

Magnetic resonance experiments on undoped and doped poly(*para*-phenylene)

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Abstract

We investigated the electron paramagnetic resonance (EPR) spectra of undoped, FeCl_3 - and iodine-doped poly(*para*-phenylene) (PPP) prepared by the method of Kovacic. EPR measurements are used to characterize electronic states relevant for carrier transport in doped PPP. We found a novel dependence of room temperature linewidth (ΔH_{PP}) and spin density (N_{spin}) on the dopant concentrations for iodine-doped PPP, namely, ΔH_{PP} first decreased and increased, and then decreased and increased again with increasing iodine concentration in the iodine-doped PPP. The corresponding value of N_{spin} first increased and decreased, and then increased and decreased again with increasing iodine concentration in PPP. However, the changes in ΔH_{PP} and N_{spin} with FeCl_3 concentration in FeCl_3 -doped PPP differ from those of iodine-doped PPP. We explain the different EPR properties in FeCl_3 -doped and iodine-doped PPP.

Introduction

It is well known that doping of a conjugated polymer with a non-degenerate ground state generates polarons and bipolarons. Due to interactions between spins on the PPP chains and dopant molecules in doped PPP, dopant-induced polarons or bipolarons exist stably, as shown by experiment [1, 2]. Theoretical computations [3, 4] and experiments [5, 6] reveal that polarons have spin ($s = \frac{1}{2}$) and charge; bipolarons are charged and spinless. EPR experiments have indicated that the Pauli susceptibility is surprisingly small and the concentration of magnetic centers is several orders of magnitude smaller than the dopant concentration in doped PPP [7]. Recently, EPR experiments have been shown to provide a very sensitive method of studying the relation between N_{spin} , ΔH_{PP} and doping.

Here we present an EPR study of novel properties of EPR spectra from iodine- and FeCl_3 -doped PPP.

Experimental

PPP was polymerized using the method of Kovacic and Oziomek [8]. Iodine and FeCl_3 doping was carried out with iodine-benzene and

FeCl_3 -nitromethane solutions, respectively, in nitrogen-protected cells to avoid oxidation [9].

EPR spectra were recorded at room temperature with an X-band (9.2–9.5 GHz) JES-FE3AX EPR spectrometer. The spin density was obtained by double integration of the signal and comparison with a calibrated reference sample (DPPH) placed in the same dual EPR cavity.

Results and discussion

The room temperature linewidth ΔH_{PP} (a) and spin density N_{spin} (b) in iodine-doped PPP vary with $\ln[N(I)]$ as shown in Fig. 1. It was found that at room temperature, the linewidth ΔH_{PP} and the spin density N_{spin} first decreased and then increased while the concentration of iodine in PPP increased. This phenomenon was repeated when the iodine concentration in the iodine-doped PPP was increased.

Iodine is a relatively weak electron acceptor so iodine molecules can have partial charge transfer with PPP chains. Furthermore, depending on the concentration of iodine in PPP, iodine may exist as I^- , I_3^- , I_2 and I_5^- . The different electric fields formed respectively in iodine-doped PPP have a different influence on the polarons and bipolarons in the chains so that relative contents of polarons or bipolarons in the PPP chains may change with increasing $N(I)$. A polaron has a spin electron and a bipolaron is spinless (see Fig. 2). As pointed out previously [10], spin-charged polarons or spinless

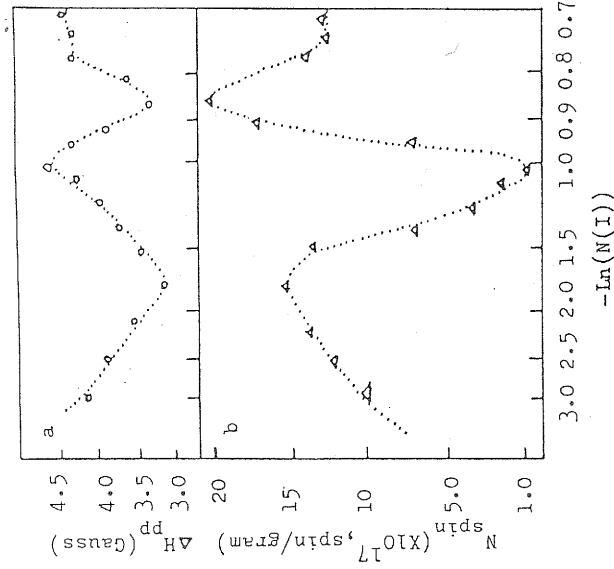
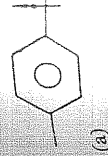


Fig. 1. Room temperature linewidth ΔH_{PP} (a) and spin density (b) in iodine-doped PPP vs. $\ln(N(I))$.

$s = 1/2$



(b) $s = 0$



Fig. 2. Paramag

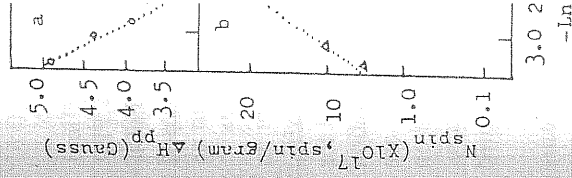


Fig. 3. Room temperature $\ln(N(\text{FeCl}_3))$.

Fig. 4. Linewidth PPP.

