Continuous wave nuclear magnetic resonance and infra-red studies of poly(phenylene sulphide) doped with $FeCl_3$

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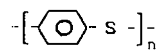
Temperature dependences of the nuclear magnetic resonance linewidth for semiconducting poly(phenylene sulphide) (PPS) doped with $FeCl_3$ have been measured. It was found that the penetration of dopant molecules into the structure caused an increase in distance between polymer chains. Moreover, for low concentration of dopant the low temperature oscillations of phenylene rings were hindered in the crystalline phase, whereas for high concentration of dopant the low temperature rotations vanished in the amorphous phase and the crystalline phase was completely destroyed. The Fourier transform infra-red spectra of the doped PPS samples showed a slight modification of the chemical structure consisting of enhanced double bond character of the C–S bond and partial chlorination of the phenylene rings.

(Keywords: n.m.r. spectroscopy; poly(phenylene sulphide); doping)

INTRODUCTION

Poly(phenylene sulphide) (PPS) is a polycrystalline, aromatic polymer composed of *p*-substituted benzene rings connected via sulphur atoms. It has the following chemical formula:



The degree of crystallinity of PPS determined by X-ray diffraction is ~65%[1]. The glass transition temperature, T_g, the recrystallization temperature and the melting point are 365, 400 and 558 K, respectively[1]. The structure and molecular dynamics of PPS have already been studied using the ^1H continuous wave nuclear magnetic resonance (CW n.m.r.)[2,3]. It was found that above 360 K, the n.m.r. resonance line was made up of two components; a broad component which was assigned to the crystalline phase, and a narrow component which was assigned to the amorphous phase of the polymer.

Unmodified PPS is an insulator with a conductivity[4] of 10^{-17} S cm^{-1}. After doping with strong electron acceptors it forms conducting complexes. One of the most effective dopants for PPS is $FeCl_3$. An amorphous PPS film doped with a 0.1 M solution of $FeCl_3$ in nitromethane has a conductivity[5] of 3.4×10^{-3} S cm^{-1}.

In a previous paper[6] we discussed the temperature and concentration effects of doping with $FeCl_3$ on the nuclear relaxation of PPS. It was found that over a wide range of temperature and for various concentrations of paramagnetic dopant the thermal relaxation exhibits a non-exponential nature which is caused by the interaction between protons and the dipole moments of the paramagnetic centres. The strong influence of interaction between protons and paramagnetic centres on the relaxation time T_1 did not allow the dynamics of segments of the PPS chains to be studied.

Broad line spectroscopy (CW n.m.r.) is one of the techniques that provides information on the molecular structure of solid polymers. Studies of the n.m.r. linewidth and its second moment as a function of temperature enables information to be obtained on the interactions between the magnetic moment of nuclei and their position in the crystalline lattice. This technique is especially useful in studies of polymers, as it provides information on both the crystalline and amorphous phases. On the other hand, the temperature dependence of the n.m.r. linewidth may provide data on the thermally activated molecular motions in polymers. For a low concentration of paramagnetic centres in conducting polymers, the broad line method has an important feature, i.e. it enables the influence of these centres on dipolar interactions to be ascertained. Here, we present the results of our measurements of the n.m.r. linewidth as a function of temperature as well as Fourier transform infra-red (*FT*i.r.) spectra of the semiconducting polymer obtained by doping PPS with a solution of $FeCl_3$ in nitromethane.

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Table 1 Results of elemental analysis for PPS doped with $FeCl_3$ (samples A and B) and for pristine PPS (sample C)

	Percentage content of elements					
Sample	C	H	S	Cl	Fe	Empirical formula
A	62.1	3.8	25.8	4.6	1.4	$C_6H_{4.37}S_{0.93}Cl_{0.15}Fe_{0.03}$
B	44.1	2.1	21.6	18.6	5.8	$C_6H_{3.40}S_{1.1}Cl_{0.86}Fe_{0.17}$
C	66.3	3.6	28.4	0.7	0.0	$C_6H_{3.92}S_{0.96}Cl_{0.02}$

