*Polymer* Vol. 37 No. 9, pp. 1529–1533, 1996

0032-3861/96/\$15.00+0.00

# Positron annihilation in polyvinylalcohol doped with $CuCl_2$

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*(Received 25 August 1995)*

Positron annihilation lifetime spectra were measured for polyvinylalcohol doped with $CuCl_2$ (0.5 to 5.0 wt%) at temperatures rising from 30°C to 160°C (heating run) and then from 160°C down to room temperature (cooling run). The data clearly revealed the glass transition ($T_g$) at around 90°C. Both $I_3$ and $\tau_3$ were decreased by the added $CuCl_2$, being interpreted as the result of inhibition and quenching. Both the inhibition coefficient $\alpha$ and the quenching rate constant $\kappa$ were smaller than the corresponding values in liquids. The diffusion constant of *ortho*-positronium (*o*-Ps) estimated from $\kappa$ implies that *o*-Ps is not very mobile in the polymer. For all the samples $\tau_3$ below $T_g$ was always larger in the heating runs than in the cooling runs, but above $T_g$ $\tau_3$ was the same for heating and cooling runs. This is due to the existence of strain brought about by the process of preparation of the samples. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: positron annihilation; polyvinylalcohol; positronium)**

## INTRODUCTION

Free volumes play an important role in determining the properties of polymers[1,2]. It is therefore interesting to apply the positron annihilation lifetime (PAL) technique, which has been shown to be very sensitive as a probe[3] of atomic-size holes (1–10 Å).

When positrons are injected into condensed matter, a fraction of them combine with an electron to form positronium atoms (Ps) which become trapped in atomic-size holes in condensed material. Ps can be formed in either a triplet state, *ortho*-positronium (*o*-Ps), or a singlet state, *para*-positronium (*p*-Ps), with lifetimes of the order of $10^{-9}$ s and $10^{-10}$ s, respectively.

Both the intensity, $I_3$, and the lifetime, $\tau_3$, of *o*-Ps are affected by many factors. For example inhibition of Ps formation by many electron scavengers is a well known fact[4] but, although not yet well understood, some structural factors are supposed to affect Ps formation in polymers, too. The lifetime of *o*-Ps is mainly determined by the size of the space in which *o*-Ps is trapped[3], but it may be further affected when *o*-Ps undergoes chemical reactions.

In this work, polyvinylalcohol (PVA) doped with various amounts of $CuCl_2$ is investigated. It is reported that doping with $CuCl_2$ promotes electrical conductivity of PVA, and this effect was analysed in terms of the free volume[5]. We were interested to compare the positron annihilation data with the result of the electrical conductivity. In this paper, however, we deal with the aspects particular to $e^+$ and Ps reactions in the doped polymer, and the comparison with the electrical conductivity data will be presented in a separate report.

## EXPERIMENTAL

Commercial PVA powder (Hayashi Pure Chemical Industries Ltd), with an average degree of polymerization of 1700, was used as the starting material. It was dissolved in distilled water by gently heating in a water bath. The water bath method was used for heating the solution to prevent thermal decomposition. The hot solution was stirred until the polymer was completely dissolved and formed a clear viscous solution. The viscous solution was coated onto polyethylene plates and left to dry in air for three days. To obtain a film of PVA containing $CuCl_2$, an aqueous solution of $CuCl_2$ was added to PVA solution, and the pH of the mixture was adjusted to the desired value (usually greater than 7) with KOH, then the mixture was well stirred for 10 h at room temperature. This mixture was coated onto polyethylene plates and left to dry in air. The concentration of the salts in the polymer was varied from 0.5 to 5.0 wt%.

