Nuclear magnetic relaxation studies of poly(*p*-phenylene sulphide) doped with sulphur trioxide

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Temperature dependences of ^1H n.m.r. spin-lattice relaxation times (T_1) were measured for poly(*p*-phenylene sulphide) (PPS) heavily doped with sulphur trioxide (SO_3). A clearly non-exponential character of the magnetization recoveries was observed. The magnetization recovery is characterized by an $\exp[-(t/T_1)^{1/2}]$ time dependence over a wide time interval and for the whole temperature range studied, indicating diffusionless relaxation of the nuclei to the paramagnetic centres. The temperature dependence of T_1 is weakly thermally activated. The annealing of doped PPS at 450 K changes the mechanism of the relaxation. In this sample the relaxation is related to the thermally activated motion of protons from phenylene rings and sulphuryl groups.

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

INTRODUCTION

Conductive polymers, such as polyacetylene (PA), poly(*p*-phenylene), polypyrole, polythiophene and poly(*p*-phenylene sulphide) (PPS), have received considerable attention. Many investigations on the physical and chemical properties and practical applications of these materials have been carried out. PPS has the advantage of being melt and solution processible.

N.m.r. studies of conducting polymers were performed to obtain information on the charge transfer defects and conduction mechanisms in these materials. The main relaxation mechanism in conducting polymers is the interaction of paramagnetic centres with nuclear spins.

The structure and molecular dynamics of pristine PPS have been studied by n.m.r. spectroscopy[1,2]. The temperature dependences of the spin-lattice relaxation times T_1 and $T_{1\rho}$ were measured. An exponential character of the magnetization recovery during the T_1 measurements was observed over the whole temperature range studied.

PPS may be doped with strong electron acceptors such as sulphur trioxide (SO_3) to form conducting complexes with a maximum conductivity[3] of 10^{-4} S cm^{-1}. Structural changes of PPS doped with SO_3 and the character of its conductivity have been studied by Kazama *et al.*[4,5]. They studied PPS doped to different degrees with liquid SO_3 and SO_3 vapour and analysed the ^{13}C cross-polarization/magic angle spinning n.m.r. and i.r. spectra obtained for the pure and doped samples. Moreover, they measured T_1 *versus* frequency for doped PPS. These measurements showed a non-exponential recovery of the magnetization in all the investigated samples. The authors explained this as being due to the inhomogeneity caused by the dopant in PPS. The linear relation between the relaxation rate T_1^{-1} and the inverse of the square root of frequency was explained in terms of the diffusion of electrons or holes in the form of polarons. However, they strongly excluded the formation of bipolarons in the PPS structure. According to them, the most probable modification of the PPS structure during doping with SO_3 is the formation of a polybenzothiophene (PBT) structure.

The mechanism of conductivity of PPS doped with SO_3 was studied by optical absorption and electron spin resonance methods[6]. Those results suggested the presence of sulphur-centred radical cations.

In a previous paper[7] we reported i.r. results and broad line ^1H n.m.r. studies for PPS heavily doped with SO_3. The doping process leads to irreversible chemical modification of the polymer due to sulphonation. The PBT structure could not be detected in the doped sample. Heavy doping with SO_3 destroyed the three-dimensional order of the crystalline areas but preserved the parallel arrangement of the polymer chains. The molecular mobility of the rigid lattice of doped PPS is restricted when compared with that of pristine PPS, however the possibility of rotation of phenylene rings in the amorphous phase has been preserved.

To shed more light on the whole question of the relaxation mechanism in the doped polymers we now report the T_1 values of protons measured as a function of temperature in PPS heavily doped with SO_3.

EXPERIMENTAL

PPS in the form of powder (Ryton V-1, Phillips Petroleum Co., USA) was purified with tetrahydrofuran and then dried at 373 K for several hours (sample I). This sample was doped with SO_3 vapour (sample II) and then annealed at 450 K (sample III). The procedure

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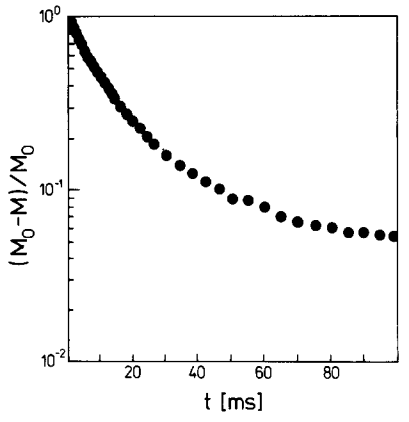

Figure 1 Magnetization recovery of protons in doped PPS (sample II) at 140 K. The difference in the magnetization at time t and the equilibrium value M_0 is plotted against t

of doping and annealing has been described in detail in our previous paper[7]. In that paper we also described the results of elemental analysis, X-ray diffraction and i.r. spectroscopy for all the samples.

