PHYSICAL REVIEW B, VOLUME 63, 064204

Positronium formation in a polymer blend of polyethylene and chlorinated polyethylene

C. L. Wang,[1] Y. Kobayashi,[1,*] W. Zheng,[1,2] C. Zhang,[2] Y. Nagai,[3] and M. Hasegawa[3,4]
[1]*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan*
[2]*Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, Shanghai 201800, China*
[3]*The Oarai Branch, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*
[4]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

(Received 5 July 2000; published 22 January 2001)

We discuss positronium (Ps) formation in a polymer blend system consisting of low-density polyethylene (PE) and chlorinated polyethylene (CPE, random copolymer with a chlorine weight content of 35%). Positron lifetime measurements were performed as a function of CPE composition (0–100%), electric field ($F = 0-40\,\mathrm{kV/cm}$), temperature ($T = 30-300\,\mathrm{K}$), and positron irradiation time ($t = 0-110\,\mathrm{h}$) at $T = 75\,\mathrm{K}$, and room temperature. We note that Ps formation occurs by recombination of electron-positron pairs with both small ($\lesssim 3$ nm) and large ($\gtrsim 3$ nm) initial separations. At low temperatures, pairs with large separations are formed not only in the positron spur (blob) but also as a result of coupling of a thermalized positron with one of the localized electrons produced by positron irradiation. For PE, the contribution of the latter process to Ps formation appears as a gradual increase in relative intensity of the long-lived *ortho*-positronium (o-Ps) component as a function of positron irradiation time. The addition of CPE appreciably reduces the contribution from pairs with large separations, and Ps formation in pure CPE occurs exclusively from pairs with small initial separations, much less influenced by external parameters such as the temperature and electric field.

DOI: 10.1103/PhysRevB.63.064204 PACS number(s): 78.70.Bj, 82.30.−b, 61.41.+e, 36.10.Dr

I. INTRODUCTION

Increasing numbers of studies have been conducted probing free volume in polymers by positron annihilation lifetime spectroscopy (PALS).[1–4] The lifetime spectrum of positrons annihilating in a polymer contains at least three exponentially decaying components. The two short-lived components are associated with the annihilation of *para*-positronium (p-Ps) and free positrons, whereas the longer-lived components are attributed to the pick-off annihilation of *ortho*-positronium (o-Ps) with characteristic lifetimes of 1–10 ns.[5] Based on a simple model of Tao[6] and Eldrup,[7] in which Ps is assumed to be localized in a spherical hole with an infinitely high potential wall, useful information on the free volume cavity in polymers has been obtained from measured o-Ps lifetimes.

In spite of successful PALS application to polymers, the Ps formation mechanism remains to be clarified. In the 1980s, the o-Ps yield was considered to be simply proportional to the free volume hole concentration.[8] More recent experiments on the effects of chemical composition,[9,10] positron irradiation,[11,12] electric fields,[13,14] and light illumination[15] revealed that early radiation chemical processes prior to Ps localization into a free volume hole play important roles in determining the long-lived o-Ps yield. According to the spur reaction model, Ps formation occurs on a time scale of 1–10 ps via a reaction between a positron and one of the electrons liberated from the medium molecules by the positron itself in the positron spur[5,16,17] or blob.[18]

The addition of a second component to a polymer matrix such as polyethylene is convenient in exploring the roles played by different parameters in Ps formation. Proper selection of an additive makes it possible to study the effect of particular parameters on Ps formation and by systematically changing its concentration more quantitative information can be obtained. We studied Ps formation in polyethylene (PE) containing different amounts of ethylene vinyl acetate copolymer (E/VA) as additives and found that Ps is formed from electron-positron pairs with different initial separations by recombination.[14,19] In this paper, we discuss the contribution from positron-electron pairs with small and large initial separations to overall Ps formation in a model polymer system consisting of nonpolar and polar components. PALS was conducted for polymer blends of polyethylene (PE) and chlorinated polyethylene (CPE) as functions of CPE concentration, external electric field, temperature, and positron irradiation time. Additional information on the positron state in PE/CPE was obtained by coincidence Doppler-broadening spectroscopy[20] and positron mobility measurements.[21]

II. EXPERIMENT

A. Samples

Low-density polyethylene (PE) (C180, UBE Industries, Ltd., Japan) was mixed with different amounts of chlorinated polyethylene (CPE) (135 A, chlorine weight content = 35%, Weifang Chemical Factory, China). The CPE weight percentage was varied from 0 to 100%, which corresponds to the CI weight content $\Phi_{\mathrm{Cl}} = 0-35\%$ (Table I). Mixtures were kept at 130–140 °C on a roller and then pressed into sheets with a thickness of about 2.5 mm at 140–150 °C. The crystallinities of the samples thus prepared were determined by x-ray diffraction (Fig. 1).

Differential scanning calorimetry (DSC) was performed on PE, CPE, and several blends with Perkin Elmer System 7. The temperature was varied from 298 to 103 K with a cooling rate of 40 K/min. On the plot of the derivative of the heat flow, a peak centered at 153 K (about 10 K width) was found for all measured samples. The peak was assigned to the secondary transition of blends. Another peak centered around

TABLE I. Positron mobilities at room temperature determined from shifts in annihilation γ-ray peaks. x is the Cl content corresponding to $CH_{2-x}Cl_x$.

CPE content (%)	Φ_{Cl} (%)	x	$\mu_+{}^a$ ($cm^2/V\,s$)	$\mu_+{}^b$ ($cm^2/V\,s$)
0	0	0	16 ± 3	25 ± 5
7	2.45	0.010	16 ± 5	24 ± 8
21	7.35	0.031	8 ± 4	12 ± 5
35	12.25	0.055	9 ± 4	12 ± 5
56	19.60	0.096	8 ± 9	10 ± 12
100	35.00	0.209	6 ± 4	7 ± 5

[a] Overall positron mobility determined from overall shift ΔE.