PAL measurements were performed using a conventional fast-fast coincidence system with a time resolution of 240 ps. The positron source was prepared by depositing about 30 $\mu$Ci of aqueous $^{22}$NaCl on a thin nickel foil of 2.2 mg cm$^{-2}$ (2.5 $\mu$m) thickness and $6 \times 6$ mm$^2$ area, and covering it with a foil of the same size after drying. The source absorption by the nickel foil was about 6% and contributed to the short lifetime components. Since we were interested in the intensity and lifetime of the long-lived component, this absorption was not separated in the analysis of the lifetime spectra. The

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source was sandwiched by two identical samples of about $10 \times 10 \times 1\,mm^3$. The sample thus prepared was put in the sample holder of a heating chamber. The heating chamber was evacuated continually while the PAL was measured. The measurements were performed from 30°C up to 160°C, and then in a cooling direction from 160°C to room temperature at 5°C or 10°C intervals. Each PAL spectrum, having about $1 \times 10^6$ total counts, was analysed into three lifetime components using the computer program PATFIT[6]. The variances of the fits ($\chi^2$) were less than 1.2.

## RESULTS AND DISCUSSION

The shortest-lived component ($\tau_1 = 0.15$–$0.20$ ns, $I_1 = 40$–$55\%$) and the intermediate component (lifetime $\tau_2 = 0.40$–$0.50$ ns, $I_2 = 35$–$45\%$) are attributed mainly to *p*-Ps and direct annihilation of positrons, but detailed analysis is difficult because of the possible formation of positron and positronium compounds contributing to both components. The long-lived component, with lifetime $\tau_3 = 1.1$–$2.1$ ns and intensity $I_3 = 8$–$20\%$, is *o*-Ps annihilation in free-volume holes.

