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Synthesis and electrical conductivities of some nitrogen- and sulphur-containing polymers

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SUMMARY

We have synthesized poly(p-azophenylene) (PPN), poly(2.4-azotoluene) (PMT), poly(2.6-pyridine) (PPy), poly(2.6-pyridine sulphide) (PPyS) and poly(ethylene vinylene sulphide) (PEVS), doped them with iodine and ferric chloride and measured the electrical conductivities. The doped polymers were also studied with ESR and IR.

INTRODUCTION

In the beginning of the seventies Heleskivi et al. (1) and Löfgren et al. (2) have studied the conductivities of different non-doped aromatic azopolymers. These polymers were synthetized by catalyzed oxidative coupling (3-5):

$$H_2N\text{-}Ar\text{-}NH_2 \xrightarrow[\text{(catalyst)}]{+O_2,\ -2H_2O} \{Ar\text{-}N{=}N\}_x$$

where Ar is an aromatic, aromatic-heterocyclic or aromatic-aliphatic bivalent radical. The conductivities of these pure polymers were in the range of 10^{-17}-10^{-9} Scm^{-1}, linear polyazophenylene being the most conductive. The authors above did not, however, use doping. In this work we have therefore chosen two of these polymers and doped them with iodine and $FeCl_3$.

Ikeda et al (6,7) have synthesized poly(vinylene sulphide) (PVS) in two different ways. In the first way they used a pressure reaction vessel, trans-1.2-dichloroethylene and $Na_2S{\cdot}9H_2O$ as starting substances and N-methyl-2-pyrrolidone as a solvent. In the second way the synthesis was carried out in a reactor equipped with a powerful stirrer under an argon atmosphere.

Boscato et al. (8) have synthesized polyphenylene polysulphur using the following method:

We have synthesized poly(p-azophenylene) (PPN), poly(2.4-azotoluene) (PMT), poly(2.6-pyridine), poly(2.6-pyridine sulphide) (PPyS) and poly(ethylene vinylene sulphide) (PEVS) (Fig. 1) using this method.

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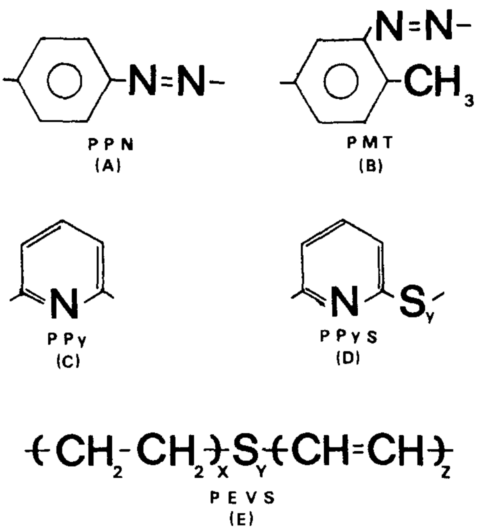


PPN (A) PMT (B) PPy (C) PPyS (D) PEVS (E)

Figure 1. The structures of PPN, PMT, PPy, PPyS and PEVS.

EXPERIMENTAL

Azopolymers were synthesized by oxidative coupling of the monomers p-phenylenediamine and 2.4-diaminotoluene in CuCl-pyridine-dimethylsulphoxide mixtures. The reaction conditions are in Table 1.

Table 1. Reaction conditions and yields of PPN and PMT.

Monomer	Monomer added (g)	DMSO/ Py (ml/ml)	Reaction time (min)	Reaction temp. (°C)	Yield (%)	$\overline{M}_n$
p-phenylenediamine	1.08	40/10	390	50	97	16200
2.4-diaminotoluene	1.22	40/10	255	50	95	20000

The products were washed twice (4 h) with boiling pyridine-ammonia solution (1:1, 4 % NH_3), three times with distilled water (4 h) to remove extra copper which comes from the used catalyst (CuCl) and finally dried under nitrogen at 140 °C.

PPy was synthesized as follows: 2.6-dichloropyridine (0.1 mol) was introduced in dry and freshly distilled THF (100 ml) under argon. 0.2 mol of lithium metal was directly added to the solution. The reaction mixture was gently heated (50 °C) for 2 hours. After this the solution was made alkaline with 1 N NaOH and a dark brown polymer precipitated. The polymer was washed with water, filtrated and dried in vacuum. The yield was 90 %. PPyS was synthesized in the same way exept in the beginning dry sulphur S_8 (0.1 mol) was also introduced in THF.

PEVS was synthesized as above exept trans-1.2-dichloroethylene and S_8 were used as the starting substances.