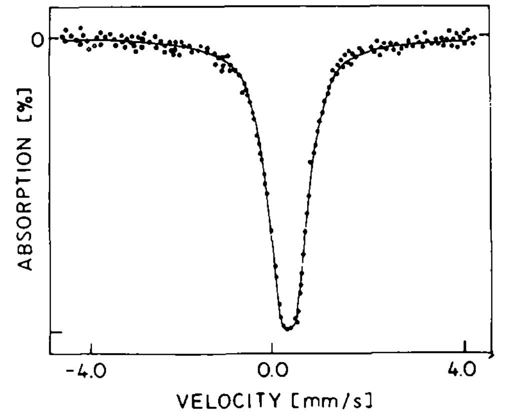

Figure 1 Mössbauer spectrum of PPS doped with a 1 M solution of $FeCl_3$ (sample B) measured at 78 K

EXPERIMENTAL

Poly(phenylene sulphide) (Ryton V-1, Phillips Petroleum Co., USA) was purified from low molecular oligomers with tetrahydrofuran in a Soxhlet column. Two semiconducting samples containing various concentrations of dopant were prepared. Sample A was prepared by doping PPS with a 0.1 M solution of $FeCl_3$ in nitromethane for 4 h, whereas sample B was doped for 18 h with a 1 M solution of $FeCl_3$. The details of the preparation procedure have been described elsewhere[6]. To determine the chemical composition of the doped samples, elemental analyses of carbon, hydrogen, sulphur, iron and chlorine were performed.

The ^1H CW n.m.r. measurements were performed with a continuous wave spectrometer with automatic field and frequency stabilization[7]. The temperature of the samples was controlled within ± 1 K in the range from 120 to 510 K.

The i.r. spectra were recorded in KBr pellets (1 mg PPS/200 mg KBr) with an *FT*i.r. spectrophotometer (model IFS 113v; Brüker, Karlsruhe, Germany) at 293 K. The KBr pellets were prepared in a carefully dried glove box under a nitrogen atmosphere. The spectra were taken under reduced pressure.

RESULTS AND DISCUSSION

Description of the doped samples

During doping the samples changed in colour from bright beige to bright green (sample A) and dark green (sample B); the green colour being characteristic[5] of doped conducting PPS. The conductivity increased several orders of magnitude to a value[6] of 6×10^{-5} S cm^{-1} for sample A. The results of the elemental analysis of both samples and pristine PPS are given in *Table 1*.

Table 2 ^{57}Fe Mössbauer parameters of PPS, polyacetylene (PA) and poly(*p*-phenylene) (PPP) doped with $FeCl_3$ measured at 78 K

Sample	IS (mm s^{-1})	QS (mm s^{-1})
PPS + $FeCl_3$	0.29 ± 0.02	0.34 ± 0.06
PA + $FeCl_3$	0.30 ± 0.01	0.36 ± 0.02^a
PPP + $FeCl_3$	0.30 ± 0.01	0.35 ± 0.01^a

[a] After reference 8

In the weakly doped sample (A) the ratio of dopant molecules to PPS mer is 1:33, whereas in the strongly doped sample (B) the ratio is 1:6. The ratio of chlorine to iron atoms is the same for both samples (5:1).

The large number of Fe nuclei allowed Mössbauer spectra to be obtained for sample B. This spectrum measured at 78 K is shown in *Figure 1*. The calculated Mössbauer parameters are given in *Table 2* and are compared[8] with those for polyacetylene and polyphenylene doped with $FeCl_3$. The values of isomer shift (IS) and quadrupole splitting (QS) observed for all these samples are consistent with the presence of tetrahedral FeX_4^- anions; the IS of FeX_4^- is in the range of 0.25–0.35 mm s^{-1} whereas QS varies between 0 mm s^{-1} and 0.4 mm s^{-1} depending on the extent of tetrahedral distortion[8]. The presence of only one line in the Mössbauer spectrum at 78 K indicates that the structure of the doped polymer is non-degraded and all the iron atoms in the polymer lattice had the form FeX_4^-.

