

Electron Paramagnetic Resonance of the I₂-Doped PBMPV Conducting Polymers

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We have studied a series of I₂-doped poly [2-butoxy-5-methoxy-1, 4-phenylenevinylene] (PBMPV) conducting polymers by means of electron paramagnetic resonance (EPR) measurements. In this work, the EPR linewidth and spin density were obtained from the EPR intensity and studied as a function of the degree of doping.

1. Introduction

The conducting polymers have been a subject of much interest for their novel properties and potential applications [1-3]. Upon doping with electron donors or acceptors, they can give remarkable electrical conductivities. The electrical conductivity is generally known to be governed by the one-dimensional diffusion of the charge-carrying solitons or polarons, and the main charge transfer mechanism in conjugated conducting polymers is known to be the intrachain diffusion and interchain hopping of polarons and/or bipolarons [4-8]. Electron paramagnetic resonance (EPR) is a powerful tool for spin dynamics and has been employed to study various conducting polymers [8-10]. In other words, the EPR lineshape and linewidth can reflect the spin-carrier motions and interactions. On the other hand, in conjugated conducting polymers like PBMPV where the charge carriers are polarons and bipolarons, the EPR intensity is proportional to the density of the spin-carrying polarons (spin 1/2, charge e). A pair of polarons can form spinless bipolarons (spin 0, charge 2e), which are energetically more stable. Of course, only spin-carrying polarons can give EPR signals, whereas the spinless bipolarons cannot make EPR transitions. In this work, we have investigated the charge/spin dynamics in a series of I₂-doped poly [2-butoxy-5-methoxy-1, 4-phenylenevinylene] (PBMPV) samples by means of EPR and electrical conductivity measurements.

2. Experiment

Figure 1 shows the repeating unit of PBMPV, which is a derivative of conjugated PPV (polyphenylenevinylene). The PBMPV conducting polymer samples were prepared by thermal elimination of polyelectrolyte precursor polymer films and iodine-doping, and the iodine concentration was determined as previously described [11]. While the doped PBMPV samples are known to have inherent inhomogeneities, relatively thick good quality samples have been obtained according to visual inspection.

The electrical conductivity was measured by the standard four-in-line-probe method, and the EPR measurements were made at 9.4 GHz using a X-band EPR spectrometer. The magnetic

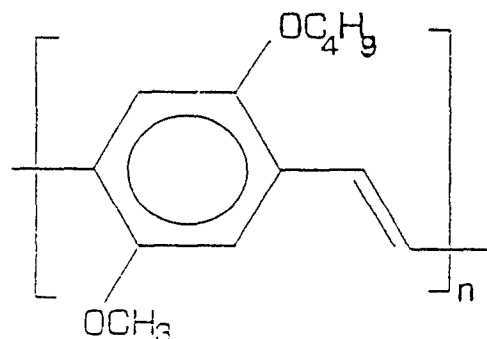


Fig. 1. The repeating unit of the PBMPV conjugated polymer.

susceptibilities were obtained by double-integrating the differential EPR lineshape.

3. Results and Discussion

Figure 2 shows the room temperature electrical conductivity for samples with various degrees of I₂-doping, in which the conductivity displays a characteristic increase with the doping. In Fig. 2 a rapid increase of the electrical conductivity is noticed around the doping degree of 10⁻²I₃⁻/RU (repeating unit). This can be attributed to the charge dynamics governing the charge conduction mechanism. In other words, the behavior of the conductivity as a function of the doping can be explained with the bond percolation model described in terms of the variable range hopping in conducting polymers like our PBMPV system [12, 13]. This model defines a percolation threshold at a critical doping degree where infinite percolation clusters are formed with infinite correlation lengths. Correspondingly, the DC conductivity can increase drastically due to the infinite percolation clusters.

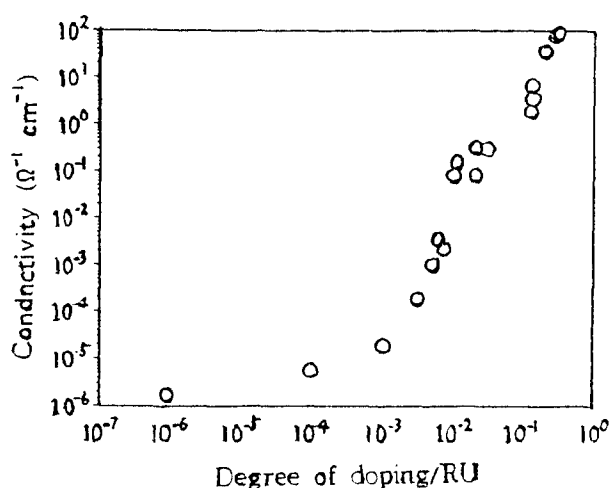


Fig. 2. The electrical conductivity as a function of the degree of doping.

Figure 3 shows the room temperature EPR lineshapes for various doping degrees, which could be fitted into Lorentzian form. The spin density for the PBMPV conducting polymers as determined by the EPR intensity is shown in Fig. 4, where a steady increase is observed as a function of the degree of doping. This indicates that more doping gives rise to more spin- and charge-carrying polarons as the spin 1/2 polarons can undergo EPR transitions as well as contribute to the electrical conductivities. Since EPR can detect only the spin-carrying polarons, direct information on polaron-bipolaron transitions can be obtained from the doping degree dependence of the spin density. Applying the polaron-bipolaron transition by spin combination in polymer chain units, the spin density is expected to decrease at doping degrees high enough for polaron-bipolaron

transitions. However, as the chain unit cannot always contain even number of spins, there will be extra spins that cannot form a pair. As a consequence, an increase of the spin density is possible even at doping degrees where the bipolaron formation is dominant. In Fig. 4 a decrease of the spin density is noticed around the doping degree around 10⁻¹I₃⁻/RU, which appears to be related to the macroscopic (or interchain) polaron-bipolaron formation at high doping degrees. Thus, EPR is shown to reflect sensitively the spin dynamics in our system.