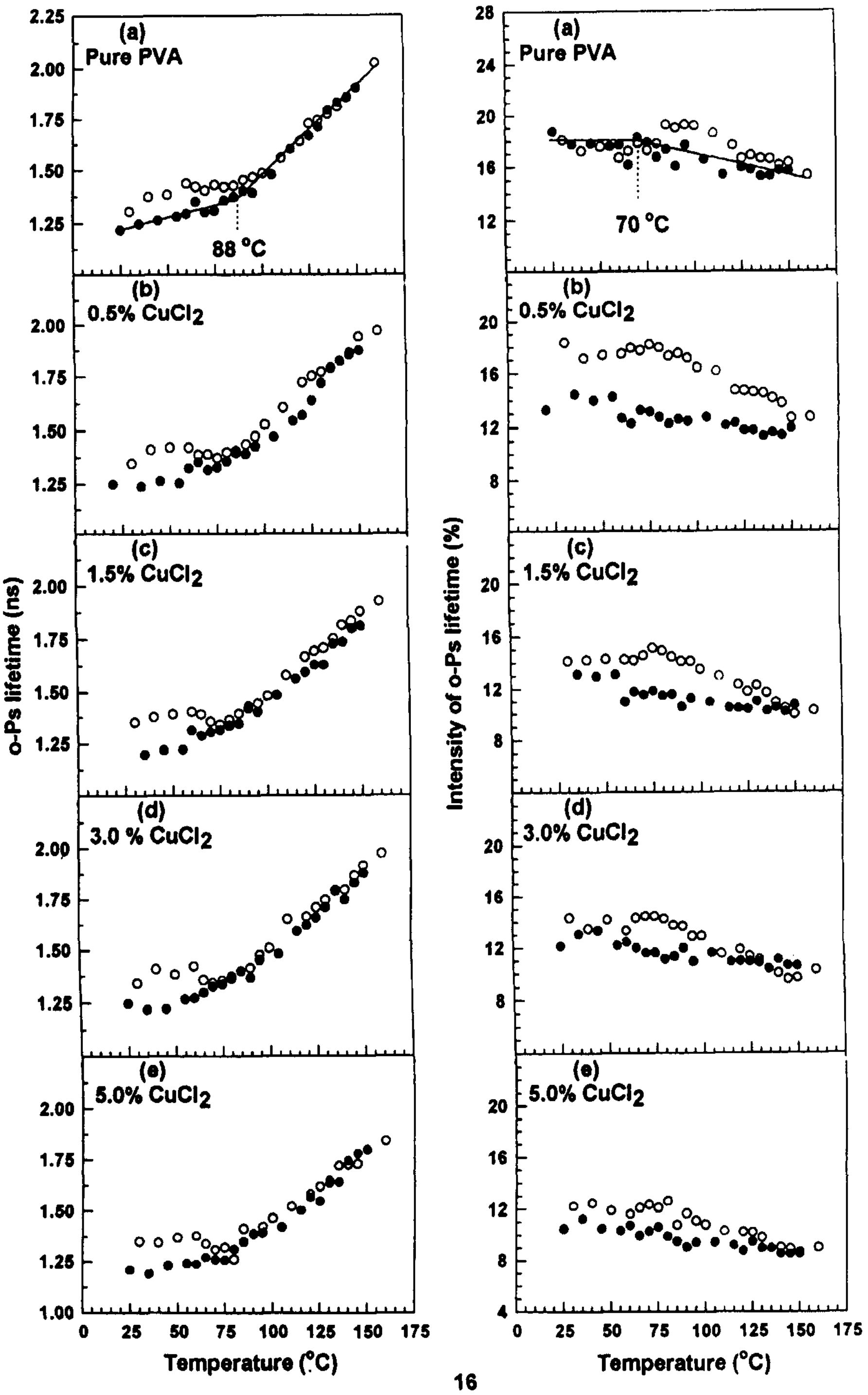

**Figure 1** Temperature dependence of *o*-Ps lifetime $\tau_3$ (left-hand column) and intensity $I_3$ (right-hand column) for pure PVA (a) and for PVAs doped with $CuCl_2$ (b–e). The concentration of $CuCl_2$ is indicated. The measurements were performed first in the heating direction from 30°C to 160°C (○) and then in the cooling direction (●). The solid lines for the pure PVA are the linear fittings to obtain transition temperatures

The temperature dependences of $\tau_3$ and $I_3$ are summarized in *Figure 1* for the pure and the doped PVAs. In the heating runs, the $\tau_3$ values rise at first then drop slightly at around 60°C to form a rounded bump, and above about 90°C start to rise with a steeper slope. In the cooling runs the $\tau_3$ values decrease with the same behaviour, but below 90°C they become smaller than in the heating runs. In another experiment, a sample was annealed in advance at 110°C, which is slightly higher than $T_g$, and PAL measurements were performed. In this case the rounded bump disappeared and $\tau_3$ was the same for the heating and the cooling runs even below 90°C. Evidently the larger $\tau_3$ values in the heating runs are attributed to the existence of strain built in during the process of sample preparation, which must have been annealed out by the annealing treatment at 110°C. For all the samples appearing in *Figure 1* the samples had not been annealed prior to the experiment and hence the effect of the built-in strain is observed. Since such strain may be partly annealed at temperatures near $T_g$, $\tau_3$ should be observed to decrease after passing 60°C. A similar drop of $\tau_3$ has also been observed for some polyimides[7]. In order to see the annealing behaviour of the built-in strain, fresh samples of pure PVA were maintained at a constant temperature of 60, 65, 70 and 75°C and PAL was measured as a function of time. As expected, the annihilation rate $\lambda_3$ increased with time and reached an equilibrium value $\lambda_{3_{eq.}}$, and the slope was steeper at higher temperatures. The Arrhenius plot of the initial slope of $\lambda_3 - \lambda_{3_{eq.}}$ is shown in *Figure 2*. The activation energy is calculated to be 0.5 eV. To the knowledge of the present authors there is little data concerning the activation energy of relaxation of built-in strain in polymers excepting a report by Hill *et al.*[8], who observed isothermal structural relaxation of compression-molded bisphenol-A polycarbonate and obtained activation energies of 0.28 and 0.014 eV for two processes with different relaxation times. While these relaxations were observed by the decrease in $I_3$, our relaxation has been observed by the change in $\tau_3$, and it is not clear whether direct comparison of these data is meaningful or not.

