Properties

The Electrical Conductivity Properties and Structures of Substituted Poly(Phenylene Sulphides), Synthesized from Phenols and Sulphur

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SUMMARY

We have synthesized polyphenylenesulphides, using phenols, xylenes, sulphur and halogens as starting materials. The substituted and partly branched polyphenylenesulphides obtained have been doped with iodine (I_2). The structures have been investigated by elemental analyses, IR, NMR and GPC. The electrical conductivities of these products were rather low in the region of 10^{-6}-10^{-11} Scm^{-1}. Higher conductivity values were observed for the polymers containing methoxy- or acetyl-substituents compared with those containing hydroxyl groups. It is suggested that this depends, at least partly, on the absence of hydrogen bonds between the sulphur atoms and the hydroxyl groups. As was expected molecular weight also had the effect of increasing the conductivity values observed.

INTRODUCTION

In recent years the electrical conductivity of polymers has attracted considerable interest. The most important of these polymers is polyacetylene, which can be doped with electron acceptors such as AsF to give a conductivity level of 1000 Scm (1,2). In addition to polyacetylene, another important polymer in this field is poly(phenylene sulphide), PPS (3), and its derivates (4,5). For several years we have been investigating the preparation of substituted PPS in our laboratories. In this report we investigate the effect of substituents in the aromatic ring on the conductivity of these polymers. A short description of the structures and properties of the polymers whose electrical conductivities have been measured is presented.

THEORY

Reactions between sulphur or sulphur-containing compounds (S_2Cl_2 and thiols) and aromatic compounds give, depending on the reaction conditions, polymeric or oligomeric compounds. Owing to the reactivity of sulphur the reactions may take place according to one of the following mechanisms:

1. As nucleophilic substitution reactions in which haloaromatic compounds react with Na_2S (6) or dithiols (7,8) in an aprotic solvent (1a), or according to the Macallum reaction in the melt (1b) (9,10).
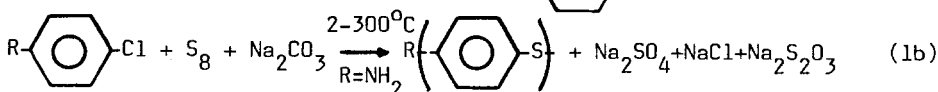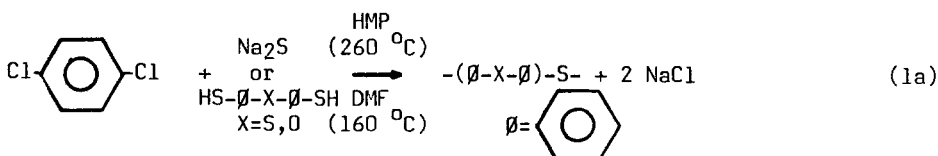
2. As electrophilic substitution reactions of the Friedel-Crafts type (11), in which sulphur or S_2Cl_2 reacts with aromatic compounds. Most of the products described in this report have been prepared by reactions between phenols and sulphur using halogens as catalysts (11).

$$R= H, CH_3, OCH_3 \qquad X= Cl, Br \qquad Y= Cl, Br \qquad (2)$$
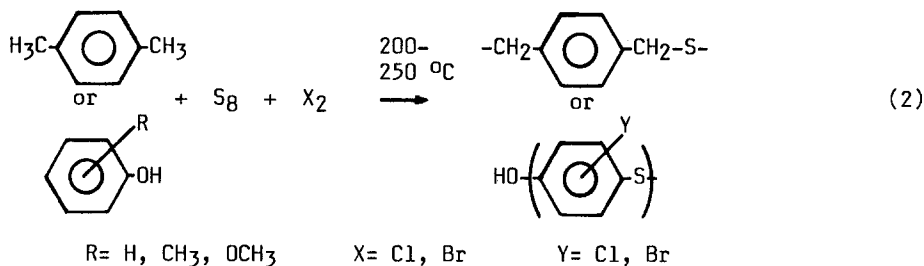
In the reaction between 1,4-dimethylbenzene and S_8 and Br_2 a radical reaction is to be expected.

