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Bipolaron saturation in polypyrrole

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Saturation of bipolaron, the species responsible for conduction in polypyrrole (PPy), has been studied using positron annihilation lifetime (PAL) spectroscopy, conductivity, and electron spin resonance (ESR) measurement. It is observed that when strong oxidizing agents are used, the defects are predominantly bipolarons as is evident from the PAL spectroscopic studies coupled with ESR measurements and its saturation occurs right at the onset of oxidation. However, in the case of a mild oxidizing agent, the dominant defects are bipolarons only at higher oxidizing strengths [$\geqslant 1.0(N)$] and no saturation is attained even at the highest strength studied. Conductivity data corroborate the findings. [S0163-1829(99)11031-2]

I. INTRODUCTION

Conducting polymers, especially polypyrrole (PPy), have recently attracted considerable attention because of the interesting properties of these materials.[1–3] The effect of doping on electronic states, conductivity, and optical properties of such polymers has been widely investigated over the past several years leading to the proposition that these properties are tremendously influenced by the soliton, polaron, or bipolaron type of defects generated in the neutral polymer chain.[3–5]

It has been observed that PPy possesses a nondegenerate ground state. A polaron is produced upon extraction of a negative charge from a neutral segment of the chain (via partial oxidation) accompanied by lattice relaxation. Formation of polaron, a radical cation, introduces two states within the band gap that are bonding and antibonding in character. Subsequent removal of further negative charges from the PPy chain that already contains a polaron, may yield more polarons or the existing polarons may be ionized to form a bipolaron via additional oxidation. Theoretical calculations done by Bredas *et al.*[6] suggest that the latter process is favored energetically. However, there exist contradictory arguments as well.[7] Nevertheless, it appears decisive that bipolarons play a fundamental role in charge transport within the PPy chain.

As more bipolarons are generated, their energies overlap leading to bipolaron bands within the forbidden gap. Electronic energy levels of such a system have been suggested by Bredas *et al.*[6] Further theoretical studies[8] have shown that in contrast to polyacetylene, the valence band and the conduction band of PPy do not merge together even upon 100% doping. Though this conclusion has been confirmed by conductivity measurement[9] no other direct experimental evidence could be found in the literature. Since bipolaron is the most fundamental species responsible for conduction in PPy, saturation of them in a PPy chain upon doping is very likely to limit the conductivity of the material to a saturation value. So it seems instructive to study bipolaron saturation in PPy for a better understanding of the conduction mechanism vis-a-vis the energy-band structure.

Recently, microstructural changes in conducting polymer matrix has been extensively studied through positron annihilation lifetime (PAL) measurements.[10–12] Because of its nondestructive nature and sensitivity to electron density fluctuations within a material, PAL measurements are being conducted widely to identify the nature of the defects, particularly the open volume defects. Doyle *et al.*[10] have studied the PAL in PPy at different temperatures and observed weak temperature dependence. Pethrick[13] has recently published an extensive review on the use of PAL measurements in polymers and has pointed out the suitability and importance of this technique for using it as a probe to study defects in polymer. Our recent investigation on microstructural lattice deformation of PPy by PAL spectroscopy indicates that the dominant defects are polarons at low oxidizing strengths [$\leqslant 0.75(N)$] and that of bipolarons at strength $\geqslant 1.0(N)$ when [$(NH_4)Fe(SO_4)_2$] is used as the oxidizing agent.[14] The aim of the present work is to study the saturation of the bipolaron type of defects in the PPy chain as a function of strength of different oxidizing agents by PAL measurements and to correlate the findings with electron spin resonance (ESR) and conductivity data.

II. EXPERIMENT

A. Materials

Pyrrole (E. Mercy, Germany) is purified twice by fractional distillation under a nitrogen atmosphere immediately prior to use. Three different oxidizing agents, viz., (i) ammonium ferric sulfate [$(NH_4)Fe(SO_4)_2$], $12H_2O$, (ii) ammonium peroxidisulphate [$(NH_4)_2S_2O_8$], and (iii) potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4 (all except H_2SO_4, procured from E. Mercy, Germany), are used. Conductivity water is used as the solvent to prepare the solutions.

