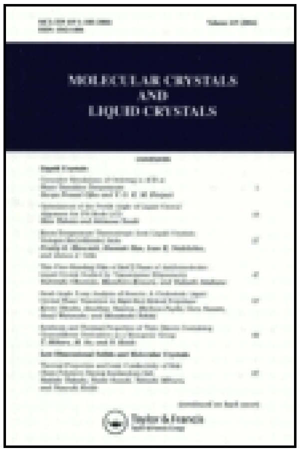

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Dyson Effect in Polyparaphenylene Heavily Doped with Rubidium in the Vapour State

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Dyson effect in polyparaphenylene heavily doped with rubidium in the vapour state

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The variation of the ESR characteristics of vapour phase rubidium doped polyparaphenylene was examined as a function of the doping duration and temperature. The Dyson effect was observed for thick ($d/\delta>1$) heavily doped compounds.

Keywords : ESR, polyparaphenylene, rubidium, doping

INTRODUCTION

Alkali metals in the vapour state react directly with insulating polyparaphenylene (PPP) to form compounds of high electrical conductivity[1,2]. Such a reaction consists in the reduction of PPP by the alkali metal and the simultaneous introduction of alkali metal species which are intercalated in columns between the polymer chains[3,4] as previously observed for polyacetylene. In the present research, the compounds obtained after reaction of gaseous rubidium with PPP were particularly examined by ESR spectroscopy. The evolution of the characteristics of the ESR signal corresponding to compounds doped to the saturation and therefore exhibiting a high electrical conductivity was studied as a function of both doping duration and temperature.

EXPERIMENTAL

Polyparaphenylene prepared by the method of Kovacic and Oziomek[5] was in the form of a brown unsoluble powder. This material was first washed out in hot concentrated HCl to remove the catalyst residues, then heated at 420°C under vacuum and finally pressed under a pressure of 2 tons/cm^2. Rubidium vapour phase doping was carried out in such PPP pressed pellets, directly in the ESR measurement tube[4]. ESR spectra were recorded at 9.78 GHz using a Bruker ER 200 D spectrometer equipped with a standard variable temperature accessory.

RESULTS AND DISCUSSION

Figure 1 shows the modifications of the room temperature ESR spectra of a pressed pellet, 280 μm thick, of rubidium doped PPP for increasing

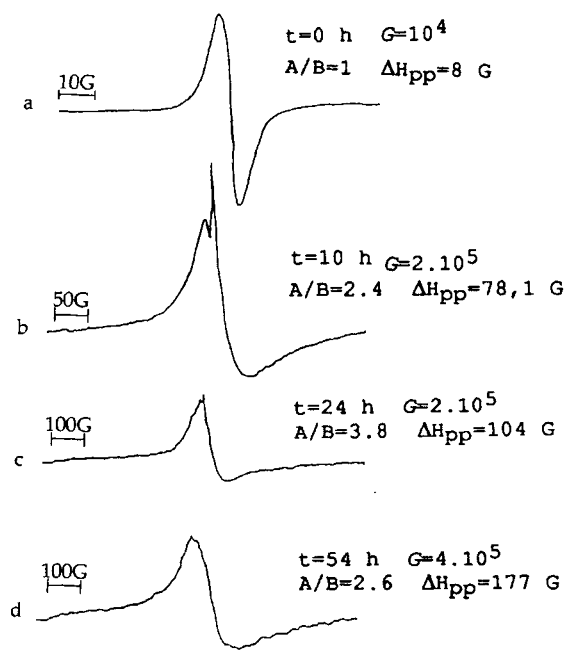

FIGURE 1 Selected ESR spectra of rubidium-doped PPP as a function of the doping time t (G=gain of the spectrometer)

doping durations t . A considerable evolution of the behaviour is noted. Before doping (1a), the spectrum of PPP exhibits the expected characteristics previously published [6] : the asymmetry ratio A/B is equal to 1 (A and B are the intensities of the first derivative absorption peak at low and high magnetic field, respectively) and the peak to peak linewidth ΔHpp is equal to 8 G. After a few hours of doping, (figure 1b), a second type of behaviour is observed : a narrow signal is superimposed on a wider and asymmetrical one. That is characteristic of a compound inhomogeneously doped, in which the Dyson effect is observed for the most doped and conductive parts of the material. The spins responsible for the narrow signal are related to the mobile paramagnetic polarons present in the less doped part of the material while the spins at the origin of the broad peak are related to the conduction electrons of the superior bipolaron band and therefore correspond to the most doped part of the polymer. A similar situation was previously found by Ghanbaja et al. in the case of alkali metal doping of polyacetylene[8].

Upon further doping (1c) and at saturation (1d), only asymmetrical and broad signals are observed. Thus, ΔHpp and A/B are respectively equal to 177 G and 2.6 for the saturated material.

