Nuclear magnetic relaxation in polyphenylene sulphide doped with $FeCl_3$

P. Hruszka, J. Jurga, J. Kubis and N. Piślewski*
Polymer Processing Laboratory, Technical University of Poznań, Piotrowo 3,
60-965 Poznań, Poland

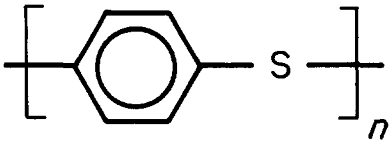
(Received 5 February 1990; accepted 8 June 1990)

The magnetization recovery function for samples of polyphenylene sulphide doped with $FeCl_3$ has been determined. It has been shown that within the whole temperature range and for various concentrations of paramagnetic dopant the relaxation is caused by direct interaction between protons and magnetic moments of the paramagnetic centres.

(Keywords: polyphenylene sulphide; doping; n.m.r.; relaxation; magnetization recovery)

INTRODUCTION

Polyphenylenesulphide (PPS) is a polycrystalline, thermoplastic polymer with high thermal and chemical resistance. It has the following chemical formula:



Unmodified PPS is an isolator with conductivity of about 10^{-17} S cm^{-1} (ref. 1). While doped with strong electron acceptors it can form conducting complexes. Iron trichloride ($FeCl_3$) is one of the effective dopants for PPS, e.g. amorphous films of PPS doped with 0.1 M solution of $FeCl_3$ in nitromethane achieve electrical conductivity σ of about 3.4×10^{-3} S cm^{-1} (ref. 2). In course of the doping process the change in polymer colour from beige via green to black is observed. The authors of ref. 2 suggest that the doping with $FeCl_3$ takes place mainly in the amorphous areas of PPS as an increase in a degree of crystallinity of the film causes a decrease in conductivity of the doped sample.

The n.m.r. studies were performed up to now for PPS doped only with the sulphur trioxide (SO_3)[3,4]. The authors report that the magnetization recovery function in this system is strongly non-exponential and explain it as caused by heterogeneous distribution of dopant in the polymer. For samples containing low concentration of dopant, a long time component of the magnetization recovery function has been separated and assigned to those areas of polymer which are slightly doped or not doped at all.

Increasing concentration of dopant diminishes the contribution of the long relaxation time component and shortens the relaxation time T_1 of the doped phase. The shortest relaxation time T_1 has been achieved for samples with maximum concentration of dopant.

The relaxation function for such a sample has been described[3,4] as a superposition of two relaxation processes. Dispersion studies of T_1 allowed the authors of these references to separate the relaxation mechanism consisting of interaction of protons with electron holes diffusing along the polymer chain and to calculate the diffusion rate of electric carriers. The spin-lattice relaxation studies in pure polymer have shown that the magnetization recovery function is mono-exponential within a wide temperature range. The temperature dependence of T_1 and $T_{1\rho}$ has been explained[5,6] as caused by the activation movements of the polymer chain and rapid spin diffusion to paramagnetic centres existing in the polymer.

The aim of this paper is to investigate the effect of PPS doping with $FeCl_3$ on the nuclear relaxation and an attempt to describe mechanisms of the observed relaxation.

EXPERIMENTAL

The powdered polyphenylene sulphide (Ryton V-1 produced by Phillips Petroleum Co., USA) purified of low-molecular oligomers with tetrahydrofuran in the Soxhlet column was used in n.m.r. studies. Chemical analysis of composition of the samples studied confirmed the high-molecular structure of the polymer.

The doping process of PPS with the $FeCl_3$ molecules affects both electrical conductivity and colour of the sample. Temporary measurements of this effect were carried out using pressed tablets of 12 mm diameter and 0.5 mm thickness. However, the doping process of pressed tablets is very heterogeneous and therefore in n.m.r. studies we used powdered polymers in which the penetration process of dopant molecules was, in our opinion, much easier.

