radical polymerizations of four *p*-styrenesulfinates as listed in Table 1 proceeded smoothly to afford water-soluble polymers of high molecular weights. The conversions were however rather low and the sulfinate contents in the polymers were reduced by possible side reactions:



The low conversion data listed in Table 1 appear to be caused by the reductive actions of the sulfinates which lead to the disappearances of growing radicals as well as the physical loss of polymers into precipitants.

The values of $[\eta]$ are, nevertheless, high, a characteristic of the aqueous polymerizations of ionic vinyl monomers.

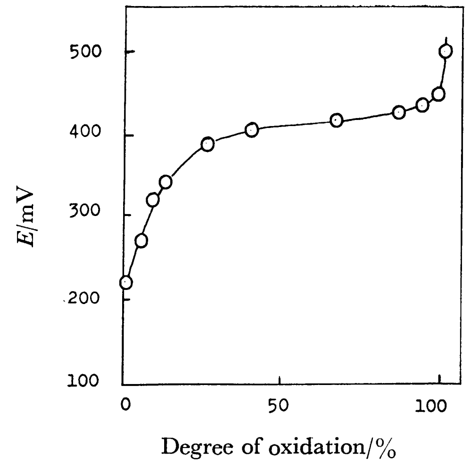


Fig. 1. Typical oxidative titration curve for sulfinate polymers. Sodium poly *p*-styrenesulfinate in aqueous solution (4×10^{-3} mol dm^{-3}) was titrated with aqueous bromine (0.0435 mol dm^{-3}) at 20 °C. *E*, oxidation potential against sat. calomel electrode.

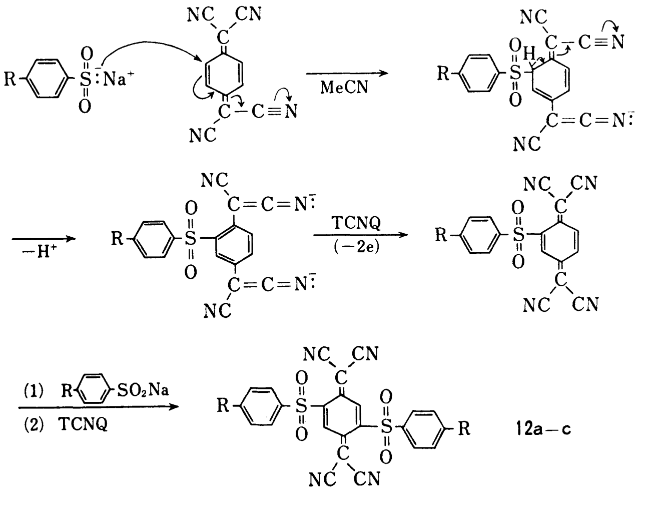
The half-oxidation potential (E_0) for each sulfinate ranges from 340 to 410 mV and is comparable with that (375 mV) for hydroquinone under the same titration conditions, indicating that these polymers are weak reductants. Figure 1 illustrates a typical oxidative titration curve for a sulfinate polymer.

The nucleophilic reactions of the sulfinate polymers and their low-molecular weight homologs investigated have been classified into three categories.

Simple Displacements (Reactions 1, 2, 3, and 7). Reactions 1, 2, and 3 are quite simple nucleophilic reactions, in which the sulfinate anions attack the activated halomethyl groups with the elimination of sodium halides. Satisfactory yields are attained for **1a** and **1b** at room temperature in dipolar aprotic solvents such as DMSO, DMF, and HMPA. In polymer **1c**, on the other hand, which was prepared from a porous crosslinked polystyrene, the swelling ability of the solvent plays a decisive role in determining the extent of reaction. Thus, in Reaction 1 conducted for 72 h at room temperature with a large excess of **2**, the **3c**-contents were 92.7, 79.7, and 31.7% in DMSO, DMF, and HMPA, respectively (on the basis of the initial **1c** unit). DMSO, the most favorable swelling solvent for polymer **1c**, provided the best results throughout the reactions. Reaction 7 with chloranil (**15**) appears to be somewhat complicated due to possible inactivation of the sulfinates and **15** as a result of oxidation to the sulfonates and reduction to tetrachlorohydroquinone, respectively. The extent of side reaction, however, appears to be small and does not appreciably affect the yield of **16c**.