3. As homolytic substitution reactions between haloaromatics or aromatics and elementar sulphur at sufficiently high temperatures (13,14).

$$(3)$$
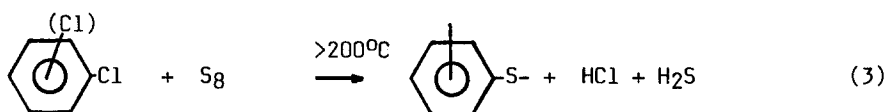
EXPERIMENTAL

a) Molecular weight measurements: Molecular weight distributions were measured by gel permeation chromatography (Sephadex G 75 in DMF), using monodisperse polystyrene samples for the calibration, as described earlier (12).
b) Thermal measurements: The melting points of the crystalline compounds were determined by differential scanning calorimetry. The softening points of the other compounds were determined visually in a melting point apparatus.
c) Doping with iodine: The doping was carried out in a vacuum. The polymers were kept under iodine vapour for three days.
d) Conductivity measurements: These measurements were carried out using a simplified four point-method and a Keithley 602 electrometer. The samples were prepared in the same way as IR-pellets, the thickness being about 0.5 mm.

RESULTS AND DISCUSSION

In the preparation of the products investigated here the methods described in the formulae 1a, 1b and 2 were used. A part of these products were methylated (15) and acetylated (16).

The structures were investigated by IR- and NMR-spectroscopy . The C-13 NMR-spectra were recorded both in solution and solid state using the CP-MAS technique (17) because the products with greater molecular weights were poorly soluble after precipitation. The results of these measurements are given in figures 1 and 2.
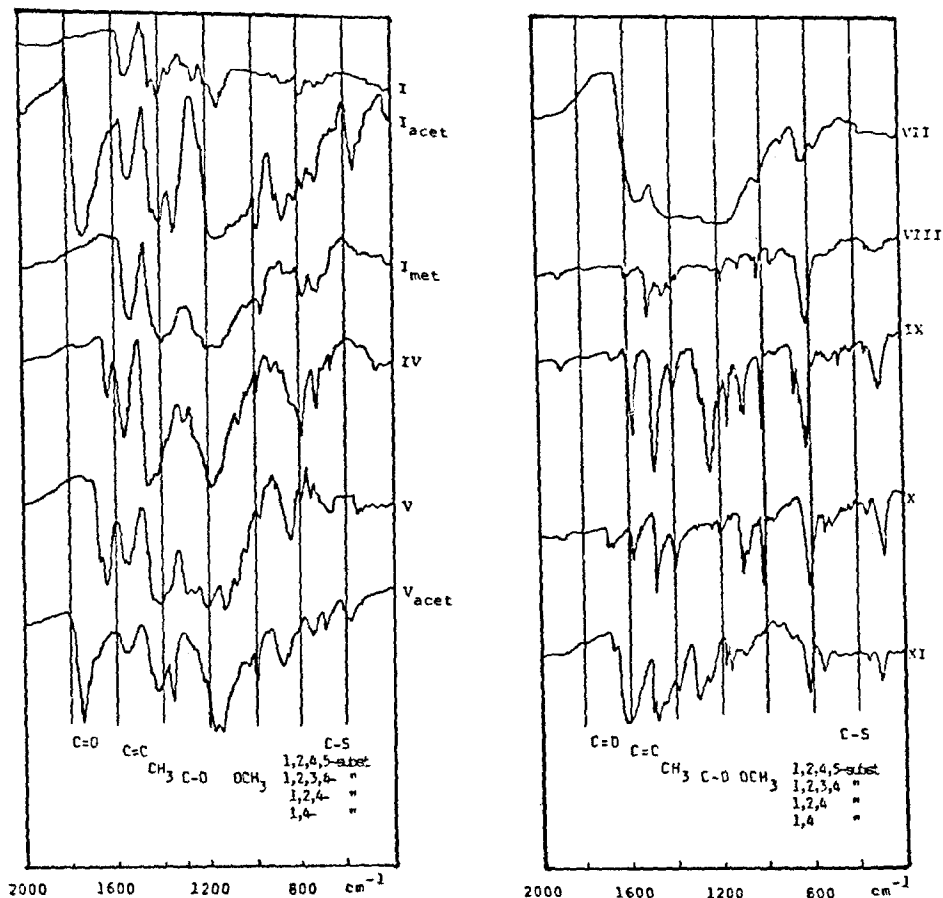
Figure 1. The IR-spectra of the products prepared according
to formulae 1 and 2. The numeration of the spectra
(I-XI) is the same as is used for the products in
table 1 and also in figures 2 and 3.

