

Study on Soluble Polyaniline by Positron Annihilation Technique

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ABSTRACT: The solubility, electrical conductivity, and other properties of polyaniline (PANI) are highly dependent on its oxidation state. In this work, polyaniline (PANI1) prepared by peroxodisulphate induced polymerization of aniline in acidic aqueous medium in presence of benzenediazonium chloride salt was found to exist in lower oxidation state than emeraldine form of PANI and was highly soluble in common organic solvents. This polymer was subjected to positron annihilation spectroscopic study to investigate the correlation between the oxidation state of the polymer and defect sites generated by different degrees of protonation that in turn affect its electrical conductivity. The positron annihilation lifetime data were resolved to yield a three-component fit for PANI1 subjected to different levels of pro-

tonation. The variation of positron annihilation parameters (τ_1, I_2) and Doppler broadening parameters (R, S) as a function of protonation level of the polymer indicate the dopant sites increase initially on protonation and reach a saturation value after a certain level of acidification. The lower value of electrical conductivity and the intensity of intermediate lifetime component (I_2) for PANI1 compared to PANI in emeraldine oxidation state indicate the presence of lesser number of quinoid-imine moieties that could undergo protonation and thus yield highly enriched trapping centers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2554–2559, 2011

Key words: polyaniline; positron annihilation; doppler broadening

INTRODUCTION

Positron annihilation lifetime spectroscopy enables us to infer the qualitative knowledge on the nature, size, and concentration of different types of defects. This technique has been widely used to characterize the structure of polymers and to study the polymer properties that are affected by free volume.^{1–4} The positron lifetime is a measure for the size of vacancy clusters and its intensity is indirectly related to the concentration of the defect. The shortest component includes annihilation of free positrons and para positronium. The largest component is attributed to annihilation of ortho positronium in the molecular matrix. The intermediate lifetime component originates from the annihilation of positrons or positronium in trapped state.

Earlier studies on polyaniline (PANI), i.e., polyemeraldine base (PEB) and its doped form Polyemeraldine hydrochloride (PEHCl)^{5–7} as well as PANI composite⁶ by positron annihilation technique showed the presence of three lifetime components (τ_1, τ_2, τ_3) when resolved without any constraint.^{5,7}

The intermediate lifetime component (τ_2) was attributed to positron annihilating from trapped states in vacancies. Variation of positron lifetime parameters (I_2, τ_1) and Doppler broadening line shape parameter (S) with protonation level of the polymer was also studied.⁸ The intensity of the intermediate lifetime component (I_2) was found to increase with protonation level of the polymer which was accounted for by the increased trapping sites in the polymer. Doppler broadening line shape parameter “ S ” was also found to increase with protonation level which was attributed to the increase in probability of annihilation occurring at a defect trap.

In our previous study,⁹ we have shown that oxidative polymerization of partially diazotized aniline with ammonium peroxodisulphate yields polyaniline (PANI1) soluble in common organic solvents which is believed to consist of relatively lesser number of imine-nitrogen compared to PEB as evidenced by spectroscopic and XPS study.

This work is a continuation of our previous work and is undertaken to understand the behavior of PANI1 that exists in lower oxidation than emeraldine toward protonation. The positron annihilation spectra and Doppler broadening of the annihilating γ energy for this polymer were measured as a function of protonation level (pH = 7 to 0.38), and the relationship between the positron parameter and conductivity of the polymer was elucidated.

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EXPERIMENTAL

Materials

Reagent grade $C_6H_5NH_2$, HCl (39%), aqueous NH_4OH solution (25%), $(NH_4)_2S_2O_8$, $NaNO_2$ were purchased from E. Merck, Mumbai, India. Aniline was vacuum distilled before use and all other reagents were used as recovered.

Preparation

Aniline was chemically polymerized in dilute HCl at 2–5°C in presence of benzenediazonium chloride using $(NH_4)_2S_2O_8$ as oxidant as described in our earlier report.⁹ Aniline was chemically polymerized in dilute HCl at 2–5°C in presence of benzenediazonium chloride using ammonium peroxodisulphate as oxidant. The reaction was carried out by partial diazotization of aniline at ~ 5°C using sodium nitrite. The mole ratio of $NaNO_2$ to aniline was maintained at 0.93 and the resulting diazotized solution containing unreacted aniline was polymerized.

