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Studies on some properties of pristine and iodine-doped poly(phenylene sulphide)

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Some properties of poly(phenylene sulphide) prepared by direct synthesis from benzene and sulphur are discussed in the light of thermal analysis, X-ray, SEM, and infrared data. Pristine poly(phenylene sulphide) is characterized by great thermal stability; it loses only 22.5% of its mass during dynamic heating to 873 K. Mass loss for iodine-doped samples increases to 41% depending on the iodine content. Doping with iodine also changes crystallinity, morphology and brings about a rise of electrical conductivity by several orders of magnitude. A conductivity of $1.45 \times 10^{-2}\,\mathrm{S\,m^{-1}}$ was obtained in air at room temperature for the poly(phenylene sulphide) sample containing 22.6% iodine.

1. Introduction

Like other macromolecular compounds containing an extended conjugated double bond region or aromatic moieties, poly(phenylene sulphide) belongs to the class of conducting polymers. The conductivity of this class of polymers is very low in the virgin state, and it increases rapidly upon doping with strong electron acceptors or donors. Arsenic pentafluoride, antimony pentafluoride or pentachloride, iodine, fluorosulphonic acid, potassium, sodium are typical doping species. Poly(paraphenylene sulphide), commercially available under the trade name Ryton^R (Phillips Petroleum Co.), is a solution and melt processible polymer in its pristine state. Moreover, it shows other interesting properties, which are important for practical applications, e.g. a great thermal and chemical resistance. These features have attracted interest in it as a material applicable in chemical industry plants running under harsh conditions [1, 2].

Properties of poly(phenylene sulphide) prepared in various ways, e.g. from 1,4-dichlorobenzene and sodium sulphide in 1-methyl-2-pyrrolidone have been described [3]. Other chemicals used as substrates are: thiophenol [4], thiophenol and thionyl chloride in the presence of Lewis acids (such as $AlCl_3$, $FeCl_3$, $SnCl_4$) as catalysts [5], *p*-dichlorobenzene 1,2,4-trichlorobenzene, sulphur, and sodium carbonate (so-called Macullum homopolymer copolymer) [6]. It would seem as if the direct synthesis from benzene and sulphur [7] can be regarded as especially simple and alluring. In the present paper, some properties of poly(phenylene sulphide) in its native and iodine-doped states, as synthesized in the manner mentioned, are reported.

2. Experimental details

The synthesis of poly(phenylene sulphide) has been accomplished according to the method described previously [7]. The product, polymer I, was used in the investigations.

The doping of the polymer with iodine was performed as follows: a loose polymer powder was mixed with iodine purified by sublimation and the mixture was placed in a specially prepared vessel. After removal of air, the mixture was left in the vessel for 48 h at room temperature. The iodine excess was removed by pumping. The dopant concentration was calculated from weight uptake.

Thermal analysis was carried out with the OD 102 MOM derivatograph, scanning electron microscopy with the Novoscan 30 microscope, infrared spectra were taken on Specord 75 IR with the KSR 4100 computer section, and X-ray spectra on DRON-1.

Pellets for electrical measurements were prepared by pressing loose powder under vacuum using a stainless steel press inside a dry box. A pressure of about 196 kPa was used. Round gold electrodes, 3 mm diameter, were made on both pellet sides by vacuum deposition. The pellets were typically less than 1 mm thick.

The current–voltage characteristics were measured in the dark both in air and in a dynamic vacuum of several Pascals, and from these data electrical conductivities of the samples were calculated. RFT 6350 electrometer (VEB Statron, Fürstenwalde, Spree, GDR) and Z-5001 power supply (Inco, Warsaw, Poland) were used in the experiment.

3. Results and discussion

High thermal resistance is an attribute of poly(phenylene sulphide). This feature also characterizes the poly(phenylene sulphide) synthesized by us. Heating for 4 h in nitrogen at temperatures up to 573 K produces virtually no change in sample, as indicated by the infrared spectra. Annealing under these conditions at higher temperatures gives at first a brown–green, and then brilliantly black incompressible loose powder product. The infrared spectra of the samples annealed at different temperatures are shown in Fig. 1, and correspond to similar results reported by other authors [6, 8]. In Fig. 2, the mass loss during static heating for 4 h in nitrogen atmosphere is plotted against heating temperature.