The molecular weight distributions have been given earlier (12) and are
collected in table 1. In table 1 are also given the results of the elemental
analysis and the softening points.

The conductivity properties of all the doped polymers are given in
table 1. It can be seen from the results in table 1 that the electrical
conductivity of these substituted polymers are in the region of 10^{-6}-10^{-11}
Scm^{-1}. The nitrogen containing polymers XI and XII have the highest conduc-
tivities. Although the conductivity values are low it is interesting to
investigate how they correlate with the different substituents.

The conductivity values of the samples from synthesis V indicate that
there is an increase in conductivity when the OH-group is replaced with
a CH_3O- or a $CH_3(CO)$-group. This can be explained by the assumption that the
absence of the intramolecular hydrogen bonds between OH-groups and sulphur

Table 1. The reaction conditions of the syntheses and the characterization of the products are given together with the conductivities with and without I_2-doping.

Product[1,2]	R[1]	X	Reaction time (min)	Reaction temperature (°C)	%X	%S	Soft. point (°C)[10]	M_n[11]	Conductivity before[12] (Scm⁻¹)	Conductivity after doping[13] (Scm⁻¹)
I[3]	H	Br	180	220	1.8	42.3	125-135	<2000	$1.4\ 10^{-12}$	$1.8\ 10^{-10}$
I acet[6]	-C-CH (O)	Br	180	220	1.8	42.3	140-150		$4.9\ 10^{-12}$	$2.4\ 10^{-10}$
I met[7]	-CH	Br	180	220	1.8	42.3	135-150		$4.9\ 10^{-12}$	$1.8\ 10^{-10}$
II[3]	H	Br	6	220			-	<2000	$2.1\ 10^{-12}$	$2.0\ 10^{-10}$
II[4]	H	Br	6	220	22.0	36.0	145-195	>2000	$2.2\ 10^{-12}$	$5.8\ 10^{-9}$
II[5]	H	Br	6	220			200-260	>2000	$2.1\ 10^{-12}$	$3.6\ 10^{-9}$
III[4]	H	Cl	80	250	5.4	20.8	75-100	2000	$3.3\ 10^{-12}$	$1.1\ 10^{-10}$
IV[4]	H	Cl	320	250	4.3	24.7	150-200	>2000	$1.5\ 10^{-12}$	$1.8\ 10^{-10}$
V[4]	H	Br	6	220	21.0	35.0	>300	>2000	$3.4\ 10^{-10}$	$1.2\ 10^{-10}$
V acet[5]	-C-CH (O)	Br	6	220			140-170		$1.5\ 10^{-11}$	$3.8\ 10^{-10}$
V met[7]	-CH	Br	6	220			120-140		$3.2\ 10^{-7}$	$8.7\ 10^{-8}$
VI[4]	H	Cl	80	250	3.7	36.4	130-190	2-3000	$2.5\ 10^{-12}$	$2.8\ 10^{-10}$
VII[4]	H	Cl	330	250				2-3000	$5.9\ 10^{-12}$	$1.1\ 10^{-11}$
VIII[8]	H	Cl	300	210		27.6		2000	$1.4\ 10^{-12}$	$2.0\ 10^{-11}$
IX[9]	O	Cl		150	0.4	21.4	170	17000	$4.3\ 10^{-12}$	$1.9\ 10^{-11}$
X[9]	S	Cl		210	0.7	30.0	210	10000	$6.8\ 10^{-12}$	$6.1\ 10^{-9}$
XI[4]	-	-	1080	220	11.5[14]	34.7	110	3000	$7.2\ 10^{-11}$	$7.5\ 10^{-7}$
XII[4]	-	-	1080	280	9.8[14]	33.2		2000	$3.2\ 10^{-10}$	$4.4\ 10^{-6}$