In a typical procedure, 8 mL of aniline (0.086 mol) was dissolved in 25 mL of 2M HCl and the mixture was cooled to below 5°C in an ice bath. A solution of 5.6 g (0.080 mol) $NaNO_2$ in 20 mL water, pre-cooled to 5°C, was added to the dilute HCl solution of aniline, maintained at 2–5°C drop wise over a period of 10 min with stirring. To the cold diazotized solution containing unreacted aniline (below 5°C), cold solution of 1.37 g (0.006 mol) $(NH_4)_2 S_2O_8$ in 25 mL of 2M HCl was added drop wise with constant stirring. The temperature of the reaction was always maintained below 5°C. The reaction was continued for 2 h. The blue-black colored precipitate thus obtained was washed with 2M HCl until the filtrate was colorless. The polymer thus obtained was purified by washing with methanol and then with THF. The solid was dried under dynamic vacuum at 50°C.

The base form of the polymer was obtained by stirring 1 g of the acid doped polymer in 160 mL 3% aqueous NH_4OH solution for 4 h at room temperature giving the unprotonated compound. The PANI powder with different protonation levels was obtained by treatment of its base form with aqueous HCl solution of different acidity (pH varying from 7 to 0.38) and compressed into 2-mm-thick pellets under 0.7 tons/sq.inch pressure for positron annihilation spectroscopic study.

Electrical conductivity measurement

The electrical conductivity of the doped polymers at room temperature was determined by collinear four-probe technique. Pellets of about 0.5–1 mm thickness were used for this purpose. A digital four-probe set

up DFP-2 instrument (S. B. Scientific CO, Kolkata, India) was used for this measurement.

Positron annihilation lifetime spectroscopy

The Positron lifetime distribution measurements have been made using a conventional arrangement with time to amplitude converter and a multichannel analyzer. The positron lifetime spectrometer used in these experiments had a prompt time resolution (FWHM) of 260 ps for the prompt 60co γ rays. Positron lifetime spectra with 10^6 counts were recorded at room temperature (25°C).

The lifetime spectra were fitted to the sum of exponential decay components deconvoluted with the Gaussian resolution function of the spectrometer. Fits of the experimental data were attempted with three components using the computer program POSITRONFIT. The variance of fit in the analysis lay between 0.9 and 1.1.

The Doppler broadening of the annihilation radiation line shape was measured by a digitally stabilized high purity Ge- spectrometer with an energy resolution of 1.17 keV at the 514 keV line of ^{85}Sr and analyzed for the standard lineshape parameters R and S . The standard lineshape parameter “ R ” is the ratio between the sum of the counts in a central region of the peak “ S ” and in the wing region, W_1 and W_2 .

$$R = 2S/(W_1 + W_2)$$

The “ S ” parameter is the ratio of the total counts near the central region of the 511 keV peak to the total counts of the whole energy spectrum after the background was subtracted.

RESULTS AND DISCUSSION

The positron annihilation lifetime data for PANI1 subjected to different protonation level were resolved to yield a three-component fit indicating positrons are annihilating from three different states. The results are listed in Table I.

Positrons are annihilation in PANI1 from three different state and the corresponding lifetime (τ_1 , τ_2 , τ_3) being the measure of average electron density ($\tau \propto n_e^{-1}$) seen by positron from each of the states. The relative intensities (I_1 , I_2 , I_3) of the components give the state population.

The shortest lifetime components of lifetime ($\tau_1 = 133$ –184 ps) which is usually attributed to positrons annihilating from free state decreases with increasing protonation level, whereas its intensity remains almost same ($\sim 8 \pm 2\%$). The intermediate lifetime component with $\tau_2 = 370 \pm 5$ ps originates from the trapped state remains almost constant with