Two samples of powdered PPS with different degree of doping were prepared for n.m.r. studies. Sample A was obtained by 4 h doping of the PPS powder with 0.1 M solution of $FeCl_3$ in nitromethane. The sample B was obtained by 18 h doping with 1 M solution of $FeCl_3$. Interaction of $FeCl_3$ with polymer leads to the formation

---

* To whom correspondence should be addressed at Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

0032-3861/91/091589-04

of $FeCl_4^-$ which is insoluble in nitromethane and forms strong complexes with the positively charged chains of the PPS polymer[7]. To break the doping process the solution was filtered off and the polymer was rinsed several times with pure nitromethane. The samples were dried in vacuum 10^{-5} Tr for several hours and sealed in glass ampoules.

To estimate the degree of doping the percentage contents of chlorine were determined in both samples. Wide-angle X-ray diffraction spectra were also registered. Moreover, for sample B the Mössbauer spectra were made at room and liquid nitrogen temperature.

Temperature studies of the spin-lattice relaxation times in the doped PPS polymer were carried out with a pulse n.m.r. spectrometer working at 30 MHz for protons[8]. The measurements were performed within the temperature range from 108 to 420 K. The sample temperature was maintained by blowing with vapour of liquid nitrogen. The relaxation times T_1 were measured with a conventional method $\pi/2$–t–$\pi/2$. The duration of $\pi/2$ pulse was 2 μs and the dead time of spectrometer was 10 μs.

RESULTS

Features of the doped samples

Elemental analysis showed that the polymer purified on the Soxhlet column has the following empirical formula: $C_6H_{3.92}S_{0.96}Cl_{0.02}$ and purity of 99%. This allows one to estimate a degree of its polymerization, assuming that the chlorine atoms are located at the ends of the PPS chain. The chains of studied polymer contained at least 100 mers. During the doping process the colour of a tablet made of the polymer changes from a pale beige via green to black and its conductivity increases several orders of magnitude, reaching the value of 6×10^{-5} S cm^{-1} after about 3 h of doping with 0.1 M solution of $FeCl_3$. This value of conductivity is close to that obtained by J. Tsukamoto and K. Matsumura[2] for the previously annealed film. The conductivity of amorphous films is, however, two orders of magnitude higher[2].

Elemental analysis of the sample A revealed the presence of 4.57% of chlorine. It means that 27 mers of the PPS chain are ascribed to one molecule of $FeCl_4^-$. The X-ray spectra of this sample showed a decrease in a degree of crystallinity in respect to the initial material preserving the same crystalline structure.

Elemental analysis of sample B revealed the presence of 18.6% chlorine. It means that about 5 mers of PPS chain are ascribed to one molecule of $FeCl_4^-$. For this sample the X-ray diffraction spectra did not reveal reflections from the crystalline phase. Large amounts of the Fe nucleus made it possible to obtain the Mössbauer spectra for sample B. These spectra showed that all paramagnetic centres built in the polymer lattice have a form of $FeCl_4^-$. They also revealed a lack of trace amounts of iron in other coordination environments.

Spin-lattice relaxation of protons in the doped samples of the PPS polymer

The spin-lattice relaxation times for samples A and B were calculated from the magnetization recovery function $M(t)$. This function was determined by measuring the amplitude of the free induction decay after the second $\pi/2$ pulse using very short intervals between pulses for initial magnetization recovery. For both samples the magnetization recovery function was non-exponential within the whole temperature range. The function $\log(M(0) - M(t))/M_0$ obtained at 260 K is shown as an example in *Figures 1* and later in *Figure 4* for samples A and B, respectively. The detailed analysis of the magnetization recovery functions revealed that they can be described as a sum of two exponential functions, e.g. for sample A the magnetization recovery $M(t)$ within the whole temperature range can be described by the following function:

$$M(t) = M_{01}\exp[-(t/T_1)^{1/2}] + M_{02}\exp(-t/T_1^*) \quad (1)$$

where M_{01} and M_{02} denote the fractions of protons relaxing with the relaxation time T_1 and T_1^*, respectively. The values of T_1 and T_1^* determined with this method are shown in *Figure 2*.

