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Conducting polymers from poly(spiro[2,4]hepta-4,6-diene)

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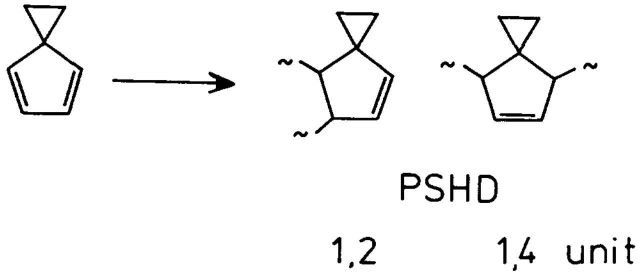
Poly(spiro[2,4]hepta-4,6-diene) (PSHD) was exposed to oxidants such as bromine, iodine and antimony pentachloride either in solution or as a film. Bromine was rapidly added to the C=C bonds of the polymer. Heating the brominated polymer to elevated temperatures resulted in dehydrobromination and the formation of a conjugated, unsaturated polymer backbone, recognizable by the formation of a black, insoluble product. Exposure of PSHD to iodine or antimony pentachloride led to the formation of a black product with a metallic appearance. The conjugation length of the resulting oxidized polymer was rather short. From optical absorption spectra a length of six to eight C=C bonds could be deduced. Infra-red spectra indicated that oxidation was accompanied by a cleavage of the cyclopropyl groups. The oxidized polymer was electrically conducting. Maximum conductivities of 10^{-5} S cm^{-1} were obtained when PSHD was exposed to iodine vapour for several hours. From electron spin resonance studies it could be derived that the conductivity is due to an electron-hopping process.

(Keywords: spiro[2,4]hepta-4,6-diene; conducting polymers; electron hopping)

INTRODUCTION

In recent years, considerable effort has been directed towards the preparation of electrically conducting polymers containing a conjugated, unsaturated backbone[1,2]. An important objective is the preparation of new processable materials. This can either be achieved by the synthesis of soluble or meltable conducting polymers[3–5], or by the preparation of tractable, non-conducting precursor polymers, which are converted into the conducting state subsequent to processing[6–9]. Our research was aimed at developing a new conducting polymer prepared by the precursor route. The precursor should be easily processable into thin films and subsequently convertible into a conducting polymer by an oxidation process.

As the precursor polymer poly(spiro[2,4]hepta-4,6-diene) (PSHD) was chosen, which is easily accessible, stable in air, and can be cast into thin films from solution[10–13]. PSHD is prepared by cationic polymerization of spiro[2,4]hepta-4,6-diene and contains a random mixture of 1,2 and 1,4 units.



There is a close structural relationship between PSHD and poly(cyclopenta-1,3-diene) (PCPD), which has already been shown to be useful as a precursor for conducting polymers[14]. However, PCPD is difficult to handle because of its instability under ambient conditions. PSHD has the advantage of being completely stable in air and therefore it was of interest to study whether this polymer can also be converted into a conducting material. In the following, the preparation and characterization of conducting polymers from PSHD will be reported.

EXPERIMENTAL

Materials

PSHD was prepared according to methods reported elsewhere[10–13]. The conditions of polymerization and characteristic data of the polymers are recorded in *Table 1*. The content of 1,4 units was determined by ^{1}H n.m.r. spectroscopy according to a method reported for PCPD[15]. The molecular weight was determined by gel permeation chromatography in tetrahydrofuran.

The polymer was reacted with oxidants either in solution or after casting into thin films. Films were cast from a solution of the polymer in toluene (0.1 g ml^{-1}). Bromine, iodine and antimony pentachloride (purchased from Fluka and used without further purification) were used as oxidants. Typical procedures are described below.