Doping with iodine was carried out by exposing the polymer pellets to an iodine atmosphere in vacuum (10^{-3} torr, room temperature). In the case of $FeCl_3$ the polymer powder was immersed in a dry saturated $FeCl_3$-nitromethane solution, filtered, washed several times with dry nitromethane and dried in vacuum. The dopant content of doped samples was calculated from their weight increase.

The electrical conductivity was measured using the four-point method and a Keithley 602 electrometer.

RESULTS AND DISCUSSION

a) Syntheses

The molecular weights, $\bar{M}_n$, (Table 1) were determined by titration of residual amine groups with perchloric acetic acid. The heat stabilities of the azopolymers were investigated by TG. The mass residues of PPN and PMT are at 510 °C 74 % and 72 %, respectively.

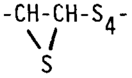
Table 2. Elemental analyses of PPy, PPyS and PEVS (%).

		C	H	N	S	Cl
PPyS	Found	36.8	2.0	7.9	26.3	
	Calcd.	55.0	2.8	12.8	29.4	
PPy	Found	76.2	3.6	16.8	-	
	Calcd.	77.9	3.9	18.2	-	
PEVS	Found	11.4	1.1	-	81.0	0.25
	Calcd.	41.4	3.4	-	55.2	-

The empirical formula for PPy and PPyS calculated from the results of the elemental analyses are $C_{4.89}H_{2.75}N_{0.92}$ and $C_{3.34}H_{2.16}N_{0.61}S_{0.89}$, respectively. The formula of PPy indicates that the elemental composition of PPy is close to the theoretical formula of PPy. The C/S-ratio (3.8) in PPyS is too small compared with the theoretical value (5.0).

Table 2 shows that there are 3 different possibilities for the structure of PEVS:

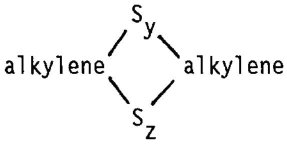
$-C=CH-S_5-$ $-CH_2-CH_2-S_6-$



$-CH-CH(-S-)-S_4-$

The interaction of sulphur with olefins below about 130 °C is extremely slow; above this temperature the primary products from mono-olefins are complex mixtures of organic polysulphides of three basic structural types (9):

alkenyl-S_x-alkyl I



II

alkenyl-S_y-alkylene-S_z-alkyl III

Traces of episulphides and cyclic disulphides may also be formed, but thiols or hydrogen sulphide have been not observed when reaction temperatures have been maintained below about 150 °C. At short reaction times, (I) is the pricipal type of product, in which the sulphur rank x has an average value of 4-5. At long times the proportions of (II) and (III) increase and the sulphur rank is reduced, monosulphides becoming apparent. Since the less-substituted olefins show reduced reactivity towards sulphur and their reaction rates are slow, this points to (II) and (III) being secondary products. The structure of PEVS was investigated with IR and solid state ^{13}C NMR. The IR spectrum shows the following bands: 1550 (vw; -C=C-), 1400 (m; CH_2-), 950 (m; -CH=), 660 (m; C-S) and 465 cm-1 (m; S-S). 13C NMR spectrum shows two different peaks: 133 and 28 ppm (7). This suggests that there are both -CH= and -CH_2- carbons in the chain. Because the sulphur content in the products was too high, the quantity of sulphur as a starting material was reduced (80, 60, 40 and 25 %). This did not, however, affect the sulphur content and the same result was obtained when sulphur and lithium were replaced by Li_2S. According to all these results it is obvious that the structure of PEVS is

$$\left(CH_2-CH_2\right)_x-S_y\left(CH=CH\right)_z$$

, where x>>z and 5<y<6.

The IR-spectra of PPN and PMT are similar to the spectra Sandholm et al. (4) have obtained: PPN, strong bands at 3430, 1600, 1505, 1280, 1130, 1015 and 835 cm^{-1}; PMT, strong bands at 3400, 1620, 1505, 1016 and 850 cm^{-1}. PPy and PPyS: 3040-3080 cm^{-1}, aromatic C-H strech; 1415-1580 cm^{-1}, C-C ring streching (skeletal bands); 790 cm^{-1}, C-H out of plane bending; 705 cm^{-1}, C-S strech; 470 cm^{-1}, S-S strech. Upon doping PPyS with iodine or ferric chloride we noted the disappearance of the fringes and the appearance of three new bands at 1000, 1027 and 1536 cm^{-1} (10). The new bands found for $FeCl_3$ doped PPyS appear exactly at the same wavenumbers. Doped PPy has the same bands except the band at 1027 cm^{-1}. Shacklette et al. (11) have studied the conducting complexes of poly(p-phenylene sulphide). There are two strong bands at 1532 and

1027 cm^{-1} and two other weaker bands at 992 and 880 cm^{-1}. They suggest that the band at 1027 cm^{-1}, which does not exist in the spectrum of poly-(p-phenylene), may be due to co-operative phenyl-sulphur vibrations.

b) Electrical conductivity

Table 3. The electrical conductivities of PPN, PMT, PPy, PPyS and PEVS.