TABLE I
Positron Annihilation Parameters for PANI1Doped with HCl of Varying pH

| pH of the acid medium | τ_1 (ns) | I_1 (%) | τ_2 (s) | I_2 (%) | τ_3 (ns) | I_3 (%) | Variance of fit |
|-----------------------|-------------------|------------------|-------------------|------------------|-----------------|-----------------|-----------------|
| 0.38 | 0.133 ± 0.018 | 8.61 ± 1.31 | 0.366 ± 0.003 | 90.41 ± 1.28 | 1.63 ± 0.07 | 1.08 ± 0.15 | 1.180 |
| 0.42 | 0.138 ± 0.024 | 8.16 ± 2.42 | 0.366 ± 0.003 | 89.90 ± 2.35 | 1.82 ± 0.07 | 1.94 ± 0.13 | 1.165 |
| 0.81 | 0.149 ± 0.021 | 8.44 ± 1.84 | 0.367 ± 0.004 | 89.62 ± 1.77 | 1.88 ± 0.07 | 1.94 ± 0.11 | 1.136 |
| 1.00 | 0.155 ± 0.024 | 6.97 ± 1.29 | 0.370 ± 0.004 | 90.87 ± 1.23 | 1.77 ± 0.06 | 2.15 ± 0.11 | 1.187 |
| 2.00 | 0.165 ± 0.032 | 7.98 ± 2.64 | 0.371 ± 0.004 | 89.78 ± 2.55 | 1.72 ± 0.06 | 2.22 ± 0.14 | 1.078 |
| 3.00 | 0.174 ± 0.019 | 8.33 ± 1.18 | 0.372 ± 0.003 | 89.58 ± 1.10 | 1.72 ± 0.06 | 2.09 ± 0.13 | 1.028 |
| 7.00 | 0.184 ± 0.019 | 13.21 ± 2.81 | 0.377 ± 0.004 | 84.84 ± 2.75 | 1.85 ± 0.06 | 1.94 ± 0.10 | 1.010 |

protonation level whereas the intensity of this components (I_2) varies with different level of protonation.

The long lived component with lifetime $\tau_3 = 1.7 \pm 0.1$ ns is identified with an intensity $\sim 2\%$ which has been rather spurious contribution due to ortho positronium in the molecular matrix of the polymer.

The variation of the intensity of intermediate lifetime component (I_2) and shortest lifetime component (τ_1) with pH is shown in Figures 1 and 2, respectively. The I_2 values increase whereas τ_1 value decrease with increase of protonation level and both attain saturation values for higher protonation level ($\text{pH} \leq 1$). These findings can be explained on the basis of chemical structure and the type of defects present in the polymer. In doped PANI, two kinds of defects, chain defect and polaron defects occur. The chain defects are formed by polaron chemically known as semiquinone radical cation which originates during protonation of PANI along quinoid-imine ($-\text{N}=\text{}$) sites with the dopant anions being localized that perturb intermolecular force in their close vicinity.¹⁰ As a result, a local distortion (polaron) is created with localized electrons which

attract the positron and serve as a trapping center (Fig. 3). The increment in the trapping sites with protonation level is due to the increase in concentration of dopant anions.

The increase of I_2 value and decrease of τ_1 value with protonation level can also be explained in terms of two state trapping model.¹¹ A positron injected into the solid moves randomly and interact with electron to form unstable electron-positron pair and then annihilate by emitting gamma rays or a positron is trapped in a vacancy type defect associated with a dislocation and then annihilate in a slower rate than delocalized positron.

The net disappearance of delocalized positron λ_1 is equal to the sum of annihilation rate of bulk positron (λ_B) plus their trapping rate $\mu_D C_D$.¹²

$$\lambda_1 = \lambda_B + \mu_D C_D \quad (1)$$

where, μ_D = trapping rate per unit dislocation. C_D = dislocation density.

If the fractions of delocalized and localized positrons present in the sample at time t are dn_B/dt and dn_D/dt , respectively.