Reaction of oxidants with PSHD in solution

Reaction with bromine. PSHD (4.61 g, 50 mmol per monomer unit) was dissolved under a nitrogen atmosphere in anhydrous carbon tetrachloride (100 ml) in a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. A solution of bromine (7.99 g, 50 mmol) in carbon tetrachloride (20 ml) was put into the

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Table 1 Preparation conditions and properties of PSHD samples

Initiator	Solvent	Yield (% of theoretical)	M_n[b]	Fraction of 1,4 units[c] (%)	Elemental analysis (% by weight)
$TiCl_4$	Toluene	98	62000	52.0	C: 90.20 H: 8.60
$TiCl_4$/TCA[a]	CH_2Cl_2	98	14000	35.1	C: 91.04 H: 8.92
$Ph_3C^+BF_4^-$	Toluene/CH_2Cl_2	65	4300	69.6	C: 89.20 H: 8.91

[a] TCA = trichloroacetic acid

[b] Determined by viscosimetry using $[\eta] = (4.5 \times 10^{-9})M_n^{1.71}$ (30°C, toluene)[13]

[c] Determined by ^1H n.m.r. spectroscopy[15]

Table 2 Elemental compositions and specific conductivities of oxidized PSHD samples

Oxidant	Elemental analysis (% by weight)	Stoichiometric composition	Specific conductivity[a] ($S\,cm^{-1}$)
Br_2	C: 31.73 H: 2.33 Br: 64.92	$C_7H_{5.7}Br_{0.14}$	8.4×10^{-8}
I_2	C: 26.33 H: 2.48 I: 67.99	$C_7H_{7.2}I_{1.46}$	1.8×10^{-5}
$SbCl_5$	C: 31.59 H: 2.03 Sb: 28.60 Cl: 33.54	$C_7H_{5.4}(SbCl_4)_{0.63}$	1.1×10^{-5}

[a] Powder conductivity at 20°C

dropping funnel. The bromine solution was then added dropwise, with stirring, at a temperature kept constant at 20°C. A yellowish precipitate was formed. When the dropwise addition was complete, the mixture was boiled under reflux for 18 h, with stirring. The precipitate gradually turned dark. The mixture was then cooled, and the precipitate was filtered off with suction in an atmosphere of nitrogen. It was rinsed three times with carbon tetrachloride (50 ml). The product was dried in a high vacuum at 30°C. A yield of 8.1 g of a black, insoluble powder was obtained. Elemental composition and specific conductivity are compiled in *Table 2*.

Reaction with iodine. PSHD (1.84 g, 20 mmol per monomer unit) was dissolved under nitrogen in anhydrous carbon tetrachloride (100 ml) in a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. A solution of iodine (12.70 g, 50 mmol) in carbon tetrachloride (500 ml) was put into the dropping funnel. The iodine solution was then added dropwise with stirring while the temperature was kept constant at 20°C. A violet-black precipitate formed after a short time. When the dropwise addition was complete, the mixture was boiled under reflux for 18 h, with stirring, and the product worked up as described above for the reaction product with bromine. A yield of 6.3 g of a black, insoluble powder was obtained. Elemental composition and specific conductivity are listed in *Table 2*.

Reaction with $SbCl_5$. PSHD (1.84 g, 20 mmol per monomer unit) was dissolved under nitrogen in anhydrous carbon tetrachloride (150 ml) in a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. A solution of $SbCl_5$ (11.96 g, 40 mmol) in carbon tetrachloride (15 ml) was put into the dropping funnel. The $SbCl_5$ solution was then added dropwise, with stirring, at a temperature kept constant at 20°C. A deep brown precipitate was formed immediately. When the dropwise addition was complete, the mixture was boiled under reflux for a further 18 h, and the product was worked up as described above for the reaction product with bromine. A yield of 5.9 g of a black, insoluble powder was obtained. Elemental composition and specific conductivity are listed in *Table 2*.

