

Quantitative and Qualitative IR Studies of Some Synthesized Aromatic Polysulfides

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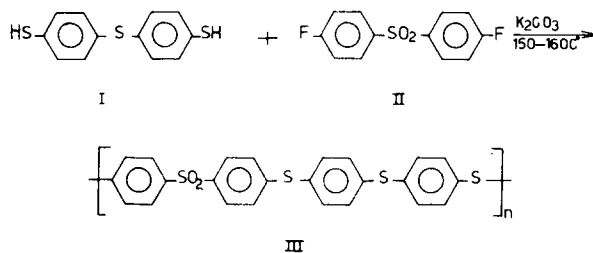
Synopsis

Quantitative and qualitative IR analysis of some synthesized aromatic homo polysulfides and copolysulfides based on 4,4-oxydibenzenethiol (IV), 4,4-dimercaptodiphenyl sulfide (I) and bis-(4-fluorophenyl) sulfone (II) in 1-methyl-2-pyrrolidone (NMP) has been done. A satisfactory agreement of experimental results with theory was observed.

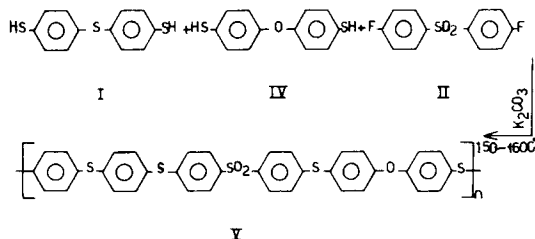
INTRODUCTION

Aromatic polysulfides have been prepared using variety of techniques that involve an aromatic nucleophilic substitution reaction,¹⁻⁶ including the use of phase transfer catalysts,⁹⁻¹³ the condensation of activated aromatic dihalides with dithiols in polar aprotic solvent by using KF as a catalyst,^{14,15} or the polycondensation of dihalobenzene or tetrahaloarenes with alkali metal sulfides in polar solvent in the presence of a reducing agent.^{14,15}

We have prepared aromatic homopolysulfides by polycondensation of the following monomers^{16,17} in NMP



and the copolymers



EXPERIMENTAL

Materials

4,4-Oxydibenzenethiol (IV) was prepared according to the reported procedure by zinc amalgam reduction of 4,4-oxydi(benzenesulfonylchloride)¹⁸ and sublimed, MP 101–102°C (literature,¹⁰ MP 101–103°C).

Similarly, 4,4-dimercaptodiphenyl sulfide¹⁷ (I) was prepared by reduction of 4,4-(disulfonyl chloride)diphenyl sulfide^{18,19} with tin and hydrochloric acid and sublimed, MP 117°C (literature,¹⁷ MP 118°C). Bis-(4-fluorophenyl) sulfone (II) was purchased from Aldrich and purified by recrystallization from methanol, MP 96–98°C (literature,^{20,21} MP 98°C). 1-Methyl-2-pyrrolidone was redistilled under reduced pressure and stored over 4-Å molecular sieves.

Preparation of Polymers

Homopolymer

A 100-ml four-necked round-bottom flask was fitted with a nitrogen inlet, a Dean-Stark trap fitted with a condenser, a thermometer, a mechanical stirrer, and a silicone oil heating bath. Anhydrous K_2CO_3 (2.5 mmol + 5% excess) was added to the stirring solution of monomer I (2.5 mmol) and monomer II (2.5 mmol) in 5 ml NMP, then to the mixture 5 ml of toluene was added under nitrogen. The reaction mixture was heated at 160°C until water was removed completely from the system by azeotropic distillation. The reflux temperature can be controlled by varying the ratio of NMP to toluene. Toluene was essentially quantitatively removed from the reactor system. The slightly colored reaction mixture was further heated at the desired temperature until the reaction mixture became very viscous. The reaction mixture was then cooled to about 90°C, diluted with NMP solvent, and filtered through a medium pore size sintered glass funnel to remove inorganic salts. The filtrate was neutralized with glacial acetic acid. The clear amber-colored solution was then coagulated in portions using a high-speed blender containing 250 ml of a 1:1 volume mixture of water and methanol. The polymer was then filtered off. This solid was worked up by boiling three times for 1 h with 250 ml methanol and then three times for 1 h with 250 ml water. Finally the powder was Soxhlet extracted overnight with water and then overnight with methanol-acetone (90:10). The product was dried overnight at 120°C in a vacuum oven to give the homopolymer (III) with 96.5% yield.

Copolymers

Using the same technique (K_2CO_3 -NMP) described above, some copolymers have been synthesized, as shown in Table I. The compositions of these homopolymers and copolymers were determined by elemental analysis for carbon, hydrogen, and sulfur. The results are shown in Table II.