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Figure 3 s) N_{spin} (b) in FeCl_3 concentration can see that ΔFeCl_3 concentration (or N_{spin}) with

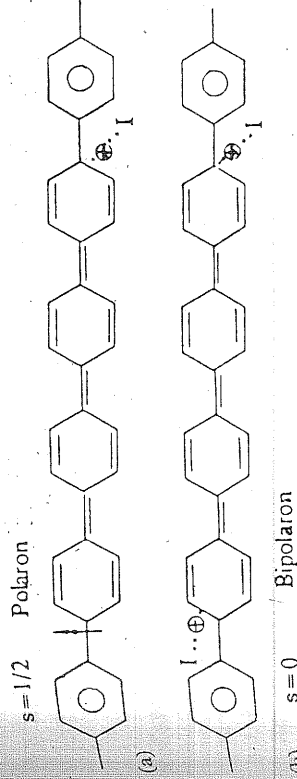


Fig. 2. Paramagnetic polarons and spinless bipolarons in doped PPP.

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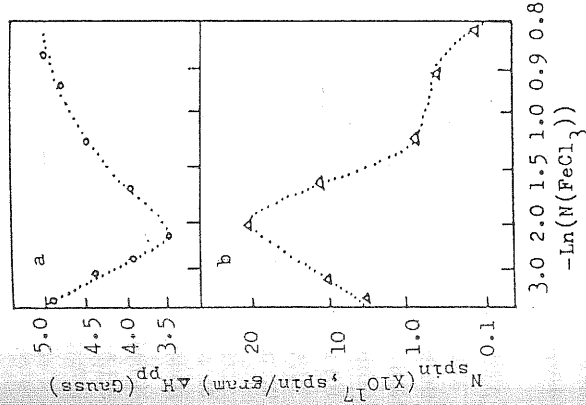


Fig. 3. Room temperature linewidth ΔH_{PP} (a) and spin density (b) in FeCl_3 -doped PPP vs. $\ln(N(\text{FeCl}_3))$.

Fig. 4. Linewidth ΔH_{PP} vs. temperature: (1) undoped PPP; (2) and (3) lightly iodine-doped PPP.

bipolarons can be formed in the PPP chains by doping and polarons and bipolarons may convert into each other. Therefore N_{spin} may vary with polaron and bipolaron contents, with the different $N(I)$ and ΔH_{PP} varying in a novel way with increases in $N(I)$.

Figure 3 shows the room temperature linewidth ΔH_{PP} (a) and spin density N_{spin} (b) in FeCl_3 -doped PPP as a function of $\ln[N(\text{FeCl}_3)]$. From Fig. 3, we can see that ΔH_{PP} and N_{spin} increased and then decreased with increasing FeCl_3 concentration in FeCl_3 -doped PPP. The dependence of ΔH_{PP} and N_{spin} on FeCl_3 concentration in FeCl_3 -doped PPP are not similar to that of ΔH_{PP} (or N_{spin}) with iodine content in the iodine-doped PPP. FeCl_3 in doped PPP

-doped PPP vs.

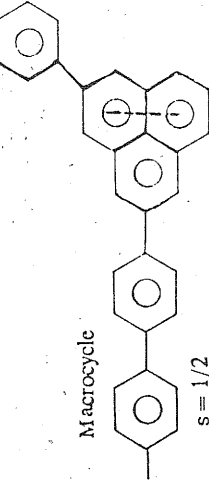


Fig. 5. Paramagnetic defects in undoped PPP.

exists only in the form of FeCl_4^- [5]. FeCl_4^- is a high-spin complex and the different EPR properties in FeCl_3 -doped PPP and in iodine-doped PPP depend on FeCl_4^- . As stated above, N_{spin} increased with increased FeCl_3 due to the production of polarons in lightly FeCl_3 -doped PPP; N_{spin} decreased with increase of FeCl_3 concentration in heavily FeCl_3 -doped PPP due to polarons converting into bipolarons.

Figure 4 shows how the linewidth ΔH_{PP} varies with temperature in undoped PPP and lightly iodine-doped PPP. The results indicate that ΔH_{PP} does not change with temperature (curve 1). EPR signals were observed for undoped PPP from macrocycle defects which were created during preparation procedure [6], i.e., due to polynuclear aromatic radicals. The defects are presented in Fig. 5, a macrocycle with one unpaired electron delocalized on a few carbon atoms leading to an EPR spectrum with no hyperfine structure. Another possibility is that a few polarons carrying a spin electron are formed in the synthesis of PPP.

For lightly iodine-doped PPP, ΔH_{PP} decreased with increasing temperature (curves 2, 3 of Fig. 4). A mobile polaron leads to EPR signals. The spin-spin relaxation and exchange interaction of spin plays a substantial role in EPR, but the effect of spin-lattice relaxation is smaller. As polarons convert into bipolarons, ΔH_{PP} increases. The results agree with theoretical predictions [3, 4]. We note that the EPR measurements of undoped PPP samples show that ΔH_{PP} values decrease with time. ΔH_{PP} is close to 7.2 G for the undoped PPP after several days. After three months, ΔH_{PP} decreased to about 5.0 G and then remains unchanged. The experimental results of the undoped PPP were in agreement with ref. 11 four months after preparation.

Acknowledgements

The authors gratefully acknowledge financial support of this work through the National Science Fund Committee of China and the Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Science.

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The authors acknowledge stimulating discussions with Professor Jing Bai Wang.

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complex and ne-doped PPP created FeCl_3 $\sqrt{v_{\text{spin}}}$ decreased in PPP due to temperature in state that ΔH_{PP} e observed for ng preparation he defects are delocalized on fine structure. on are formed ig temperature The spin-spin ul role in EPR, s convert into al predictions samples show r the undoped o about 5.0 G undoped PPP n.

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