The Use of Positron Annihilation Lifetime Technique to Study the Effect of Doping Metal Salts on Polyhydroxamic Acid Polymers

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ABSTRACT: Polyhydroxamic acid (PHA) from polymethacrylamide (PMAA) was prepared. Chromium chloride ($CrCl_3$) and ferric chloride ($FeCl_3$) salts were added to the polymer in order to increase its electrical conductivity, i.e., the dopants help produce semiconducting properties. The positron annihilation lifetime technique spectroscopy (PALS) was used to study the changes in the free volume as a function of $FeCl_3$ and $CrCl_3$ concentrations. *ortho*-Positronium lifetime components were used to estimate the free volume parameters. It was found that the hole size and the total free volume fraction decreased with $FeCl_3$ concentration. On the other hand, the hole size increased slightly with $CrCl_3$ concentration and then decreased, while the total free volume fraction increased continuously. The free volume distributions were determined from *ortho*-positronium distributions. The electric conductivity as a function of $FeCl_3$ and $CrCl_3$ concentrations showed fluctuation behavior and showed a continuous increase with the increase in temperature. The correlation between positron annihilation parameters and electric conductivity were discussed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2095–2101, 2001

Key words: positron annihilation; polyhydroxamic acid; polymethacrylamide; electrical conductivity; free volume distribution

INTRODUCTION

In positron annihilation lifetime spectroscopy (PALS) one employs the antiparticle of electron—i.e., the positron—as a nuclear probe to the free volume hole size of polymers.[1,2] Because of the positively charged nature of the positron and positronium atom (a bound atom that consists of an electron and positron), they were repelled by the core electrons of the polymer and trapped in open spaces, such as holes, free-volume, and voids. Therefore, the positron and positronium

(Ps) annihilation signals were found to be contributed mainly from the free-volume holes in a polymer. Ps has two spin states called *ortho*-positronium (o-Ps) and *para*-positronium (p-Ps), which have lifetimes of 140 and 0.125 ns in vacuum, respectively. In polymers, the o-Ps lifetime is shortened to 1–5 ns due to the pick-off process.[3]

Currently, PALS has been mainly developed in monitoring the o-Ps annihilation lifetime for polymeric applications. Free-volume hole sizes V_f, fractions f, and distributions in a variety of polymers have been reported using PALS methods.

A PAL spectrum of a polymer usually consists of three different mean lifetimes—τ_1, τ_2, and τ_3—which have relative intensities (I_1, I_2, and I_3),
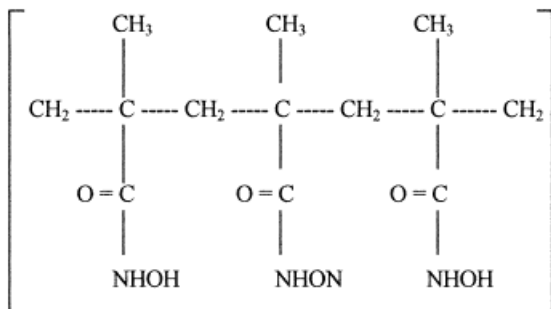
Figure 1   PHA from PMAA.

indicating the relative number of positrons annihilating with that lifetime to the different annihilation processes. While the lifetime of o-Ps τ_3 can be related to the size of the cavity V_f, its intensity I_3 is considered to be related to the fraction f of cavities such that

$$f = AI_3V_f$$

where A is a parameter that can be determined by calibrating with the specific volume expansion coefficients below and above T_g.[3]
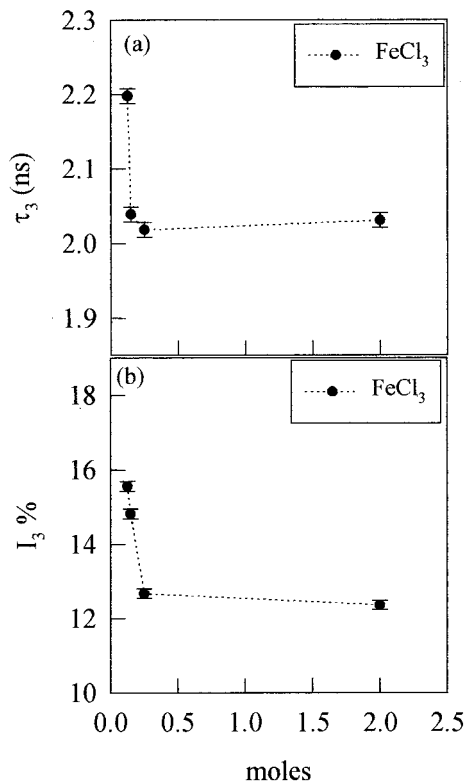