TABLE I
Preparation of the Homopolymers and Copolymers

Polymers	Monomer I (mmol; g)	Monomer II (mmol; g)	Monomer IV (mmol; g)	K ₂ CO ₃ (g)	NMP (ml)	Polymerization time (h)	Temperature (°C)	[Inv.] _{0.5% NMP} 30°C (dL/g)	Yield (%)
Homopolymer (III)	2.5 (0.625)	2.5 (0.635)	0	3.617 (0.5)	5	15	160	0.476	96.5
Copolymers contain									
10% of (IV)	2.25 (0.562)	2.5 (0.635)	0.25 (0.0585)	3.617 (0.5)	5	16	160	0.4496	87.4
20% of (IV)	2 (0.59)	—	0.5 (0.117)	—	—	16	—	0.2123	82
30% of (IV)	1.75 (0.4375)	—	0.27 (0.1755)	—	—	16	—	0.4245	85.4
40% of (IV)	1.5 (0.375)	—	1 (0.234)	—	—	16	—	0.2272	86
50% of (IV)	1.25 (0.3125)	—	1.25 (0.2925)	—	—	16	—	0.271	81

TABLE II
Quantitative Elemental Analysis of C, H, and S in Homopolymers and Copolymers^a

Polymer	Calculated (%)			Found (%)		
	C	H	S	C	H	S
Homopolymer (III)	62.04	3.47	27.6	59.77	3.33	26.81
Copolymer containing						
10% (IV)	62.26	3.48	26.98	59.74	3.68	24.60
20% (IV)	62.48	3.49	26.36	60.60	3.43	25.23
30% (IV)	62.70	3.50	25.74	61.93	3.52	23.72
40% (IV)	62.92	3.52	25.12	60.90	3.52	24.20
50% (IV)	63.15	3.53	24.51	61.59	3.42	23.69

^a Analysis was done in Analytical Laboratories, Postfach 135, D5250 Engelskirchen, West Germany.

RESULTS AND DISCUSSION

IR Studies

Characteristic peaks in the IR spectra of the homopolymer (III) (Fig. 1) and copolymer (V) (Figs. 2 through 6) are assigned as given in Table III.

Quantitative and Qualitative Analysis

In the spectra of the polymer samples, the band at 1160 cm^{-1} ($-\text{SO}_2-$), peak a, is apparently independent of the configuration, and this can be used as an internal standard. It was found in the present work that the absorption intensity of the bands at 1240 cm^{-1} of the (C-O-C) peak b is proportional to the percentage of the monomer 4,4-oxydibenzenethiol (IV) in the feed of the copolymer.

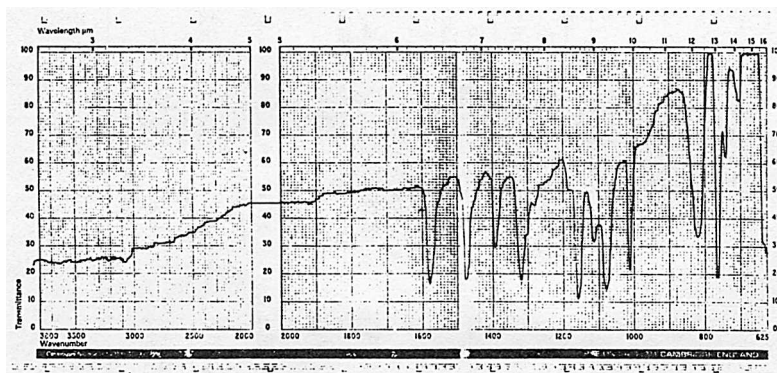


Fig. 1. Infrared spectrum of the homopolymer (III), 3 mg homopolymer per 120 mg KBr.

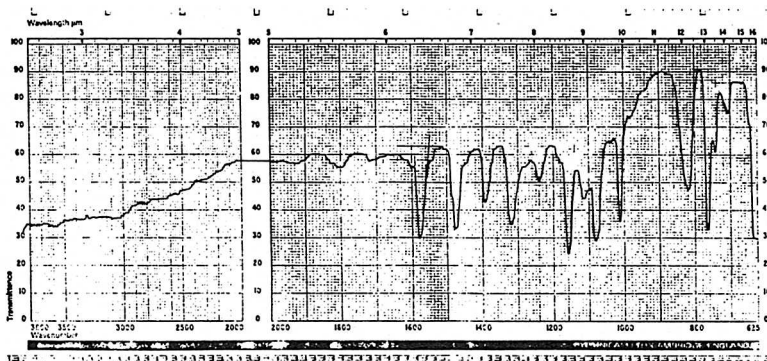


Fig. 2. Infrared spectrum of the copolymer containing 10% (IV), 3 mg copolymer per 120 mg KBr.