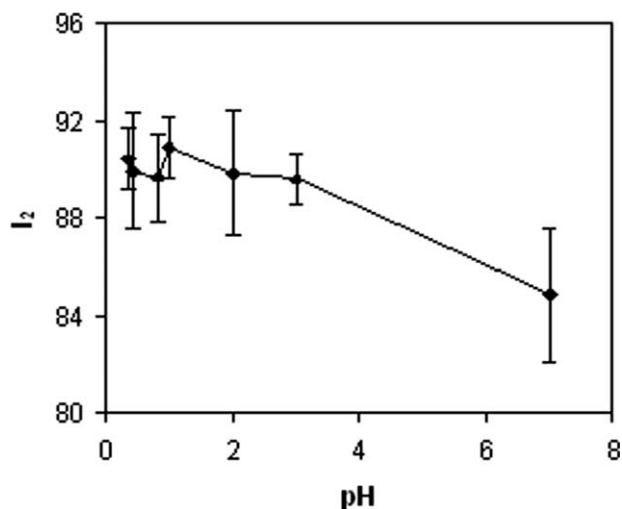


Figure 1 Variation of intensity of intermediate lifetime component (I_2) with protonation level.

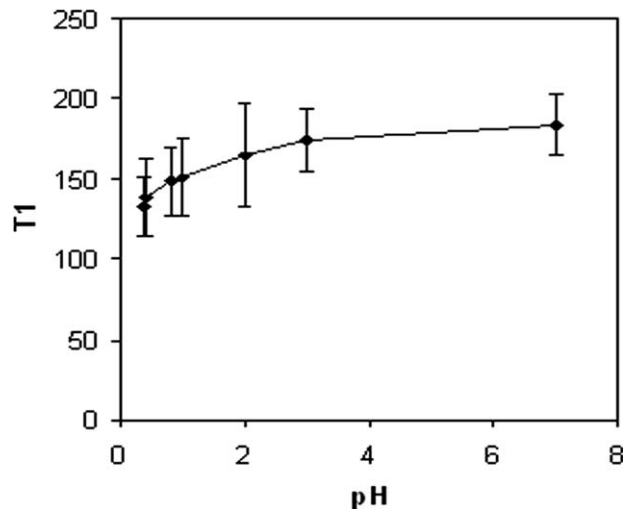


Figure 2 Variation of shortest lifetime component (τ_1) with protonation level.

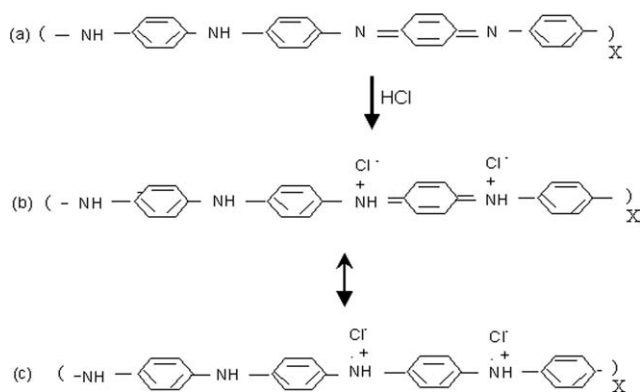


Figure 3 Structural unit of PANI 1 ($X = 0.38$) (a) unprotonated form, (b) protonated polaronic form, (c) protonated bipolaronic form.

$$dn_B/dt = -\lambda_1 n_B \quad (2)$$

where, n_B = total number of bulk positron.

$$dn_D/dt = -\lambda_2 n_D + \mu_D C_D n_B \quad (3)$$

where, λ_2 = rate of annihilation for localized positrons. n_D = total number of localized positrons, $\mu_D C_D n_B$ = total number of positrons trapped at defect site.

Solving eqs. (2) and (3) with the initial condition that $n_B(t=0) = 1$, it has been found that,⁶ $n = n_B + n_D$ may be expressed as,

$$n(t) = (1 - I_2)e^{(-t/\tau_1)} + I_2 e^{(-t/\tau_2)} \quad (4)$$

where,

$$I_2 = \mu_D C_D / (\lambda_1 - \lambda_2) \quad (5)$$

$$\text{and } \tau_1 = \lambda_1^{-1}, \quad \tau_2 = \lambda_2^{-1} \quad (6)$$

The rate of annihilation for delocalized positron, $\lambda_B = (I_1/\tau_1 + I_2/\tau_2)$ as obtained by solving eqs. (1), (5), and (6) is found to be independent of protonation level as obtained by calculating using the data in Table I. From equations (1), (5), and (6) it is found that I_2 and λ_1 are determined by dislocation density $\mu_D C_D$. The increase of dislocation density with protonation level is clearly reflected by decrease in τ_1 value and increase of I_2 value. It is pertinent to mention the fact that after a certain level of protonation (beyond pH = 1), the defect sites do not increase as evidenced by the saturation of I_2 value. The fact is further corroborated in the conductivity studies whether the conductivity values do not increase after a certain level of protonation. The variation of conductivity of PANI1 powder at room temperature versus the protonation level is shown in Figure 4. However the I_2 values of polyemeraldine-HCl (PE