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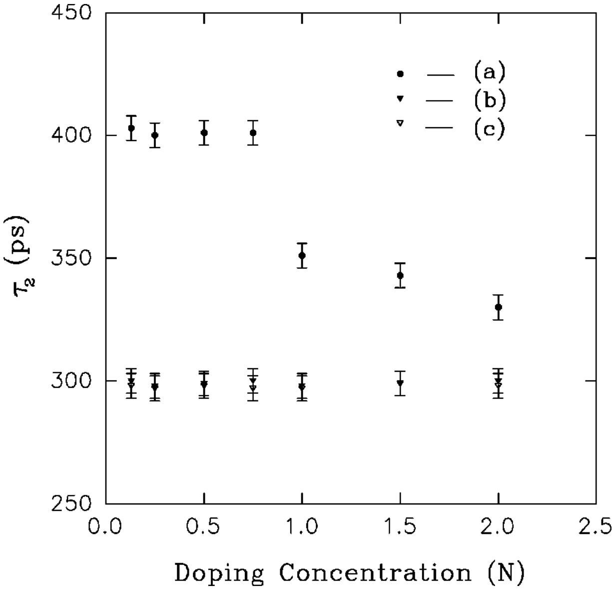

FIG. 1. Variations of the second lifetime components of polypyrrole as a function of the strength of the oxidizing agents: (a) ammonium ferric sulfate, (b) potassium dichromate, and (c) ammonium peroxidisulphate.

B. Polymer synthesis

PPy is synthesized by mixing solutions of pyrrole with the solutions of different oxidizing agents at different strengths, viz., 0.13(N), 0.25(N), 0.5(N), 0.75(N), 1(N), and 2(N). In each case, pyrrole is added to such an extent that the molar ratio of an oxidizing agent to the pyrrole is 50:1. This ratio is maintained to ensure complete conversion of pyrrole monomer to PPy.[15] In each case, polymerization is allowed to proceed for an hour. PPy, formed as a black precipitate, is collected by filtration in a sintered bed crucible. Polymer thus obtained is rinsed thoroughly with water and dried for 24 h at room temperature under a vacuum. Dried polypyrrole powder doped with different oxidizing agents at different strengths, as stated above, are subjected to 6 ton/cm^2 pressure for 10 min to make the pellets that are subsequently used for conductivity as well as PAL measurements.

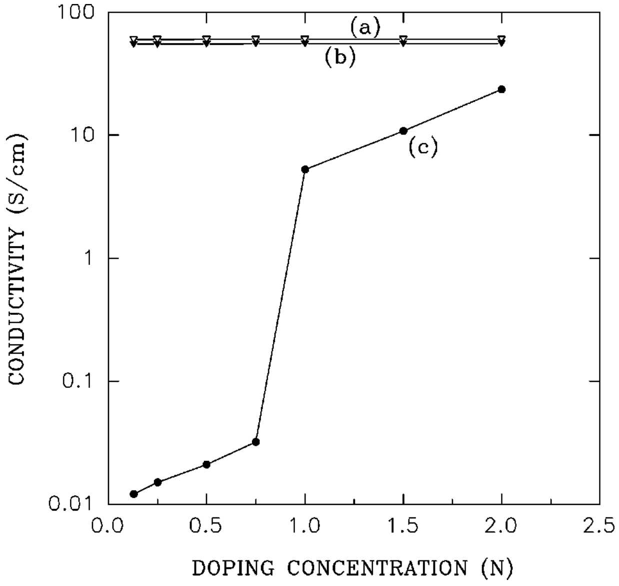

FIG. 2. Plot of conductivity of polypyrrole with the strength of the oxidizing agents: (a) ammonium peroxidisulphate, (b) potassium dichromate, and (c) ammonium ferric sulfate.