Figure 2   (a) O-Ps lifetime τ_3 and (b) o-Ps intensities I_3 of PHA vs FeCl$_3$ concentrations.
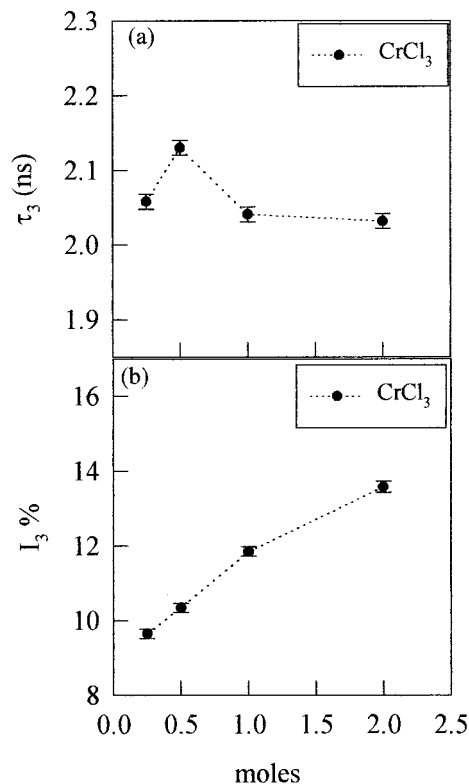

Figure 3   (a) O-Ps lifetime τ_3 and (b) o-Ps intensities I_3 of PHA vs CrCl$_3$ concentrations.

Recently, PALS has been shown to be a useful technique for studying the structural properties of electronic and ionic conducting polymers.[4] These studies indicate that the macroscopic properties of conducting polymers can be related to the atomic scale free volume holes.[4] In the case of the polyhydroxamic acid (PHA) polymer; due to addition of CrCl$_3$ or FeCl$_3$ solutions, the two hydrogen atoms of OH groups of the hydroxylamins were replaced by a metal ion Cr^{2+} or Fe^{2+}.[5] When an electric current is passed, these metallic ions become mobile and increase the electric conductivity of the polymer. Accordingly, the conductivity is an ionic conductivity. It is meant by the macroscopic electric properties that the electric conductivity of the polyhdroxamic acid prepared form polymethacrylamide plays a role especially when metal salts were added.