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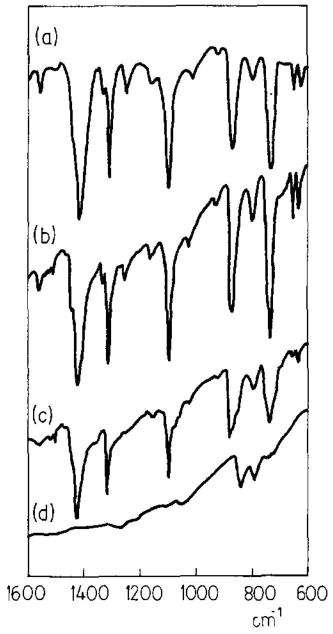

Figure 1 Infrared spectra of poly(phenylene sulphide): (a) pristine polymer, (b) sample annealed at 513 ± 10 K, (c) sample annealed at 708 ± 5 K, (d) residue after annealing at 863 ± 10 K. Annealing was carried out in nitrogen atmosphere for 4 h.

Doping with iodine, as shown in Table I, drastically changes the thermal properties of the polymer. A new peak appears on the DTG curve in the temperature range 393 to 435 K, which grows with increasing iodine content. We found a linear relationship between the total mass loss to 473 or to 873 K and iodine mass fraction (Fig. 3). These straight lines are nearly parallel, which means that the mass loss above 473 K is independent of iodine content. It is characteristic that at higher temperatures the course of the TG and DTA curves is very similar to the course of corresponding curves of the pristine polymer. It becomes obvious that mass loss below 473 K is connected mainly with removal of iodine.

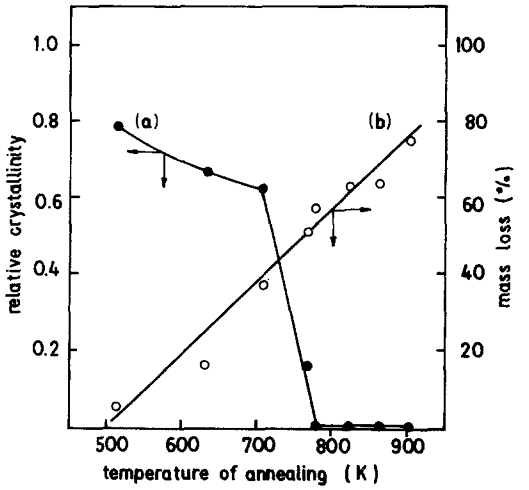

Figure 2 Properties of poly(phenylene sulphide) samples annealed at different temperatures in nitrogen for 4 h. Relative crystallinity (a) was estimated from X-ray diffractograms as the ratio of the areas under the highest peak at the angle $2\theta = 13.7°$ for the annealed and thermally untreated samples. The mass loss (b) was referred to the total mass loss during static annealing performed under the above conditions.

X-ray spectra indicate that, unlike poly(para-phenylene sulphide), poly(phenylene sulphide) prepared by us is crystalline to a very low degree. Both annealing and iodine doping lead to the gradual vanishing of the crystalline phase (Figs 2 and 3). The quickest destruction of the crystalline phase in the undoped polymer is observed in the temperature range 710 to 770 K. These temperatures correspond to the temperature range of intensive mass loss obtained from the thermal analysis data (see Table I). Changes already detectable in the infrared spectrum at temperatures slightly below this temperature region lead next to thermal destruction of the material. This is revealed in both infrared spectra (Figs 1c, d) and X-ray diffractograms, which indicate completely amorphous samples. Chiu *et al.* [9] observed that the organic dopant molecules of chloranil or tetracyanoethylene (TCNE) can penetrate into the crystalline region, followed by the partial destruction of crystallites. Decrease of crystallinity of the iodine-doped samples in comparison with the undoped polymer suggests that iodine exhibits the same behaviour as a dopant species.