The longer relaxation time T_1^*, amounting to about 4 s, represents about 8% of protons. In our opinion it can be recognized as a measure of the relaxation processes taking place in those areas of the polymer which are not modified by a paramagnetic dopant. This hypothesis is supported by the value of T_1^*, which is close to the value of T_1 obtained in pure polymer[5]. Temperature dependence of T_1^*, similar to that presented in ref. 5, and the exponential nature of the magnetization recovery function in respect to time indicate that, despite careful purification, the relaxation processes in this phase are mainly caused by trace amounts of paramagnetic centres.

The first term of equation (1) describes the relaxation taking place in phase containing 92% of protons. Time dependence of the magnetization recovery function described by the composed function $\exp[-(t/T_1)^{1/2}]$

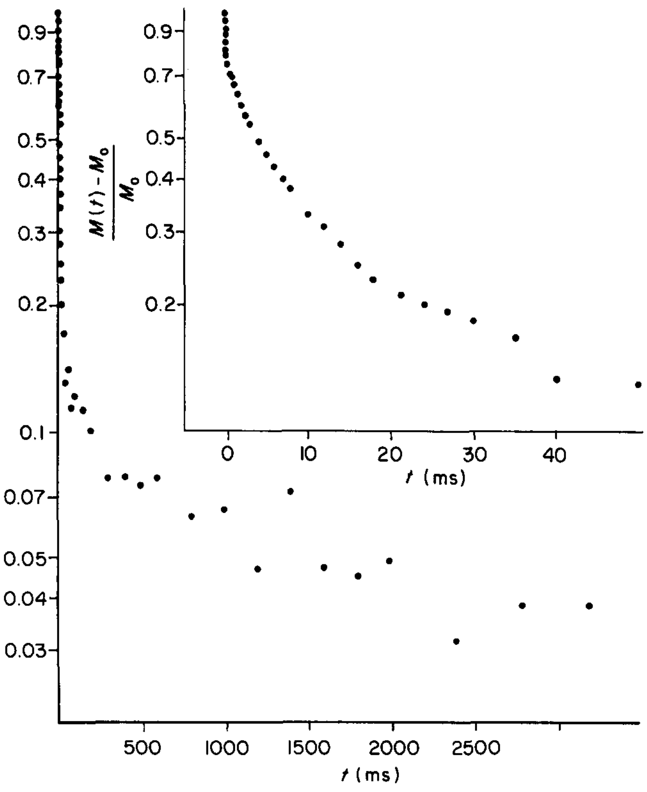


Figure 1 Dependence of the amplitude of the normalized magnetization recovery function on the time t between $\pi/2$ pulses for sample A at 260 K. Inset shows the initial amplitude changes in extended time scale

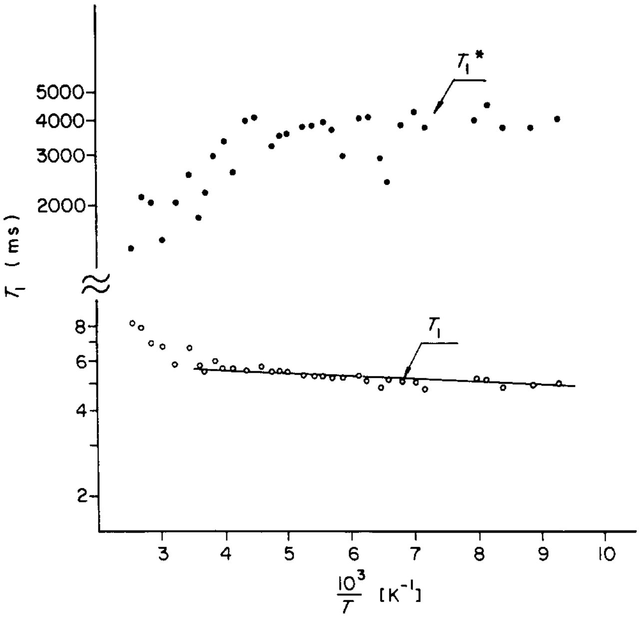


Figure 2 Relaxation times T_1 and T_1^* for sample A as a function of $1/T$. A slight increase in T_1 caused by a contribution of thermal movements of the polymer chains in the spin-lattice relaxation of protons is observed above the room temperature