The aim of the work is to establish the effect of adding salts such as FeCl$_3$ and CrCl$_3$ on the electric conductivity of PHA prepared from polymethacrylamide (PMAA). Also, this work showed a correlation between the electric conductivity and the free volume parameters of PHA using PALS.
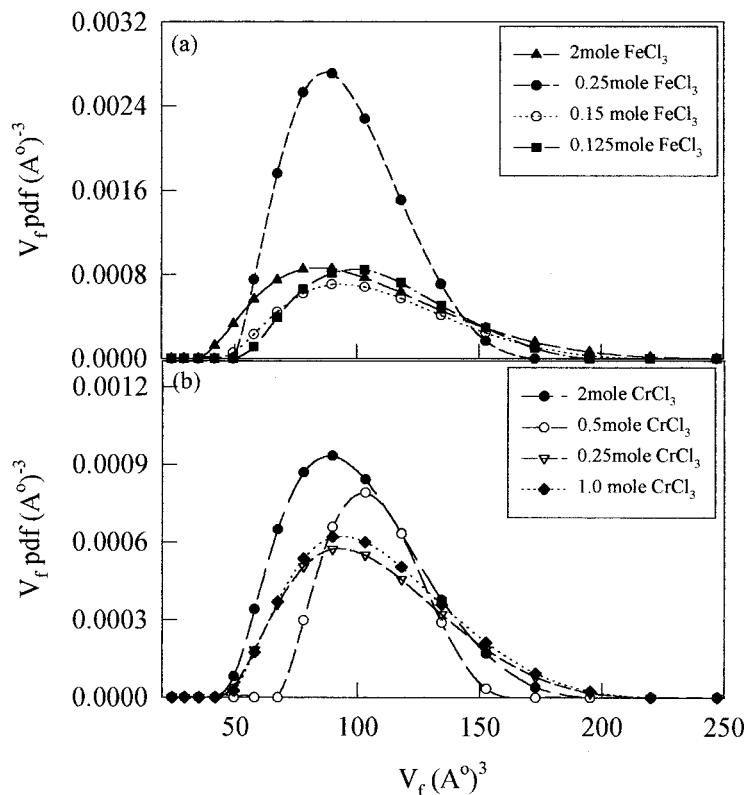
Figure 4 Free-volume hole distributions V_f pdf *vs* V_f for (a) PHA–FeCl$_3$ and (b) PHA–CrCl$_3$. Smooth curves are drawn through data points for clarity.

EXPERIMENTAL

Preparation of Methacrylamide

One hundred grams (1 mole) of methylmethacrylate (MMA) was added in a round-bottomed flask. One hundred eighty milliliters of concentrated ammonia solution (sp.g. 0.88) was then poured in the flask. The mixture is allowed to stand with occasional shaking until it became homogeneous (1–2 days, a longer period of standing is not harmful). The MMA was purified by distillation under vacuum to rid of the inhibitor, any polymer present, or any other impurities.[5] The method of preparation of MAA was made by making use of the procedure[6] for preparing acetamide from ethylacetate.

Preparation of Polymethacrylamide

One hundred grams of MAA was added in a round-bottomed flask. Add 200 ml of chloroform and 1 g of benzoylperoxide were added and refluxed for 30 min. The polymer is separated by distillation.

Preparation of Polyhydroxamic Acid from PMAA

Polymethacrylamide was dissolved in chloroform and poured into 1 L. beaker. The amount of g of hydroxylamine hydrochloride was dissolved in a mixture of water and ethyl alcohol, and added to the above solution in a beaker. Forty-five grams of sodium hydroxide was dissolved in a small amount of water and added into the beaker such that the pH > 11 and then left for 24 h. The bulk is acidified to pH 1–3 by 3 N HCl, and the precipitate was washed several times with water and dried. The polymer was dissolved in dichloromethane and the solution was divided into fractions.

1. Fractions were made by adding 0.125, 0.150, 0.250, and 2.0 mole per gram of FeCl$_3$ of polymer, respectively. The ferric salt solution of PHA from PMAA were poured into petro dishes; films of 1 cm diameter and 1 mm thickness were obtained.
2. Other fractions were made by adding 0.25, 0.50, 1.0, and 2.0 mole per gram of CrCl$_3$ of polymer, respectively. The chorium salt solution of PHA from PMAA were poured in

petri dishes; films of 1 cm diameter and 1 mm thickness were obtained.

Measurement of the Specific Electric Conductivity of the Polymers

The specific electric conductivity of thin films of the polymers was measured by the method mentioned before.[7] Specimens of 1 cm diameter and 1 mm thickness were tightly adjusted between the plates of two copper electrodes of an electric cell. The temperature was measured by a thermocouple adjusted into the cell near the sample. A thermocouple temperature probe of the type TP-30 (BK PRECISION) attached to a millivoltmeter was used to measure the temperature. The electric cell was put in an electric furnace in order to measure the resistivity at different temperatures. An electric circuit was used composed of a regulated DC power supply a high impedance electrometer (Keithley electrometer of the type 610c), and the cell.