Based on the work of Dyson[9], Kodera[10] numerically calculated the lineshape parameters of the absorption ESR signal and the first derivative for different values of d/δ and $(T_D/T_2)^{1/2}$ (d is the sample thickness, δ the skin depth, T_D the diffusion time of the paramegnetic centres through δ and T_2 is the spin-spin relaxation time).

Figure 2 shows the evolution of the asymmetry ratio A/B as a function of the doping duration for a heavily Rb doped pellet of 280 μm thick. The shape of this curve is coherent with the theoretical ones of Kodera (A/B = f (d/δ). A/B increases first from 1 (undoped material) to a maximum of about 3.9 and then decreases to about 2.5. These variations can be related to the monotonic increase of the electrical conductivity σ during the doping and thus to the increase of the ratio d/δ since δ varies as σ^{-1}. According to the curves of Kodera, the maximum observed value of A/B indicates that, in the present samples, the $(T_D/T_2)^{1/2}$ ratio is higher than 10 and that the spin diffusion process through δ is slow.

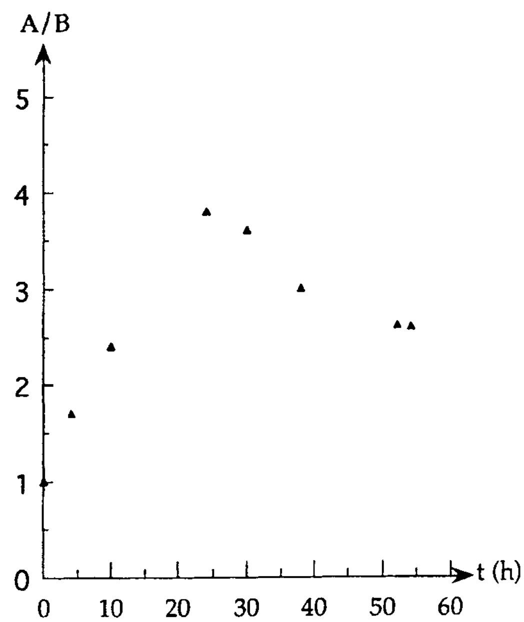

FIGURE 2 Evolution with the doping time t of the asymmetry ratio A/B for heavily rubidium doped PPP compounds

Figure 3 presents the evolution of A/B as a function of temperature T between 280 and 100 K. This curve behaves similarly as the one presented in figure 2. The A/B variation is related to the decrease of σ when T decreases, and therefore to the d/δ decrease. As T decreases, the results follow the curve of Kodera, showing that the Dyson theory can be applied to the present rubidium-PPP samples. The maximum value of A/B is close to 3.9. That is typical of samples for which the $(T_D/T_2)^{1/2}$ ratio is higher than 10, as also observed in fig. 2. The electrical conductivity at 9.78 GHz can be estimated from the curve of Kodera. Thus, for a Rb saturated PPP sample of thickness equal to 280 µm, the A/B ratio of 2.6 yields σ equal to 154 S/cm. Such a value is very similar to the one, 140 S/cm, measured directly with a four probe technique[4].

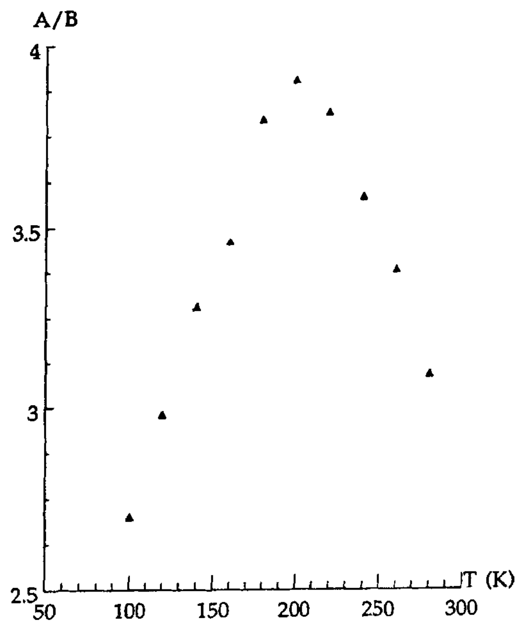

FIGURE 3 Evolution with temperature T of the asymmetry ratio A/B for heavily rubidium doped PPP compounds

CONCLUSIONS

The ESR parameters of pressed pellets of rubidium doped PPP have been examined as a function of the doping duration and temperature. Dysonian ESR signals have been observed for heavily doped samples for which $d/\delta>1$. The evolution with T or with the doping duration of the asymmetry ratio A/B for such samples is comparable with that presented in the curves of Kodera relating A/B with d/δ. Therefore, the Dyson theory can be applied to rubidium doped PPP which can exhibit, for high doping levels, a metallic character. A good agreement is found between the values of σ obtained by direct contact methods and those calculated from the ESR data recorded at 9.78 GHz. It appears that the behaviour of the present Rb-PPP compounds is comparable to that of doped polyacetylene materials studied previously in details[8].

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