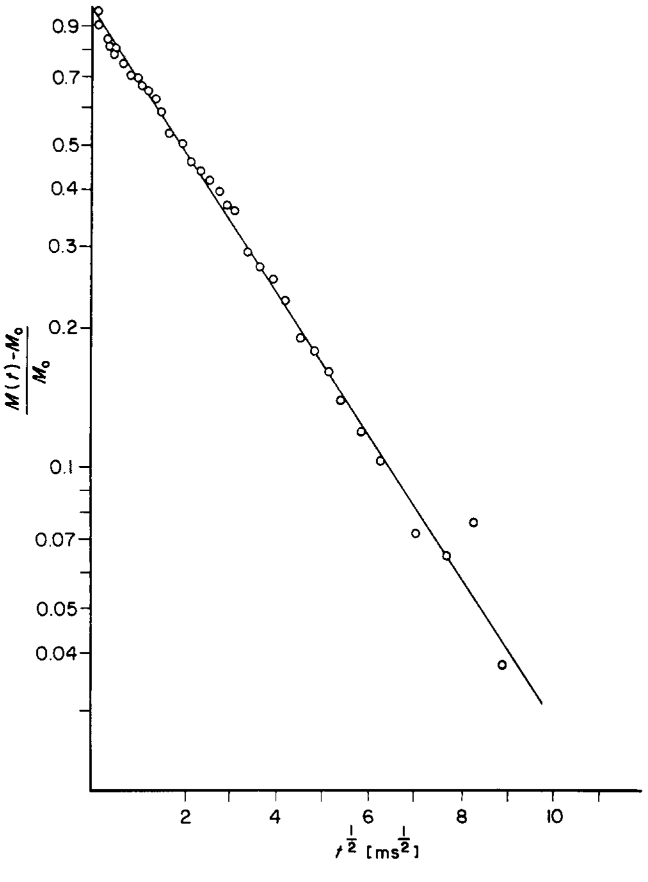


Figure 3 Example dependence of the normalized magnetization recovery function on the time interval t between $\pi/2$ pulses obtained at 360 K for sample A annealed at 460 K

suggests that the relaxation takes place in conditions of the direct dipolar interaction of protons and the magnetic moment of dopant. The above dependence was proposed by Tse and Hartmann[9] for cases without a spin diffusion and then used by Miller and Dybowski[10] to explain the relaxation processes in poly-p-phenylene. The relaxation time T_1 determined by us for sample A results from interaction between the localized magnetic moments of the $FeCl_4^-$ ions and protons, as well as from interaction between the conducting electrons and protons. However, a recognition of particular contributions to the interpreted relaxation seems to be impossible on the basis of a simple n.m.r. experiment.

The idea in which the time T_1^* is assigned to the undoped regions of polymer is supported by studies of the magnetization recovery function for sample A annealed at 460 K for 1 h. The results for the treated sample obtained at 360 K are shown in *Figure 3*. Annealing of the sample is causing a steady distribution of paramagnetic dopant and the magnetization recovery function can be described by a simple formula proposed by Tse and Hartmann[9]

$$M(t) = M_0 \exp[-(t/T_1)^{1/2}] \qquad (2)$$

The relaxation time T_1 determined for this sample at 360 K amounts to 8 ms and differs only slightly from the value obtained before annealing of the sample.

The studies of relaxation for B sample show that the magnetization recovery function can be well approximated with the two-component function of type

$$M(t) = M_{01} \exp[-(t/T_1')^{1/2}] + M_{02} \exp[-(t/T_1'')^{1/2}] \qquad (3)$$

The percentage contribution of the phase relaxing with the very short relaxation time T_1' (about 30 μs) amounts to 70% within the whole range of studied temperatures

