

POSITRON ANNIHILATION AND CONDUCTIVITY MEASUREMENTS ON POLYANILINE*

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ABSTRACT

The positron lifetime spectra and electrical conductivities have been measured for polyaniline as a function of protonation level ($[H^+]$ from 10^{-7} — $10^{0.8}$ mol/L). We observed that (1) the short lifetime τ_1 , which was related to electron density in bulk, decreased with the protonation level; (2) the intermediate lifetime $\tau_2 \approx 360$ ps, almost remaining constant, whereas its intensity I_2 increased with increasing protonation level which was related to the conductivity of material. These results are discussed in terms of conducting island model.

Keywords Positron annihilation, Polyaniline, Conductivity

1 INTRODUCTION

The polyaniline family of polymers have been the focus of recent investigation due to the special structural characteristics and applications^[1]. First, its doping

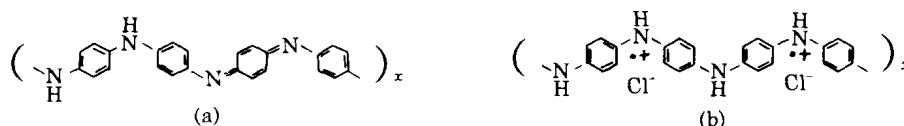


Fig.1 (a) Emeraldine base polymer (unprotonated); (b) polaron lattice on emeraldine salt polymer (fully protonated $[Cl]/[N] = 0.5$)

mechanism is different from that of previously studied polymer. Unlike the conventional conducting polymers, there is no change in the number of electrons in the backbone chain after protonation; second, both forms, emeraldine base (EB) and emeraldine salt (ES), as shown in Fig.1, are very stable in air; third, possibility of application as electronic materials is very high. Although serious corresponding

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variation in physical properties with the protonation level has been reported^[2,3], the conducting mechanism is not very certain.

In recent years, positron annihilation technique (PAT) was emerged as one of the novel methods currently available for the study of polymers at a molecular level^[4,5] because of its sensitivity to the microstructural changes in the polymer matrix. To the best of our knowledge, only Y.F. Nicolau *et al.* have studied the compressed pellet samples of polyaniline (EB and ES) in the temperature range 77–400K by PAT. In order to understand the nature of physical processes which occur in polyaniline due to protonic doping, we have measured the electrical conductivity and positron annihilation parameters in polyaniline as functions of protonation level over a range of $[H^+]$ from 10^{-7} – $10^{0.8}$ mol/L, and discussed the relation of the conductivity σ with positron lifetime parameter.

2 EXPERIMENT

Polyaniline powder was prepared by chemical synthesis as described by Macdiamid *et al.*^[6]. The powder obtained was extracted with CH_3CN , dried and then equilibrated with constant stirring in 0.1mol/L $NH_3 \cdot H_2O$ for 24h giving deprotonated. The polyaniline powder with different protonation states was obtained by treatment of its base form of powder with aqueous HCl solution of different acidity and compressed into 1mm thickness pellets under $150kg/cm^2$. The conductivity of samples at room temperature was measured by four-probe method or high resistance instrument.

A 0.74 MBq ^{22}Na positron source, which was sealed between two aluminum foils, was used in the experiments. Positron lifetime spectra were measured using a fast-fast coincidence system. The time resolution of the system was determined to be 245ps using a ^{60}Co source. Each spectrum contained one million counts. The obtained lifetime spectra were resolved using the PATFIT computer program^[7] with a three component model.

3 RESULTS AND DISCUSSION

3.1 Conductivity at room temperature

The variation of the conductivity of polyaniline powder at room temperature versus the protonation state is shown in Fig.2. the emeraldine base form of polyaniline (EB) has a conductivity of 10^{-10} S / cm. Through the treatment with aqueous HCl of $[H^+]$ varying from 10^{-7} – $10^{0.8}$ mol/L, protons were added to a fraction of formerly unprotonated nitrogen sites, while Cl^- remained interstitially for charge neutrality^[1]. Though the number of electrons on the polymer chain remains constant, the conductivity increases with increasing protonation level and then remains nearly constant at high degree of the protonation level ($pH < 1$). Therefore, an insulator to metal transition on

conductivity at room temperature for samples was observed when the base form of polyaniline powder was protonated by aqueous HCl solution. The transition to a metallic state was suggested to coincide with a change in electronic structure to form metallic polaron lattice (with disorder).

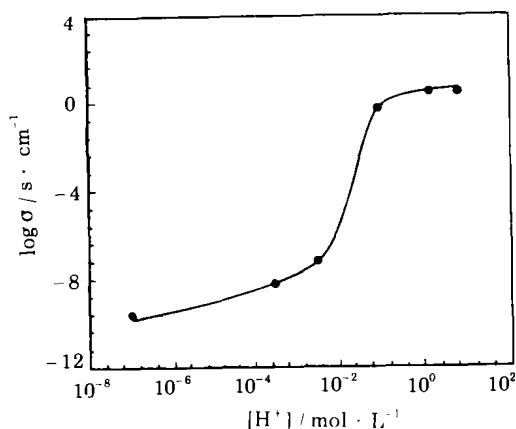


Fig.2 The variation of conductivity with protonation level in polyaniline

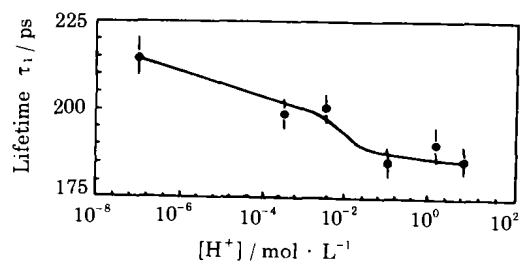


Fig.3 The positron lifetime τ_1 against protonation level in polyaniline

3.2 Positron annihilation measurement

We have measured the positron lifetime spectra in polyaniline as a function of protonation level. Three positron lifetimes were resolved for the spectra, that is to say, positron are annihilating from three different states. The lifetimes are then measures of the average electron density ($\tau \propto n_e^{-1}$) seen by positrons annihilating from each of these states. The relative intensities of the components give the state populations. Since the intermediate lifetimes remain nearly 360ps when fitting without any constraint for the intensities and lifetimes, we fixed τ_2 at 360ps to reduce the statistical error.