Lifetime Measurements

The lifetime measurements have been performed in air at room temperature using a fast–fast coincidence system with a lifetime resolution of 230 ps full width at half maximum (FWHM). A 20 microcurie (μCi) ^{22}Na positron source is deposited on Kapton foil, then sandwiched between two similar pieces of the sample. PAL spectra containing 10^6–10^7 counts were collected on each sample. All of the PAL spectra obtained were analyzed using the PATFIT[8] program, which is a finite term lifetime analysis, with $\tau_1 = 0.125$ ns constraint and continuous lifetime analysis using the Laplace inversion program CONTIN.[9]

In finite-term lifetime analysis, three lifetime results were obtained giving variance < 1.1. The shortest lifetime $\tau_1 \sim 0.125$ ns is the lifetime of p-Ps and the intermediate lifetime $\tau_2 \sim 0.35$ ns is the lifetime of the free positron. The longest lifetime $\tau_3 \sim 2$ ns is due to o-Ps annihilation. The mean free-volume hole radius obtained from the results of o-Ps lifetime by using the following semiempirical equation[10]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1}$$

where the cavities were assumed to be spherical with a radius of R. R_0 equals $R + \Delta R$, where ΔR is the fitted empirical electron layer thickness ($=0.166$ nm).
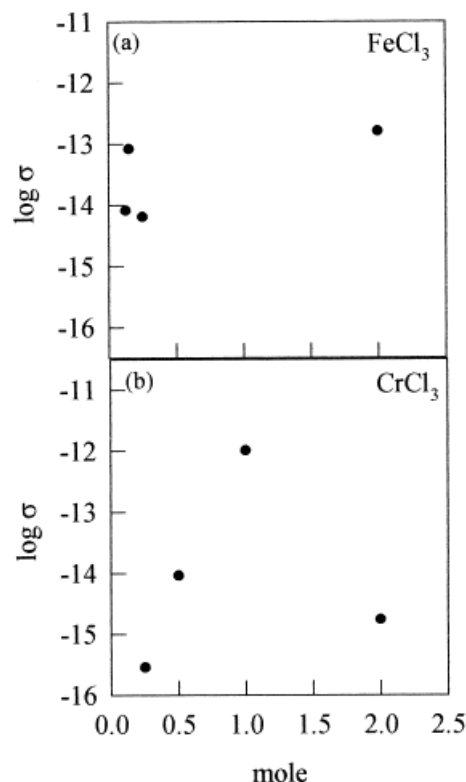

Figure 5 Plot of log σ vs concentrations of (a) PHA–$FeCl_3$ and (b) PHA–$CrCl_3$.

The computer program CONTIN was employed to provide the free-volume probability density function V_f pdf vs free-volume size V_f, for a PAL spectrum by using the measured reference spectrum in Al.

RESULTS AND DISCUSSION

The microstructure of PHA from PMAA which is a polymer containing polar groups (NHOH) is shown in Figure 1.

This polymer can be linked metal salts (e.g. $FeCl_3$ and $CrCl_3$) which possess paramagnetic properties.[3] Salt-polymer composites are characterized by interaction of the salt with a polar matrix polymer which give rise to complex formation. These interactions have major effects on the electrical conduction of the composites due to chemical instability of the salt linked to the polymer matrix as well as on the crystal state of the salt in the polar polymer.