[b] Free positron mobility determined from shift ΔE_f.

253 K (about 20 K width) due to glass transition was observed for all samples except PE.

B. PALS

Positron lifetime measurements were conducted with a conventional fast-fast coincident positron lifetime spectrometer with a time resolution of about 280 ps full width at half maximum (FWHM). A ^{22}Na source with an activity of about 0.74 MBq, deposited on an area of about 10 mm^2 between two 0.8-mg/cm^2 Kapton foils, was sandwiched between two identical pieces of the sample; 1.2–1.8 million counts were accumulated in each lifetime measurement.

The resolution function of the spectrometer, assumed to be a sum of three Gaussians, was determined several times from analysis of the lifetime spectra of Kapton with a single component (381–385 ps) using the RESOLUTION program.[22] Lifetime spectra of PE, CPE, and their blends were decomposed into three components using the PATFIT routine[22] after correction of a source component (7%). The longest-lived component with lifetime τ_3 was easily attributed to o-Ps, so its yield is given as I_3, the relative intensity of the longest-lived component.

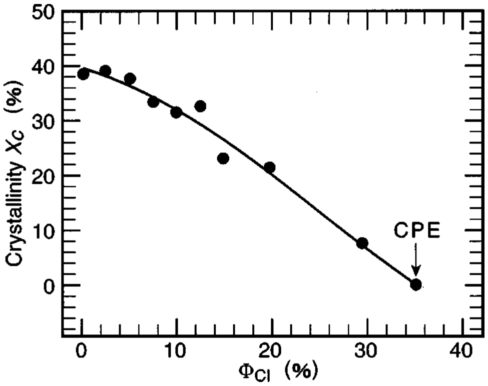

FIG. 1. Plot of crystallinity versus Cl concentration for PE/CPE blends. Crystallinities were evaluated from the relative intensity of (110) and (200) reflections in x-ray-diffraction spectra. The gradual decrease in crystallinity by the addition of CPE was observed also by DSC up to 200 °C (data not shown).

PALS in the presence of an external electric field was conducted at room temperature $(295\pm2\ K)$. Two pieces of the sample were clamped, with the positron source, between a pair of silver electrodes to which static electric fields (F) up to 40 kV/cm were applied. Temperature dependence of lifetime parameters was measured at 30–300 K. The source-sample assembly was mounted on a cryostat and cooled to 30 K within about 30 min. Then, the temperature was raised to 300 K with an interval of 10 K. After a sample was kept at each temperature for 1 h, a positron lifetime spectrum was collected for 8 h. Another temperature scan was done on fresh samples in the cooling process from 300 to 30 K with a step of 90 K. After the scan, samples were rapidly heated to 300 K and lifetimes measured again during cooling to 30 K in a step of 45 K. Positron irradiation time dependence of lifetime spectra was studied at 75 K and room temperature. Data were repeatedly recorded as a function of measurement time $(t=0-110\,h)$. The time scan at 75 K was started right after quenching of the sample from room temperature to this temperature, while that at room temperature was started immediately after setting the source-sample assembly between the two detectors.

C. Determination of positron mobilities

A weaker positron source with an activity of about 0.37 MBq was used for positron mobility measurements. The peak position of 511-keV annihilation radiation was precisely determined for six selected samples including PE and CPE as a function of static electric field (F) up to 20 kV/cm at room temperature. The source-sample assembly was placed at 20 cm from a high-purity Ge detector with a resolution of about 1.3 keV FWHM. Detailed procedures for data collection and analysis are described elsewhere.[23] The positron mobility μ_+ was determined from the relation

$$\mu_+=\nu_d/F=2c\Delta E/(E_{511}F),$$

where ν_d is the positron drift velocity, ΔE is the overall shift of the annihilation γ-ray peak due to the field F, E_{511} is the energy of the annihilation radiation at $F=0$, and c is the velocity of light. To deduce the free positron mobility, we used the shift ΔE_f for the ‘‘free’’ positrons instead of the overall shift ΔE,

$$\Delta E_f=\frac{\Delta E}{1-f}. \tag{1}$$

Here, f is the fraction of the positrons forming Ps. For simplicity, we assumed $f=(\frac{4}{3})I_3$, although this $\frac{4}{3}$ ratio may slightly vary from one sample to another.[24]

D. Coincidence Doppler-broadening spectroscopy

Coincidence Doppler-broadening (CDB) spectra were measured using two high-purity Ge detectors at Tohoku University. The overall energy resolution of the apparatus was about 1.1 keV FWHM. Selection of the coincidence events that fulfilled the condition

$$2E_{511}-2.4\,\text{keV}<E_t<2E_{511}+2.4\,\text{keV}$$

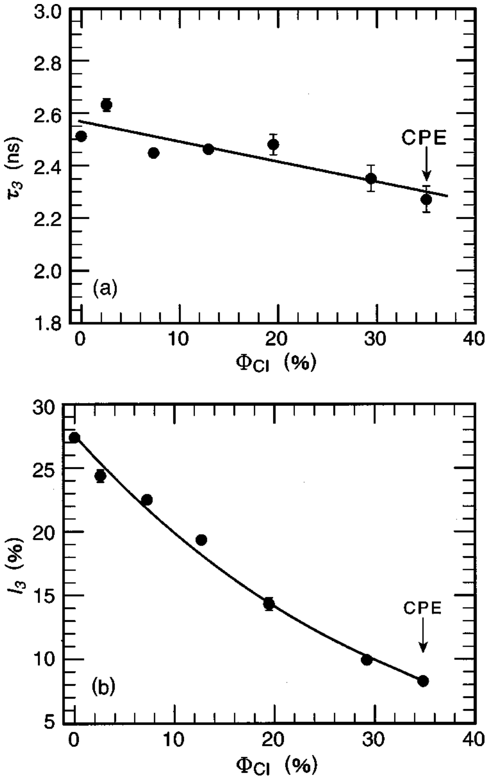

FIG. 2. Variations in (a) *o*-Ps lifetime and (b) intensity as a function of Cl content for PE/CPE polymer blends at room temperature. The curve in (b) was obtained by fitting experimental data to Eq. (5).