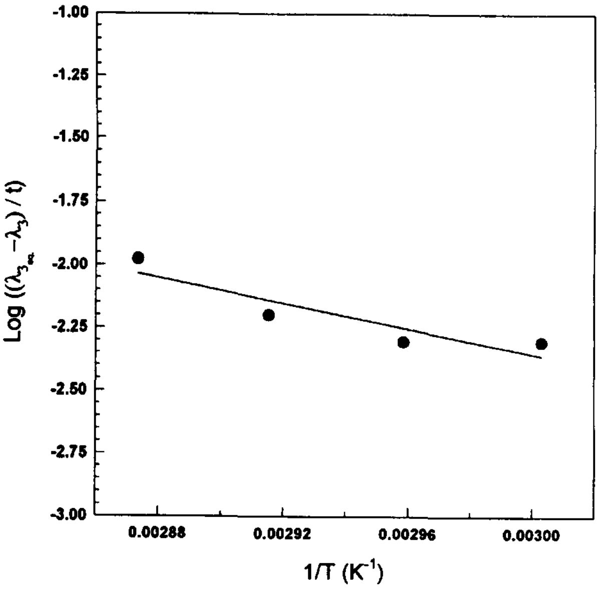

**Figure 2** Arrhenius plot of the rate of change in the annihilation rate $\lambda_3$ at temperatures 60, 65, 70 and 75°C at which the free-volume holes relax to equilibrium values $\lambda_{3_{eq.}}$ due to release of the built-in strain in pure PVA samples

Clearly there are two regions with different temperature dependences of $\tau_3$. We will consider the data of the cooling runs, which are thought to be free from the effect of built-in strain. The slopes of the two regions for the pure PVA (*Figure 1a*) meet at 88°C. This meeting point agrees with $T_g \approx 87$°C reported as the glass transition temperature, $T_g$ (ref. 9).

For all the samples $I_3$ decreases with increasing temperature. $I_3$ is often thought to be a measure of the number of free-volume holes, but the latter is not the sole reason for the variations of $I_3$. The probability of Ps formation itself may be affected by various conditions of the polymer. It is difficult to attribute the drop of $I_3$ with increasing temperature to a change (decrease) in the number of free-volume holes. A more plausible explanation would be dissociation of hydrogen bonds of PVA leading to an increased number of sites that can trap precursors of Ps. But the nature of the trapping sites has yet to be examined in detail.

The $I_3$ values in the heating runs also appear to be composed of two regions: at lower temperatures the dependence is almost flat, and at higher temperatures $I_3$ decreases with temperature. The meeting point of the two regions is about 70°C, which is much smaller than the $T_g$ measured by the $\tau_3$ values. This may be interpreted in terms of stimulated dissociation of the hydrogen bonds near the strained sites. The release of the strain starts at about 60°C, as was discussed before, and the sites around the released strain will behave as a locally rubbery state. The hydrogen bonds around them will dissociate leading to a decreased $I_3$. Such a transition may be regarded as a kind of $T_g$ specifically related to the built-in strain. In fact the literature values of $T_g$ vary from 70 to 90°C (ref. 10), and it is not surprising that the $T_g$ connected with the strains belongs to the lower values.

The $I_3$ values in the cooling runs do not show a marked bend, connect smoothly from the rubbery to the glassy state, and are always smaller than in the heating runs. This might be attributed in part to the existence of built-in strain in the heating runs, but it is more probable that PVA has dissociated during measurements above 150°C and the probability of Ps formation has become smaller due to enhanced crystallinity. It is known that PVA does not melt to a thermoplastic, but decomposes by loss of water from two adjacent hydroxyl groups at temperatures above 150°C (ref. 11). It is also possible that $CuCl_2$ has formed some complex with PVA and has become an inhibitor of Ps formation. Indeed, the colour of the PVA containing doped $CuCl_2$ became dark brown after heating up to 160°C, while the colour of pure PVA became pale yellow with the same heating.

Although the bend of $I_3$ in the heating runs, i.e. the transitions corresponding to the annealing of the built-in strains, are observed for all the samples, the transitions corresponding to the bend of $\tau_3$ are observed only for pure PVA. This is because, as is discussed later, the value of $\tau_3$ in the doped PVA contains the effect of quenching and information about the volume factors is made obscure.