As pointed out earlier, the ratio of Fe:Cl was found by means of elemental analysis to be 1:5. On the other hand the Mössbauer spectroscopy results showed that only one type of anion is present in the doped polymer with a Fe:Cl ratio of 1:4. This difference clearly indicates that the chlorination of the phenylene ring occurs during the doping process.

X-ray diffraction studies[6] showed that the degree of crystallinity of sample A is lower than that of pristine PPS, providing that the same crystalline structure is maintained. However, sample B does not exhibit any signals originating from the crystalline phase. The studies of the relaxation time T_1 showed that in both samples the distribution of the $FeCl_3$ dopant is heterogeneous[6].

CW n.m.r. studies

A single, broad resonance line, characteristic of the rigid polymer structure, is observed for both samples within the low temperature range. At higher temperatures, an additional narrow line (<0.1 mT) appears. This line is assigned to the rotation of phenylene rings in the amorphous phase[9] (*Figure 2*). In spectra of sample with low concentration of dopant (A) and of pristine polymer the narrow component is clearly visible from ~ 200 K, whereas in spectra of highly doped sample (B) this line appears at temperatures above 400 K.

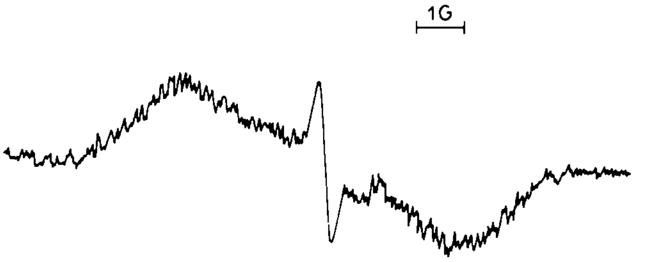

Figure 2 A CW n.m.r. spectrum of PPS doped with a 0.1 M solution of $FeCl_3$ (sample A) at 260 K

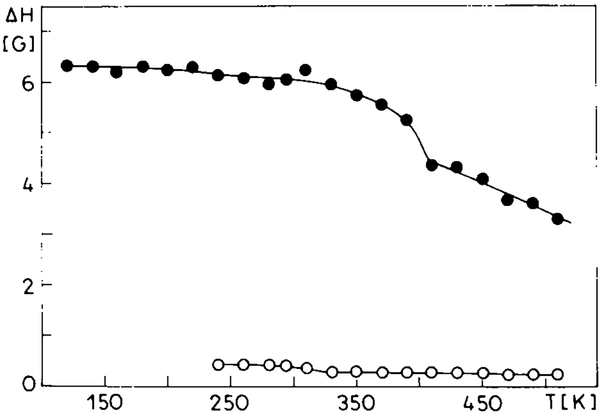

Figure 3 Temperature dependence of the n.m.r. linewidth of PPS doped with a 0.1 M solution of $FeCl_3$ (sample A): (●) broad line component; (○) narrow line component

The temperature dependences of the n.m.r. linewidth for the doped PPS samples are shown in *Figures 3* and *4*. *Figure 5* shows the analogous results[9] for pristine PPS.

In both samples A and B, i.e. for low and high concentrations of dopant, a distinct narrowing of the n.m.r. line (>0.1 mT) is observed within the low temperature range. This indicates that doping reduces the interactions between protons. Since the structure of the polymer chains is essentially the same after doping, the observed decrease in linewidth is interpreted as being due to the increasing distance between protons in the neighbouring polymer chains.

The degree of doping considerably affects the manner in which the linewidth depends on temperature. For low concentration of dopant (sample A) the linewidth remains almost constant up to 320 K, and then gradually decreases due to glass transition (365 K) and recrystallization (400 K) processes. The constant value of the linewidth observed in the low temperature range indicates hindering of the random oscillations of the phenylene rings by the dopant molecules inserted into the crystalline structure of the polymer. We have previously shown using X-ray diffraction measurements[6] that the crystal structure of the slightly doped PPS (sample A) is unchanged and only a lower degree of the crystallinity is observed in comparison to pristine PPS. Hence, even a small amount of dopant molecules inserted in the polymer chain reduce the random oscillations of the phenylene rings. The increasing energy of the molecular motions in the vicinity of the T_g activates these oscillations and leads to a reduction in the linewidth.