The T_1 of protons was measured on a home-made n.m.r. pulse spectrometer[8] at a frequency of 30 MHz. The measurements were made using the standard $\Pi/2-\tau-\Pi/2$ method over the temperature range of 130–500 K. The width of the pulse was $\sim 2\ \mu s$ and the receiver dead time was 8 μs.

RESULTS AND DISCUSSION

The magnetization recovery for sample II was clearly non-exponential within the whole temperature range studied (*Figure 1*). There are two possible reasons for this behaviour: the first is the presence of a few independently relaxing regions with different relaxation times[5]; the second is the interaction of protons with paramagnetic centres for the diffusionless case. In this situation the magnetization recovery should be described by the expression $\exp[-(t/T_1)^{1/2}]$ which is valid for a limited time period[9]. For doped sample II the magnetization is found to approach its equilibrium value in this manner for all temperatures studied. *Figure 2* shows the magnetization recovery as a function of the square root of time. Similar magnetization recoveries were observed in calcium fluoride crystals doped with paramagnetic centres[9], in organic solids like diphenyl with paramagnetic free radicals[10], in dilute copper–manganese alloys[11] and in iodine-doped *trans*-PA[12].

The relaxation of the total magnetization in the presence of paramagnetic centres can occur in different ways[11].

Diffusion case. Most of the observed nuclei are outside the diffusion barrier. These nuclei interact with paramagnetic centres through spin diffusion. The recovery of the magnetization is exponential.

Diffusionless case. Most of the nuclei are inside the diffusion barrier. These nuclei take place in direct relaxation to paramagnetic centres without spin diffusion. The relaxation is non-exponential and the recovery of the magnetization over a long time is given by the expression $\exp[-(t/T_1)^{1/2}]$. Deviations from this expression appear for short times. A more general result has been calculated by MacHenry *et al.*[13] for small paramagnetic contents and can be written as:

$$\ln\frac{M_0-M}{M_0} = n_0C\left\{1-\exp\left[-\frac{t}{\pi T_1(n_0C)^2}\right]\right\} - \left(\frac{t}{T_1}\right)^{1/2}\operatorname{erf}\left[\frac{t}{\pi T_1(n_0C)^2}\right]^{1/2} \quad (1)$$

which has the asymptotic form:

$$\ln\frac{M_0-M}{M_0} \cong n_0C - \left(\frac{t}{T_1}\right)^{1/2} \quad (2)$$

where M is the magnetization, M_0 is the equilibrium value, C is the concentration of the paramagnetic centres in the sample and n_0 is the number of unobserved nuclei close to the paramagnetic centres. In pulse technique experiments some nuclei close to the paramagnetic centres are not observed as they experience local fields from these centres stronger than the rotating radio-frequency field.

The intermediate case. The magnetization recovery is exponential for long times and diffusionless for short times.

For our doped sample II we deal with the intermediate case III. However any discrepancy from the expression $\exp[-(t/T_1)^{1/2}]$ for long times is not too great and therefore we did not take into account the last experimental points which describe the spin diffusion case. Under this assumption we believe to have the diffusionless case. We computed from equation (2) the values n_0C and T_1 for all the temperatures studied and fitted the experimental points of the magnetization recoveries to equation (1). The example of the fit for a temperature of 140 K is shown in *Figure 3*. For this and other temperature points the MacHenry equation, equation (1), describes very well the magnetization recoveries in doped sample II. The average value of n_0C, determined from equation (2) for different temperatures, is 0.39 ± 0.06.

In our sample the paramagnetic centres can be sulphur-centred radical cations, whose concentration increases monotonically with increasing SO_3 concentration[6].