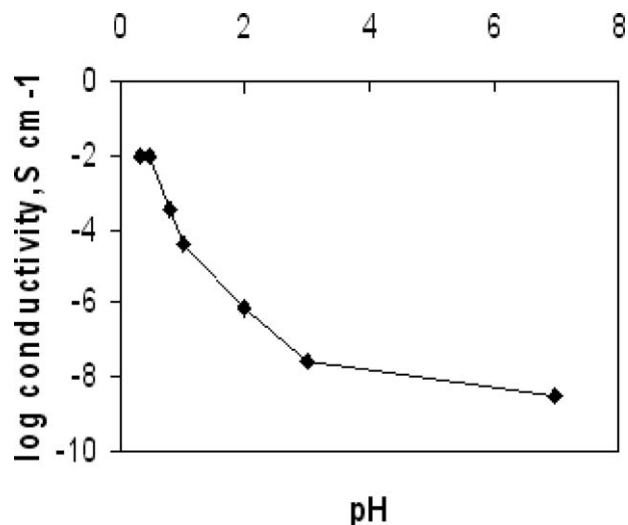


Figure 4 Variation of logarithm of electrical conductivity ($\log \sigma$) of PANI1 with protonation level.

HCl) form of PANI are higher than that of PANI1 which is due to the presence of higher number of quinoid-imine moieties that could undergo protonation and thus would yield highly enriched trapping centers. Accordingly, the sole positron annihilation lifetime component for PEHCl was due to these defect sites and was found to be more than 90%.⁵ Therefore, there is a direct correlation between the protonation level of the polymer and positron parameters I_2 .

The probability of annihilation from trapped state may be written as the ratio of the trapping rate to the net disappearance of delocalized positrons.⁸

$$P_D = \mu_D C_D / \lambda_1$$

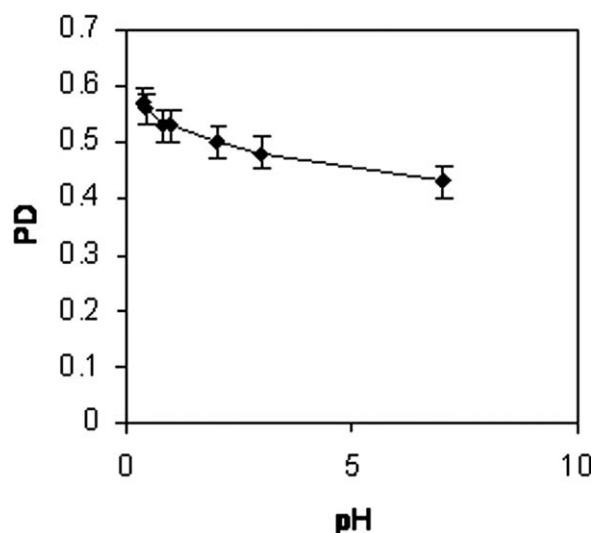


Figure 5 Variation of probability of annihilation (P_D) with protonation level.

$$= I_2(\lambda_1 - \lambda_2)/\lambda_1 \text{ with } \tau_1 = \lambda_1^{-1} \text{ and } \tau_2 = \lambda_2^{-1}$$

The probability P_D is found to increase with increasing protonation level as shown in Figure 5.