1) The numbering and significance of the substituents for the structures are given in figure 1.
2) The molar ratio of monomer:sulfur:halogen in synthesis I-VIII was 1:2:2 apart from in synthesis I where it was 1:2:1.
3) Fraction soluble in ethanol precipitated with water + 0.1 M HCl.
4) Fraction soluble in 50 ml of DMF (insoluble in ethanol), precipitated with water.
5) Fraction insoluble in 50 ml of DMF during 4 h, but soluble in an additional amount (100 ml) of DMF after 24 h and precipitated with water.
6) Samples from II and V which were acetylated with aceticanhydride in pyridine.
7) Samples from II and V which were methylated with dimethylsulfate in NaOH.
8) Fraction soluble in hot toluene precipitated with ethanol.
9) Fractions insoluble in toluene at room temperature.
10) The softening points were determined visually apart from in synthesis IX and X where the crystalline melting point was determined by DSC (Perkin Elmer DSC II).
11) The molecular weight distributions were investigated by GPC (Sephadex G-75 and G-50) in DMF or DMFD. Calibration of the columns was performed using monodisperse polystyrene samples. The molecular weight distributions were broad. There were two fractions in all samples; one with $M_n>2000$ and one with $M_n<2000$. The dominating fraction is given in the table. M_n was determined by end group analysis in the syntheses IX and X.
12) Results of the electrical conductivity measurements before doping with I_2.
13) Results of the electrical conductivity measurements after doping with I_2.
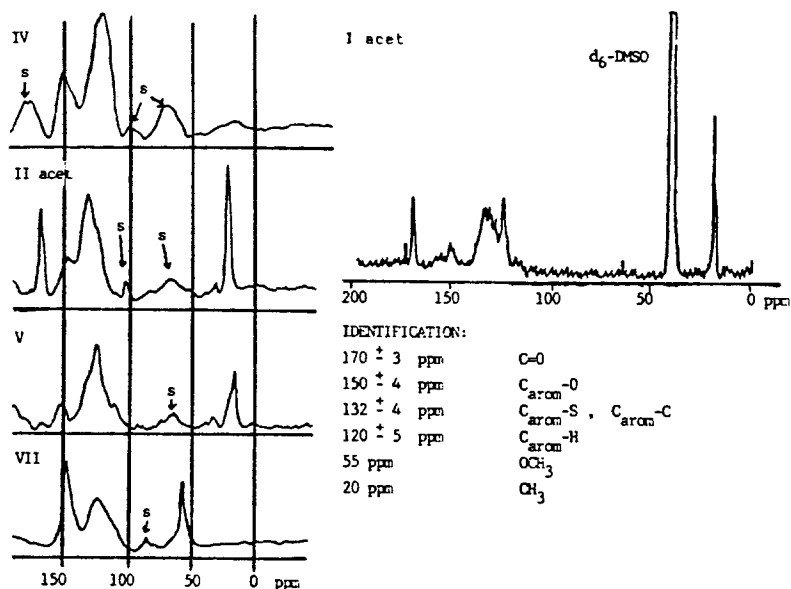14) X= nitrogen for these products.