As we usually know, the short component ($\tau_1 = 0.18 - 0.21$ ns) and the intermediate component ($\tau_2 = 360$ ps) are attributed to positron annihilation mainly from the bulk and trapped state, respectively, and the long-lived component ($\tau_3 = 1.93 \pm 0.12$ ns, $I_3 = 1.8 \pm 0.3\%$) is due to o-Ps annihilation on the surface of the material which is nearly independent of protonation level.

The results of positron lifetimes τ_1 and the intensity of the intermediate components I_2 resolved in the spectra measured for polyaniline are shown as a function of protonation level in Figs.3 and 4, respectively. The τ_1 lifetime decreases with the protonation level, whereas I_2 increases with the protonation level and then remains nearly constant for higher protonation level ($\text{pH} < 1$). The decrease of the τ_1 lifetime with the increase of protonation level indicated the increase of the electron

density in bulk of material. Comparing Fig.2 and Fig.4, we found that the intermediate intensity I_2 is related to the conductivity of our sample, so we pay the special attention to the variation of the intermediate component with respect to protonation level.

In the base form of polyaniline, the trapping sites might be chain defects which are formed by the coiling, bending or overlapping of the polymer chains; in protonated emeraldine, the localized chlorine dopant anions should perturb the intermolecular force in its vicinity and create local lattice distortions (polaron) in a manner so as to create local negatively charged regions that localize positrons. It is well known, the polaron, which are chemically named "semiquinone cation radicals" are commonly considered as the conduction structure in this polymer. Because the size of the chlorine anion is small (the ionic volume of a Cl^{-1} anion $\sim 25 \times 10^{-3} \text{ nm}^3$,^[8] it is not unreasonable to consider that the doping anions have little affect on the existed trapping sites, and the increased concentration of the trapping sites in our polymer is essentially determined by the concentration of the dopant anion. Therefore, the increment of I_2 is just an indicator of the protonation level. According to the model of conducting island proposed by Epstein^[9], in polyaniline, partial protonation leads to phase segregation into metallic (fully protonated) regions and insulating (unprotonated) regions. The conduction mechanism is dominated by the presence of barriers in the sample leading to charging energy limited tunneling among small metallic regions. We could infer that the increment of I_2 is in proportion to the amount of metallic regions. At lower protonation level ($1 < \text{pH} < 7$), I_2 increases as the equilibrium pH of aqueous HCl solution decreases, that is, more metallic regions will be formed with increasing protonation level. The formation of large amount of metallic regions will reduce potential barrier and leads to the increase in conductivity; at higher protonation level ($\text{pH} < 1$), I_2 remains nearly constant, that indicated the polyaniline was almost fully protonated. The amount of the metallic regions will no longer increase, so the conductivity almost remains constant, too. Therefore, the positron parameter I_2 has the same tendency as the conductivity.

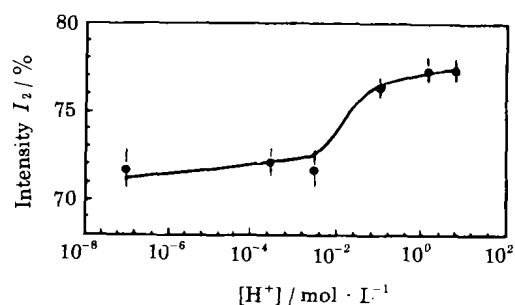


Fig.4 The positron intensity I_2 against protonation level in polyaniline

4 CONCLUSION

We have presented changes of the positron annihilation parameters in protonated

emeraldine polymer with the protonation level. It is very valuable that the characters of the positron parameter, such as I_2 , closely interrelated with the conductivity. These phenomena are in agreement with the model of conducting island proposed by Epstein, where the metallic particles formed due to polaron separated by insulating medium.

Further investigations in order to elucidate the nature of the conduction mechanism and chemical changes brought about by proton doping are continued.

REFERENCES

- 1 Chiang J C, MacDiarmid A G. Synth Met, 1986; 13:193
- 2 MacDiarmid A G, Chiang J C. Mol Cryst Liq Cryst, 1985; 121:173
- 3 Choi H Y, Mele E J. Phys Rev Lett, 1987; 59:2188
- 4 Levay B, Lalovic M, Ache H J. J Chem Phys, 1989; 90:3282
- 5 Kobayashi Y, Zheng W, Meyer E F *et al.* Macromolecules, 1988; 22:2302
- 6 MacDiarmid A G, Chiang J C, Richter A F *et al.* Conducting Polymer, Special Applications. Proceedings of the workshop held at Sintra, 1986. Reidel, Dordrecht, 1987, p105
- 7 Ginder J M, Richter A F, MacDiarmid A G. Solid State Communications, 1987; 63:97
- 8 Pouget J P, Jozefowicz M E, Epstein A J. Macromolecules, 1991; 24:279
- 9 Epstein A J, MacDiarmid A G. Mol Cryst Liq Cryst, 1988; 160:165