significantly improved the peak-to-background ratio over conventional one-detector measurement, which enabled us to observe element-specific high-momentum positron annihilation with core electrons. Here E_t is the total energy of the two γ rays. Details are given elsewhere.[20,25]

III. RESULTS

Figure 2 shows the *o*-Ps lifetime (τ_3) and intensity (I_3) in PE/CPE blends versus CPE concentration at room temperature. The *o*-Ps lifetime is slightly shortened from 2.51 to 2.27 ns with increasing CPE concentration, whereas the *o*-Ps formation probability I_3 is appreciably decreased from 27.3 to 8.4%. We relate the gradual shortening of the lifetime to the shorter *o*-Ps lifetime in CPE. The approximately linear variation of τ_3 in Fig. 2(a) shows that the cavity size in the blend is given as the weighted average of the free volume in PE and CPE.[7] The variation of I_3 in Fig. 2(b) cannot be related, however, to the free volume, because the amount of the amorphous region and hence the total free volume increase with increasing CPE concentration, as shown by the crystallinity data in Fig. 1.

The effects of the electric field on *o*-Ps parameters τ_3 and I_3 are shown in Fig. 3. Note that the electric field does not change the *o*-Ps lifetime τ_3 except CPE, for which a systematic reduction of τ_3 is observed [Fig. 3(a)]. Perhaps the polar C-Cl bond in CPE causes an anisotropic structural change in the presence of an external field,[26] leading to the reduced free-volume size.[27] The application of an electric field appreciably reduces the Ps formation in PE, while its effect becomes progressively weaker with the increase in Cl content [Fig. 3(b)].

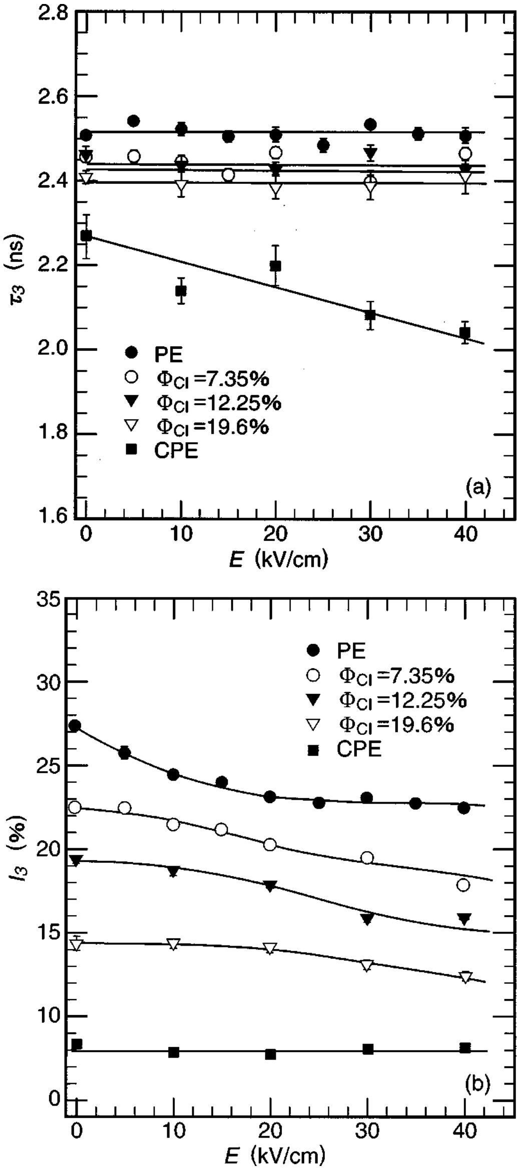

FIG. 3. Variations in (a) *o*-Ps lifetime and (b) intensity as a function of external electric field *F* for PE/CPE polymer blends. Lines are purely for visual guidance. Some data have been omitted to ensure clarity.

Variations of the *o*-Ps lifetime τ_3 in pure PE, CPE, and some of their blends as a function of temperature during slow heating are shown in Fig. 4. No difference was observed between the data in Fig. 4 and those obtained during rapid cooling. Qualitatively, the increase of τ_3 with temperature is attributed to the thermal expansion of the free volume, where Ps is localized. For simplicity, we approximate the $\tau_3(T)$ curves by three straight lines. Thus relaxation temperatures are obtained from the inflection points of the two neighboring lines. Using the straight line equation, i.e., $\tau_3(T)=aT+b$, the secondary transition temperature T_s and

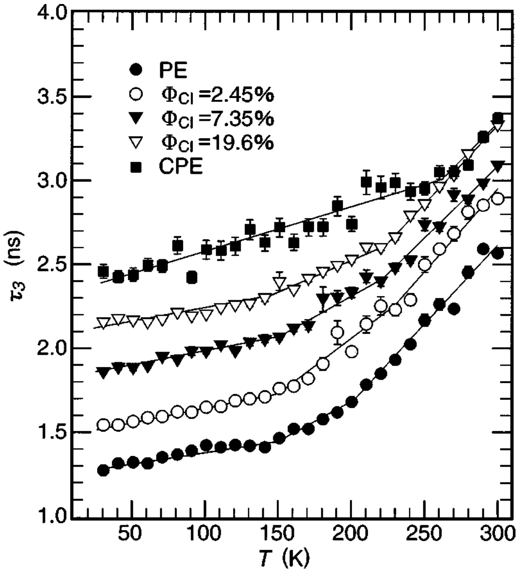

FIG. 4. Variations in *o*-Ps lifetime as a function of temperature during slow heating. Curves for the blends with Φ_{Cl}=2.45, 7.35, 19.6% and CPE are moved upward, respectively, by 0.3, 0.6, 0.9, and 1.2 ns for clarity. Data obtained during rapid cooling every 45 and 90 K (not shown) are the same as those obtained during slow heating.