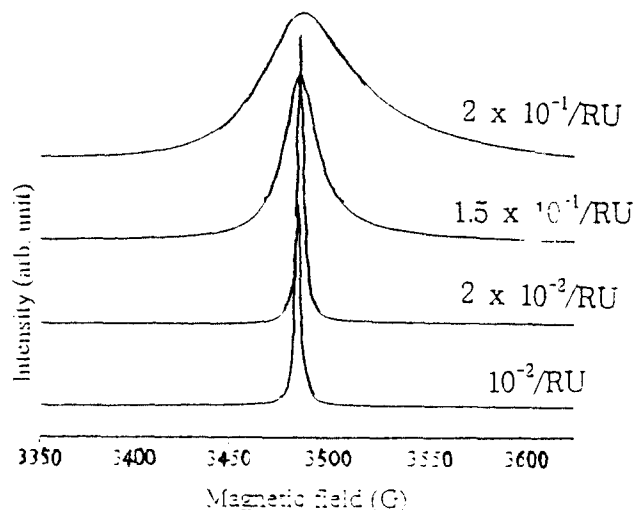


Fig. 3. EPR lineshapes for samples of various degrees of doping.

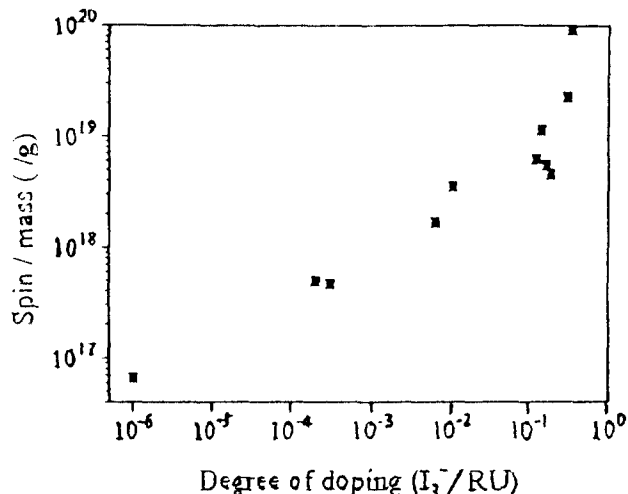


Fig. 4. Spin density as a function of the degree of doping.

A semi-quantative analysis can be made here on the polaron-bipolaron recombination. Figures 2 and 4 show that as the degree of doping change by 10ⁿ, the conductivity changes by 10⁸ and the EPR intensity by 10³. Assuming that each dopant can give rise to a polaron, then the difference between the degree of doping and the spin density, on the order of 10³, may be accounted for by the polaron-bipolaron recombination.

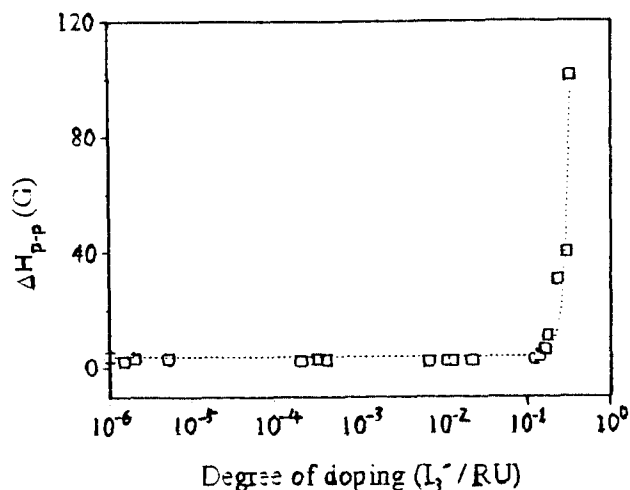


Fig. 5. Peak-to-peak EPR linewidth as a function of the degree of doping.

As Fig. 3 shows the doping dependence of the linewidth, the peak-to-peak EPR linewidth ΔH was plotted as a function of the degree of doping in Fig. 5. While the linewidth stays nearly constant before showing a rapid increase as the doping proceeds, it can be well fitted into the form of $y = a + bx^2$. In conducting polymers main contributions in the linewidth are hyperfine interaction between the hydrogen nucleus (proton) and the electron spin, and the dipolar interaction between the electron spins. For low enough doping the interspin distances are so large that the dipolar linewidth $\Delta H_d \sim 1/r^6$ cannot contribute significantly, and the linewidth will mostly be the hyperfine interaction between the proton and the polaron, which is really independent of the doping degree. However, for high enough doping, the interspin distance will be small and ΔH will be dominated by the spin dipolar interaction, resulting in a rapid increase in the doping dependence. Assuming a homogeneous spin distribution, the average interspin distance is given by $r_0 = (V/N)^{1/3}$, where N is the total number of spins and V is the volume. As a consequence, the ΔH due to the spin-spin interaction will be proportional to the square of the dopant density as observed in this work.

In summary, PBMPV conjugated polymers were synthesized and iodine-doped for high electrical conductivities for electron paramagnetic resonance studies. As a result, characteristic

behaviors were observed in the lineshape, linewidth, and spin susceptibilities. Further work is in progress to elucidate the nature of spin dynamics in the systems.

Acknowledgments

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