Increment of the value of I_2 as well as conductivity with protonation indicates formation of more metallic region (metallic polaron lattice) through protonation of unprotonated nitrogen sites, i.e., quinoid-imine sites. The lower I_2 value of fully protonated PANI1 compared to polyemeraldine salt form of PANI ($I_2 > 90\%$) may be due to the presence of lesser number of quinoid-imine moieties that undergo protonation yielding polaron defects and thus decreasing the probability of positron annihilation in trapping sites. In our earlier study,⁹ we have found that the elemental analysis of fully protonated PANI1 show a low value of Cl/N ratio, i.e., 0.16 compared to 0.44 for polyaniline¹³ as well as XPS study of N_{1s} core level spectrum showed the proportion of quinoid-imine structure is lower compared to benzenoid-amine structure as determined from the integrated area under binding energy peaks. The oxidation level of the polymer as calculated from the relative intensities of the deconvoluted N_{1s} spectra of PANI1 in the undoped form is 0.38.

Results on the protonation level dependence of the Doppler broadening parameters are presented in Figures 6 and 7. The S parameter studied essentially signifies contribution due to the low electron momenta of the labile electrons trapped at defect sites and thus less likely to encounter high momentum core electrons. Therefore, presence of defects in a material usually produces a high S parameter compared to defect free material. The experimental results show that S parameter increase with respect to pH of the acid medium up to 1 after which the

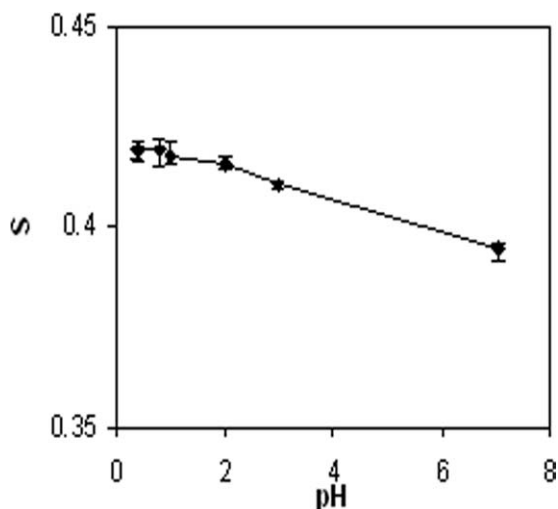


Figure 6 Variation of Doppler broadening parameter (S) with protonation level.

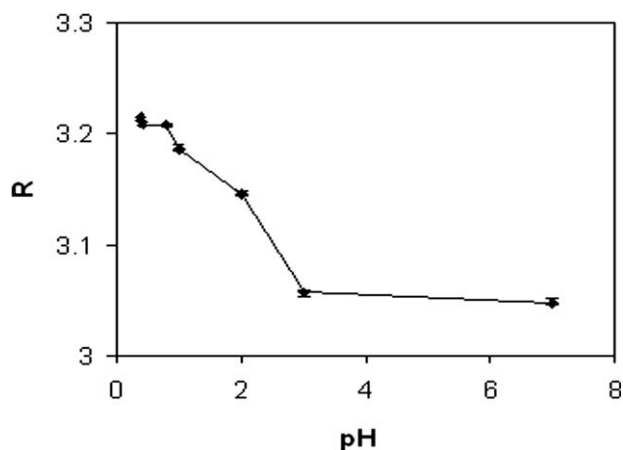


Figure 7 Variation of Doppler broadening parameter (R) with protonation level.

values level off (Fig. 6). Similarly the " R " parameter that is sensitive to the low momentum component of the electrons is also found to show the similar trends (Fig. 7). Therefore, the increase of the values of " S " and " R " parameter with protonation level is an indication of the increase in the defect sites with protonation. The measurement of the " S " and " R " parameters also support the interpretation of the lifetime data.

CONCLUSIONS

Study on positron annihilation parameters of PANI1 as a function of protonation level revealed that the defect sites generated on HCl doping do not increase to any substantial extent with decrease in pH of the acid medium beyond 1 as indicated by the increase in I_2 value and Doppler broadening parameters (R , S) related to the protonation level of the polymer. This behavior of the polymer towards protonation can be explained by the presence of fewer number of quinoid-imine moieties in the polymer that could undergo protonation. This fact is corroborated by the relatively lower conductivity of PANI1 compared to PANI in emeraldine oxidation state that is explained by the generation of relatively lesser number of polarons on HCl doping as the polymer contains relatively lesser number of imine-nitrogens.

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