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Positron and Positronium Annihilation in Polymers Studied by Age-Momentum Correlation Spectroscopy

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Positron (e^+) and positronium (Ps) annihilation processes in polymers are studied by positron age-momentum correlation spectroscopy, which can sensitively probe momentum distributions of e^+ , p -Ps, and o -Ps. For polyether sulfone and ethylene tetrafluoroethylene copolymer belonging to oxygen-containing polymers (O group) and fluorine-containing polymers (F group), respectively, significant effects of positron trapping by polar element are observed. The Doppler profile of o -Ps pick-off annihilation is strongly influenced by F atoms, giving rise to anomalous broadening. The results are discussed together with our previous data of the $S-I_3$ correlation in order to explore the feasibility of chemical analysis around the free volumes by age-momentum correlation spectroscopy.

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1. Introduction

In positron annihilation spectroscopy, a well-known technique for metals and intermetallic compounds, the defect and electronic structure is probed with high sensitivity [1]. After thermalization, positrons become localized in open-volume defects [1] or certain defect-free nanoparticles [2], and are annihilated therein. The two emitted γ rays provide us information on these trapping sites.

In polymers, the situation is more complex because a fraction of energetic positrons forms the bound state with an electron, so-called positronium (Ps). Singlet *para*-positronium (p -Ps) with the spins of the positron and electron antiparallel and triplet *ortho*-positronium (o -Ps) with parallel spins are formed at

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a ratio of 1 : 3. In vacuum, *p*-Ps annihilates into two γ rays with a lifetime of 125 ps, whereas *o*-Ps decays into three γ rays with a longer lifetime of 142 ns. The *o*-Ps lifetime is shortened to a few ns in polymers, because the positron in *o*-Ps undergoes two-photon pick-off annihilation with one of the bound electrons with opposite spin. The annihilation of Ps is of great potential for polymer studies, since the positron lifetime of *o*-Ps and the momentum distribution of *p*-Ps give information on the free volume.

We have systematically investigated Ps formation in polymers by employing coincident Doppler broadening and positron lifetime spectroscopy [3, 4]. A correlation between Doppler broadening line-shape S parameter and *ortho*-positronium fraction, I_3 (S - I_3 correlation) [5] has been introduced to examine intrinsic momentum distributions of positrons (e^+), *para*-positronium (*p*-Ps), and *ortho*-positronium (*o*-Ps). The correlation has been found to be classified into the following groups depending on the chemical element which polymers contain: (1) polymers consisting of only carbon and hydrogen, (2) oxygen-containing polymers, and (3) fluorine-containing polymers [3]. In addition, low energy Ps formed by recombination of weakly bound Mott-Wannier (MW) positron-electron pairs with large separations becomes visible by the S - I_3 correlation [4].

In the present work, the Ps formation in polymers is further studied by age-momentum correlation (AMOC) spectroscopy, which can sensitively probe momentum distributions of e^+ , *p*-Ps, and *o*-Ps. The results are discussed together with our previous data of the S - I_3 correlation in order to explore the feasibility of chemical analysis around the free volumes by AMOC spectroscopy.

2. Experiments

SiO₂ fused quartz and the following polymers were examined in this study.

(1) Polyolefin polymers: high-density PE (HDPE), polypropylene (PP), polyethylene (PE), ultrahigh-molecular-weight PE (UHMW), low-density PE (LDPE), polystyrene (PS), and syndiotactic PS.

(2) O-containing polymers: kapton, polyetherimide (PEI), poly(ether ether ketone) (PEEK1), PEEK2 (crystallinity: 50%), poly(ethylene terephthalate) (PET), poly(vinyl alcohol) (PVA), polyether sulfone (PES), poly(methyl methacrylate) (PMMA), polyestercarbonate (PEC), and polycarbonate (PC).

(3) Teflon, polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene copolymer (ETFE), tetrafluoroethylene perfluorovinyl ether copolymer (PFA), tetrafluoroethylene perfluoropropylvinyl ether copolymer (FEP), polyvinylidene fluoride (PVDF), and polyvinyl fluoride (PVF).