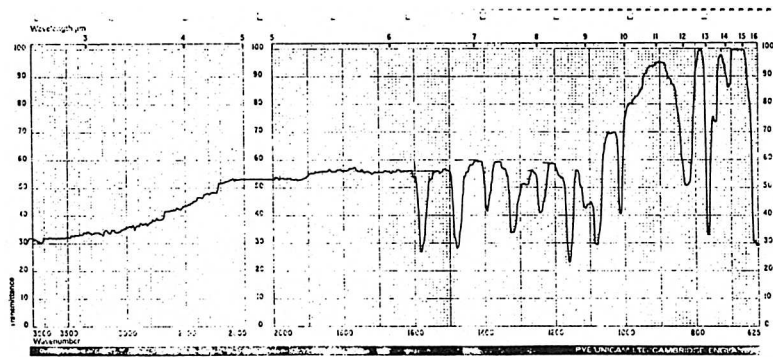


Fig. 3. Infrared spectrum of the copolymer containing 20% (IV), 3 mg copolymer per 120 mg KBr.

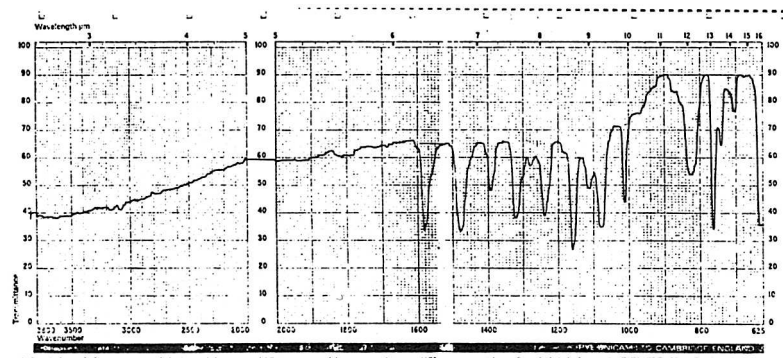


Fig. 4. Infrared spectrum of the copolymer containing 30% (IV), 3 mg copolymer per 120 mg KBr.

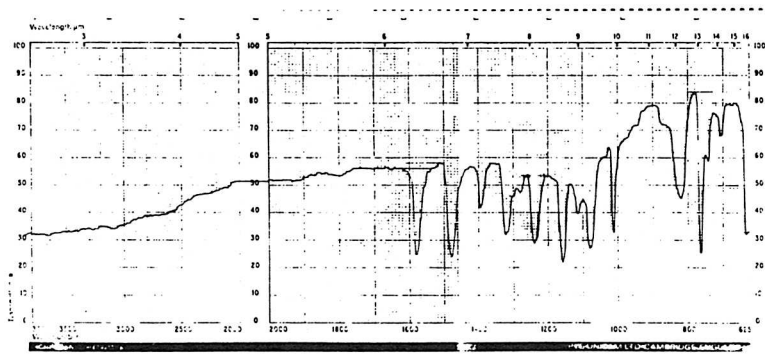


Fig. 5. Infrared spectrum of the copolymer containing 40% (IV), 3 mg copolymer per 120 mg KBr.

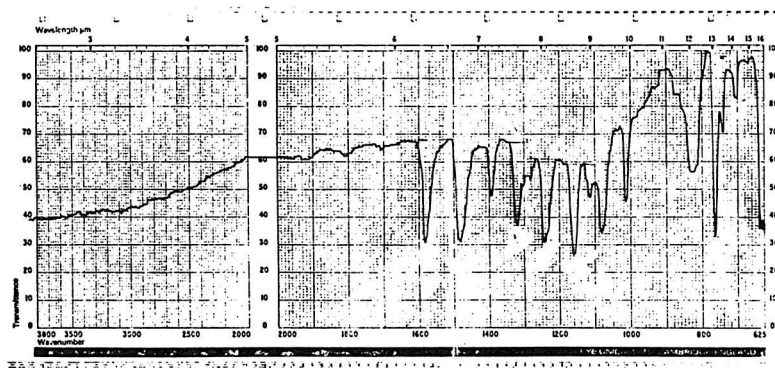


Fig. 6. Infrared spectrum of the copolymer containing 50% (IV), 3 mg copolymer per 120 mg KBr.