For high concentration of dopant (sample B) narrowing of the resonance line begins above 180 K. This effect is similar to the narrowing of the n.m.r. line in solids due to the appearance of additional motions and may be described by the following phenomenological formula[10]:

$$\ln\left(\frac{1}{W}-\frac{1}{A}\right) = -\frac{E_a}{kT} + \ln\left(\frac{1}{B}-\frac{1}{A}\right) \qquad (1)$$

where W denotes the linewidth at temperature T, A is the limit linewidth at low temperature, E_a is the activation energy and B is the limit linewidth at high temperature. Application of this formula to sample B allows the determination of the E_a (9.6 ± 2.2 kJ mol^{-1}) within the range from 180 to 330 K. This value of E_a is characteristic of the oscillations of the phenylene ring in pristine PPS[3]. In this case the crystal structure of the doped polymer is completely destroyed as shown by X-ray diffraction studies[6]. Thus, in such a disordered sample, the random oscillations occur much easier in comparison to a sample with crystalline structure in spite of the higher concentration of dopant molecules.

It is worthwhile stressing that in both doped samples all the temperatures characteristic of the pristine PPS, i.e. glass transition and recrystallization, remain unchanged; temperature dependences of linewidth show inflection points in the vicinity of these temperatures. This indicates that the chain structure is not affected by doping.

Above the recrystallization temperature (400 K), the doped polymer undergoes essential modifications: its

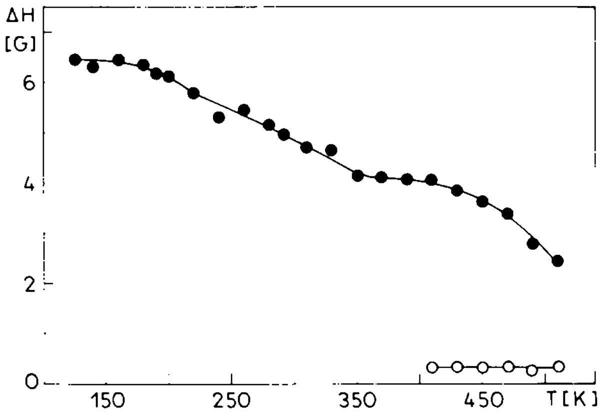

Figure 4 Temperature dependence of the n.m.r. linewidth of PPS doped with a 1 M solution of $FeCl_3$ (sample B): (●) broad line component; (○) narrow line component

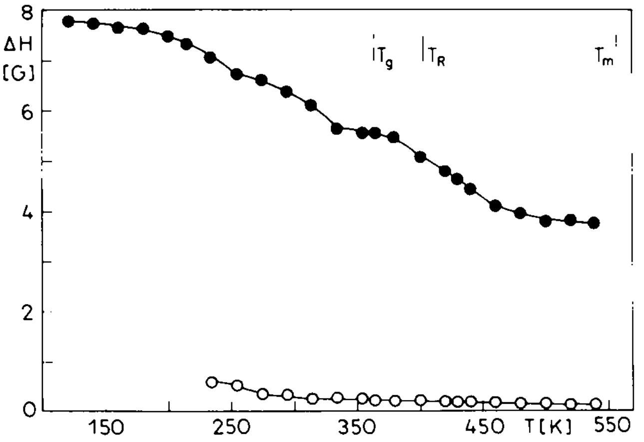

Figure 5 Temperature dependence of the n.m.r. linewidth of pristine PPS[9]: (●) broad line component; (○) narrow line component