The electrical conductivity of poly(phenylene sulphide) samples varies greatly when the samples are doped with iodine. Fig. 4 shows the dependence of bulk conductivity at room temperature plotted against iodine mass fraction. Typical σ against y curves were obtained. They exhibit very distinct conductivity changes at low doping levels and saturate in the range of higher doping levels. It is notable that the conductivity in vacuum is lower than that in air, which may

TABLE I Thermal analysis results for iodine-doped poly(phenylene sulphide)

Iodine content (%)	Temperature range of the most intensive mass loss (K)	Temperature of maximum loss rate* (K)	Mass loss rate (10^{-2} mg sec^{-1})
undoped	718–760	748	1.1
5.4	718–751	738	0.83
10.8	393–438	418	0.53
	718–743	733	0.90
15.2	393–431	411	0.79
	713–751	735	0.72
22.6	393–431	413	1.02
	731–755	743	0.94
29.4	391–431	411	1.44
	725–751	738	0.85

*From the DTG curve.
All samples were heated in nitrogen ($20\,\mathrm{l\,h^{-1}}$), heating rate $3\,\mathrm{K\,min^{-1}}$.

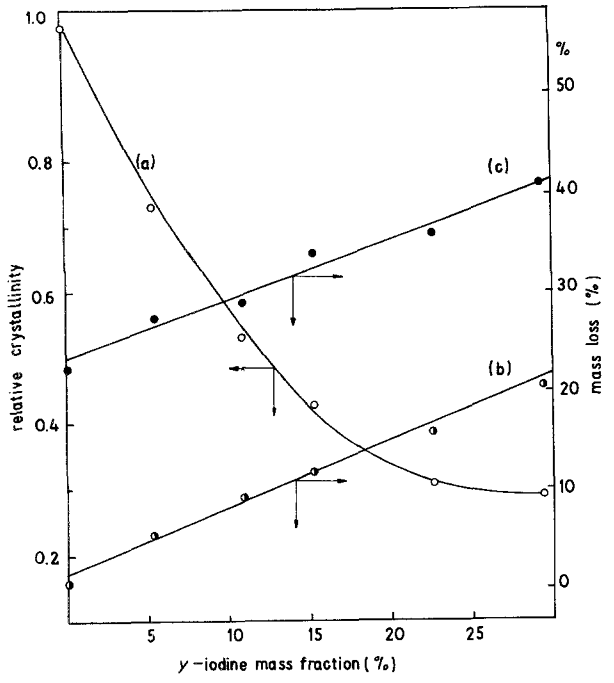

Figure 3 Properties of iodine-doped poly(phenylene sulphide). Relative crystallinity (a) was estimated analogously as for annealed samples. The mass loss (◑) to 473 K (b) and that (●) to 873 K (c) were referred to dynamic heating in nitrogen (20 l h^{-1}, heating rate 3 K min^{-1}).

be connected with the absence of oxygen. Oxygen can play a role of a weak dopant, which was observed in the case of poly(para-phenylene sulphide). Saito *et al.* [10] found the conductivity of this polymer to be very sensitive to oxygen atmosphere. The difference in conductivity measured under high vacuum and in air was about three orders of magnitude, proving that absorbed oxygen is a weak electron acceptor.

The current–voltage characteristics measured in the dark at different temperatures are shown in Fig. 5. These characteristics are practically linear, which leads to the conclusion that the samples of poly(phenylene sulphide) doped with iodine obey Ohm's law.

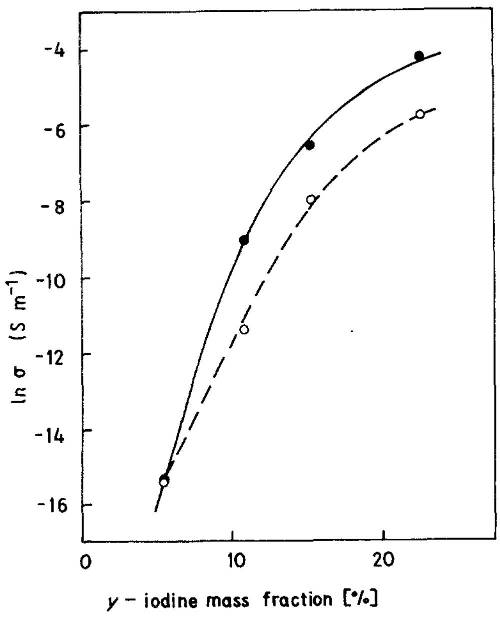

Figure 4 ln conductivity plotted against iodine mass fraction at room temperature, in (●) air, and (○) vacuum.