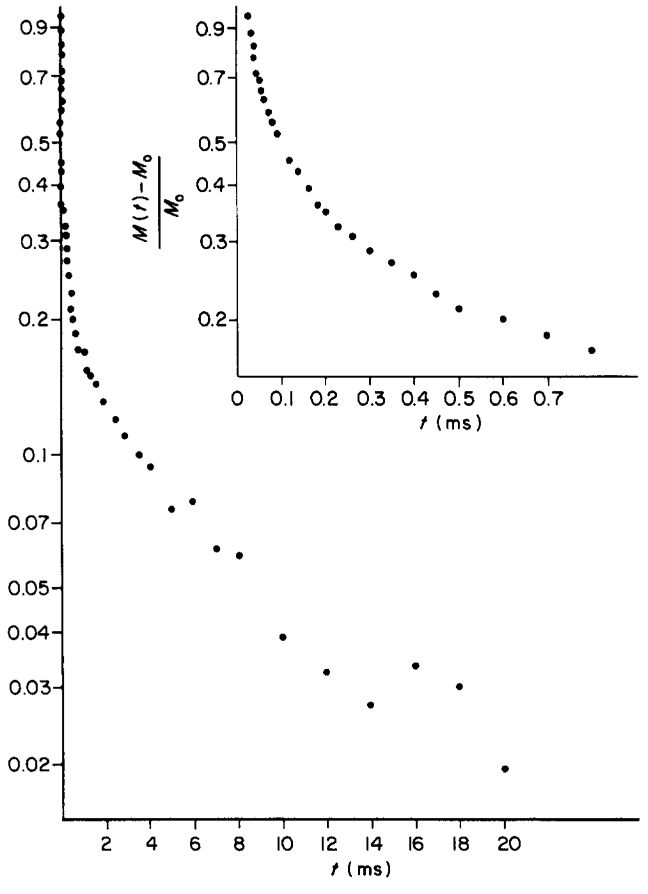


Figure 4 Dependence of the normalized magnetization recovery function on the time t for sample B at 260 K. Inset shows the initial amplitude changes in extended time scale