TABLE III
Assignment of Characteristic Frequencies in IR Spectra

Spectrum no.	Wavenumber (cm ⁻¹)	Intensity	Assignment	Reference
1	1340	Sharp, strong	—SO ₂ —	22
2	1160	Sharp, strong	—SO ₂ —	22
3	1240	Sharp, strong	C—O—C	22
4	700	Sharp, medium	C—S—C	23

TABLE IV
Relationship Between Percentage of 4,4'-oxydibenzenethiol Feed and Absorbance at 1160 cm^{-1} in Copolymer

% (IV) in copolymers	$\log(I_0/I)_{\text{C—O—C}}$ in copolymer (1240 cm^{-1})	$\log(I/I_0)_{\text{SO}_2}$ in copolymer (1160 cm^{-1})	$\log(I/I_0)_{\text{C—O—C}} / \log(I/I_0)_{\text{SO}_2}$
10	0.0763	0.3654	0.21
20	0.1441	0.3770	0.38
30	0.2074	0.3601	0.58
40	0.2747	0.3689	0.75
50	0.3058	0.3479	0.88

TABLE V
Relationship Between Percentage of 4,4'-oxydibenzenethiol Feed and Absorbance at 1160 cm^{-1} in Homopolymer (III)

% (IV) in copolymers	$\log(I/I_0)_{\text{C—O—C}}$ in copolymers (1240 cm^{-1})	$\log(I/I_0)_{\text{SO}_2}$ in homopolymer (III) (1160 cm^{-1})	$\log(I/I_0)_{\text{C—O—C}} / \log(I/I_0)_{\text{SO}_2}$
10	0.0763	0.6446	1.184
20	0.1441	0.6446	2.234
30	0.2074	0.6446	3.218
40	0.2747	0.6446	4.262
50	0.3058	0.6446	4.744

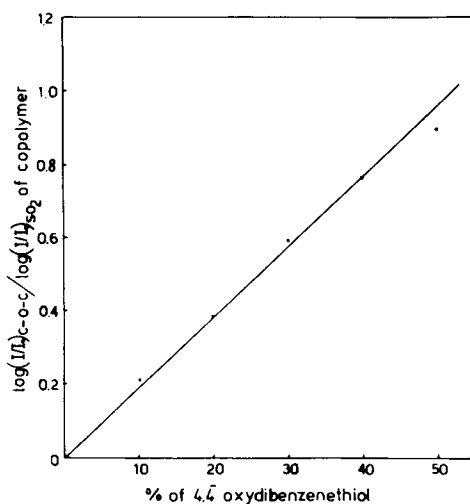


Fig. 7. Relationship between the percentage of 4,4'-oxydibenzenethiol copolyether sulfide composition and the ratio of the absorption bands $\log(I/I_0)_{\text{C—O—C}} / \log(I/I_0)_{\text{SO}_2}$; copolymer at 1240 and 1160 cm^{-1} .

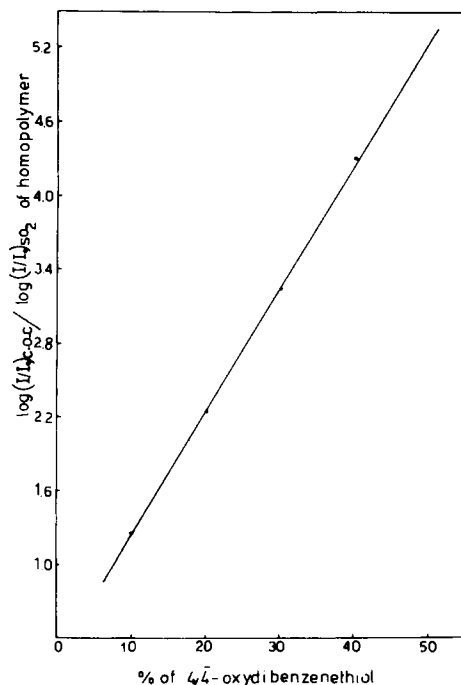


Fig. 8. Relationship between the percentage of 4,4'-oxydibenzene-thiol in copolyether sulfide composition and the ratio of the two absorption bands ($\log(I/I_{OC}) / \log(I/I_{SO_2})$; homopolymer at 1240 and 1160 cm^{-1}).

%4,4'-oxydibenzene-thiol in the copolymer is proportional to \propto

$$\frac{\text{absorption of peak b}}{\text{absorption of peak a}}$$

According to the Beer-Lambert law, the absorbance A is defined as follows.^{22,23}

$$A = \log \frac{I_0}{I}$$

Where I_0 is the intensity of the incident infrared radiation and I is the infrared radiation transmitted through the sample. By using the tangent baseline, the results of these calculations are shown in Tables IV and V.

It is clear from Figs. 7 and 8 that a good straight line was obtained, leading to the conclusion that the percentage of compound (IV) in the copolymer is closely similar to that in the feeds to the reactions.

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