Reaction of iodine with a PSHD film

Iodine crystals (1.0 g) were initially placed in a thoroughly dried vessel (700 ml) flushed with argon and equipped with a stirrer. Glass supports coated with PSHD (film thickness approximately 1 μm) were then put into the vessel. Coating was effected by spin coating (concentration of the PSHD solution 0.1 g ml^{-1} in toluene; speeds of rotation 30 s at 1200 rev min^{-1} and then 30 s at 3000 rev min^{-1}). After about 1 h the PSHD films assumed a brown colour, and after about 10 h they were completely black and exhibited a metallic appearance. After 21 h, 1 mg of the polymer had taken up 3.89 mg of iodine. The specific conductivity was 2.4×10^{-6} S cm^{-1} (determined on powder samples).

Methods

For conductivity measurements, the polymer samples were pressed into pellets and measured at room temperature using a two-probe technique.

Optical absorption spectra were taken from polymer samples cast onto glass slides using a Perkin–Elmer Lambda 7 spectrometer. Attenuated total reflection Fourier transform infra-red (ATR *FT*i.r.) spectra were monitored from polymer samples cast onto germanium plates using a Nicolet spectrometer.

Electron spin resonance (e.s.r.) spectra were measured on powdered samples using a Varian E-9 X-band spectrometer. Prior to measurement, the samples were evacuated and exposed *in situ* to an argon atmosphere saturated with iodine vapour at room temperature until a constant signal intensity was reached.

RESULTS AND DISCUSSION

Reaction of PSHD with various oxidants

Reactions in solution. Addition of bromine to a polymer solution in carbon tetrachloride led to a rapid decoloration of the bromine owing to its addition to the C=C bonds of the polymer. If the reaction was carried out at temperatures below 20°C, a yellowish solution of the brominated polymer was formed. The brominated polymer could be isolated as a yellowish powder, which gradually decomposed under ambient conditions with the evolution of hydrogen bromide. Bromination of the dissolved polymer at higher temperatures, or heating the solution of the brominated polymer to elevated temperatures, led to a rapid precipitation of a black, insoluble polymer accompanied by the evolution of hydrogen bromide. A different behaviour was observed when iodine or antimony pentachloride was added to a solution of PSHD in carbon tetrachloride. In both cases, the addition of small amounts of oxidant led to the precipitation of a black, insoluble polymer. The polymer precipitated even if the oxidants were added at temperatures below 0°C. The elemental compositions of the reaction products with bromine, iodine and $SbCl_5$ are listed in *Table 2*.

Reaction with PSHD films. Films of PSHD were prepared by casting a toluene solution onto glass plates and evaporating the solvent. In this way, thin films of 1 to 50 μm in thickness were obtained. Upon exposure to an argon atmosphere saturated with iodine vapour, the films gradually turned brownish red and finally, after several hours, became black and exhibited a shining, metallic appearance. Films exposed to an argon atmosphere saturated with $SbCl_5$ vapour behaved similarly and turned brownish purple. Although the original PSHD films were very flexible, the deeply coloured films were brittle and tended to crack after exposure to ambient conditions for a few days.

Specific conductivity of oxidized PSHD

Although the black polymer obtained upon the reaction with bromine was only poorly conducting, the reaction products with iodine and $SbCl_5$ exhibited specific conductivities of up to 10^{-5} S cm^{-1}. In *Table 2*, typical conductivity values are listed. Conductivities measured from powdered samples and films (surface conductivity) were nearly identical. Also, it was observed that neither the concentration of 1,4 units in PSHD nor the molecular weight had any significant effect on the reaction behaviour or the specific conductivity.

Dependence of the specific conductivity on the iodine content. In *Figure 1*, the specific conductivity of a 5 μm thick PSHD film is plotted *versus* its iodine content. The curve indicates that the uptake of one iodine atom per two monomer units is accompanied by an increase in the conductivity of six orders of magnitude. Further uptake of iodine increases the conductivity only little until at about 2.5 iodine atoms a maximum σ value of about 10^{-5} S cm^{-1} is reached. The ability of PSHD to take up large amounts of iodine is due to its low density, which makes the polymer highly permeable to iodine and allows the C=C bonds to be attacked easily. The low density originates from the completely amorphous, rigid backbone structure of PSHD.

