I.r. spectroscopy and ^{1}H n.m.r. broad line studies of poly(*p*-phenylene sulphide) doped with sulphur trioxide

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I.r. spectra and temperature dependences of ^{1}H n.m.r. linewidths were measured for poly(*p*-phenylene sulphide) (PPS) heavily doped with sulphur trioxide (SO_3) in the form of vapour and liquid. X-ray diffraction studies confirmed the total destruction of the crystalline phase as a result of the doping process. I.r. spectra show that doping with SO_3 leads to irreversible chemical modifications of the polymer by sulphonation. A comparison of the experimental values of the n.m.r. second moment determined for a rigid structure of the doped PPS with the poly(benzothiophene) excludes the formation of the latter as a result of doping. Doping with SO_3 in the vapour form leads to structural changes in the polymer with its two-phase character preserved. Annealing of the doped sample at 450 K results in the removal of chemically unbonded SO_3. However, the annealed polymer still has a different structure from the pristine polymer. PPS doped with liquid SO_3 shows a monophase structure indicated by a liquid-like resonance line.

(Keywords: i.r.; n.m.r.; poly(*p*-phenylene sulphide); sulphur trioxide; doping)

INTRODUCTION

Organic conducting polymers have recently become a popular subject to research. Interest in them has been stimulated by the possibility of their wide applications in electronics and electrical engineering as well as by the fascinating nature of their specific mechanism of electric conduction. At present the most popular organic conducting polymers are polyacetylene, polyphenylene, polypyrrole, polythiophene, polyacrylonitrile and poly(*p*-phenylene sulphide) (PPS).

PPS is a crystalline aromatic polymer with a rigid backbone chain consisting of *p*-substituted benzene rings linked by a single sulphur atom (*Figure 1a*). The structure of crystalline PPS was determined by X-ray diffraction[1,2]. Its molecular structure is assumed to be a zigzag chain in which sulphur atoms are arranged in the (1 0 0) plane. The degree of crystallinity determined by Brady[3] by X-ray diffraction is ~65%. The glass transition temperature (T_g) estimated by differential thermal analysis is 365 K, the recrystallization temperature (T_R) is 400 K and the crystalline melting point (T_m) is ~558 K[3]. The structure and molecular dynamics of PPS have been studied by n.m.r. pulse and broad line methods[4,5]. Above 360 K the resonance line was found to have a two-phase character, the broad and narrow line components being ascribed to the crystalline and amorphous phases of the polymer, respectively.

PPS is a good insulating material with a conductivity[6] of 10^{-17} S cm^{-1}. PPS may be doped with strong electron acceptors such as AsF_5, SbF_5 (ref. 7) and SO_3 (ref. 8) giving conducting complexes with a maximum conductivity of 25–10^{-4} S cm^{-1}, respectively. Structural changes in PPS doped with SO_3 and the character of its conductivity were studied by Kazama *et al.*[9,10]. They analysed ^{13}C cross-polarization/magic angle spinning n.m.r., i.r. spectra and frequency dependence of spin-lattice relaxation times of doped PPS, showing that the most probable modification is the formation of a poly(benzothiophene) (PBT) like-structure (*Figure 1b*). However, i.r. studies by Schoch *et al.*[8] indicated the occurrence of sulphonation and possibly crosslinking during light doping of PPS films with SO_3. Also Shimizu *et al.*[11] suggested from X-ray photoelectron spectroscopy measurements that doping with SO_3 seemed to mainly induce sulphonation on the PPS chain, although a charge transfer structure also appeared.

Since the possible structure of the PPS doped with SO_3 proposed by Kazama *et al.*[9,10] is quite different from that suggested by Schoch *et al.*[8] and Shimizu *et al.*[11] we have undertaken i.r. and ^{1}H n.m.r. experiments to shed more light on the structural changes in PPS induced by heavy doping with SO_3. One of the n.m.r. methods giving

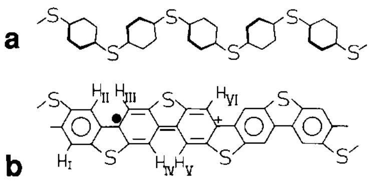

Figure 1 Molecular structure of (a) PPS and (b) PBT with a partial quinoid-like structure. The dot denotes an electron or a hole

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information on the molecular structure of a solid polymer is broad line spectroscopy. Studies of n.m.r. resonance linewidth and the second moment support data for dipole–dipole interactions of nuclear spins and positions of nuclei in the crystal structure. This method can give information on the crystalline and amorphous phases in polymers. On the other hand, the temperature dependence of the resonance linewidth can provide information about thermally activated molecular processes in polymers.