In case of doping $FeCl_3$ and $CrCl_3$ salt to the polymer (PHA), the positron lifetimes at room temperature were measured as a function of
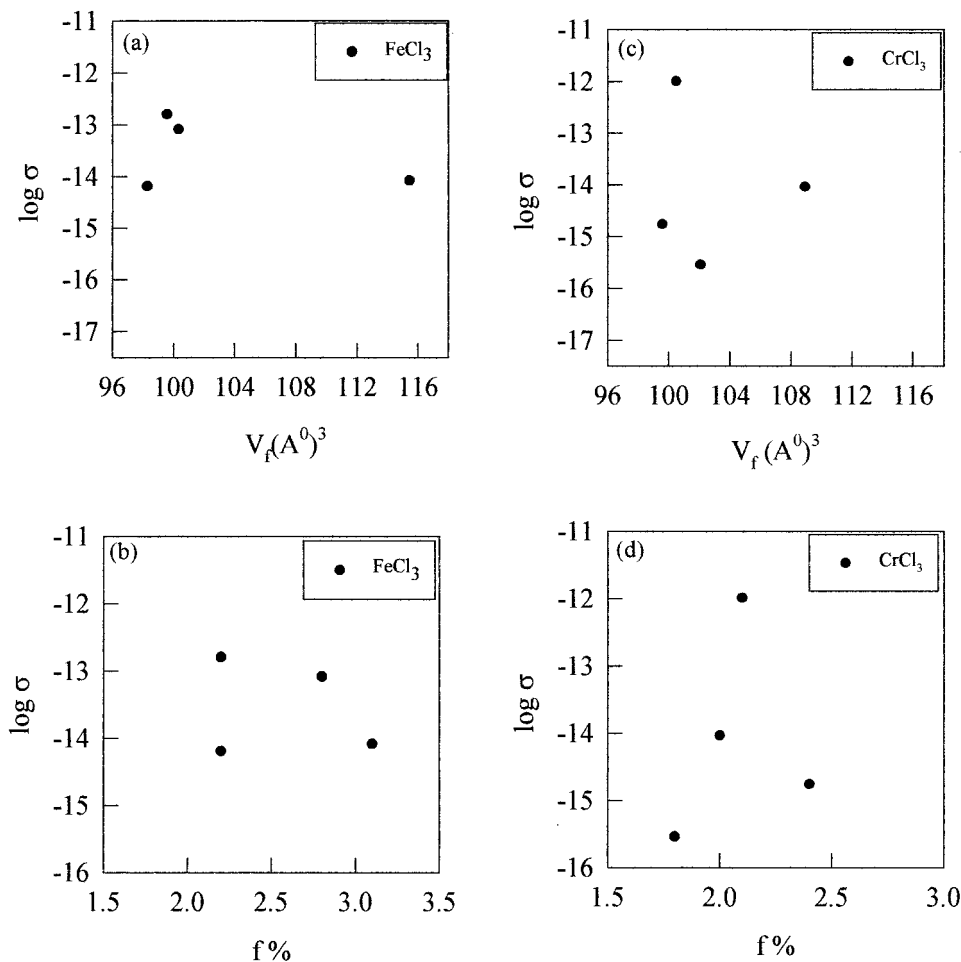
Figure 6 Plot of log σ *vs* (a) free-volume size V_f, (b) free-volume fraction f for PHA–FeCl$_3$, (c) free-volume size V_f, and (d) free-volume fraction f for PHA–CrCl$_3$.

FeCl$_3$ and CrCl$_3$ salt concentrations in the range from 0.125 to 2 mole.

The second components (τ_2, I_2) were not mentioned here because they are nearly constant. However, the third components, i.e. o-Ps lifetime τ_3 and its intensity I_3 were strongly affected by the dopants FeCl$_3$ and CrCl$_3$. The variation of τ_3 and I_3 with FeCl$_3$ salt concentration are shown in Figure (2a,b). One can observe that both τ_3 and I_3 decrease sharply for concentrations less than 0.25 mole while they almost constant for higher concentrations. This fact indicated that the FeCl$_3$ salt mainly diffuses into the amorphous region and the concentration 0.25 mole is an inflection point. Firstly, before the inflection point FeCl$_3$ has formed some complex with PHA. Fe^{+3} is a high spin ion and has a half filled d-subshell. This has a stabilizing effect on the electron density, and the Ps formation is inhibited to a greater extend. On the other hand, the quenching of Ps

lifetime due to FeCl$_3$ or Fe^{+3} ions is observed due to both spin-conversion and oxidation reactions.[3] Secondly, after the inflection point the paramagnetic property of FeCl$_3$ is appeared. The interaction of o-Ps with paramagnetic material flips the spin of o-Ps electron.[11]

In the case of doping the polymer by CrCl$_3$, it was noticed that there was a reflection point at concentration 1 mole. Before it, τ_3 was increased slightly and then the quenching of Ps lifetime due to CrCl$_3$ or Cr^{+3} ions is observed (Fig. 3a). After the reflection point the paramagnetic properties of CrCl$_3$ appeared[11] and the o-Ps lifetime is almost constant. These properties did not affect the intensity of o-Ps such that they increased with increasing the concentration as shown in Fig. (3b).