Reductive Additions to Quinonoids (Reactions 4, 5, and 6). The nucleophilic addition reaction of sulfinic acid to *p*-benzoquinone[3)] was applied to polysulfinic acid (**8**) in ethanol–water (1: 1) to afford a 91 mol% addition of the hydroquinone unit (Reaction 4). Similarly, the reaction of oxidized alizarin with sulfinate[4)] was applied to the polymer **1c** and gave satisfactory extents of Reaction 6.

The reactions of **1a** *and* **1b** *with TCNQ (***11***) in* acetonitrile giving the disubstituted products **12a** and **12b** which were analytically pure (Reaction 5) appears to proceed as follows:



The reaction of polymer **1c** with TCNQ also appears to take place in a similar manner.

Displacement of Aromatic Nitro Groups (Reactions 8, 9, and 10). The displacement reactions of aromatic nitro groups with arenesulfinate[5] were applied to **1a**—**c**. Thus, *o*-nitrobenzonitrile (**17**) possessing an activated nitro group reacted with polymer **1c** in DMSO at room temperature (Reaction 8). In the reactions of **1a** and **1b** with TNF (**19**) (Reaction 9), only single monosubstituted products (**20a** and **20b**) were isolated, indicating that the most activated 7-nitro group of **19** was predominantly replaced. The effect of the solvent on the extent of reaction for polymer **1c** (70 °C, 12 h) was also in the order: DMSO >DMF >HMPA. As anticipated, the reaction of **1c** with tetranitrofluorenone (**21**) was easier than that with TNF, but a product of unidentified structure was obtained.

The results indicate that the nucleophilic reactions of **1a**—**c** are generally very easy and provide satisfactory yields of products, sometimes with apparent selectivity.

The polymerization behavior of the styrenesulfonyl derivatives synthesized here has also been examined. The results so far obtained, however, indicate the predominance of polymer reactions.

Experimental

The IR, ^{1}H-NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively, all under standard measurement conditions. Elemental analyses were conducted using a Perkin-Elmer 250 instrument.

p-Styrenesulfinates. *p*-Styrenesulfinic acid, synthesized as in a previous paper,[1] was neutralized in aqueous or *t*-butyl alcoholic solutions with equimolar sodium hydroxide, potassium hydroxide, ammonia, and triethylamine and the resulting solutions freeze-dried to isolate the respective salts.

Polymerization of p-Styrenesulfinates. A solution of the monomer (0.5 g) and potassium persulfate (KPS, 0.005 g) in water (5 ml) was placed in a glass ampoule, which was evacuated twice by a standard freeze-thaw method, sealed, and maintained at 70 °C for 24 h. The viscous solutions were precipitated into appropriate precipitants (Table 1) to afford the polymers.

Preparation of Sodium Polystyrenesulfinate (1c) from Crosslinked Polystyrene. To a suspension of crosslinked polystyrene beads (1.2 g; 10 mmol; Aldrich Macroporous) in chloroform (50 ml) was added dropwise chlorosulfuric acid (8 ml; 100 mmol) and the mixture refluxed overnight. The brown reaction mixture was filtered and washed with chloroform, acetonitrile, and finally with cold water to leave white beads. The weight increase and IR data [disappearance of the absorption peaks at 680 and 740 cm^{-1} attributable to the monosubstituted styrene and appearance of a strong 820 cm^{-1} peak (*p*-disubstitution)] indicated that reaction was practically quantitative.

Poly(*p*-styrenesulfonyl chloride) thus prepared (2.0 g, 10 mmol) was converted to sodium poly(*p*-styrenesulfinate) (**1c**) by stirring in a solution of sodium sulfite (13 g, 100 ml) in water (50 ml) at 50—60 °C for 24 h. The **1c**-polymer was filtered and washed with water thoroughly to leave light brown beads (2.0 g). Iodometry on the sample stirred in excess aqueous bromine at room temperature overnight provided 90.9% of the sulfinate unit on the basis of available reaction sites.

Oxidative Titration. Oxidative titrations of the soluble sulfinate polymers were conducted in aqueous solutions with bromine (0.05 mol dm^{-3}) potentiometrically (electrodes: Pt–sat. calomel at 20 °C). Figure 1 illustrates a typical titration curve.