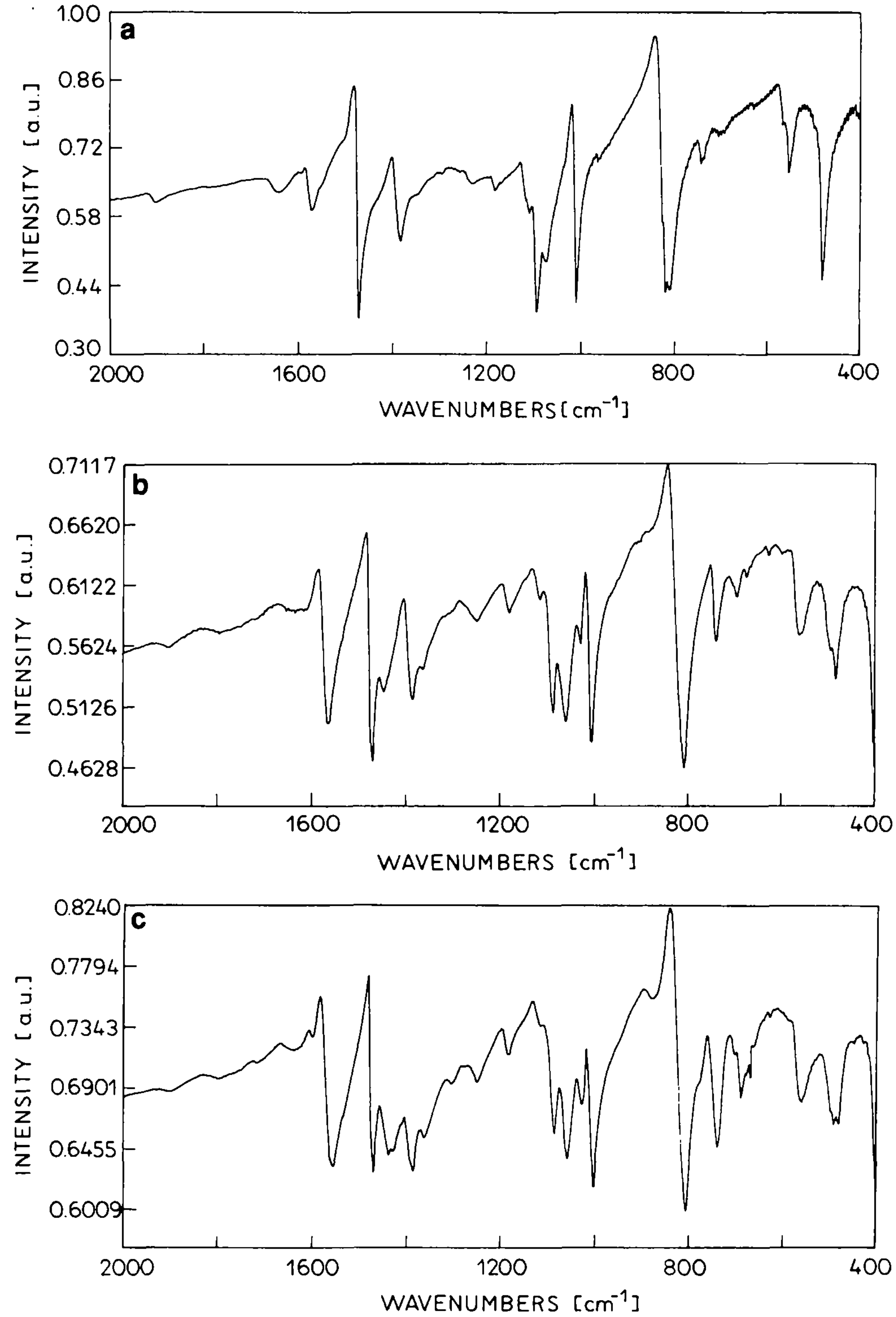

Figure 6 Infra-red spectra of pristine PPS and its $FeCl_3$-doped modifications: (a) *FT*i.r. spectrum of pristine PPS; (b) *FT*i.r. spectrum of PPS doped with a 1 M solution of $FeCl_3$; (c) *FT*i.r. spectrum of PPS doped with a 1 M solution of $FeCl_3$ and annealed for 1 h at 510 K

colour changes from green to beige (indicating a decrease in conducting properties), and broad resonance lines narrow in both samples, whereas in the highly doped sample a narrow component appears. All these phenomena are related to a considerable increase in energy of molecular motions in the PPS molecule, which exceeds the energy of bonding between dopant molecules and the polymer chain. This leads to separation of the $FeCl_4^-$ ion from the polymer macromolecule, and to rotation of the phenylene rings.