EXPERIMENTAL

PPS powder (Ryton V-1 grade, Phillips Petroleum Co., USA) was purified with tetrahydrofuran and then dried at 373 K for several hours (sample I). Doping with SO_3 was carried out using either SO_3 vapour or liquid SO_3.

To carry out the reaction with SO_3 vapour, fine grain PPS powder was put in a glass reactor connected to a reservoir filled with fuming sulphuric acid (65%, reagent grade, Merck, Germany). The reactor was continuously evacuated (10^{-4} Pa) for several hours. Then the SO_3 vapour from the fuming sulphuric acid was distilled into one chamber in the reactor and frozen. The frozen SO_3 was the source of vapour used for doping. The doping process was stopped when the PPS powder changed from light beige to black. In the next step the reactor was evacuated and the doped polymer was transferred directly from the reactor into an n.m.r. probe connected to it. The probe was then sealed under vacuum (sample II).

PPS doped with SO_3 vapour was annealed in a closed glass ampoule up to 450 K in order to remove chemically unbonded SO_3. At that temperature the ampoule broke due to the pressure of the released SO_3 vapour, and the colour of the doped PPS changed from black to brown. The powder annealed at 450 K was then placed in an n.m.r. probe which was sealed under vacuum (sample III).

Doping with liquid SO_3 was carried out in the evacuated (10^{-4} Pa) glass reactor. The source of SO_3 was the same fuming sulphuric acid. The SO_3 vapour was distilled into one chamber of the reactor and frozen. Solid SO_3 was then melted and poured into the chamber with PPS powder. The polymer saturated with liquid SO_3 was put into the n.m.r. probe connected to the reactor and the content of the probe was frozen and sealed under vacuum (sample IV).

Samples I and II were subjected to elemental analysis (C, H and S). The analysis for carbon and hydrogen was performed on a Perkin-Elmer 240 apparatus and the sulphur content was determined by titration.

For samples II and III the X-ray diffraction study was performed on a diffractometer (type TUR M62, Zeiss, Germany) with Ni-filtered CuKα radiation.

I.r. spectra were taken using KBr pellets (1 mg per 200 mg) and a Fourier transform i.r. (*FT*i.r.) spectrophotometer (model Bruker IFS 113v) at 293 K. KBr pellets were prepared in a carefully dried glove box under nitrogen atmosphere and i.r. spectra were taken under reduced pressure.

^{1}H n.m.r. studies were carried out by the broad line method on a home-made continuous wave spectrometer with automatic stabilization of the ^{1}H field level and frequency[12]. The measurements were performed in the temperature range from 140 to 500 K at a frequency of 30 MHz.

RESULTS AND DISCUSSION

Elemental analysis and X-ray diffraction

The results of elemental analysis are given in *Table 1*. The analysis shows that the purity of sample I is ~99%. The amount of SO_3 in sample II corresponds to one molecule of SO_3 per PPS unit and four hydrogen atoms correspond to six carbon atoms.

The X-ray diffraction study of samples II and III revealed no reflections in the crystalline phase. It clearly shows that the crystalline phase was destroyed during heavy doping and after the removal of chemically unbonded SO_3, recrystallization process does not occur. Similar results have been reported[8] for PPS films doped with SO_3.

