

NMR observation of critical delocalization in a disordered conducting polymer system

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A critical behavior associated with the delocalization of the charge-carrier wave function was manifested in our study of the spin/charge dynamics for a series of I₂-doped poly[2-butoxy-5-methoxy-1,4-phenylenevinylene] conducting polymers employing conductivity and nuclear-magnetic-resonance measurements. Our results represent a demonstration of a critical behavior near a percolation threshold in a disordered system.

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The topic of localization/delocalization in a disordered medium has fascinated many researchers over the years. However, while critical behaviors near the percolation thresholds have been theoretically described in a comprehensive manner, only sporadic and indirect evidences have been experimentally observed for inherently homogeneous systems, although some examples have been reported in polymer composite systems.^{1,2} Especially, close examination of the critical behavior in the percolation threshold regime in a disordered medium caused by inhomogeneous doping would be of considerable interest. In this work, we report a comprehensive observation of the fractal and critical behavior associated with the delocalization in a disordered conducting polymer system. Doping up to controllable degrees showing metallic behavior around room temperature in a polyphenylenevinylene (PPV) derivative, for which heavy doping is possible, provided us with a unique opportunity for such a study.

Conducting polymers show remarkable electrical conductivities upon doping with electron donors or acceptors.³⁻⁵ 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.⁶⁻¹⁰

Nuclear magnetic resonance (NMR) is a powerful tool for spin dynamics, and has been employed to study various conducting polymers as it can sensitively reflect the spin carrier motions and interactions.¹⁰⁻¹² NMR measurements have proven to be very successful in investigating the local environments and lattice dynamics in a variety of systems including polymer systems.

Poly [2-butoxy-5-methoxy-1,4-phenylenevinylene] (PBMPV) is a derivative of the conjugated PPV polymer. It can be easily doped to controllable degrees and provides a unique opportunity to systematically study the doping as well as conductivity dependence of various properties including the dopant kinetics and spin/charge dynamics. In this work, we have investigated the charge/spin dynamics in a series of I₂-doped PBMPV samples by means of NMR as well as electrical conductivity measurements. While there have been some indirect indications of bipolaron formation

in some electrochemically synthesized conducting polymers through the electron paramagnetic resonance (EPR) and susceptibility measurements,^{13,14} this work is believed to represent a comprehensive observation of the collective critical behavior of spin-charge-carrier delocalization in an iodine-doped conjugated polymer.

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.¹⁵ While the doped PBMPV samples are known to have inherent inhomogeneities, relatively thick good quality samples have been obtained. The room-temperature NMR line shape and spin-lattice relaxation measurements were made at 30 MHz using a home-built pulsed spectrometer.

Figure 1 shows the room-temperature electrical conductivity as a function of the degree of I₂ doping, in which the conductivity displays a characteristic increase with the doping. In Fig. 1 prominent changes of the electrical conductivity are noticed around the dopings of $p_{c1} = 4 \times 10^{-3} \text{ I}_3^-/\text{RU}$ (repeating unit) and $p_{c2} = 5 \times 10^{-2} \text{ I}_3^-/\text{RU}$, which can be attributed to the dynamics governing the charge conduction mechanism. 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 such as our PBMPV system.^{16,17} This model defines percolation thresholds at critical doping degrees where infinite percolation clusters are formed with infinite correlation lengths. Correspondingly, the dc conductivity can increase drastically due to the infinite percolation clusters. In bulk samples with three-dimensional network structures such as PBMPV, the dc conductivity can increase rapidly at the percolation threshold only when infinite percolation clusters are formed, because charge carriers diffuse principally perpendicular to the polymer chains. The bulk electrical conductivity in those structures is limited by the interchain diffusion rather than the fast diffusion along the main chain.⁸ As will be further elucidated, the two percolation thresholds in the iodine-doped PBMPV system,¹⁸ p_{c1} and p_{c2} , corresponds to the evolution of the local environments as the concentration of the conducting islands near the dopants increases with the degree of doping.

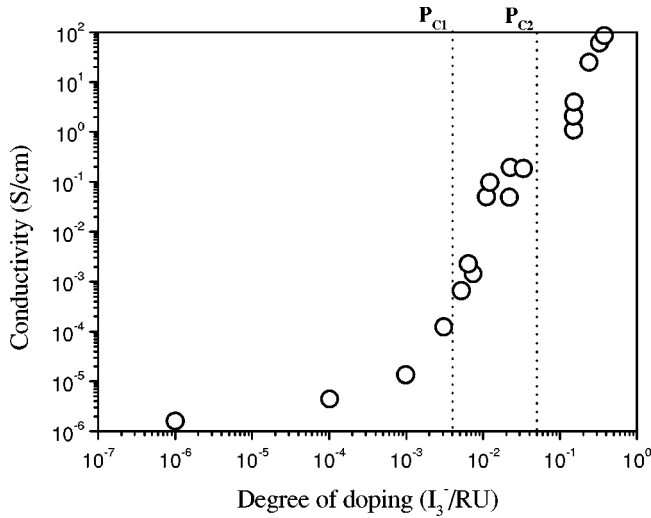


FIG. 1. The electrical conductivity of I₂-doped PBMPV as a function of the degree of doping showing the two percolation thresholds.