Figure 4 presents T_1 *versus* the inverse of temperature. Moreover, an analogous dependence of T_1 relaxation times for sample I[14] is presented in *Figure 5*. The values

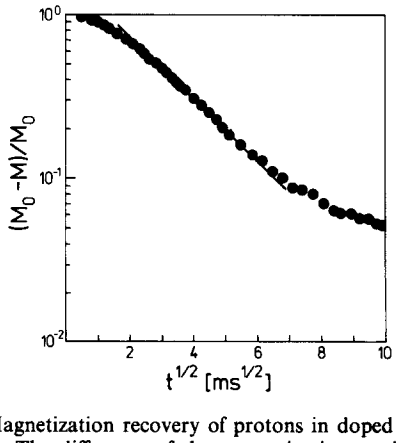

Figure 2 Magnetization recovery of protons in doped PPS (sample II) at 140 K. The difference of the magnetization at time t and the equilibrium value M_0 is plotted against $t^{1/2}$

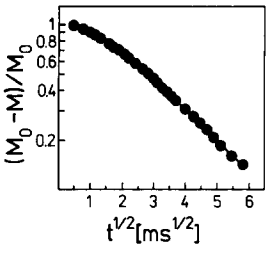

Figure 3 Fitting of the magnetization recovery in doped PPS (sample II) at 140 K by the MacHenry equation. The solid line fits the experimental points for the following parameters: $T_1 = 5.27$ ms, $n_0C = 0.56$

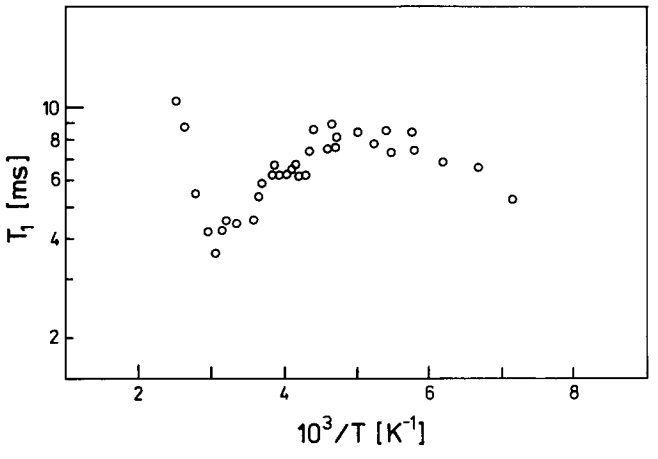

Figure 4 Temperature dependence of relaxation times T_1 in doped PPS (sample II)

of the relaxation times for doped sample II are considerably lower than those for pristine sample I and do not exceed 10 ms. This confirms the influence of paramagnetic centres on the relaxation process in the doped sample. In the low temperature region the relaxation in sample II is insignificantly thermally activated which is typical of paramagnetic centres induced relaxation. In the high temperature region a characteristic minimum of T_1 relaxation times was observed. A similar character of the temperature behaviour of T_1 was observed in iodine-doped *trans*-PA[12]. In our opinion the high temperature minimum is not a classical minimum related to molecular motion. The rapid increase in T_1 above this minimum can be explained by the release of the dopant from the polymer. This process is related to an increase of molecular motion energy near the glass transition temperature of PPS. This energy is higher than the interaction energy between the dopant and the polymer chain. A decrease in the amount of dopant causes a decrease in the paramagnetic centres concentration and an increase in T_1. Simultaneously, the colour of the sample changes from black to brown which is characteristic of non-conducting PPS. The end of this process is the breaking of the ampoule containing the doped sample due to the pressure of the released SO_3 vapour.

For the annealed sample III the magnetization recovery is quite different than for sample II (*Figure 6*), but is still non-exponential. However, the two components describe sufficiently well the observed non-exponential recoveries of magnetization for this sample over the whole temperature range studied. *Figure 7* presents the temperature dependence of the two components of the T_1 relaxation time.

Higher values and considerable changes in relaxation times *versus* temperature (a deep minimum) show that the relaxation in sample III is not determined by the interaction of protons with paramagnetic centres. This indicates that the radical cations disappear and proves that the annealing of the doped sample is the reason why the conducting properties disappear. The linear slopes of the dependence of the relaxation times *versus* temperature give values for the activation energies of ~ 17 and ~ 10 kJ mol^{-1} for the short and long components, respectively. These values are similar to those for pristine PPS[2,14] and indicate that the relaxation process in sample III is mainly related to the reorientation of phenyl rings. The short component of the relaxation times could probably describe molecular motion in the regions with high density of the chain arrangement and the longer one the motion in the mobile phase. The existence of two molecular regions in the polymer which differ from each other by the density of the chain arrangement and their mobility confirm the results of the broad line n.m.r. studies on the same sample[7].