Reaction 1. As a typical example, 4-(vinylbenzylsulfonyl)styrene (**3b**) was prepared as follows: a solution of sodium *p*-styrenesulfinate (1.0 g, 5 mmol; **1b**) and vinylbenzyl chloride (1.0 g, 7 mmol; **2**, Seibi Chem. Co., *m*/*p*=60/40) in DMF (30 ml) was stirred at room temperature overnight. The reaction mixture was poured into water and the resulting precipitates were filtered and recrystallized from benzene–hexane to afford colorless crystals (mp 162—165 °C) in 26% yield. Found: C, 71.15; H, 5.59%. Calcd for $C_{17}H_{16}O_2S$: C, 70.82; H, 5.67%. IR (KBr): 3100—3000 (aryl), 3000—2920 (alkyl), 1310, 1150 (SO_2), 990, 910 (vinyl) cm^{-1}. NMR ($CDCl_3$) δ 4.4 (s, 2H, CH_2), 5.0—6.2 (m, 4H, 2×(-CH=$C\underline{H}_2$)), 6.7 (m, 2H, 2×(-C$\underline{H}$=CH_2)), 7.1—7.8 (m, 8H, ArH) ppm. Mass (*m*/*e*): 284 (M$^+$, 1.5), 117 (100).

4-(Vinylbenzylsulfonyl)toluene (**3a**) was synthesized in the same manner to afford colorless crystals (mp 147—148 °C) in 46% yield. Found: C. 70.44; H, 6.02%. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.89%. IR (KBr): 3100—3000 (aryl), 2920—2980 (alkyl), 1310, 1150 (SO_2), 990, 910 (vinyl) cm^{-1}. NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 4.4 (s, 2H, CH_2), 5.3 (d, 1H, $C\underline{H}_2$=CH-), 5.8 (d, 1H, $C\underline{H}_2$=CH-), 6.7 (q, 1H, CH_2=C$\underline{H}$-), 7.1—7.8 (m, 8H, ArH) ppm. Mass (*m*/*e*): 273 (M$^+$, 2.4), 117 (100).

In the case of polystyrenesulfinate (**1c**; 0.1 g), 72 h-reactions at room temperature with a large excess of **2** (1 ml) provided 92.7, 79.7, and 31.7% of **3c**-content in DMSO, DMF, and HMPA (each 10 ml), respectively. These were determined by the remaining $-SO_2Na$ in IR (960 cm^{-1}) on the basis of the initial **1c** unit. IR (KBr) indicated vinyl (1620, 990, 910 cm^{-1}) and SO_2 (1310 cm^{-1}) absorptions.

Reaction 2. **1a** (1.5 g, 7 mmol) was reacted for 15 h with vinyl chloroacetate (**4**, 1.0 g, 8 mmol) in HMPA solution (20 ml) at room temperature. Subsequent purification of the product by extraction with ether–water, washing of the colorless organic layer with aqueous sodium hydrogencarbonate, drying over anhydrous sodium sulfate, removal of the ether, extraction of the residue with petroleum ether, and vacuum drying afforded a colorless viscous oil in 65% yield. Found:

C, 54.83; H, 5.21%. Calcd for $C_{11}H_{12}SO_4$: C, 55.00; H, 5.00%. IR ($CHCl_3$): 1760 (ester); 1640, 940 (vinyl); 1320 (SO_2), 1120 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 4.3 (s, 2H, CH_2), 5.0 (t, 2H, $C\underline{H}_2$=CH–), 7.1—8.6 (m, 5H, CH_2=C$\underline{H}$–+ArH) ppm. Mass (*m*/*e*): 240 (M$^+$).

In the case of polymer **1c** (0.1 g) using a large excess of **4** (1.0 g) in DMSO (10 ml) at room temperature, the extent of reaction (IR) was 86 mol % over 72 h. IR (KBr) indicated 1760 (ester), 1310 (SO_2), 1120 (SO_2), 990, 950 (vinyl) cm^{-1}.

Reaction 3. 4-(Phenacylsulfonyl)toluene (**8a**; mp 109—110 °C) was synthesized in quantitative yield by allowing a solution of **1a** (1.5 g, 7 mmol) and phenacyl bromide (1.0 g, 5 mmol; **6**) in DMSO (30 ml) to stand for 20 h at room temperature. Subsequent precipitation into water and recrystallization from benzene–petroleum ether gave the product as colorless crystals. Found: C, 65.35; H, 5.26%. Calcd for $C_{15}H_{14}SO_3$: C, 65.69; H, 5.11%. IR (KBr): 3050 (aromatic) 3000—2850 (alkyl), 1660 (C=O), 1580 (aromatic), 1305, 1140 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 4.8 (s, 2H, CH_2), 7.2—8.2 (m, 9H, ArH) ppm. Mass (*m*/*e*): 274 (M$^+$).