AMOC measurements were performed by acquiring the Doppler broadening and the positron lifetime data coincidentally. The birth γ ray and the annihilation γ ray were detected by BaF₂ scintillators with 2'' diameter \times 1'' thickness coupled with photomultiplier tubes (PMT1 and PMT2). The PMT1 and PMT2 detecting 1.27 MeV and 511 keV γ rays were squarely aligned to each other. For

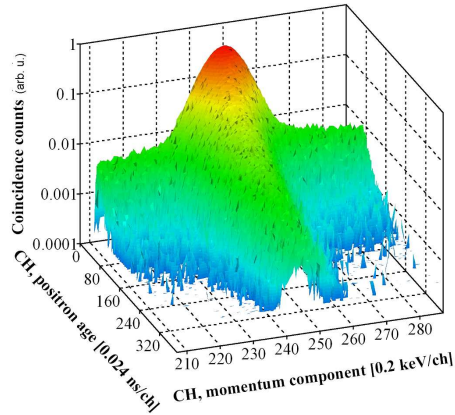


Fig. 1. Age-momentum correlation spectrum observed for polystyrene. The counts are plotted in the logarithmic scale as a function of both the positron age and the momentum component of the annihilation γ rays.

the simultaneous measurement, a high purity Ge detector with 1.0 keV (FWHM) energy resolution was located collinearly to PMT2 and detects the annihilation γ ray. A time resolution of 250 ps FWHM was obtained. Figure 1 shows typical AMOC spectrum observed for PS. In the present experiments, positron-age dependent Doppler broadening spectra were analyzed by the S parameter ($S(t)$), which was determined by the ratio of the central area over $(-2.5 \text{ to } +2.5) \times 10^{-3} m_0 c$ to the total area of the Doppler broadening spectrum. For the clarification of presentation, 3 neighboring-point-averaging smoothing was applied.

3. Results and discussion

AMOC measurements were performed for PS, PES, and ETFE belonging to C, O, and F groups, respectively. Any effects due to positron irradiation [6] were not observed during our measuring time of 24–48 hours. In Fig. 2 the $S(t)$ parameters as a function of positron age are shown for PS, PES, and ETFE. Similar results were found in earlier papers [7–10]. The $S(t)$ parameters indicate high values around $t = 0$ arising from self-annihilation of p -Ps commonly for three polymers. They rapidly decrease in the positron age from 0 to 0.5 ns due to the disappearance of p -Ps. There appear significant dips for PES and ETFE, but not for PS in the positron age around 0.6 ns. The $S(t)$ parameters are saturated above the positron age of 2.0 ns for the three polymers.

Figure 3 shows the correlation between the S parameter obtained by coincident Doppler spectroscopy and the o -Ps fraction ($S-I_3$ correlation) obtained by lifetime spectroscopy for a number of polymers. As indicated by straight lines determined by the least-squares method (see Fig. 3), $S-I_3$ correlation was classified into the following three groups, depending on the chemical element the polymers contained: (1) polyolefines consisting only of carbon and hydrogen (C group),

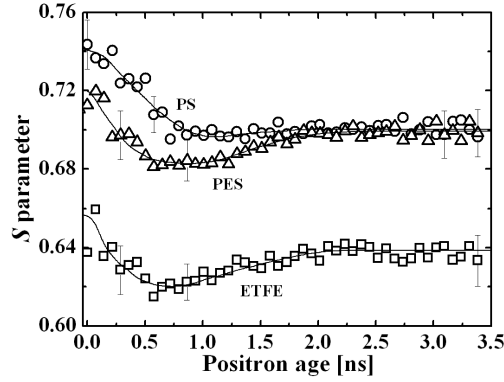


Fig. 2. Positron age dependence of $S(t)$ parameter in PS (open circles), PES (open triangles), ETFE (open squares). Solid lines are drawn for guiding the eye.

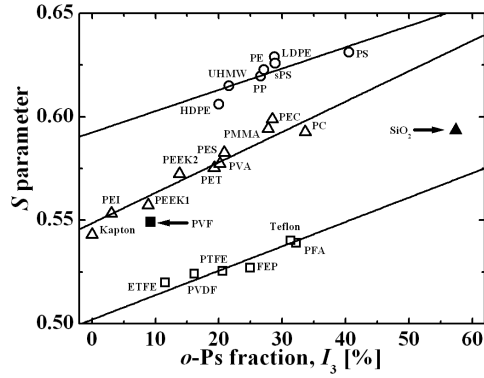


Fig. 3. Correlation between the S parameter and o -Ps fraction for C (open circles), O (open triangles), and F (open squares) groups [3, 4]. Solid lines are results of the least-squares fit for respective polymer groups. The data for SiO_2 fused quartz and PVF are newly plotted with a solid triangle and square, respectively.

(2) oxygen-containing polymers (O group), and (3) fluorine-containing polymers (F group). The strongly element-dependent correlation can be understood from the perspective that each of these three polymer groups has its own Doppler profiles of e^+ and Ps.