the glass transition temperature T_g were determined by the least-squares method. The transition temperatures and constants *a* and *b*, thus deduced, are listed in Table II. For CPE, the $\tau_3 - T$ curve was best fitted by two lines and only T_g was obtained. Secondary transition temperatures (T_s) are in rough agreement with the results by DSC and low-frequency dielectric spectroscopy,[28] but the glass transition temperatures (T_g) are 20–30 K lower than the corresponding values obtained by DSC and dielectric measurements. Table II shows that the addition of CPE to PE slightly increases the glass transition temperature. Similar values of *a* among different samples excluding CPE imply that the thermal expansion coefficient of the free volume cavity is not significantly influenced by CPE.

Figure 5 shows variations of the *o*-Ps formation probability I_3 versus temperature. The data in Fig. 5(a) exhibit smooth variations with temperature, and slight enhancement in I_3 is observed for PE and some blends at low temperatures. In the course of these rapid scan PALS measurements every 45 and 90 K, samples were exposed to the positron source for a short time, so smooth variations reflect the temperature dependence of I_3 only. Later we briefly discuss why I_3 in PE is slightly enhanced at low temperatures. When the temperature is slowly increased from 30 to 300 K, more pronounced variations arising from long-term positron irradiation are observed for most samples [Fig. 5(b)]. $I_3(T)$ of PE shows a peak (of ''Λ'' shape) around 80 K and two valleys (of ''V'' shape) around 180 and 250 K, which is similar to previous results for high-density polyethylene (HDPE),[29] polystyrene (PS),[30,31] and other polymers.[11] Note that with the increase in CPE content, the difference of I_3 between data obtained for slowly heated and quenched samples becomes less obvious and negligible for pure CPE [Fig. 5(b)].

Figure 6 shows variations of I_3 at 75 K and room temperature as a function of positron irradiation time. At $T = 75\,\mathrm{K}$, for PE and the blend with Φ_{Cl}=2.45% I_3 rapidly increases within initial 20 h and later tends to saturate, indicating that Ps formation is enhanced by positron irradiation. For blends with larger CPE contents and pure CPE, I_3 is less enhanced [Fig. 6(a)]. At room temperature, I_3 in PE exhibits a pronounced decrease from 27.3 to 23.2%, indicative of suppressed Ps formation. The decrease becomes less obvious as the CPE concentration increases, and there is little change in I_3 for CPE [Fig. 6(b)].

Results of positron mobility measurements are presented in Table I. The free positron mobility μ_+ in PE is 25 $\pm 5\ \mathrm{cm^2/Vs}$. The mobility gradually decreases with increasing CPE concentration, somewhat different from our previous result for PE containing E/VA, where 47% decrease of μ_+ is observed at an extremely low vinyl acetate concentration of 0.4%;[14] in PE/CPE blends, the corresponding reduction of μ_+ is seen at a much higher concentration of $\Phi_{Cl} = 7.35\%$. The dramatic effect of E/VA on the positron mobility is attributed to efficient trapping of positrons by E/VA.[14,25] The much weaker effect of CPE revealed in the present study suggests that CPE may not trap positrons, and the gradual decrease in mobility may be due to the reduced positron mean free path caused by efficient positron scattering by polar C-Cl bonds.

CDB spectra of blends and CPE relative to the PE spectrum are shown in Fig. 7. Ratio curves for most samples rapidly increase in the momentum range $16–22\times10^{-3}mc$, decrease in the range $22–30\times10^{-3}mc$, and are constant

TABLE II. Secondary transition temperatures (T_s), glass transition temperatures (T_g), and parameters *a* and *b* in the fitting equation $\tau_3(T) = aT + b$ for five samples including pure PE and CPE.

	T_s (K)	T_g (K)	$30\,\mathrm{K} \leqslant T \leqslant T_s$ 10^3a (ns K^{-1})	b (ns)	$T_s \leqslant T \leqslant T_g$ 10^3a (ns K^{-1})	b (ns)	$T_g \leqslant T \leqslant 300\,\mathrm{K}$ 10^3a (ns K^{-1})	b (ns)
PE	151	205	1.37±0.16	1.25±0.01	4.79±0.41	0.73±0.07	9.38±0.54	−0.21±0.14
Φ_{Cl}=2.45%	153	231	1.70±0.08	1.18±0.01	7.14±0.96	0.34±0.17	9.38±0.73	−0.17±0.19
Φ_{Cl}=7.35%	148	233	1.72±0.12	1.21±0.01	5.31±0.60	0.68±0.11	8.63±0.64	−0.10±0.17
Φ_{Cl}=19.6%	137	222	1.62±0.25	1.18±0.01	3.58±0.42	0.92±0.08	9.39±0.25	−0.38±0.06
CPE		262			2.60±0.20	1.12±0.31	7.99±1.24	−0.30±0.34