In the case of polymer **1c** (0.2 g), a large excess of **6** (1.0 g) in DMSO (10 ml) at room temperature gave a quantitative yield in 72 h as determined by IR (960 cm^{-1}). IR (KBr) also indicated 1660 (C=O), 1600 (aromatic), and 1310 (SO_2) cm^{-1} absorptions.

Reaction 4. Crosslinked poly(*p*-styrenesulfinic acid) (0.2 g, **8c**) was stirred in a solution of *p*-benzoquinone (**9**, 1 g) in ethanol–water (30 ml, 1: 1 v/v) for 48 h at room temperature. The brown reaction mixture was filtered and extracted with acetone to afford a brown powder, in which the hydroquinone unit existed in 91 mol %, as determined by both remaining –SO_2Na and weight increase. IR (KBr) indicated absorptions at 1450 (hydroquinone), 1300 (SO_2), and 1200 (hydroquinone) cm^{-1}.

Reaction 5. 7,7,8,8-Tetracyanoquinodimethane (TCNQ, **11**; 1 g, 5 mmol) and **1a** (1 g, 5 mmol) in acetonitrile (50 ml) were refluxed for 8 h. The dark green solution containing a precipitate was poured into aqueous hydrochloric acid and the resulting precipitate extracted with chloroform. The red extract was filtered and evaporated *in vacuo* at 50 °C to give a green powder (**12a**) in 15% yield. Found: C, 61.37; H, 3.63: N, 10.82%. Calcd for $C_{26}H_{16}N_4S_2O_4$: C, 60.82; H, 3.12; N, 10.92%. IR (KBr): 2200 (CN), 1590 (aromatic), 1340, 1140 (SO_2) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$) δ 2.5 (s, 6H, 2 CH_3), 7.2—8.3 (m, 10H, ArH+quinonoid) ppm. Mass (*m*/*e*): 512 (M$^+$).

The same procedure was applied for **1b** also to afford the disubstituted product **12b**. Polymer **1c** (0.1 g) and TCNQ (**11**, 0.5 g) in acetonitrile (25 ml) were refluxed for 24 h. The dark green product was extracted with hot acetonitrile. The extent of reaction, as determined by the remaining –SO_2Na in IR and N-analysis, was 48%. IR (KBr) indicated absorptions at 2150 (CN), 1600 (aromatic), 1330 (SO_2) cm^{-1}.

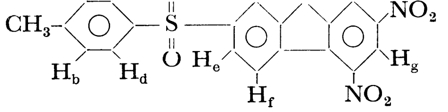
Reaction 6. To a solution of alizarin (**13**, 1 g) in DMSO (25 ml) was added a solution of sodium periodate (0.8 g) in water (5 ml). The mixture was stirred for a short time, then the polymer **1c** (0.2 g) was added. Stirring was continued at 70 °C overnight. The red reaction mixture was filtered and the polymer extracted with acetone to leave an orange powder. Weight increase and the remaining –SO_2Na in IR indicated that the polymer contained 95 mol % of the **14c** unit. IR (KBr) indicated absorptions at 1660, 1630 (quinone), 1430 (phenol), 1340 (SO_2) cm^{-1}.

Reaction 7. A mixture of **1a** (1 g, 5 mmol), chloranil (**15**, 1.2 g, 5 mmol), and DMF (20 ml) was stirred at 50 °C for 15 h. The resulting brown solution containing a white precipitate was poured into water to give a gray powder. Recrystallization form benzene–petroleum ether containing bromine gave a yellow powder (**16a**, mp 140—142 °C) in 52% yield. Found: C, 42.89; H, 1.98%. Calcd for $C_{13}H_7SO_4Cl_3$: C, 42.68; H, 1.92%. IR (KBr): 1690 (quinone), 1580 (aromatic), 1370, 1160 (SO_2), 1100, 900 cm^{-1}. NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 7.0—8.3 (m, 4H, ArH) ppm. Mass (*m*/*e*): 290 (M$^+$—74).