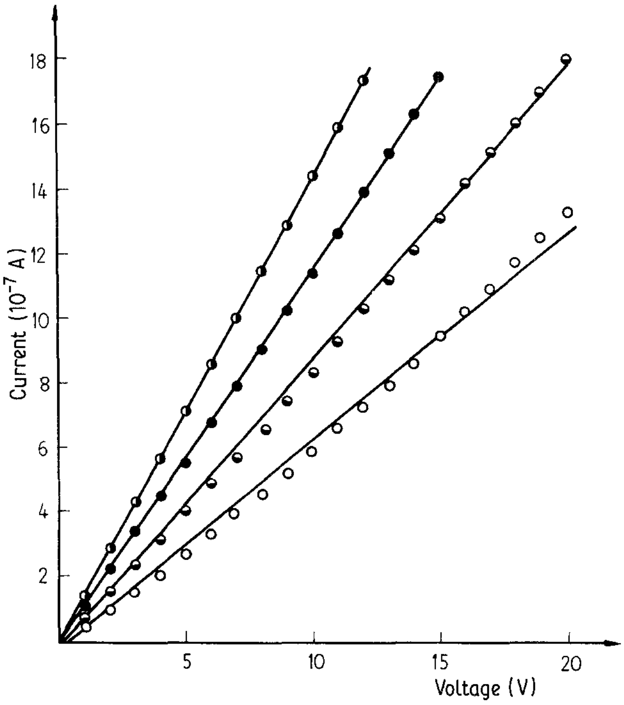

Figure 5 Current–voltage characteristics for the poly/phenylene sulphide/sample containing 10.8% iodine. In vacuum: (○) 298.5 K, (⊖) 319 K, (●) 375 K; In air: (◑) 305 K.

The temperature dependence of specific conductivity for some samples is shown in Fig. 6. The experimental data cannot be described by the simple Arrhenius equation: ln $\sigma \propto T^{-1}$. Also, the equation of the type ln $\sigma \propto T^{-1/2}$ does not give a good description of the conductivity–temperature dependence. This suggests a complex conduction mechanism in the samples under study. Generally, it can be stated that temperature weakly influences electrical conductivity, but causes a striking decrease of conductivity in the temperature region above 320 K. It can be connected with the onset of dopant removal. Derivatographic results indicate that mass loss up to 353 K for a sample

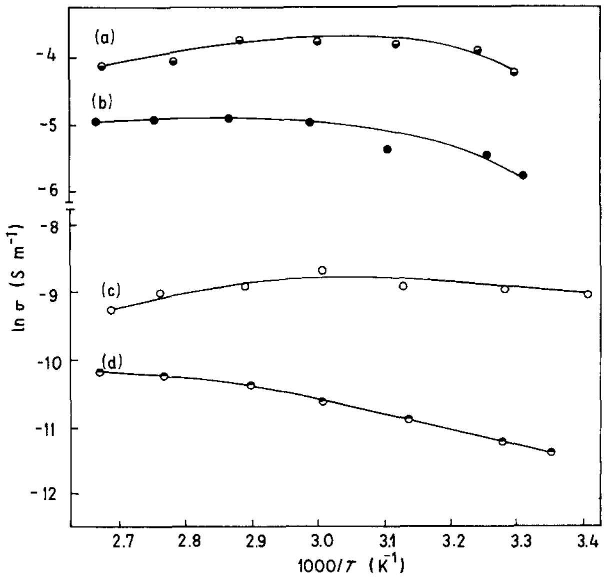

Figure 6 Examples of the temperature dependence of the conductivity for poly(phenylene sulphide) samples doped with different levels of iodine: (a) $y = 22.6\%$, air, (b) $y = 22.6\%$, vacuum, (*c*) $y = 10.8\%$, air, (d) $y = 10.8\%$, vacuum.