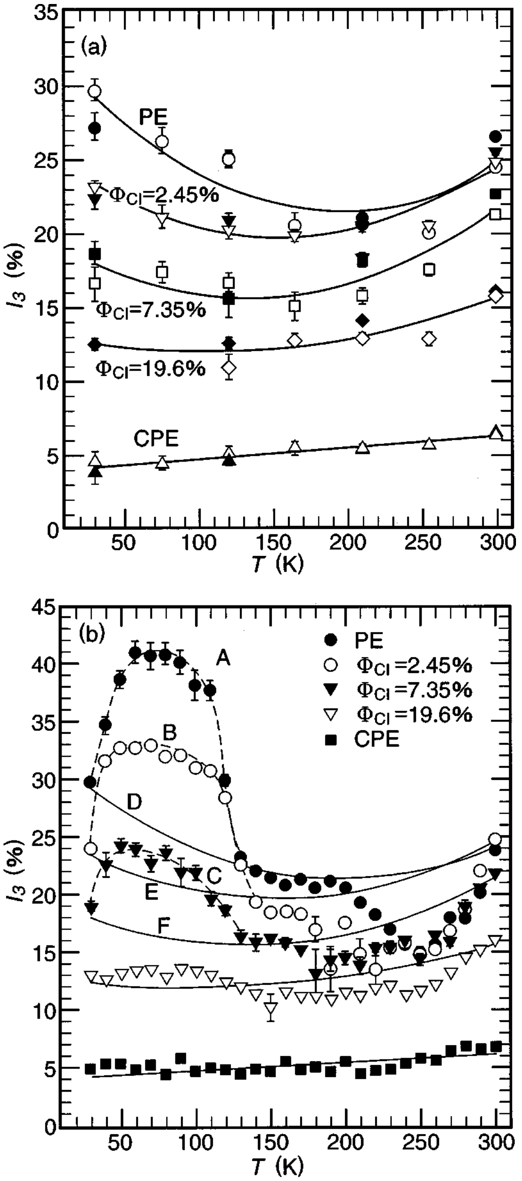

FIG. 5. Variations in *o*-Ps intensity as a function of temperature during (a) rapid cooling and (b) slow heating. Curves in (a) show the results of polynomial fitting. These curves are also shown in (b).

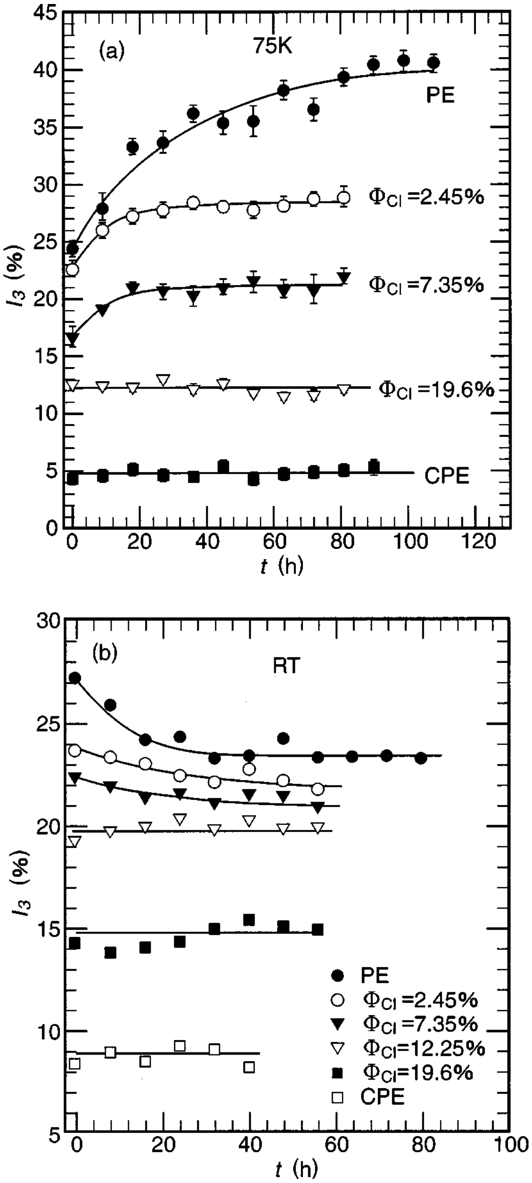

FIG. 6. Variations in *o*-Ps intensity as a function of time *t* at (a) $T=75$ K and (b) room temperature. Curves in (a) are the results of fitting to Eq. (7), while those in (b) are purely for visual guidance.

above $30\times10^{-3}mc$, where m is the mass of an electron. For blends of PE with E/VA, somewhat different spectra with a peak at $16\times10^{-3}mc$ due to oxygen were observed.[25] As is seen from the inset of Fig. 7, the peak centered around $22\times10^{-3}mc$ is systematically enhanced with increasing CPE concentration, indicating that it is due to positron annihilation with core electrons of chlorine.

IV. DISCUSSION

A. Electric-field effect on Ps formation

Based on the electric-field dependence of I_3, it is convenient to distinguish two contributions, one sensitive and the other insensitive to the electric field, to overall Ps formation.[14] In Fig. 3(b), the difference of I_3 in PE/CPE blends between 0 and 40 kV/cm becomes smaller with increasing CPE concentration. The increase of CPE concentration results also in appreciable reductions of I_3 at all fields studied. These results show that both contributions, which are sensitive and insensitive to the fields as high as 40 kV/cm, are gradually suppressed by the addition of CPE.

Field-dependent Ps formation is associated with the recombination of electron-positron pairs with large initial separations in the positron spur (blob). Because of weak Coulomb interaction between the two particles, they are easily separated by an electric field. At low fields, only a fraction of pairs are separated and Ps formation is slightly reduced from that at $F=0$ kV/cm. With increasing field strength, more and more pairs are separated and Ps formation is progressively reduced. The strong-field effect on Ps formation has been observed for nonpolar polymers such as polyethylene and