I.r. spectroscopy

*FT*i.r. spectra of samples I and II are shown in *Figure 2*. The spectrum of sample I is quite similar to those reported previously[9,13–15]. The ring stretching vibrations at 1471 and 1570 cm^{-1} and the out-of-plane vibrations of the two paired hydrogen atoms in a phenyl ring at 819 cm^{-1}, as well as the vibrations in plane of the paired hydrogens at 1091 cm^{-1}, confirm the structure of PPS determined by X-ray crystallography[1]. An additional absorption at 3450 cm^{-1} is due to the OH stretching vibration. This comes from the traces of water, which could not be removed from PPS, even after drying at 333 K under reduced pressure (10 Pa) for 48 h.

A dramatically different spectrum is obtained for the heavily doped PPS (sample II). The most characteristic feature of this spectrum is a broad absorption in the 3700–1650 cm^{-1} region which is attributed to the strongly associated OH groups, undoubtedly coming from SO_2–OH groups. The above suggestion is confirmed by the presence of a high intensity band at 1169 cm^{-1} that can be assigned to the asymmetric stretching vibrations of the SO_2–OH group in arene sulphonic acids. The strongly reduced intensity of the out-of-plane vibrations of the two paired hydrogen atoms in the phenyl ring at 819 cm^{-1} clearly indicates that only a small part of PPS remains unchanged upon

Table 1 Results of elemental analysis for pristine PPS (sample I) and doped PPS (sample II)

Sample	Carbon (%)	Hydrogen (%)	Sulphur (%)	Empirical formula
I	66.0	3.8	28.9	$C_6H_{3.96}S_{0.95}$
II	36.4	2.1	31.4	$C_6H_{4.08}S_{1.95}$

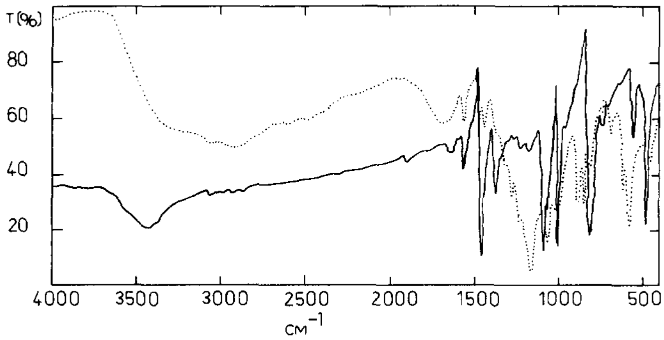

Figure 2 I.r. spectra of pristine PPS (sample I, ——) and doped PPS (sample II, · · ·)

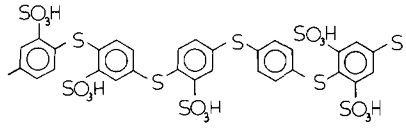

Figure 3 The possible molecular structure of sulphonated PPS as a result of doping with SO_3

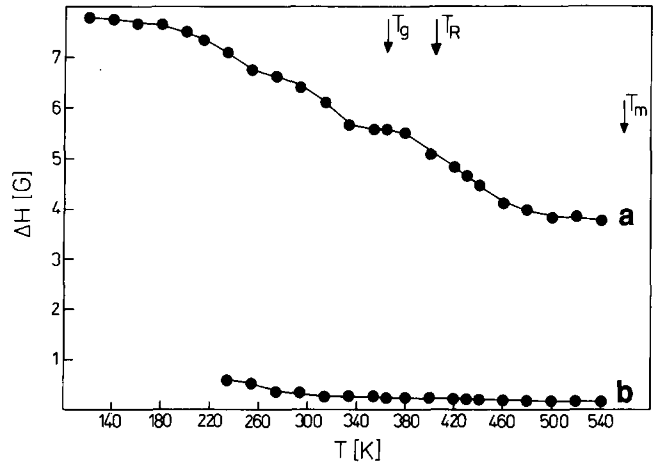

Figure 4 Temperature dependence of the n.m.r. linewidth for sample I (pristine PPS)[16]: (a) broad line component; (b) narrow line component