Comparison of the results given in *Figures 5* and *7* shows that the temperature dependences of T_1 for samples I and III are different. In sample I the short component of the relaxation time exists only in the limited low temperature region and its contribution to the total relaxation process is small. As we mentioned earlier the

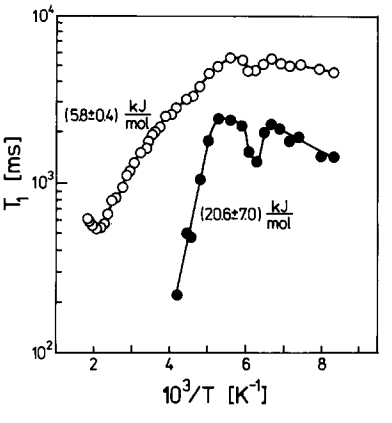

Figure 5 Temperature dependence of relaxation times T_1 in pristine PPS (sample I)[14]

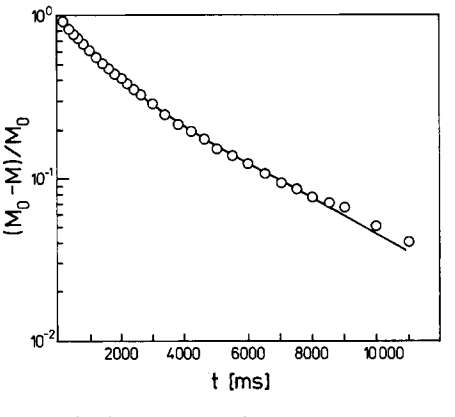

Figure 6 Magnetization recovery of protons in doped and annealed PPS (sample III) at 140 K. The solid line fits the experimental points computed for two relaxation times: $T_{1S} = 1041$ ms; $T_{1L} = 4039$ ms

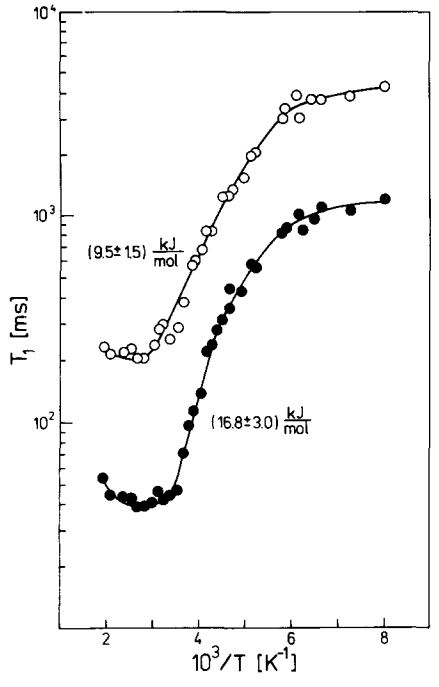

Figure 7 Temperature dependence of relaxation times T_1 in doped and annealed PPS (sample III)

magnetization recovery in sample III is clearly non-exponential over the whole temperature range. In general, the relaxation times in sample III are shorter than those in sample I. The relative change in the relaxation times in sample III is greater than that in sample I. This indicates that not only protons from phenyl rings but also the more mobile protons from sulphuryl groups can take part in the relaxation process. Thus, side groups might have been attached to the polymer chain during the doping process[7]. The high temperature minima observed for sample III are considerably broader than those of sample I. This proves a very wide correlation time distribution in the doped and annealed sample. This is connected to the considerable inhomogeneity of the molecules taking part in the molecular motions.

CONCLUSIONS

The nuclear relaxation rate in SO_3-doped PPS is much faster than in pristine PPS. The magnetization recovery over the whole temperature range studied is clearly non-exponential. The dominant process of relaxation in the doped sample is the interaction of protons with paramagnetic centres without spin diffusion, which is confirmed by the fact that the magnetization recovery is described by a square root law over a broad time interval and for all the temperatures studied. A very good fitting of the initial points of the magnetization recoveries to the MacHenry equation was obtained. The temperature dependence of T_1 is weakly thermally activated. The paramagnetic centres in PPS doped with SO_3 can be sulphur-centred radical cations as confirmed by Shimizu *et al.*[6] using the electron spin resonance method.

Annealing doped PPS at 450 K results in the disappearance of these paramagnetic centres through the release of dopant. This is a reason for the change in the relaxation mechanism in that sample. The relaxation is clearly thermally activated and related to the molecular motion of protons of phenylene rings. The relaxation rate at the minimum of the T_1 in this doped polymer is greater than in the pristine sample. This is due to the presence of mobile protons from sulphuryl groups. Two components of relaxation times over the whole temperature range studied prove the presence of two different molecular regions in the polymer. The existence of the two molecular regions, which differ in their molecular mobility, is also proved by our broad line n.m.r. investigation[7]. A very wide minimum of relaxation times indicates the inhomogeneity of the molecular structure of doped and annealed PPS.

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