Most of the iodine is taken up reversibly. Evacuating a sample which is highly loaded with iodine leads to a decrease of the iodine content from 2.5 to 1.4 atoms per monomer unit. Simultaneously the conductivity drops to the corresponding σ value given in the plot of *Figure 1*.

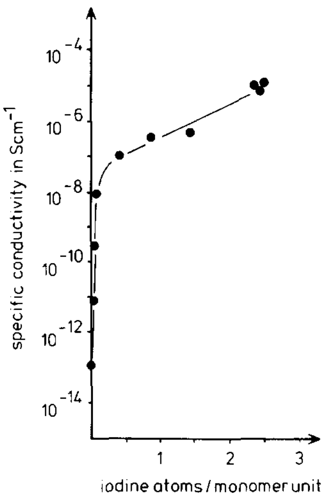


Figure 1 Plot of specific conductivity *versus* iodine content for a thin film of PSHD

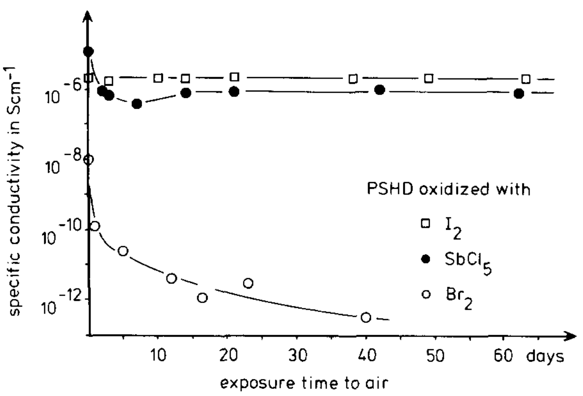


Figure 2 Long-term stability of PSHD films in air after treatment with bromine, iodine and $SbCl_5$

After an additional solvent treatment with toluene overnight, only 0.5 iodine atoms per monomer unit are left. The residual iodine cannot be leached out even upon a prolonged solvent treatment, probably because it is covalently bound to the polymer.

Long-term stability of conductivity. The conductivity of the iodine-treated or $SbCl_5$-treated polymer is rather constant under ambient conditions, while the polymer treated with bromine exhibits a lower conductivity which further decreases in air. As shown in *Figure 2*, the iodine treatment produces a material which does not show any decrease in conductivity even after three months in open air.

Spectroscopic characterization of the oxidized polymer

The oxidized polymer was characterized by u.v./visible, e.s.r. and i.r. spectroscopy.

U.v./visible absorption spectra. These were taken from thin polymer films cast onto glass plates at a thickness of about 0.1 μm. Upon exposure to iodine vapour, the originally transparent films gradually turned brownish red (*Figure 3*). Within 3 h, a strong absorption built up in the visible region showing a broad maximum at about 400 nm. PSHD films exposed to $SbCl_5$ vapour turned brownish purple (*Figure 4*). A broad absorption appeared with maxima at about 400 and 500 nm and a shoulder

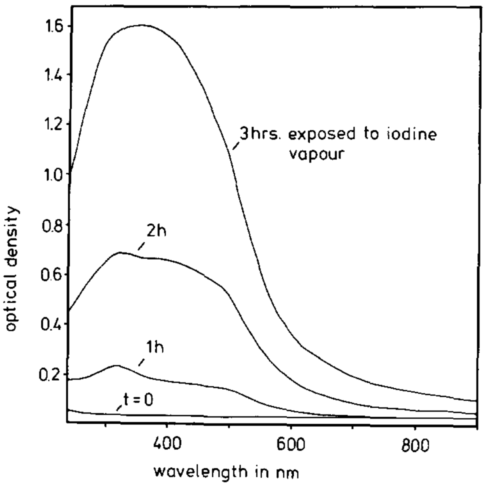


Figure 3 U.v./visible absorption spectra of a thin PSHD film after different exposure times to iodine vapour (film thickness 0.1 μm)