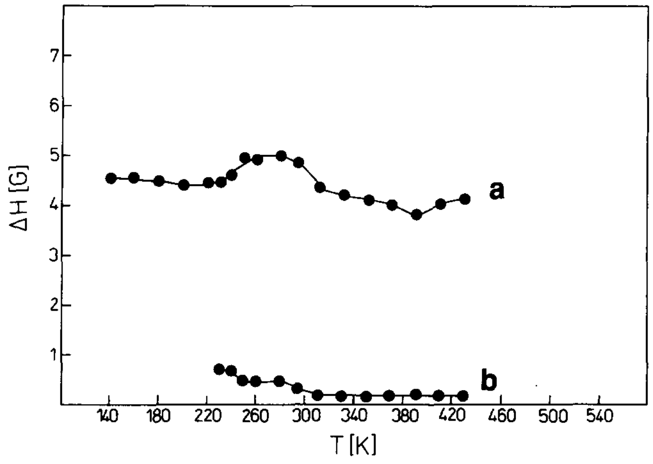

Figure 5 Temperature dependence of the n.m.r. linewidth for sample II (PPS doped with SO_3 vapour): (a) broad line component; (b) narrow line component

doping with SO_3. As can be seen from *Figure 2*, new bands at 851 and 885 cm^{-1} appear in SO_3-doped PPS. Thus, it may be concluded that the 1,2,4-trisubstituted benzene structure is predominantly formed upon doping with SO_3. Finally, the decrease in the intensity of the ring stretching vibrations at 1471 cm^{-1} is probably caused by introducing an electron-withdrawing substituent to the phenyl ring. However, the formation of the intermolecular crosslinks can also give a similar effect.

All the above findings clearly indicate that heavy doping of PPS with SO_3 gives mainly a sulphonation product where the SO_3 group is directly attached to a phenyl ring (*Figure 3*).

It has previously been suggested that heavy doping of PPS with SO_3 leads to a PBT structure with some quinoid-like character and a polymer with additional crosslinks via sulphuryl groups[9]. However, no bands corresponding to olefinic $\nu_{C=C}$ stretching vibrations or olefinic ν_{C-H} bending vibrations could be detected in the spectra to confirm the presence of a quinoid-like structure. Similarly, no bands were found in the 1350–1300 and 1160–1120 cm^{-1} regions for asymmetric and symmetric SO_2 stretching vibrations, respectively, to prove the formation of a structure with additional crosslinks via sulphuryl groups.

The i.r. spectrum of sample II shows no changes in the 'fingerprint' region in comparison to that of sample III which has been heated at 450 K. This is strong evidence that the doping-induced molecular modification is irreversible.

^1H *n.m.r. broad line studies*

Figures 4–7 show the results of n.m.r. linewidth measurements *versus* temperature for samples I–IV. The presence of two components in the line was observed for samples I–III above 220 K. We have graphically determined the contributions of the protons belonging to the particular phases. These contributions are proportional to the area limited by the appropriate component of the resonance line. Examples illustrating the change in shape of the resonance lines at various temperatures are shown in *Figure 8* and the phase contributions for the samples studied are given in *Figures 9–11*. These phase contributions were determined only for the temperatures at which simultaneous recording of

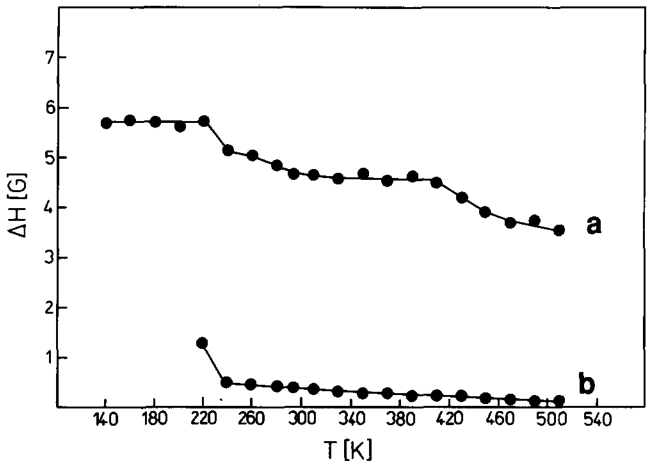

Figure 6 Temperature dependence of the n.m.r. linewidth for sample III (PPS doped and annealed): (a) broad line component; (b) narrow line component