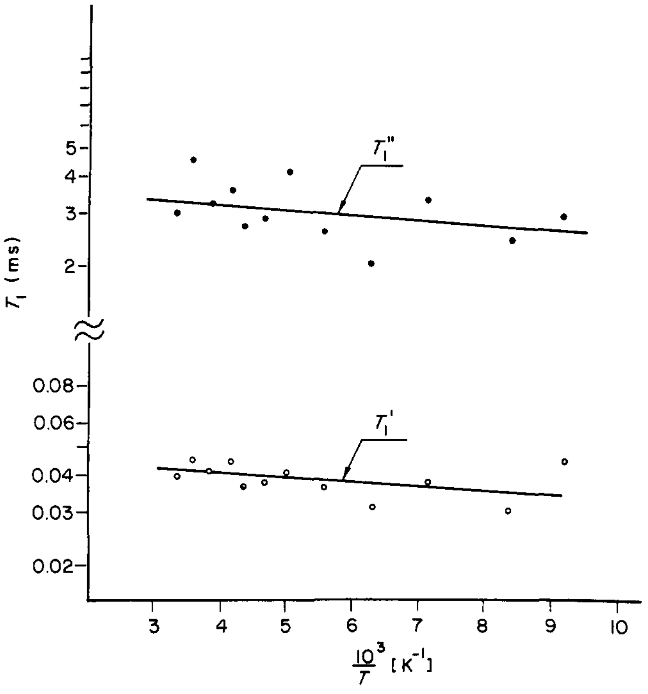


Figure 5 Relaxation times T_1' and T_1'' for sample B as a function of $1/T$

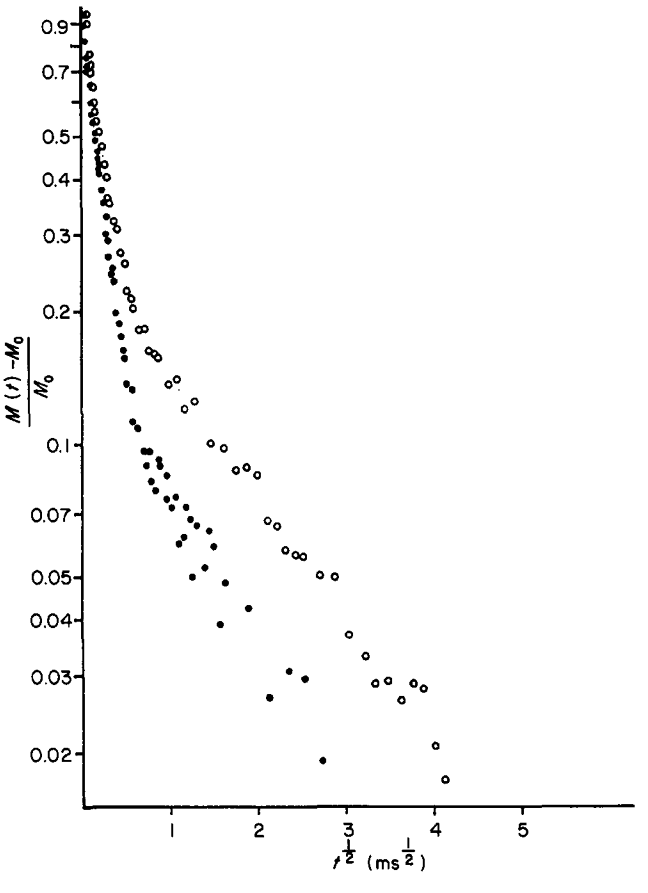


Figure 6 Dependence of the amplitude of the normalized magnetization recovery function on $t^{1/2}$ obtained at room temperature for sample B. Empty circles denote the values obtained before annealing, full circles denote the values obtained after annealing at 510 K

(*Figure 5*). It means that the larger part of paramagnetic dopant is localized in this phase of polymer.

A much longer relaxation time T_1' amounting to about 3 ms is similar in value to the time T_1 for sample A and can be assigned to those protons which interact with the paramagnetic dopant, as in the doped phase of sample A.

The above results do not allow one to explain the existence of the two doped phases with different relaxation times. A simple model, assuming the two doped phases result from heterogeneous distribution of dopant in the amorphous and crystalline phases of polymer, has been to some extent verified by studies of the magnetization recovery function for sample B annealed at 510 K for 1 h. The results obtained for this sample at room temperature before and after annealing are shown in *Figure 6*.

In both cases the magnetization recovery function is a two-component type with similar values of relaxation times, however in the annealed sample the content of the slowly relaxing phase is lower. Moreover, it is worth noticing that both relaxation processes, i.e. before and after annealing are described by equation (3). It may mean that the relaxation processes take place in the proton reservoir of both phases and result from direct interaction with the paramagnetic centres. Lack of effects caused by the fast spin diffusion is understandable because, in case of the PPS chains, the sulphuric bridges can extinguish the fast spin diffusion between protons of the neighbouring phenylene rings. Further n.m.r. studies of the PPS polymers doped with $FeCl_3$ performed at various frequencies should provide a better description of a nature of the relaxation processes and explain a role of the conducting electrons in these processes.

ACKNOWLEDGEMENTS

This work was carried out under the CPBP project 01.14. The authors are grateful to Prof. J. Garbarczyk from Poznań Technical University for making the X-ray spectra and to Dr J. Kucharski from the Atomic Energy Institute for providing the Mössbauer spectra.

REFERENCES

1 Tsu Tsui, T., Nitta, N. and Saito, S. *J. Appl. Phys.* 1985, **57**, 5367
2 Tsukamoto, J. and Matsumura, K. *Jpn. J. Appl. Phys.* 1984, **23**, 584
3 Kazama, S., Arai, K. and Maekawa, E. *Synth. Met.* 1986, **15**, 299
4 Kazama, S. *Synth. Met.* 1986, **16**, 77
5 Jurga, J., Eckert, H. and Müller-Warmuth, W. *Z. Naturforsch* 1979, **34a**, 1216
6 Schlick, S. and McGarvey, B. R. *Polym. Commun.* 1984, **25**, 369
7 Proń, A., Billaud, D., Kulszewicz, J., Budrowski, C., Przyluski, J. and Suwalski, J. *Mat. Res. Bull.* 1981, **16**, 1229
8 Jurga, J. and Jurga, S. *Scientific Instrumentation* 1989, **2**, 23
9 Tse, D. and Hartmann, S. R. *Phys. Rev. Lett.* 1968, **21**, 511
10 Miller, J. B. and Dybowski, C. *Solid State Commun.* 1983, **46**, 487