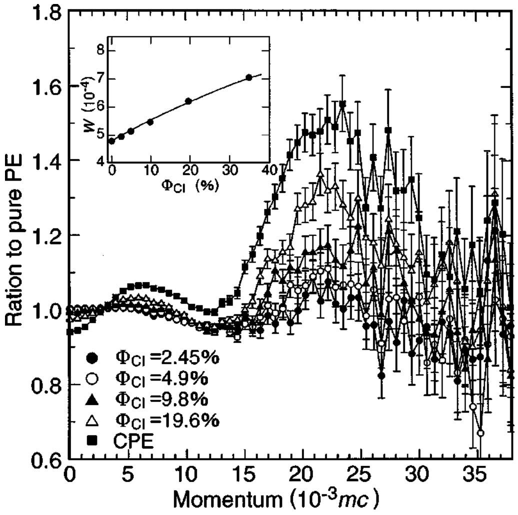

FIG. 7. Ratio curves of CDB spectra for PE/CPE blends and CPE relative to PE. The horizontal axis expresses the momentum of the annihilating positron-electron pair in units of $10^{-3}mc$. The inset shows the variation of the W parameter, defined as the fraction of signals at $22-24\times10^{-3}mc$ to those over the whole range as a function of chlorine concentration. Note that the increase in W is not linear with chlorine concentration, indicating that the intensity of the peak at $22\times10^{-3}mc$ varies differently from what is expected simply as a result of mixing the two components.

polypropylene with high positron mobility.[14,32,33] The field-independent contribution, however, is attributed to the recombination of electron-positron pairs with smaller separations ($\lesssim$3 nm). Here we cannot rule out the possibility that the field-independent contribution involves Ps atoms formed by the Ore process.[13] Obviously, relatively low fields used in this study are not strong enough to separate such pairs because of the stronger binding of the two particles in them.

The effect of the external electric field on the recombination probability of a thermalized charge-separated pair with mutual separation r is expressed as[19,34]

$$P(F)=1-\exp(-r_c/r)(1+eEr_c/2k_BT), \tag{2}$$

where $r_c=e^2/(4\pi\varepsilon\epsilon_0k_BT)$ is the Onsager length, e is the electronic charge, ϵ is the relative dielectric constant of the sample, and ϵ_0 is the dielectric constant in vacuum. Thus, for example, for a pair with 10-nm separation in PE ($\varepsilon=2.30$), $P(F)/P(0)$ is reduced by 7.95% at $F=40$ kV/cm. For a pair with a separation of 3 nm, $P(F)/P(0)$ is reduced only 0.03% at the same field.

As was discussed in previous papers,[14,19] the separation of electron-positron pairs into only two contributions is an oversimplification and more strict treatment should take the distribution of the initial separations into account. Based on an exponential distribution function of initial separations, we analyzed the electric-field dependence of I_3 for PE and estimated the average initial distance (r_0) for positron-electron pairs to be $\approx$25 nm at room temperature.[19] However, it is difficult to apply such analysis for a complicated system such as polymer blends. At present, it is more realistic to simplify the problem by approximating the distribution function with two components associated with electron-positron pairs with large ($\gtrsim$3 nm) and small separations ($\lesssim$3 nm).

TABLE III. Best-fit values of parameters α and β in Eq. (5) at $F=0$ and 40 kV/cm. Additive concentration y was equated to Cl content x.

F (kV/cm)	α	β
0	9.45 ± 0.45	1.18 ± 0.08
40	8.24 ± 0.19	1.05 ± 0.04

Effects of chlorinated compounds (R-Cl) on overall Ps formation, from pairs both with small and large separations, have been studied for a number of molecular substances.[10,35–39] The observed reduction of Ps formation in the presence of R-Cl was explained by the following reactions:[5,39]

$$e^-+\mathrm{R}-\mathrm{Cl}\rightarrow\mathrm{Cl}^-+\mathrm{R}, \tag{3a}$$

$$e^++\mathrm{Cl}^-\rightarrow[\mathrm{ClPs}]\rightarrow\mathrm{Cl}+2\gamma. \tag{3b}$$

Here, dissociative electron attachment to R-Cl is followed by positron capture by the chloride ion, which is released from R-Cl as a result of the first reaction. Reaction (3b) is possible because the Ps affinity of Cl is positive (1.91 eV).[40] Since the electron and positron participating in the above reactions are more or less coupled, it is more appropriate to describe them as follows:

$$e^- \text{---} e^+ +\mathrm{R}-\mathrm{Cl}\rightarrow\mathrm{Cl}^- \text{---} e^+ + R, \tag{4a}$$

$$\mathrm{Cl}^- \text{---} e^+\rightarrow[\mathrm{CIPs}]\rightarrow\mathrm{Cl}+2\gamma. \tag{4b}$$

Here, $e^-\text{---}e^+$ denotes an electron-positron pair with a certain mutual distance and $\mathrm{Cl}^-\text{---}e^+$ is a similar pair between a chloride ion and a positron.

Concentration dependence of I_3 in different solutions of chlorinated compounds is well reproduced by the empirical relation[5,39]

$$I_3(y)=\frac{I_3(0)}{1+(\alpha y)^\beta}, \tag{5}$$

where y represents the additive concentration, α is the inhibition coefficient, proportional to the scavenging cross section of the electron-positron pair by the additive, and β is an additional fitting parameter. Our data of I_3 for PE/CPE at 0 and 40 kV/cm in Fig. 3(b) was found to follow the same formula as α and β in Table III. Further, the increase of positron annihilation with core electrons of chlorine in Fig. 7 is not linear with CPE concentration and the larger increase in the W parameter is observed at lower CPE concentrations (inset of Fig. 7), where a larger decrease in I_3 is observed. These results suggest that reactions (4) are responsible for reduced Ps formation, and increased positron annihilation with core electrons of chlorine may be due to formation of the Ps complex [ClPs].

Table III shows that α at $F=40$ kV/cm is smaller than that at $F=0$ kV/cm. The larger α at 0 kV/cm indicates that scavenging efficiency of electron-positron pairs with large separations is higher than that of pairs with smaller separations. The *o*-Ps intensity I_3 in CPE is not affected by the electric field at room temperature [Fig. 3(b)], is only slightly influenced by temperature (Fig. 5), and is independent of positron irradiation (Fig. 6). These results show that in CPE, Ps is formed exclusively by the recombination of electron-positron pairs with short separations, which is much less influenced by external parameters such as temperature.