Figure 2 shows the electrical conductivity as a function of $(p - p_{c1})$, where p is the doping degree and $p_{c1} = 4 \times 10^{-3}$ I₃/RU. It is noticed in Fig. 2 that for doping levels higher than p_{c1} , the conductivity is proportional to the square of $(p - p_{c1})$, in agreement with the case of conduction due to the fractal network between conducting islands.¹⁹ Thus, p_{c1} is seen to act as a percolation threshold for the I₂-doped PBMPV conducting polymer samples.

While the spin-lattice relaxation patterns of the undoped and the heavily doped samples were well fitted into a single-exponential form, those for the intermediate doping levels were clearly nonexponential, and were well fitted into a stretched-exponential form, $M(t) = M_o(1 - \exp[-(t/T_1)^{1-n}])$. The exponent $n=0$ corresponds to the single-exponential type, and the greater values of n are indicative of higher degrees of nonexponentiality, and of inhomogeneity, as will

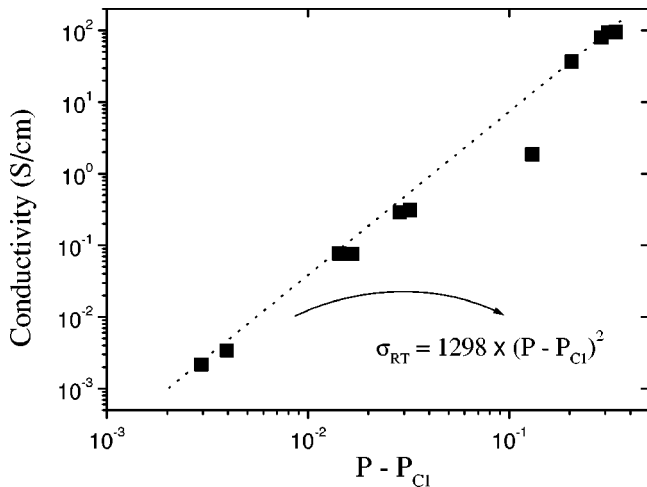


FIG. 2. Log-log plot of the conductivity vs $(p - p_{c1})$ where p is the degree of doping and $p_{c1} = 4 \times 10^{-3}$ is a percolation threshold. The dotted line is a linear fit corresponding to a $(p - p_{c1})^2$ dependence.

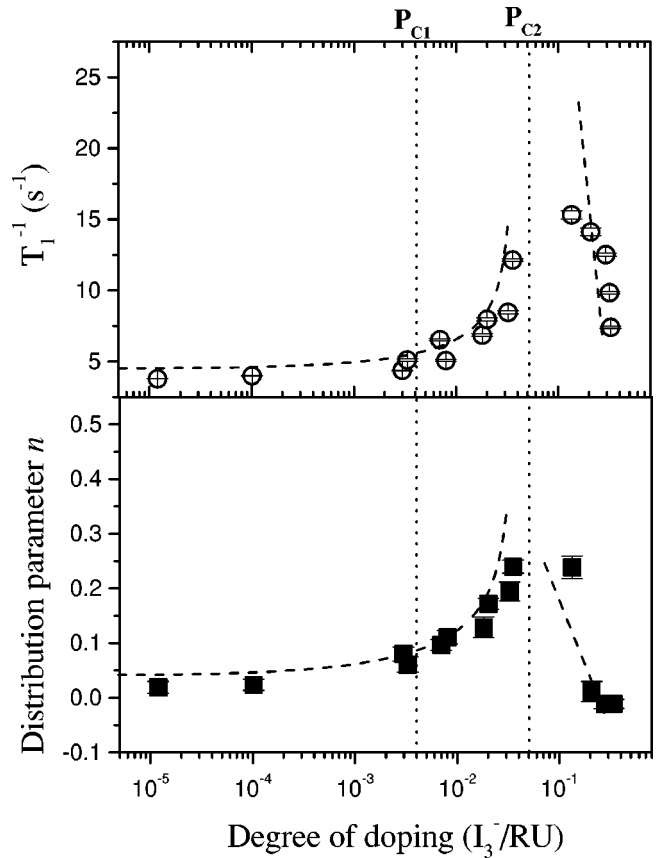


FIG. 3. ¹H NMR spin-lattice relaxation rate ($1/T_1$) and the exponent n as a function of the degree of doping, both showing a $|p - p_{c2}|^{-\nu}$ dependence where p_{c2} is a percolation threshold.

be further discussed. Figure 3 shows the results of the fitting, i.e., the exponent n and the spin-lattice relaxation rate ($1/T_1$). Both of them initially increase with doping, abruptly decreasing around p_{c2} .