The effect of various additives on Ps formation has been extensively studied for molecular liquids[12]. One of the most important findings is that the addition of electron acceptors such as nitrobenzene derivatives and halogenated hydrocarbons causes a marked reduction of the Ps yield. The $I_3$ values are shown in *Figure 3* as a function of the concentration of $CuCl_2$. The data in this figure indicate that $CuCl_2$ is having an inhibiting effect in the polymer as it does in aqueous solution[13]. The results were fitted with the empirical functions which are often used to describe the inhibition effect[14–17]:

$$I_3 = I_3^0/[1 + (\alpha C)^{\beta}] \qquad (1)$$

where $C$ is the additive concentration, $I_3^0$ is the *o*-Ps intensity at $C = 0$, and $\alpha$ and $\beta$ are constants dependent on the solute and matrix. The value of $\alpha$ varies for different PVAs (see the $\alpha$ values shown in *Figure 3*) and it is not possible to extract any trend of temperature dependence. The average of the inhibition coefficients was $\alpha = 0.64\,\mathrm{mol}^{-1}$ which is smaller than the corresponding values in liquid (3.3 $\mathrm{mol}^{-1}$ for $Cu^{2+} \cdot 6H_2O$ in water, 0.9 $\mathrm{mol}^{-1}$ for $Cu^{2+} \cdot 4NH_3 + 2H_2O$ in water[14] and 2.5 $\mathrm{mol}^{-1}$ for $Cu^{2+}$ or $CuCl^+$ or $CuCl_2$ in aqueous solution[13]).

The variation of the *o*-Ps annihilation rate, $\lambda_3$, in PVA by adding $CuCl_2$ at different temperatures is shown in *Figure 4*. It is clear that $\lambda_3$ slightly increases with increasing $CuCl_2$ concentration. Quenching of positronium lifetime due to $CuCl_2$ or $Cu^{2+}$ ions in aqueous solution is well known[13,14,18–20]. DeNatale *et al.*[14] confirmed that the quenching by $Cu^{2+}$ ions is due to both spin-conversion and oxidation reactions. Also, Ps is supposed to react with three reacting species, $Cu^{2+}$, $CuCl^+$ and $CuCl_2$ in aqueous solutions, Ps reaction with $CuCl_2$ and $CuCl^+$ being stronger than with $Cu^{2+}$ (ref. 17).

The rate constant of the Ps reaction, $\kappa$, is determined using the following equation[21,22]:

$$\lambda_3 = \lambda_3^0 + \kappa C \qquad (2)$$

Where $\lambda_3$ and $\lambda_3^0$ are the *o*-Ps annihilation rates at concentration $C$ of doped matrix and in pure matrix, respectively. The rate constant was determined as the slope of the $\lambda_3$ *versus* concentration relationships, and is $0.0676 \pm 0.0029\,\mathrm{mol}^{-1}\,\mathrm{ns}^{-1}$. This rate constant is much smaller than the corresponding values in liquid (3.19 for $Cu^{2+} \cdot 6H_2O$ in water, 2.86 for $Cu^{2+} \cdot 1EDTA + 1H_2O$ in water[14] and $2.7 \pm 0.5$ for $Cu^{2+}$, $5 \pm 3$ for $CuCl^+$ and $12 \pm 7\,\mathrm{mol}^{-1}\,\mathrm{ns}^{-1}$ for $CuCl_2$ aqueous solutions[13].

If we assume that the reaction is diffusion controlled and is entirely due to reaction with $Cu^{2+}$, the rate constant can be written as[13,23]:

$$\kappa = 4\pi(D_{Ps} + D_{Cu})(r_{Ps} + r_{Cu}) \qquad (3)$$

where $D_{Ps}$ and $D_{Cu}$ are the diffusion coefficients of Ps and $Cu^{2+}$, and $r_{Ps}$ and $r_{Cu}$ are the reaction radii of Ps and $Cu^{2+}$, respectively. Assuming $D_{Ps} \gg D_{Cu}$ and $r_{Ps} + r_{Cu} \sim 1.9$ Å, the diffusion coefficient of Ps is $0.5 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. $CuCl_2$ may not be completely ionized to $Cu^{2+}$ in PVA and $CuCl_2$ might be a stronger quencher. In such a case the diffusion coefficient becomes much smaller. Kobayashi also observed that the quenching effect of dinitrobiphenyl becomes smaller in polycarbonate than in liquid benzene, and attributed it to a reduced *o*-Ps mobility[23]. It is interesting to see whether the quenching efficiency is different for the glassy (below about 90°C) and the rubbery (above 90°C) states, but the data of *Figure 4* do not reveal any trend on this point. The quenching efficiency of $CuCl_2$ in PVA is not much different within the accuracy of the experiment.