The distribution of free volume shifts from a large to smaller size as the FeCl$_3$ concentrations increase as shown in Fig. (4a). The distribution

Table I Positronium Lifetime Results Obtained by Finite-Term Analysis in PHA

| Mole	σ (ohm^{-1} cm^{-1})	τ_3 (ns)	I_3 (%)	V (A')^3	f (%)
FeCl$_3$					
0.125	8.30×10^{-15}	2.1982	14.816	115	3.1
0.150	8.30×10^{-14}	2.0394	15.557	100	2.8
0.250	6.48×10^{-15}	2.0185	12.671	98	2.2
2.000	1.60×10^{-13}	2.0314	12.365	99	2.2
CrCl$_3$					
0.250	2.89×10^{-16}	2.0582	9.643	102	1.8
0.500	9.28×10^{-15}	2.1298	10.341	108	2.0
1.000	1.02×10^{-12}	2.0412	11.848	100	2.1
2.000	1.70×10^{-15}	2.0322	13.583	99	2.4
Pure PHA	5.90×10^{-16}	2.1700	11.393	112	2.3

also becomes broader. At 0.25 mole of FeCl$_3$ concentration, the distribution is narrower and above it the free volume size becomes constant, where this is an inflection point.

The distribution of free volume shifts from a small to a larger size at 0.5 mole as a function of CrCl$_3$ concentrations [Fig. 4(b)], then it becomes almost constant, which is consistent with the results obtained by the finite-term analysis.

These characters are also confirmed by the variation of the electric conductivity with salts concentrations and free volume parameters (Fig. 5 and Fig. 6). The presence of transitional elements such as Fe and Cr in PHA increase the ionization which leads to the increase of conductivity (Figure 5). The correlation between the electric conductivity, the free volume sizes, and fractions indicated that PHA has higher conductivity or exhibits semiconducting properties at small size and fraction as shown in Figure 6. The highest conductivity at 100 Å^3 free volume size and 2% free volume fraction in both 2 mole FeCl$_3$ and 1 mole CrCl$_3$ concentrations as listed in Table I. These results indicated that PHA can be used as a semiconductor at these two concentrations.

The specific electrical conductivity of PHA in presence of FeCl$_3$ and CrCl$_3$ at different concentrations was between 10^{-15} and 10^{-13} ohm^{-1} cm^{-1} at room temperature.