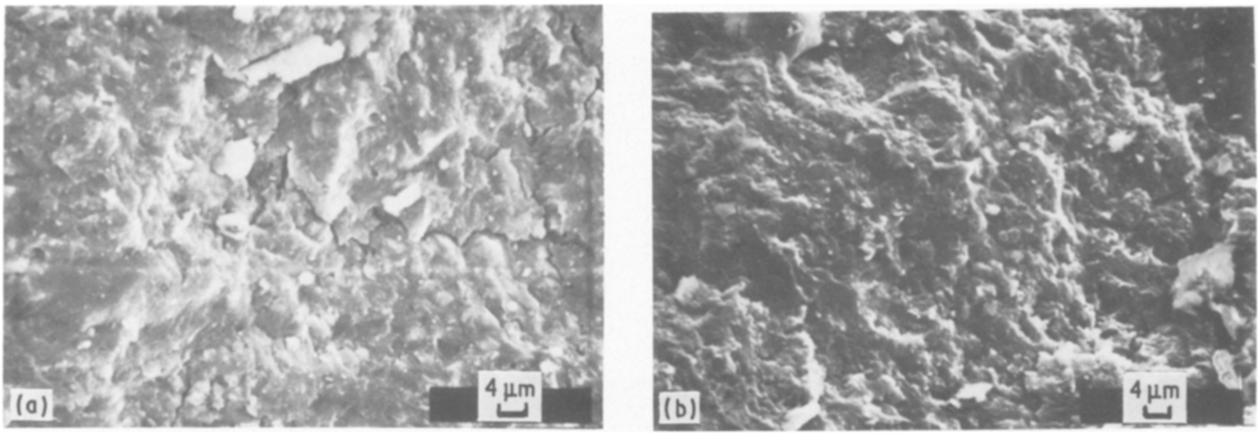

Figure 7 Cross-sectional scanning-electron micrographs of (a) undoped, (b) iodine-doped (y = 29.4%) samples.

containing 22.6% iodine is 0.5%. Although the mass loss is very little it can influence conductivity. As an explanation of the conduction mechanism was not the aim of our research, we did not perform further detail investigations, and concentrated on the experimental determination of the temperature behaviour of the doped samples, which is necessary to characterize the doped polymer as a novel conducting material.

Some authors emphasize that not only dopant content but also morphological aspects of doped polymers should be taken into consideration [11]. Monaco [12] found that doping with antimony pentafluoride (SbF_5) modified the morphology of poly(*m*-phenylene disulphide) samples (PMDS). The PMDS samples before doping and those doped to a very low degree, reveal a globular morphology which changes completely upon doping to a high level with liquid SbF_5. These samples show a morphology with edged particles in place of the previous globules. Scanning electron micrographs of the pellets' cross-section showed that the morphology of poly(phenylene sulphide) samples does not change so greatly (Fig. 7). The fact that iodine is a more moderate doping species than antimony pentafluoride may be the reason why only very small morphological changes are observable.

4. Conclusions

An experimental study was carried out on some properties of poly(phenylene sulphide) in its pristine and iodine-doped states as synthesized from benzene and elemental sulphur. The conclusions are as follows:

1. Poly(phenylene sulphide) exhibits high thermal stability, which decreases in direct proportion to the increase of iodine content in the doped samples. A linear relationship between mass loss and iodine content was established.

2. Both annealing and iodine doping cause decline of crystallinity of poly(phenylene sulphide).

3. Conductivity of an undoped sample is of the order $10^{-10}\,\mathrm{S\,m^{-1}}$. It can be varied in the range from this value to $10^{-2}\,\mathrm{S\,m^{-1}}$ by doping with iodine.

4. No distinct change in the morphology of iodine-doped samples occurs.

Acknowledgement

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