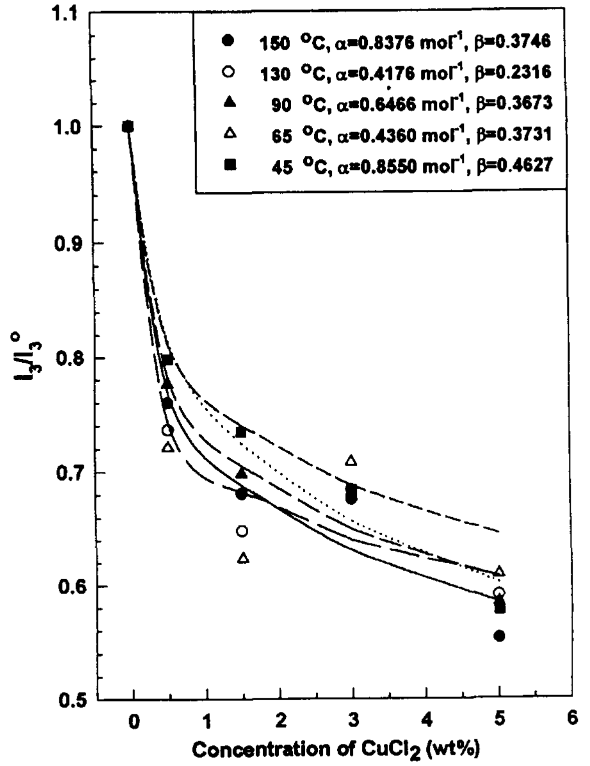

**Figure 3** Effect of $CuCl_2$ on *o*-Ps intensity in PVA. The lines are the result of fitting the equation $I_3 = I_3^0/[1 + (\alpha C)^{\beta}]$

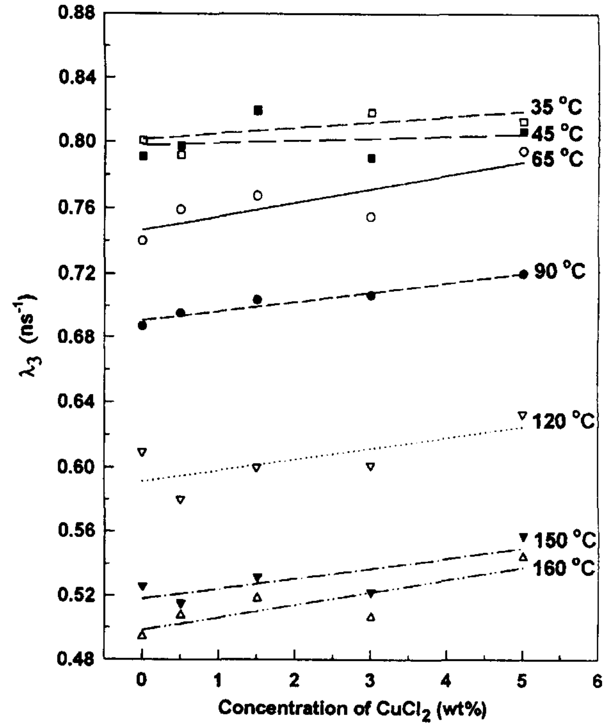

**Figure 4** Variation of *o*-Ps annihilation rates in PVA by addition of $CuCl_2$ at different temperatures

## CONCLUSION

Positron annihilation in PVA has been shown to be very sensitive to physical and chemical perturbations. Firstly, it is chemically affected by the dopant. As in liquids the dopant $CuCl_2$ has two effects, inhibition of Ps formation and quenching of *o*-Ps lifetimes, although their efficiencies are smaller in the polymer than in liquids. Positron annihilation is also affected by the strain brought about by the process of sample preparation and by degradation at high temperatures. Taking the sensitive nature of positron annihilation into consideration, it becomes possible to use it as a probe of polymer structures. The glass transition temperature $T_g$ has been determined in agreement with the literature value and, moreover, an earlier transition associated with the built-in strain has been determined.

## ACKNOWLEDGEMENT

We are grateful to Drs K. Tanaka and M. Imai for valuable discussion.

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