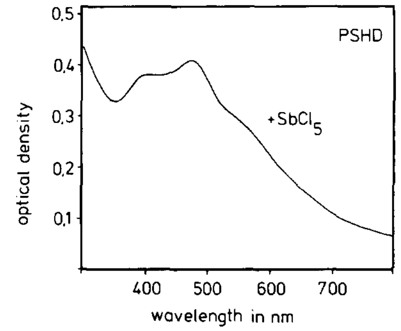


Figure 4 U.v./visible absorption spectrum of a thin PSHD film after exposure to $SbCl_5$ vapour for 3 h

at 560 nm. The bandshape and positions of the absorption maxima were very similar to those reported for PCPD after exposure to $TiCl_4$ vapour[16]. The iodine-exposed polymer films showed a much higher optical density than the $SbCl_5$-exposed films. This is due to the strong absorption of the iodine, which is present in the polymer either in the form of I_2 molecules or I_3^- and I_5^- chains. On the other hand, the colour of the $SbCl_5$-exposed films must originate from the optical absorption of the oxidized polymer itself. As already discussed for PCPD[16], it can be concluded from the wavelength positions of the absorption maxima that short conjugated sequences of six to eight C=C bonds have been formed.

E.s.r. measurements. Measurements on powdered samples indicated that the spin concentration increased by a factor of 20 when PSHD was exposed to iodine or $SbCl_5$ vapour. However, even in the strongly exposed samples the radical concentration remained rather low and did not exceed about one radical per 3000 monomer units at 77 K. As shown in *Figure 5*, the e.s.r. signals exhibit an asymmetric lineshape and are rather broad. Samples treated with iodine vapour exhibit a g value of 2.0058. From this high value a localized position of the radicals can be concluded. Radicals in samples exposed to $SbCl_5$ vapour exhibit a lower g value (2.0030), and are thus more delocalized. Owing to the low concentration and localized position it seems unlikely that these radicals will play an important role in the conduction mechanism. Instead, charge transport is more likely dominated by an electron-hopping process between cations (positively charged solitons) present in the oxidized polymer, as similarly proposed for other conjugated polyenes[17].

I.r. spectroscopy. From this it was hoped to obtain further information on the molecular structure of the oxidized polymer. Therefore, thin PSHD films (thickness smaller than 0.5 μm) were cast onto germanium crystals and ATR *FT*i.r. spectra were taken prior and subsequent to iodine treatment. In *Figures 6a* and *6b* the corresponding spectra are shown. The spectrum of pure PSHD in *Figure 6a* is in accord with a spectrum reported in the literature[10]. The i.r. spectrum of the iodine-treated polymer is completely different (*Figure 6b*). The band at 3000 cm^{-1} can be ascribed to C–H stretching vibrations. The strong, broad band at about 1450 cm^{-1} probably

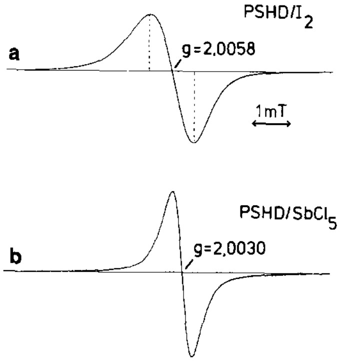


Figure 5 E.s.r. signals of powdered PSHD after exposure to (a) iodine vapour and (b) $SbCl_5$ vapour