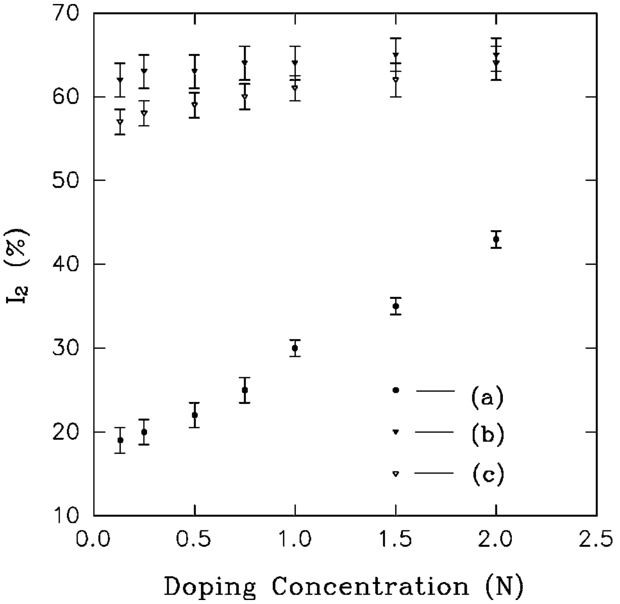

FIG. 3. Variation of I_2 with the strength of the oxidizing agents: (a) ammonium ferric sulfate, (b) potassium dichromate, and (c) ammonium peroxidisulphate.

C. Positron annihilation lifetime measurements

The positron annihilation lifetimes have been measured with a fast–slow coincidence assembly. The detectors are 25 mm dia, 25 mm long cylindrical BaF$_2$ scintillators coupled to Philips XP2020Q photomultiplier tubes (PMT). The negative pulses from the anodes of the PMT's are fed directly to constant fraction differential discriminators and then to the inputs of a time-to-amplitude converter. The resolving time (full width at half maximum), measured with a ^{60}Co source and with the windows of the slow channels of the fast–slow coincidence assembly set to select pulses corresponding to 300 keV to 550 keV in one channel and 700 keV to 1.32 MeV in the other, is 190 ps.

The experimental positron source is prepared from carrier free ^{22}NaCl solution in water by depositing a drop of the solution and then drying it on a thin nickel foil 2 μm thick to obtain a source strength of 10 μCi. A similar nickel foil is placed on the source to cover it.

The contribution of the source in the lifetime spectrum, which has been ascertained by referring to the measured value of the lifetime of positrons in an Al single crystal sample, is $\leqslant 2\%$. The lifetimes and their relative intensities have been extracted from the recorded spectra using the PATFIT-88 program.[16]

III. RESULTS AND DISCUSSIONS

On analysis of the positron lifetime spectra, it is seen that each of them is resolvable into only two lifetime components τ_1 and τ_2. According to the theory of the two state trapping model,[17] τ_2 originates from the annihilation at the defect site,

TABLE I. ESR spectroscopic data of PPy samples.

Oxidizing agent	Strengths (N)	Gain setting	Peak to peak derivative amplitude (cm)	Peak to peak width (G)
$NH_4Fe(SO_4)_2$	(a) $\leqslant 0.75$	4×10	8.7	2.1
	(b) $\geqslant 1.0$	4×10	2.8	4
$(NH_4)_2S_2O_8$	0.13–2.0	4×10	2.6	4.2
$K_2Cr_2O_7$	0.13–2.0	4×10	2.45	4.1

i.e., the distorted part of the lattice and τ_1 is due to the free annihilation in the material. In this context Sharma *et al.*[18] suggest that trapping sites for the positrons in the sample are created as a consequence of spatially localized dopant ions. These dopants create local lattice distortion in such a way so as to create a local negatively charged domain that localized positrons. Further it appears certain that the presence of the dopant ion is strongly associated with the process of negative charge extraction from the PPy chain (i.e., formation of polarons and bipolarons). So, it seems instructive to consider the trapping sites for positrons as the dopant ions having a polaronic or bipolaronic environment, i.e., τ_2 originates from positron annihilation at the dopant site with a polaronic or bipolaronic environment. Since the lifetime components τ_1 and τ_2 are affected by the structure of the dopant ion, we have chosen the oxidizing agents with SO_4^{-2} as the dopant ion in all the cases.