I.r. spectra

The i.r. spectra of the pristine PPS and its doped forms are shown in *Figure 6*.

The positions and intensities of the i.r. absorption bands for pristine PPS (*Figure 6a*) are in good agreement with literature data[11–14]. Doping with a 0.1 M solution of $FeCl_3$, leading to an increase in conductivity and decrease in the n.m.r. linewidth, only slightly affects the i.r. spectrum. The shift of the skeleton vibration band from 1570 to 1567 cm^{-1}, without changes in the intensity and position of the remaining bands, suggests that the PPS structure undergoes only a minor change after doping or the contribution from a modified structure is small. The lack of changes in the PPS structure is understandable after taking into account the results of diffraction studies and elemental analysis which show that the ratio of dopant molecules to the PPS mers is 1:33.

However, doping with a 1.0 M solution of $FeCl_3$ considerably affects the *FT*i.r. spectrum of PPS (*Figure 6b*). Fundamental changes concern the shift of the skeleton vibration band from 1570 to 1563 cm^{-1} with an increase in its integral intensity. The band assigned to the deformation out-of-plane vibrations of the two hydrogen atom pairs of the phenylene ring also shifts from 814 to 808 cm^{-1}, losing its characteristic doublet splitting. Moreover, the new bands appearing at 1446, 1251, 1060 and 1028 cm^{-1} as well as relative changes in intensities of the remaining bands suggest major structural changes in such a doped sample. The absence of the band at 1298 cm^{-1} assigned to the quinoid structure[15,16] and the band of the out-of-plane deformational vibrations of a single hydrogen atom in the phenylene ring located at $\sim$850 cm^{-1} indicates that the formation of the polybenzothiophene structure, suggested previously for the polymers doped with SO_3 (ref. 12) and AsF_5 (ref. 17), is improbable in this case.

A shift of the skeleton vibration band towards lower frequencies and the increase of its integral intensity as well as the appearance of a new band at 1060 cm^{-1} with a simultaneous shift in the out-of-plane deformational vibration of the phenylene ring hydrogen atoms towards lower frequencies suggest that the formation of the conducting polymer structure is caused by an enhancement of the double bond character of the C–S bond. Similar changes were observed[18] in PPS doped with TaF_5. Doping with $FeCl_3$ can also lead to partial chlorination of the phenylene ring[19]. In the case of PPS doped with $FeCl_3$ this suggestion is supported by the results of elemental analysis and the presence of a band situated at 1050 cm^{-1} in the i.r. spectrum which can be assigned to the C–Cl vibrations.

The presence of the band at 1438 cm^{-1} and the characteristic bands at 850 and 710 cm^{-1} in the *FT*i.r. spectrum (*Figure 6c*) of the annealed polymer indicates that the decay of conductivity after annealing is also partially caused by formation of additional bridges between the polymer chains.

CONCLUSIONS

The PPS polymer doped with a solution of $FeCl_3$ in nitromethane not only has its electrical conductivity inhibited but also undergoes structural changes. Doping increases the distance between protons due to separation of the polymer chains by $FeCl_4^-$ molecules. Low concentration of dopant does not destroy the crystalline structure, but hinders the low temperature oscillations of the phenylene rings, characteristic of pristine PPS in the crystalline phase. Due to large intermolecular distances the rotations of rings in the amorphous region are not affected by low concentration of dopant. However, for high concentration of dopant, e.g. caused by doping with a 1 M solution of $FeCl_3$, the PPS crystalline structure is completely destroyed. This destruction releases the phenylene ring oscillations in the low temperature range, however full rotations are blocked by the large number of dopant molecules in the polymer.

Heating the doped samples above the T_g of PPS breaks the bonds between dopant and polymer molecules. This leads to a decrease in electrical conductivity and releases the molecular motions characteristic of pristine PPS.

The described modifications refer to the macromolecular structure of PPS. The chemical structure of the chain in $FeCl_3$-doped PPS undergoes only a slight modification consisting of enhanced double bond character of the C–S bond and partial chlorination of the phenylene rings.

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