Figure 2. The C-13 NMR-spectra were obtained with a Jeol
FT-NMR-spectrometer. The spectra of the products IV,
II$_{acet}$, V and VII (see table 1), were obtained in
the solid state using the CP-MAS-technique.
The observation frequency was 50.1 MHz, the spectral
width 15000 Hz, 4 k data points were used and 750
pulses collected. The pulse width was 6.1 us (90°),
the contact time 5 s, the pulse delay 5 s, and
the spinning speed 3.2 kHz (s=spinning sideband).
The solution spectra of I$_{acet}$ was recorded in a 5% (w/v)
solution of d -DMSO. The pulse width was 8 us (45°),
the pulse delay time 5 s and 10000 pulses were collected.
The spectral width was 10 kHz and 8 k data points were
used.

atoms and intermolecular hydrogen bonds between different OH-groups improves
the possibility for I$_2$ to affect the conductivity properties of the aromatic
π-electrons. The above effect is not observed in the case of the substituted
samples of synthesis I, which may be due to their low molecular weight. It is
known that the electrical conductivity of polyacetylene increases with in-
creasing molecular weight (18).

According to the results from syntheses I and II, and III and V, the
amount of covalently bonded halogen in the polymers does not affect the
conductivity. Bromine can thus be used in the syntheses to give products
with higher molecular weights when using reaction (2) for preparing the pro-
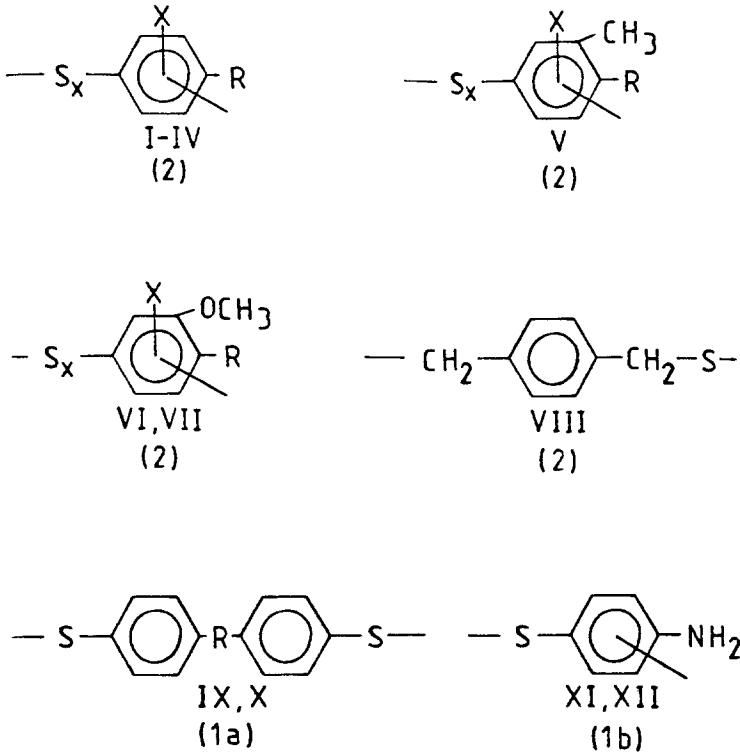ducts.

Figure 3. The structures of the polymers prepared according
to the mechanisms la, lb and 2.

The well-known fact that replacing the sulphur atom with an oxygen atom
in a linear poly(phenylene sulphide) should lower the conductivity, is clear-
ly evident in the results of syntheses VIII and IX. A similar effect is also
expected when a sulphur atom is replaced by a $-CH_2-S-$group, as can be seen
from the results of synthesis X. The introduction of methylene linkages de-
creases the conductivities of the doped polymers. These changes in the back-
bone are expected both to increase the ionization potential of the polymer
and to interrupt electronic delocalization. The decrease in conductivity is
thus not surprising.

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