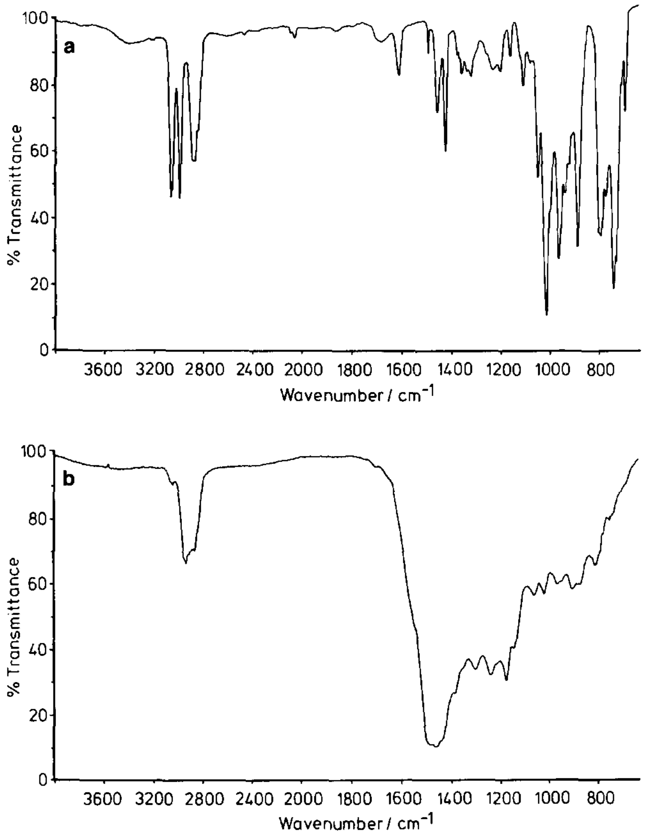


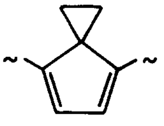
Figure 6 ATR *FT*i.r. spectra of <0.5 μm thick PSHD films (a) prior and (b) subsequent to iodine exposure for 3 h

originates from C–H bending and C–C stretching vibrations of the polymer backbone. Peaks due to the cyclopropyl ring appearing at 810, 1012, 1045 and 3080 cm^{-1} (see *Figure 6a*) are almost completely lacking in the oxidized polymer (*Figure 6b*). This may indicate a partial cleavage of the cyclopropyl ring during the oxidation process. Other bands between 1400 and 800 cm^{-1} are only poorly resolved and do not allow us to draw further conclusions on the polymer structure.

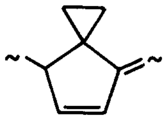
Structure of the oxidized polymer

From the experimental observations it is evident that PSHD becomes oxidized to give a polymer with a conjugated, unsaturated structure. Since the molecular structure of PSHD is rather complex because it contains a random mixture of 1,2 and 1,4 units, both as *cis* and *trans* isomers, the structure of the oxidized polymer will be even more complex. At present, we can only speculate on the structure of the oxidized polymer.

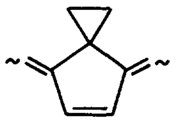
In the case where the cyclopropyl ring remains uncleaved, the oxidation of the 1,2 and 1,4 units of PSHD should lead to structural units such as **I** to **VI** with endocyclic and exocyclic C=C bonds, as similarly proposed for oxidized PCPD.



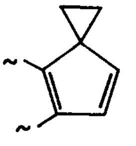
I



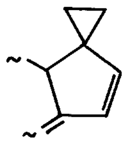
II



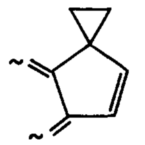
III



IV



V



VI

The opening of the cyclopropyl group would lead to diradical species which could give rise to the formation of a variety of other structures. Isomerization of the C=C bonds, crosslinking of polymer chains and new ring formation[18] can occur.

SUMMARY AND CONCLUSIONS

Our study shows that PSHD can be used as a tractable precursor for conducting polymers. Treatment with oxidants leads to simultaneous dehydrogenation and formation of an oxidized (doped), conjugated, unsaturated polymer with a specific conductivity of up to $10^{-5}\,S\,cm^{-1}$. While the reaction with bromine proceeds according to an addition/elimination mechanism, reactions with iodine and $SbCl_5$ immediately lead to a dehydrogenated product. It can be inferred that PSHD reacts analogously with other oxidants such as AsF_5 and $FeCl_3$. Also, it seems likely that PCPD behaves similarly and can be converted into a conducting polymer when exposed to iodine or strong Lewis acids such as AsF_5 and $SbCl_5$.

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