B. Increased Ps formation in PE at low temperatures

Here we briefly discuss why I_3 in PE is enhanced at low temperatures in Fig. 5(a). The recombination probability of a charge-separated pair in the absence of an external field is written as[34]

$$P(r)=1-\exp\left(-\frac{r_c}{r}\right). \tag{6}$$

At low temperatures, the Onsager length r_c is enhanced by factor $4\pi\epsilon\epsilon_0 k_B T$. Simple calculation taking account of the temperature dependence of ϵ (Ref. 41) shows that at room temperature $r_c = 25\,\mathrm{nm}$, but at 210, 75, and 30 K it is 35, 125, and 329 nm, respectively. The enhancement of r_c appears to favor the recombination and Ps formation. However, freezing of molecular motions at the same time enhances the thermalization distance of the positron and electron, thereby increasing their initial separation r. From the temperature dependence of the ratio $I_3(T)/I_3(295\,\mathrm{K})$ for PE, it is possible to estimate the temperature dependence of the ratio r_c/r. Our estimation based on the exponential distribution function of r (Ref. 19) gave $r_c/r_0 = 2.2$ at 30 K, 1.2 at 75 K, and 0.9 at 210 K as compared to $r_c/r_0 = 1.0$ at room temperature. We concluded that the enhancement of I_3 in PE at low temperatures is a reflection of different behaviors of r_c and r with temperature as well as the temperature dependence of the dielectric constant. The absence of the enhancement of I_3 for CPE indicates that the tail of the distribution function with larger r is responsible for the temperature dependence of I_3 in PE.

C. Effects of positron irradiation on Ps formation

The gradual enhancement of Ps formation in some polymers at low temperatures ($T < 120\,\mathrm{K}$ for PE) is due to recombination of positrons with localized electrons produced by positron irradiation.[11,15] The absence of the positron irradiation effect in CPE at 75 K [Fig. 6(a)] indicates that the increased Ps formation in PE/CPE blends is exclusively due to Ps formation from electron-positron pairs with large separations. Coupling of a positron, thermalized in a polymer containing a certain number of trapped electrons, with one of the nearby electrons leads to the formation of an electron-positron pair with a certain mutual distance. The concentration of localized electrons produced by several kGy γ-ray irradiation is about $10^{15}\,\mathrm{cm}^{-3}$ in PE.[15] Therefore the mutual distance of the electron-positron pairs formed as a result of coupling of a positron with one of the localized electrons may be on the order of 50 nm at a dose of several kGy.

TABLE IV. Best-fit values of τ, I_c, and aR in Eq. (7) for PE/CPE blends at 75 K, and blends of PE with E/VA (random copolymer, with a vinyl acetate weight content of 14%) at 100 K (Ref. 45).

	T (K)	τ (h)	I_c (%)	aR (%/h)
PE	75	32.9 ± 5.7	16.14 ± 0.98	0.49 ± 0.06
$\Phi_{\mathrm{Cl}}=2.45\%$	75	10.8 ± 1.5	5.72 ± 0.16	0.53 ± 0.07
$\Phi_{\mathrm{Cl}}=7.35\%$	75	10.5 ± 2.8	4.41 ± 0.22	0.42 ± 0.10
$\Phi_{\mathrm{Cl}}=19.6\%$	75		0	0
CPE	75		0	0
PE	100	9.3 ± 0.2	8.85 ± 0.71	0.95 ± 0.06
$\Phi_{\mathrm{E/VA}}=3\%$	100	16.0 ± 1.9	6.53 ± 0.24	0.41 ± 0.04
$\Phi_{\mathrm{E/VA}}=6\%$	100	23.6 ± 7.0	6.57 ± 0.79	0.28 ± 0.05
$\Phi_{\mathrm{E/VA}}=12\%$	100	137 ± 66	11.34 ± 4.37	0.08 ± 0.01
$\Phi_{\mathrm{E/VA}}=60\%$	100	157 ± 39	14.09 ± 2.78	0.09 ± 0.01
E/VA	100	250 (fixed)	15.10 ± 0.43	0.06 ± 0.01

It is well known in radiation chemistry that charge-separated pairs generated by low temperature irradiation of molecular solids with photons in the visible or x-ray region cause isothermal luminescence (ITL) via mutual recombination. Due to very slow recombination of electrons with parent ions, ITL lasts hours or even months.[42,43] The characteristic lifetime of ITL, approximately matches that of increasing Ps formation in polymers, which enables us to relate the enhancement of I_3 at 75 K to shallowly trapped electrons produced by positron irradiation that survive ion-electron recombination (IER).

It is possible to describe the enhancement of I_3 during the isothermal process at $T = 75\,\mathrm{K}$ with a simple formula. Assume that (i) at low temperatures, positron irradiation produces localized electrons with a constant rate R, which is proportional to the positron source activity; (ii) all electrons produced by positron irradiation are localized and distributed randomly, and their disappearance rate is given as C/τ, where C and τ are the concentration and characteristic lifetime of the trapped electrons, respectively;[44] (iii) the formation probability of Ps from trapped electrons produced by positron irradiation is proportional to concentration C. Then *o*-Ps formation versus time is written as

$$I_3(t)=I_3(0)+aC=I_3(0)+I_c[1-\exp(-t/\tau)], \tag{7}$$

where $I_3(0)$ denotes the *o*-Ps yield in the absence of an irradiation effect, a is the specific *o*-Ps formation probability and $I_c = aR\tau$ corresponds to the increment of I_3 at extremely long positron irradiation.