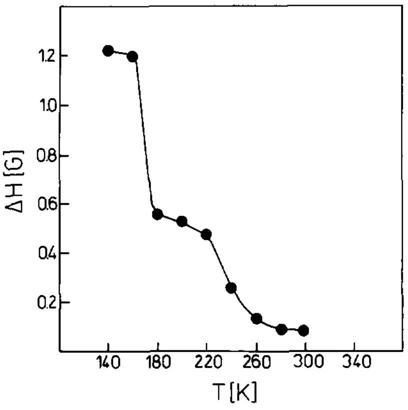

Figure 7 Temperature dependence of the n.m.r. linewidth for sample IV (PPS doped with liquid SO_3)

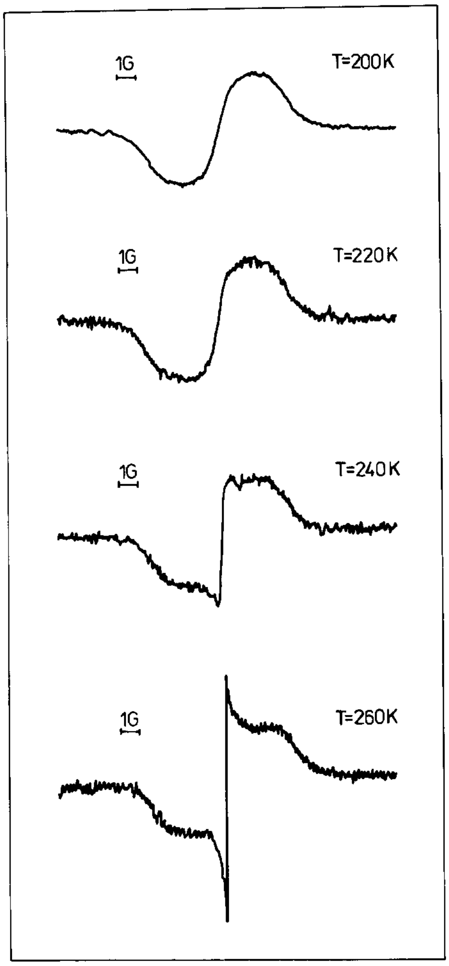

Figure 8 N.m.r. lines for sample II (PPS doped with SO_3 vapour) at various temperatures

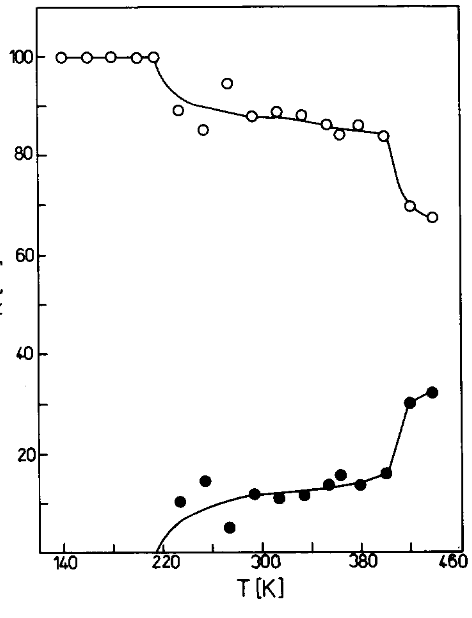

Figure 9 Percentage contributions of protons responsible for broad (○) and narrow (●) components of the n.m.r. linewidth for sample I (pristine PPS)[16]

both components was possible without the effects of the overmodulation of the narrow component. Thus, the range of temperatures at which the phase contributions were determined is narrower than that for which the measurements were made.

We have discussed the temperature dependence of the resonance linewidth obtained for pristine PPS in detail in another paper[16]. In this paper we only present it to be able to draw a comparison between pristine PPS and the doped samples.