Polymer	Dopant	Conductivity (S/cm)
PPN	-	$1.4\cdot10^{-8}$
	iodine	$2.0\cdot10^{-5}$
	ferric chloride	$9.6\cdot10^{-6}$
PMT	-	$3.3\cdot10^{-10}$
	iodine	$7.4\cdot10^{-7}$
	ferric chloride	$9.1\cdot10^{-8}$
PPy	-	$1.5\cdot10^{-11}$
	iodine	$8.9\cdot10^{-3}$
	ferric chloride	$5.2\cdot10^{-4}$
PPyS	-	$2.1\cdot10^{-11}$
	iodine	$9.2\cdot10^{-4}$
	ferric chloride	$4.4\cdot10^{-5}$
PEVS	-	$5.0\cdot10^{-9}$
	iodine	$6.6\cdot10^{-6}$
	ferric chloride	$9.8\cdot10^{-6}$
	sulphuric acid	$9.2\cdot10^{-6}$

The conductivity of pure PPN is $1.4\cdot10^{-8}$ Scm^{-1} and of pure PMT $3.3\cdot10^{-10}$ Scm^{-1}. The difference depends on linearity and the substituent. Heleskivi et al. (1) found this same behavior. The influence of the substituent is here, however, greater. Satoh et al. (12) have studied the conductivity of poly(o-azophenylene) (POP) and poly(p-azophenylene) films and they noted that the conductivity of PPN was higher than that of POP, just expected from their molecular structures.

From Table 3 it is evident that the sulphur in the polymer chain lowers the conductivity of both pure and doped polymer. The same phenomenon can be seen in the case of poly(p-phenylene) and poly(p-phenylene sulphide) (13,14). The conductivity of doped polypyrrole is higher than that of PPy. It has been suggested that the hydrogen on the nitrogen is important in the conductivity process (15). When the sulphur link in PPS is replaced by a methylene unit, one which does not have p-orbitals to overlap with the π-system of the aromatic rings, only an insulating material is formed (16-18). The same is obtained even if only every other sulphur atom in PPS is replaced with a methylene link. This can be seen in the case PEVS.

Though extra iodine is pumped off the polymer samples (pellets), they still loose their weights and electrical conductivity in air. This is caused by the chemical equilibrium and diffusion phenomena which depend on time. $FeCl_3$ doped polymers are quite stable in air.

For pure PPN the ESR signal exhibits a symmetrical lineshape and during the iodine doping the g-factor increase from 2.0038 to 2.0059. Barbarin et al. (19) have noticed this same effect and they suggest these results can be explained by:

- a lightly anisotropic g tensor, its effect on the lineshape being small because of the intrinsic linewidth
- the existence of radicals the g-factor of which depends on the chain length distribution or on their position in the chain

Table 4 shows the A/B-ratios of the ESR signals of PPN and PMT. The increasing asymmetry of the lineshapes during the doping is consistent with increasing conducting behavior of the PPN pellets. $FeCl_3$ doped polymers have initially the same trend but after 5 h the A/B-ratio begins to decrease.

Table 4. The A/B-ratios of iodine and $FeCl_3$ doped PPN and PMT.

Dopant	Doping time (h)	A/B-ratios PPN	PMT
-	-	0.65	0.55
iodine	1	0.67	0.58
	8	0.71	0.62
	18	0.71	0.62
	72	0.71	0.62
ferric chloride	2	1.00	0.95
	5	2.50	2.40
	19	1.00	0.95
	72	0.95	0.90

Pure PPy and PPyS have one symmetrical line in ESR spectra (in air, room temperature) and the shape of the lines is Lorentzian. The g-factor of the both polymers is 2.0028. During the doping with iodine the linewidhts first decrease and then increase (Table 5) but the shape remains Lorentzian. Czerwinski et al. (20) have observed this same phenomenon in PPP.

Table 5. The linewidhts of PPy and PPyS during the doping with iodine.

Doping time (h)	-	2	5	24	48	72
PPy	14.0	14.8	14.3	14.5	15.0	16.0
PPyS	13.5	13.0	15.5	17.0	18.7	19.2

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