For Ps-forming polymers, the overall momentum distribution (P) is described as the summation of individual momentum distribution contributed from the e^+ (P_{e^+}) and Ps (P_{Ps}), as given by the equation

$$P = (1 - f)P_{e^+} + fP_{\text{Ps}}, \quad (1)$$

where f is the fraction of Ps formation. Since p -Ps and o -Ps are formed at a ratio of 1 : 3, Eq. (1) is rewritten as

$$P = P_{e^+} + f\Delta P \quad (2)$$

with

$$\Delta P = \frac{1}{4}P_{p\text{-Ps}} + \frac{3}{4}P_{o\text{-Ps}} - P_{e^+}, \quad (3)$$

where $P_{p\text{-Ps}}$ and $P_{o\text{-Ps}}$ are contributions from *p*-Ps and *o*-Ps, respectively. Equation (1) directly explains the three different lines in Fig. 3, which are characterized with different intersection points, one at $I_{o\text{-Ps}} = 0\%$, corresponding to the intrinsic S parameter of the e^+ (S_{e^+}), and one at $I_{o\text{-Ps}} = 75\%$, corresponding to the intrinsic S parameter of Ps (S_{Ps}).

In the case of the O and F groups, positrons may be attracted by the negative charge (δ^-) localized on these elements due to an inductive effect, which has already been suggested for O-containing polar groups [5, 10, 12]. As is evidenced by the high positron mobility in PE [11], this polarity effect is small for the C group, in which positron annihilation with the electrons of carbon atoms is most probable in light of the fact that the number of electrons bound to hydrogen is much smaller than the number of electrons on carbon atoms. The dips observed for PES and ETFE in the positron age around 0.6 ns well agree with the $S-I_3$ correlation (see Fig. 3) where positron annihilation with the electrons of O and F atoms occurs yielding significantly broader Doppler profiles than for C-containing polymers.

At the positron age longer than 2.0 ns in Fig. 2, where the $S(t)$ parameters are saturated, they are dominated by pick-off annihilation of *o*-Ps. One may therefore say that the saturated values of the $S(t)$ parameter are caused by the Doppler broadening of *o*-Ps pick-off annihilation, leading to the possibility to probe chemical elements surrounding free volumes by extracting the momentum distribution contributed by *o*-Ps pick-off annihilation.

For the O-containing polymers, at most 30% of constituents are oxygen and the rest are carbon or hydrogen. Thus, neutral Ps should be annihilated mostly with electrons of carbon, and consequently the *o*-Ps profile similar to that of the C group is obtained [4]. Essentially, the same values of $S(t)$ parameter at the higher age between PS and PES consistent with our earlier data [4] suggest that the chemical environment around free volumes in the two polymers are very similar to each other and are largely composed of C atoms. On the other hand, the $S(t)$ parameters of *o*-Ps for ETFE are well distinguishable from other two polymers. Remarkably low $S(t)$ parameters of *o*-Ps for ETFE compared with other two polymers at longer positron age demonstrates that the Doppler profile of the *o*-Ps pick-off annihilation process is unusually broad. The anomalous broadening of *o*-Ps indicates that the pick-off annihilation process is strongly influenced by F atoms, implying they are located around the free volumes.

It is finally worth mentioning the deviation of the data of SiO₂ fused quartz and PVF from the $S-I_3$ correlation in O and F groups (see arrows in Fig. 3). SiO₂ and PVF containing O and F atoms seem to be classified into O and F groups, respectively. As mentioned above, three polymer groups, C, O, and F groups have

their own Doppler profiles of e^+ and Ps. The distinct classification into the three polymer groups thus appears. Here we may hypothesize that *o*-Ps Doppler profiles for SiO₂ and PVF differ from the others in O and F groups, respectively, which is supposed to originate from different gradient in the $S-I_3$ correlation (see Fig. 3). At any rate the significant deviation of SiO₂ and PVF in the Doppler broadening will be the subject of our future study by AMOC.

4. Conclusion

AMOC spectroscopy was applied for the study of e^+ and Ps annihilation processes in polymers. The results were discussed together with the data of $S-I_3$ correlation. The $S(t)$ parameters indicate high values around $t = 0$ arising from self-annihilation of *p*-Ps. Significant dips in the positron age around 0.6 ns were observed for PES and ETFE due to positron trapping by polar element. The Doppler profile of *o*-Ps pick-off annihilation was found to be strongly influenced by F atoms, giving rise to anomalous broadening.

Acknowledgments

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