Polymer **1c** (0.1 g) was stirred in a solution containing an excess of **15** (0.5 g) in DMSO (20 ml) for 24 h at room temperature. This was followed by filtration and subsequent extraction with acetone which gave a light orange powder. Weight increase and IR indicated that the extent of the reaction was 91% based on the available reaction sites of **1c**. IR (KBr) indicated characteristic absorptions at 1680 (quinone), 1580 (aromatic), 1370, 1180 (SO_2), 1120, 900 cm^{-1}.

Reaction 8. The polymer **1c** (0.1 g) was stirred in a solution of *o*-nitrobenzonitrile (**17**, 1 g) in DMSO (10 ml) for 72 h at room temperature. The reaction mixture was filtered and the polymer extracted with acetone to afford a light brown powder. IR and N-analysis indicated the presence of 43 mol % of the **18c** unit. IR (KBr) indicated 2200 cm^{-1} (CN) absorption.

Reaction 9. A solution of 2,4,7-trinitrofluorenone (**19**; 1 g, 32 mmol) and **1a** (0.57 g, 32 mmol) in DMSO (25 ml) was stirred at room temperature for 12 h. The brown solution was poured into iced hydrochloric acid to afford a white precipitate, which was recrystallized from acetonitrile–water. A yellow powder (**20a**) of mp 220—222 °C was isolated in 52% yield. Found: C, 56.49; H, 2.86; N, 6.78%. Calcd for $C_{20}H_{12}N_2SO_7$: C, 56.60; H, 2.83; N, 6.60%. IR (KBr): 3060 (aromatic), 2960—2840 (CH_3), 1720 (C=O), 1510 (NO_2), 1340, 1150 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ 2.5 (s, 3H, CH_3), 7.5 (d, 2H, H_a, H_b), 8.0 (d, 3H, H_c, H_d, H_f), 8.4 (s, 1H, H_e), 8.7 (s, 2H, H_h, H_i), 8.9 (s, 1H, H_g) ppm. Mass (*m*/*e*): 424 (M$^+$, 11), 149 (100).



The same reaction procedure was applied to **1b** to afford a yellow powder (**20b**, mp 200—204 °C) in 44% yield. Found: C, 57.70; H, 2.79; N, 6.75%. Calcd for $C_{21}H_{12}N_2SO_7$: C, 57.80; H, 2.75; N, 6.42%. IR (KBr): 1720 (C=O), 1580 (aromatic), 1520 (NO_2), 1320, 1140 (SO_2), 990, 910 (vinyl) cm^{-1}. NMR (DMSO-d_6) δ 5.5 (d, 1H, $C\underline{H}_2$=CH–) 6.1 (d, 1H, $C\underline{H}_2$=CH–), 6.8 (q, 1H, CH_2=C$\underline{H}$–), 7.8 (d, 2H, H_a, H_b), 8.2 (d, 3H, H_c, H_d, H_f), 8.4 (s, 1H, H_e), 8.7 (s, 2H, H_h, H_i), 9.0 (s, 1H, H_g) ppm. Mass (*m*/*e*): 436 (M$^+$, 30), 104 (100).

Polymer **1c** (0.1 g) was stirred in a solution of **19** (1 g) in DMSO (25 ml) at 70 °C for 12 h. The yellow-brown reaction mixture was filtered and the polymer extracted first with acetone, then with acetone–water (1: 1), and finally with acetone. A light yellow powder containing 77% of the **20c** unit, as determined by the remaining –SO_2Na and N-analysis, was obtained. Reactions for 72 h at room temperature in DMSO, DMF, and HMPA provided 77.0, 57.8, and 35.0% extents of reaction, respectively. IR (KBr) indicated characteristic absorptions at 1730 (C=O), 1600 (aromatic), 1530 (NO_2), 1340 (SO_2) cm^{-1}.

Reaction 10. Polymer **1c** (0.2 g) was stirred in a solution of 2,4,5,7-tetranitrofluorenone (**21**, 1 g) in DMSO (25 ml) for 72 h at room temperature. The green reaction mixture was filtered and the polymer extracted first with acetone, then with acetone–water (1: 1), and finally with acetone. A brown powder with the extent of reaction of 83 mol %, as determined by $-SO_2Na$ in IR, was obtained. IR indicated that the reaction proceeded *via* the formation of the SO_2 linkage (1350 cm^{-1}), but the number of replaced nitro groups in **21** was not established.

Characteristic absorptions in IR (KBr) were located at 1740 (C=O), 1600 (aromatic), 1540 (NO_2), 1350 (SO_2) cm^{-1}.

References

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