The temperature dependence of the n.m.r. linewidth obtained for sample II (*Figure 5*) has a very specific character. Especially surprising is an unusual maximum of the n.m.r. linewidth at ~280 K, which is difficult to explain. The n.m.r. linewidth at 140 K is narrower for sample II than for sample I pointing to a structural change in PPS after doping. However, on the basis of our n.m.r. results, we cannot say whether the change involves chemical structure or only crystalline structure of the polymer. Moreover, for sample II no significant increase in n.m.r. linewidth with decreasing temperature

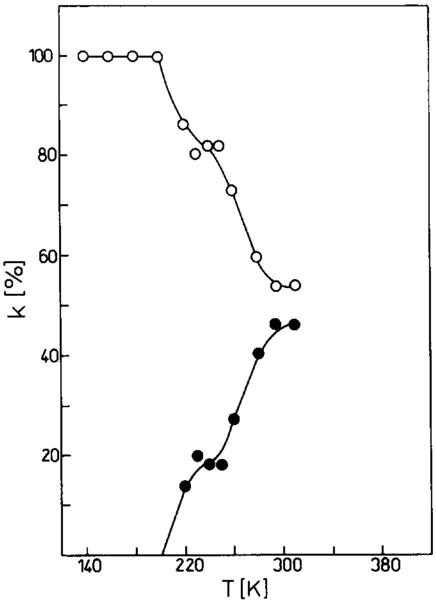

Figure 10 Percentage contributions of protons responsible for broad (○) and narrow (●) components of the n.m.r. linewidth for sample II (PPS doped with SO_3 vapour)

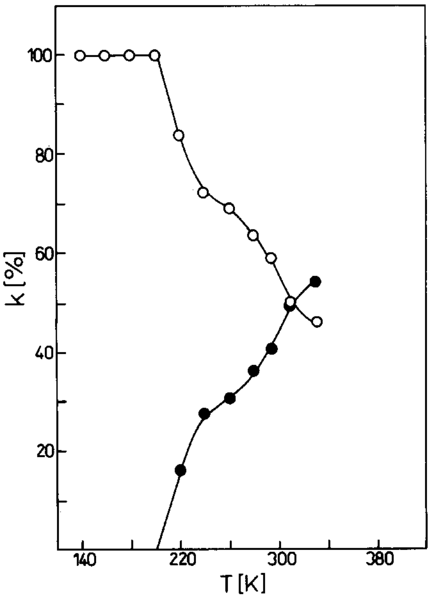

Figure 11 Percentage contributions of protons responsible for broad (○) and narrow (●) components of the n.m.r. linewidth for sample III (PPS doped and annealed)

Table 2 Distances (in Å) between hydrogen atoms, r_{ij}, in a PBT molecule (*Figure 1b*)

	H_{I}	H_{II}	H_{III}	H_{IV}	H_{V}	H_{VI}
H_{I}	0.00	4.96	6.06	6.75	8.54	12.57
H_{II}	4.96	0.00	1.79	6.06	7.43	8.54
H_{III}	6.06	1.79	0.00	4.96	6.06	6.75
H_{IV}	6.75	6.06	4.96	0.00	1.79	6.06
H_{V}	8.54	7.43	6.06	1.79	0.00	4.96
H_{VI}	12.57	8.54	6.75	6.06	4.96	0.00

has been observed within the studied temperature range. This fact suggests the disappearance of the reorientation of phenyl rings characteristic of PPS[4] in the polymer phase described by the broad component.

The phase contributions presented in *Figures 9* and *10* prove that the amount of mobile phase in sample II described by the narrow component is greater than in sample I. The X-ray diffraction study of sample II showed a complete absence of reflections in the crystalline phase. The observed two components in the n.m.r. resonance line may come from two molecular regions which differ from each other in the density of the chain arrangement and their mobility. It seems that the broad component of the n.m.r. line can be related to those polymer areas in which molecules are arranged parallel but without three-dimensional order. The narrow component in this case can be ascribed to molecules which enhance the mobility characteristic in the amorphous phase of PPS.