At lower strengths of $(NH_4)Fe(SO_4)_2$ polarons are formed along with the chemical defects while at higher strengths, the chemical defects cease to exist and the number of bipolaronic states increases in the PPy chain. In the latter case, the effective delocalization of positive charge (two unit) reduces the annihilation lifetime, though the polaronic state contains unit positive charge that remains centered, in contrast to the bipolaronic state. When $(NH_4)_2S_2O_8$ or $K_2Cr_2O_7$ is used as the oxidizing agent, τ_2 remain almost constant throughout the range of strength of oxidation studied (Fig. 1) leading one to accept that a state of saturation has been reached at the very onset of oxidation. In both these cases, even at low strengths, no chemical defects exist in the PPy chain due to the higher formal reduction potential of these oxidizing agents, making τ_2 much smaller than when the oxidation is brought about by using $(NH_4)Fe(SO_4)_2$.

The conductivity data for different strengths of the oxidizing agents, presented in Fig. 2, show that with $(NH_4)Fe(SO_4)_2$ as the oxidizing agent, the conductivity linearly increases with strength up to $0.75(N)$ and then rises sharply (by ~170 times) at a strength of $1.0(N)$ and thereafter again takes a slow linear rising course up to $2.0(N)$. However, with $(NH_4)_2S_2O_8$ and $K_2Cr_2O_7$ as oxidizing agents, the conductivity practically remains constant within the concentration range $0.13(N)-2.0(N)$. The variation of τ_2 shows an identical trend as that obtained from the corresponding conductivity measurement for all three oxidizing agents.

The ESR spectra of the samples have been taken under identical experimental conditions (e.g., gain setting 4×10 in all the cases). ESR spectra of PPy have been a matter of controversy over the last two decades. Different explanations have been put forward to explain the nature of ESR signals in such samples. In a review article, Saunders *et al.*[9] have ascribed the ESR activity of PPy to polarons and not to accidental defects. An ESR spectrum of a sample having polaronic defects would show a signal with high intensity and narrow linewidth. However, as bipolaron to polaron ratio increases in a sample, the corresponding spectrum would have smaller intensity and greater linewidth in comparison to a sample having predominantly polaronic defects. Our findings (as mentioned in Table I) also lend support to the above view, which is in good agreement with that suggested by Genoud *et al.*[19] So, one may conclude that τ_2 is a consequence of the annihilation of positron at the dopant site with a bipolaronic environment in the samples prepared by using the oxidizing agents $(NH_4)_2S_2O_8$ and $K_2Cr_2O_7$ at all the strengths and $(NH_4)Fe(SO_4)_2$ only at higher oxidizing strengths.

The nature of variation of the relative intensity (I_2) pertaining to the lifetime component τ_2 (Fig. 3) in the respective samples also lends support to the above view. The values of I_2 in samples prepared by using $(NH_4)_2S_2O_8$ as the oxidizing agent do not significantly change over the range of strength studied. The same is true of the samples prepared by using $K_2Cr_2O_7$ as the oxidizing agent. This constancy of I_2 indicates that a saturation of bipolaronic states ensues at a very low oxidizing strength in each of these two sets of samples. This is in contrast to the case of samples prepared by using $(NH_4)Fe(SO_4)_2$ where I_2 shows a large rate of increase with increasing the oxidizing strength.

IV. CONCLUSIONS

While saturation is found to set in the two sets of samples, it is unattainable in samples prepared using $(NH_4)Fe(SO_4)_2$. This is because the formal reduction potential of the Fe^{+3}/Fe^{+2} system is not large enough to initiate saturation even at a strength of $2.0(N)$. Unfortunately its solubility does not allow preparation of solutions having higher strengths. Hence, it has not been possible to prepare a sample at some higher oxidizing strength at which saturation might have been attained. It seems that we have presented convincing evidence in favor of bipolaron saturation in PPy, which naturally requires further development for a more detailed description of experimental data.

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