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The electrical conductivities of poly(3.6-pyridazine) and poly(3.6-pyridazine sulphide)

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SUMMARY

We have chemically synthesized poly(3.6-pyridazine) ,(PPd), and poly(3.6-pyridazine sulphide), (PPdS), and studied the electrical conductivities of these polymers.

INTRODUCTION

We have earlier studied the effect of a substituent on the electrical conductivity of poly(p-phenylene sulphide), PPS (1), and the electrical differences between poly(2.6-pyridine), PPy, and poly(2.6-pyridine sulphide), PPyS (2).

We have now continued this work and synthesized poly(3.6-pyridazine), PPd, and poly(3.6-pyridazine sulphide), PPdS, in the same way (fig. 1). The polymers have been characterized and the electrical conductivities of both pure and doped polymers have been measured.

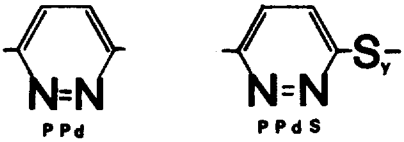

Figure 1. The structures of poly(3.6-pyridazine) (PPd) and poly(3.6-pyridazine sulphide) (PPdS).

EXPERIMENTAL

PPd and PPdS were synthesized as before (2) except 3.6-dichloropyridazine was used as a starting monomer. The yields of PPd and PPdS were 91% and 89%, respectively. The polymers were doped with iodine as described before (2) and the conductivity measurements were done using the four probe method.

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RESULTS AND DISCUSSION

Elemental analyses (%)

		C	H	N	S
PPd	Found	59.2	3.4	32.2	-
	Calcd.	61.5	2.6	35.9	-
PPdS	Found	41.0	1.4	23.8	25.9
	Calcd.	43.7	1.8	25.4	29.1

According to the elemental analyses the empirical formula for PPd and PPdS are $C_{3.85}H_{2.62}N_{1.79}$ and $C_{3.76}H_{1.56}N_{1.87}S_{0.88}$, respectively.

These polymers are black and insoluble in common solvents. The molecular weights, $\bar{M}_n$, were determined by titration of the end groups (chlorine). M_n was 4000 for both polymers. The thermal degradation of both polymers begins at 200 °C (3).

Figure 2 shows the IR-spectra of PPd and PPdS: 3200-3400cm^{-1}, -N= strech; 3050-3080cm^{-1}, aromatic C-H strech; 1600-1625cm^{-1}, C-C ring streching; 1515cm^{-1}, -N=N- strech; 1150cm^{-1}, C-N strech; 835cm^{-1}, 1.4-disubstituted; 710cm^{-1}, C-S strech; 480cm^{-1}, S-S strech.

Table 1 shows the electrical conductivities of iodine doped PPd and PPdS.

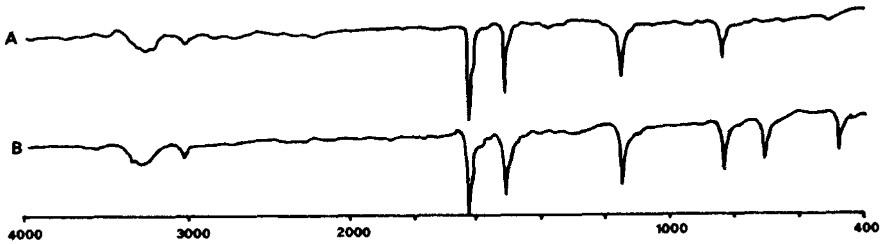

Figure 2. The IR-spectra of PPd (a) and PPdS (b).

Iodine doped polymers are not stable in air suggesting slow reduction of dopant from the sample. A sulphur atom in the chain increases the nonplanarity of a polymer (1) and the electrical conductivity decreases. This can be seen in table 1. Using the same method we synthesized poly(3.6-pyridazine oxide), which does not have "p" orbitals to overlap with the π-systems of the aromatics. This change in backbone structure increases the ionization potential of the polymer and interrupts electronic delocalization and only an insulating material is obtained.

Table 1. The electrical conductivities of pure and iodine doped PPd and PPdS.

Polymer	Doping time (h)	Conductivity (S/cm)
PPd	-	$9.8 \cdot 10^{-11}$
	5	$6.9 \cdot 10^{-6}$
	24	$5.8 \cdot 10^{-4}$
	72	$1.2 \cdot 10^{-3}$
PPdS	-	$1.3 \cdot 10^{-11}$
	5	$9.8 \cdot 10^{-8}$
	24	$7.7 \cdot 10^{-7}$
	72	$7.5 \cdot 10^{-4}$

Like PPy and PPyS (2), pure PPd and PPdS have one symmetrical line in ESR-spectra and the shape is Lorentzian.

Satoh et al. (3) have synthesized PPd electrochemically and the conductivity of it was 6 S/cm. They also found that the doped samples are not stable in air.

As in the pyridine molecule, the C-N bonds of the diazines are short when compared with the C-C bonds. Heats of combustion indicate a considerable conjugation energy arising from the delocalized 6π-electron system; the energy appears to be less in pyridazine than pyrimidine or pyrazine (4).

If M_n increases 2000, conductivity increases only 0.5 decade. This result prove that intrachain carrier migration does not strongly determine the transport properties of either undoped or doped polymer. Otherwise the difference of 2000 fold in chain should affect δ. This means that interchain hopping of carriers is a very important process (5).

Shacklette et al. (6) have shown that doping induces the formation of dibentzothiophene linkages in PPS by adjoining aromatic rings:

They have also have shown that the sulphur links not only provide the necessary chain conformation and inductive activation for the bridging process to occur but support conduction along the polymer chain. This can not be directly applied to PPdS because there are 1-3 sulphur atoms in the polymer chain. However, the sulphur atoms next to the pyrazine rings might form similar dibentzothiophene linkages.

Kao et al. (7) have calculated that poly(p-pyrazine) and poly(p-pyridine) have similar intrinsic conductivities as poly(p-phenylene). They have also found that a -NH- group is the most effective in lowering the ionization potential (IP) values. This same phenomenon has been found in polypyrrole (8). It has been suggested that the hydrogen on the nitrogen is somewhat important in the conductivity process.

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