In order to verify the suggestion of Kazama *et al.*[9] on the formation of the PBT structure in PPS strongly doped with SO_3, we have calculated the value of the n.m.r. line second moment for the rigid structure of PBT and compared it with the experimental value obtained[17] for sample II at 140 K. Since we did not have results from X-ray diffraction studies of PBT, we calculated only the intramolecular part of the second moment on the grounds of the planar model of the PBT chain proposed in reference 9 (*Figure 1b*) using the lengths of bonds: $C{-}C_{arom}$, $\geqslant C{-}C \leqslant$ and C–H given in reference 18. The distances, r_{ij}, obtained between the six hydrogen atoms which are responsible for the intramolecular part of the second moment are given in *Table 2*. The intramolecular part of the second moment calculated for these distances from the Van Vleck formula[17] is 7.4 G^2 which is almost two times greater than the experimental value (4.8 G^2) for sample II at 140 K. Hence, the formation of a PBT structure as a result of PPS doping was disregarded.

In the sulphonated PPS structure (*Figure 3*) the distances between the hydrogen atoms are far greater than for PBT. Therefore the theoretical value of the proton second moment for PPS is much lower and closer to the experimental value. However, the calculation of this value would require crystallographic data, which are unavailable since the doped polymer is amorphous.

Figure 6 presents the temperature dependence of the n.m.r. linewidth for sample III. The removal of chemically unbonded SO_3 by heating the doped PPS results in an insignificant increase in the n.m.r. linewidth when compared with that for sample II. This may be explained by an increase in intermolecular interactions resulting from the removal of SO_3 molecules separating polymer chains. After the removal of SO_3 molecules, the resonance line decreases significantly with increasing temperature which proves an enhanced molecular mobility in sample III compared with sample II.

It is noteworthy that annealing the doped sample did not result in restoring the structure of unmodified PPS. This conclusion follows directly from a comparison of *Figures 4* and *6* and *Figures 9* and *11*. They reveal essential differences between the n.m.r. linewidth and phase contribution for samples I and III.

Since the X-ray diffraction study for sample III gives the same results as for sample II, the two components observed in the resonance line have to come from two amorphous regions in sample III which differ from each other by their molecular mobility.

The temperature dependence of the n.m.r. linewidth for sample IV (*Figure 7*) reveals a character typical of liquid. This proves that the doping of PPS with liquid SO_3 results in the total destruction of the crystalline structure of the polymer. The liquid-like line indicates that the dipole–dipole intermolecular interactions were reduced almost to zero because of the chain separation by SO_3 molecules.

At 140 K the n.m.r. linewidth for sample IV is about four times lower than for sample II. This leads to the conclusion that the chemical structure of PPS doped with liquid SO_3 and SO_3 vapour is the same, but in sample II the molecular motion is frozen because of strong intermolecular interactions.

CONCLUSIONS

Considerable amounts of dopant (one molecule of SO_3 per PPS unit) were found to remain inside the polymer sample subjected to heavy doping with SO_3 vapour.The doping process leads to the irreversible chemical modification of the polymer due to sulphonation. The PBT structure could not be detected in the doped sample from the i.r. spectra. A comparison of the experimental value of the second moment determined for a rigid structure of the doped PPS with the theoretical second moment value for the planar structure of PBT also excludes the formation of the latter.

The doping of PPS with SO_3 vapour brings about a change in the polymer structure with the two-phase character of the sample being preserved. The contribution of the mobile phase is enhanced which is confirmed by n.m.r. studies. On the other hand, X-ray diffraction confirmed the total destruction of the crystalline phase of the polymer. This means that the doping process destroyed three-dimensional order in the crystalline areas but preserved the parallel arrangement of the polymer chains.

Small changes observed in the temperature dependence of the n.m.r. linewidth for the doped sample suggest that the molecular mobility has been restricted compared with the pristine polymer. However, the possibility of the rotation of phenylene rings in the amorphous phase has been preserved.

Annealing the doped sample at 450 K leads to removal of chemically unbonded SO_3. The different width of the resonance line at 140 K than that recorded for the pristine polymer confirms the irreversible character of structural changes in PPS induced by doping. A greater linewidth for the annealed sample compared with that for the doped and unheated sample results probably from an increase in intermolecular interactions due to the removal of SO_3 molecules during annealing.

Doping of PPS with liquid SO_3 results in the total destruction of the crystalline phase of the polymer. For this sample a monophase structure is observed and the corresponding resonance line is liquid-like.

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