The stretched-exponential type of relaxation is characteristic of inhomogeneous environments such as glassy systems and can be attributed to a distribution of the microscopic correlation time.²⁰ In our PBMPV conducting polymer systems, the inhomogeneity is caused by the inhomogeneous I₂ doping. In other words, the dopants are believed to form around them inhomogeneous glassy regions, which are the metallic conducting islands. These regions under the direct influence of the dopants will be in environments different from those less directly affected by the dopants. Our spin-lattice relaxation data are well interpreted in this physical picture. The nonexponentiality in the spin-lattice relaxation can be attributed to the inhomogeneous distribution of conducting islands arising from the I₂ doping. Then, the spin-lattice relaxation would reflect corresponding transitions in the local environments.

The exponent n , indicative of the degree of inhomogeneity, and the spin-lattice relaxation rate $1/T_1$ initially increase with doping, both showing a $|p - p_{c2}|^{-\nu}$ dependence in Fig. 3. This concentration dependence is in agreement with the bond percolation model, in which percolation clusters of various sizes form fractal dimensions as the concentration approaches the percolation threshold, which is p_{c2} in our

case. In such cases, the proton spin-lattice relaxation is given by the cluster size distribution. The change in the cluster sizes defined by the volume to surface area ratio is described by the correlation length, which varies as $\xi \propto |p - p_c|^{-\nu}$. It then follows that the concentration dependence of the spin-lattice relaxation rate, $1/T_1 \propto |p - p_{c2}|^{-\nu}$, observed in Fig. 3 is a good indication that our system forms fractal dimensions in intermediate doping ranges where more of the inhomogeneous conducting islands are formed.¹⁹ It is interesting to note that the distribution parameter n shows a similar dependence, which suggests that it is a sensitive indicator of the evolution of the microscopic local environments, presumably the cluster size distribution of the conducting islands in our case.²⁰

In Fig. 3, the abrupt decrease in both the spin-lattice relaxation rate and the exponent n around p_{c2} is indicative of a transition in the local environments. In particular, the abrupt drop in the exponent n indicates that the system suddenly becomes quite homogeneous, pointing to a transition associated with the spin/charge carriers, which dictate the local environments in conducting polymer systems. Furthermore, as heavier doping will give rise to more spin/charge carriers and to more inhomogeneous regions in general, the sudden transition to a more homogeneous environment indicated by a sudden drop in the exponent n to zero can only be explained by a sudden globalized delocalization of the spin-charge-carrier wave functions. In other words, the delocalization of the wave functions would render the carrier environments quite homogeneous in the whole system. The sharp and abrupt transition then can be attributed to the presence of a critical carrier density for the carrier delocalization.

The inhomogeneous morphology of even the most highly conducting polymer samples is known to lead to disorder-induced localization and percolation effects, dominating the transport. In a metallic conductivity study of doped poly-

aniline and polypyrrole conducting polymers, it has also been shown that the metal-insulator transition results from a percolation of metallic regions in the presence of inhomogeneous disorder.²¹

The magnetic susceptibility of our I₂-doped PBMPV systems were also studied by means EPR measurements. In addition to an abrupt increase of the linewidth, the magnetic susceptibility per charge created by the doping showed a sharp minimum around p_{c2} . This indicates that spin carriers recombine into spinless states around this percolation threshold.

In summary, a disordered conducting polymer system of a PPV derivative arising from inhomogeneous iodine doping was carefully studied near the percolation thresholds by means of conductivity and nuclear magnetic resonance measurements. Two percolation thresholds were identified in this work. The first one at the lower doping degree corresponds to the formation of the fractal network between the conducting islands: the local environment becomes more inhomogeneous as the doping further proceeds until the second percolation threshold is reached. On the other hand, the second one at the higher doping degree turned out to correspond to the sudden globalized delocalization of the spin/charge carrier wave function, which renders the whole environment quite homogeneous. The current systematic study provided us with unique and comprehensive evidences for fractal and critical behaviors apparently associated with the evolution of the inhomogeneous local environments and with the charge-carrier delocalization.

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