The relation between log σ and $1/T$ is linear for PHA in the presence of FeCl$_3$ and CrCl$_3$, as shown in Figure 7(a,b) at different temperatures. No significant variation in σ is observed less than 40°C. The relation between the electric current and voltage in presence of FeCl$_3$ and CrCl$_3$ was Ohmic for PHA from PMAA as shown in Figures 8(a,b).
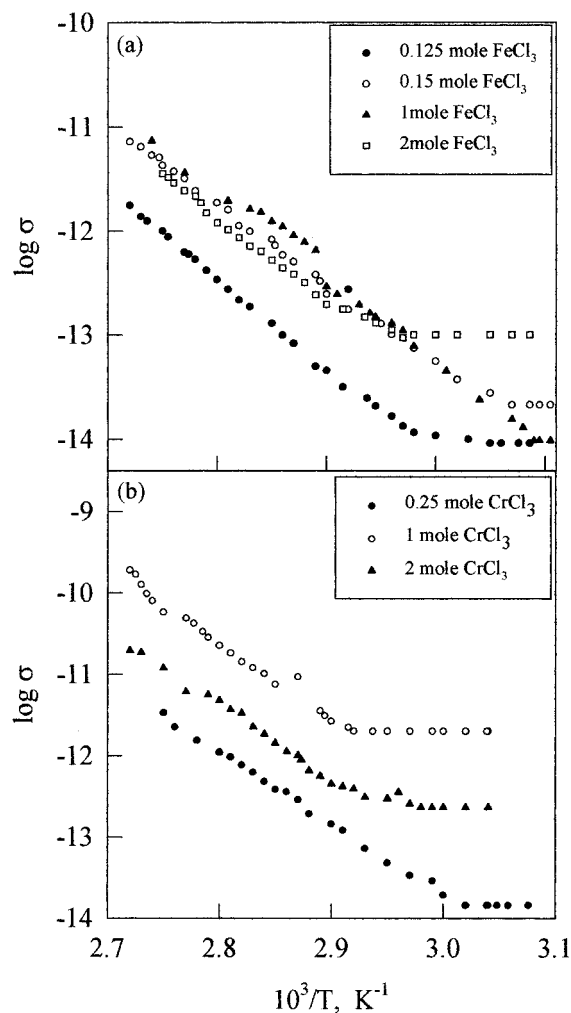
Figure 7 Plot of log σ vs reciprocal temperature for (a) PHA–FeCl$_3$ and (b) PHA–CrCl$_3$.
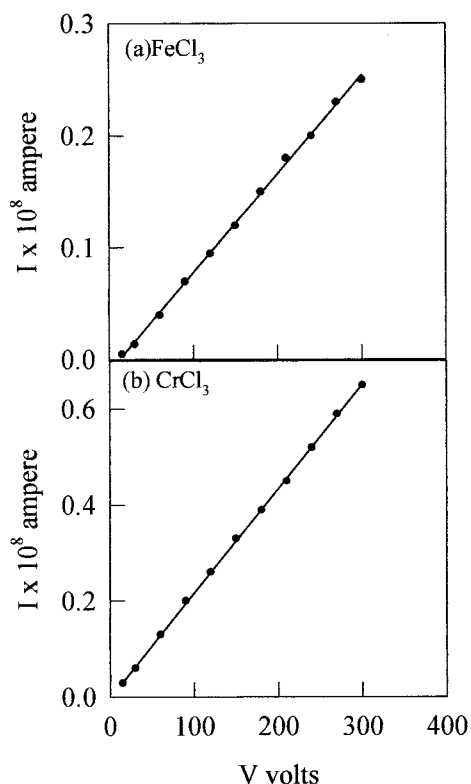
Figure 8 Plot of I vs V for (a) PHA–FeCl$_3$ and (b) PHA–CrCl$_3$.

These experimental results imply that the increase of the salt concentration was connected to an increase in the number of charge carriers and a reduction of the size and fraction of free volume. The former factor is necessary and useful to the conductivity, but the latter factor will limit the segmental motion.[4] At a certain concentration, when the increase of the charge carriers predominate over the reduction of the size and fraction of free volume, the conductivity was increased.

However, for another concentration, the interaction of salt with polymer segment suppress the segmental motion. This induced a reduction of charge transport in the polymer and consequently causes a decrease in the conductivity. These results were confirmed by the correlation between the conductivity and the free volume parameters, and by the probability density function of free volume distributions.

CONCLUSIONS

The free-volume and conductivity mechanism of two conducting polymers have been studied by PALS. For the polymer PHA prepared from PMAA and doped with FeCl$_3$ and CrCl$_3$ salts, the τ_3 and I_3 were strongly affected by the dopant. The concluding remarks are as follows:

1. When the salts used as dopant, at low concentration ($<$0.25 mole for FeCl$_3$ and $<$1 mole for CrCl$_3$), there was an inhibition of the Ps formation in free volume holes of amorphous region. On the other hand, the quenching of the Ps lifetime due to both spin conversion and oxidation reaction was observed.
2. At high concentration ($>$0.25 mole for FeCl$_3$ and $>$1 mole for CrCl$_3$), there was no change in cavity size due to the appearance of paramagnetic properties of the salts.
3. The free-volume probability density functions were consistent with the results obtained by the finite term analysis.
4. The conductivity changed with the concentration, which depended on the charge carrier numbers, the size and fraction of free volume, and the interaction of the salt with the polymer segments.

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