We found that Eq. (7) gives satisfactory fits to the $I_3(t)$ data for our PE/CPE blends at 75 K as well as our previous data for blends of PE with E/VA at 100 K.[45] The best fits of τ, I_c, and aR are listed in Table IV. The addition of small amounts of CPE to PE reduces the characteristic lifetime τ but the factor aR is basically unchanged within the error range. This result is in contrast to that of the blends of PE with E/VA, where τ increases but aR decreases with increasing E/VA concentration. In the former system, electrons produced by positron irradiation undergo dissociative attachment to CPE and resultant chloride ions capture positrons, which effectively reduces the lifetime of electrons available for Ps formation. This accounts for the decrease of τ with the increase in CPE concentration. In the latter system, electrons produced by positron irradiation may be weakly captured by E/VA but still available for Ps formation, which lengthens the lifetime of trapped electrons. The decrease of the factor aR is attributed to a reduction of a rather than R. The addition of E/VA to PE appreciably decreases positron mobility due to positron capture,[14,25] which should considerably reduce the recombination probability of an electron-positron pair with large separation.

At room temperature, positron irradiation suppresses Ps formation in PE and blends containing relatively low concentrations of CPE [Fig. 6(b)]. The reduction of I_3 in PE may arise from positron capture by trapping centers formed by the decay of electrons.[46–48] The candidates of these positron trapping centers are chemical traps such as free radicals[49,50] and physical traps such as nonuniform potentials produced by positron irradiation.[43,51] One may argue that cross linking formed by positron irradiation may be responsible for the decrease of I_3. However, there is no clear indication that cross linking reduces Ps formation.

The respective increase and decrease of I_3 at 75 K and room temperature due to positron irradiation are absent for the blend with $\Phi_{\mathrm{Cl}}=19.6\%$ and pure CPE. In these samples, the CPE concentration is probably so high that all electrons produced by positron irradiation are captured by CPE before they combine with a positron to form Ps or form positron traps. Note that the above explanation does not contradict the nonzero values of intrinsic I_3 of the blend with $\Phi_{\mathrm{Cl}}=19.6\%$ and CPE, because Ps formation in these samples exclusively occurs from a smaller number of positron-electron pairs with short initial separations.

As the temperature is gradually raised from 75 K, the increased Ps formation due to positron irradiation in PE is replaced by a decrease in I_3 around 110–140 K [Fig. 5(b)], where because of the local molecular motion, e.g., the crankshaft motion involving several carbon atoms,[52] localized electrons start to be detrapped. One can assume that the removal of localized electrons and the formation of positron traps above are responsible for the transition from the ‘‘positive’’ to ‘‘negative’’ positron irradiation effect. For simplicity, assume that the reduction of I_3 observed during slow heating is solely due to detrapping of localized electrons. We then estimate the activation energy E_a of localized electrons using $\Delta I_3 \sim \exp(E_a/k_B T)$, where ΔI_3 is the contribution of localized electrons to I_3 at different temperatures. Assuming ΔI_3 is given as the difference between curves A, B, C and D, E, F in Fig. 5(b) between 110 and 140 K, we obtained $E_a \sim 30-80\,\mathrm{meV}$ for PE and the PE/CPE blends with $\Phi_{\mathrm{Cl}}=2.45$ and 7.35%, in consistent with the activation energy of spin rotation in electron spin resonance (ESR) for polymers.[53] Note that activation energies of localized electrons in PE and polyethylene terephthalate (PET) as determined by photon ionization are, respectively, 0.6–2.5 eV (Ref. 54) and above 2 eV,[55] much higher than activation energies determined by Ps formation. In photoionization, the Franck-Condon effect must be considered, and the difference is attributed to the additional energy for nuclear relaxation required in photoionization.[55,56]

V. CONCLUSION

We measured positron lifetime spectra for PE/CPE polymer blends as functions of external electric field, temperature, and positron irradiation time. Complimentary information on the positron states and annihilation sites was obtained by positron mobility and coincidence Doppler-broadening measurements. We found that the addition of CPE significantly changes the temperature, electric field, and positron irradiation time dependences of I_3.

The time dependence of I_3 at 75 K was quantitatively modeled by considering the formation and disappearance of localized electrons produced by positron irradiation. Comparison of the result for PE/CPE to that for the blends of PE with E/VA revealed important differences between the two systems. The addition of CPE to PE shortened the lifetime of localized electrons available for Ps formation, while the addition of E/VA resulted in an elongation of the lifetime, accompanied by a decrease of the specific Ps formation probability. In the former system, electrons produced by positron irradiation undergo dissociative attachment to CPE and resultant chloride ions capture positrons to form the complex [ClPs], as evidenced by coincidence Doppler broadening spectroscopy. In the latter system, E/VA traps not only the electrons produced by positron irradiation but also the positron. The electrons trapped on E/VA form Ps, but positron trapping on E/VA results in suppression of Ps formation. From the temperature dependence of the I_3 increment due to positron irradiation, the activation energies of the localized electrons in the shallow traps were determined to be 30–80 meV for PE and PE/CPE blends containing relatively small amounts of CPE.

The observed weakening of temperature and positron irradiation effects by the addition of CPE, is understandable considering different contributions of electron-positron pairs with small ($\lesssim 3$ nm) and large ($\gtrsim 3$ nm) initial separations to Ps formation. Based on the electric field dependence of I_3, we concluded that Ps in CPE is formed exclusively from electron-positron pairs with short initial separations ($\lesssim 3$ nm) including that formed by the Ore process, whereas Ps in PE originates from pairs with both short and large initial separations. The average initial separation in PE was estimated to be 25 nm at room temperature, based on the exponential distribution function. The relative contribution from pairs with large initial separations is progressively reduced with increasing CPE concentration.

ACKNOWLEDGMENTS

We thank Dr. T. Kumagai, Dr. T. Ihara, and Y. Ohte for their aid in x-ray diffraction and DSC measurements. This work was supported financially by the Science and Technology Agency (STA) and the Agency of Industrial Science and Technology (AIST). Two of us (C.L.W. and W.Z.) are grateful to STA for financial assistance.

[*] Corresponding author. Email address: kobayashi@nimc.go.jp

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