Characterization of the melting process of PTFE using positron annihilation spectroscopy

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Abstract. Poly(tetrafluoroethylene) (PTFE) is a semi-crystalline polymer and the lifetime of ortho-positronium (o-Ps) is known to be able to be separated into two components due to annihilation in the crystal region and in the amorphous region. The melting process of PTFE was investigated using positron annihilation spectroscopy and X-ray diffraction. The results indicated that volume expansion with an increase of temperature is dominantly due to the expansion of the amorphous region and a Ps bubble is formed at melting in both regions. The o-Ps relating to the crystal region definitely remains on the surface of crystal at the time of annihilation. The production of lower energy electrons at melting was deduced by the analysis of the Doppler broadened annihilation photopeak, and the increase in the number of such electrons was found to have great influence on the formation of the o-Ps and annihilation processes of positron and o-Ps.

1. Introduction

Whenever some properties related to the functional polymers are evaluated by using positron annihilation spectroscopy (PAS), special attention must be paid to the annihilation sites of positron and ortho-positronium (o-Ps), which is a triplet state of the electron-positron bound state. In many functional polymers, polarization due to functional groups or impurities would induce inhomogeneous formation of o-Ps and the annihilation of positron/o-Ps. We investigated the annihilation process of positron/o-Ps in perfluorinated polymer electrolyte membranes through the degradation process and found that the dominant part of o-Ps remains and annihilates near the hydrophilic site, i.e., just in the “skin” of inverse micelle that is formed by aggregation of the hydrophilic site [1], indicating that the lifetime of o-Ps is not significantly influenced by the condition of the hydrophilic site, but is sensitive to that of the micellar skeleton. Such localization of o-Ps would be caused by the presence of a local electric field due to hydrophilic groups. Because no such local electric field is found in poly(tetrafluoroethylene) (PTFE), which is a base polymer of the above-mentioned electrolyte membrane, annihilation of positron/o-Ps expects to occur homogeneously in PTFE. However, PTFE is known to be a semi-crystalline polymer, having a crystal region of hexagonal form and an amorphous region, and two types of lifetimes of o-Ps are known to be responsible for the space sizes of the crystal region and the amorphous region. PTFE is a well-known polymer that has several advantages, such as good chemical stability, high heat resistance and biocompatibility, and widespread use. The characterization of the melting process of PTFE is important not only from the academic perspective.
but also from an industrial application perspective. In such semi-crystalline polymers, special attention is on the individual behavior of the crystal region, the amorphous region and their interface during the melting process, and a recent theoretical model was also focused on the peeling of the crystal region during melting [2]. Many studies involving positrons for the characterization of PTFE have been reported so far. In particular, Dlubek et al. attempted to locate a precursor of deformation appearing on the surface of the crystal region at the phase transition in the range below the melting point [3]. In this work, the behavior of each region during melting is discussed.

2. Experimental setup

The measured sample was a homo PTFE plate brought from DAIKIN industries Ltd. In PAS, sodium-22 solution was dropped onto the sample with a thickness of 3 mm. The source was dried on the sample and then sandwiched with another homo PTFE plate, followed by wrapping with aluminum foil to prevent contamination. This source assembly was also sandwiched in between two ceramic heaters to suppress the temperature gradient and was heated to a temperature exceeding the melting point. The temperature was monitored using a thermocouple inserted between the PTFE plate and the aluminum foil. The intensity of the source was ca. 560 kBq. The temperature was controlled within a fluctuation of ±0.5 °C for the PAS and X-ray diffraction measurements mentioned below. The annihilated γ-rays were detected by the assembly of a BaF2 scintillator and a photomultiplier tube together with a conventional time measuring system using a constant fraction differential discriminator and a time to pulse-height converter. Data analysis of the lifetime was mainly performed using the PATFIT program, in which a lifetime spectrum is represented by the formula of

\[ N(t) = \sum_i \left( \frac{1}{r_i} \right) \exp \left( -\frac{t}{r_i} \right) \]

where the index \( i \) denotes each annihilation process of positron. The time resolution was approximately 290 ps throughout the measurements. Differential scanning calorimetry (DSC8270; RIGAKU) was used to evaluate the melting point. The temperature dependence of the structure was also investigated using X-ray diffraction (SmartLab; RIGAKU), where the applied temperature was monitored by the attached thermocouple to the sample.

3. Results and discussion

3.1. Differential Scanning Calorimetry (DSC)

DSC measurements were performed to evaluate the melting point. The rate of temperature increase was 10 °C per minute and endothermic peak appeared at 330 °C (Figure 1). The heat of fusion was evaluated to be 25 J/g based on the area of endothermic peak between 277.1 °C and 345.9 °C. As the heat of fusion for melted PTFE was reported to be 93 J/g elsewhere [4], the crystallinity of the sample was estimated to be 26.9 %. However, in a semi-crystalline polymer, it is better to describe the melting process based on a three-phase model consisting of a crystal region, an amorphous region and a rigid amorphous region rather than a two-phase model consisting of a crystal region and an amorphous region, and it would be difficult to evaluate crystallinity precisely by using the usual DSC. This point will be discussed in a later section.

3.2. Positron Annihilation Spectroscopy (PAS)
3.2.1. Positron Annihilation Lifetime Spectroscopy (PALS). There are many works related to the lifetime of o-Ps in PTFE; four-component analysis is known to be suitable, i.e., the lifetimes of o-Ps annihilations in the crystal region, $\tau_3$, and in the amorphous region, $\tau_4$, in addition to the lifetimes of para-Ps (the singlet of Ps), $\tau_1$, and free annihilation, $\tau_2$. Because our attention was focused on the temperature dependence of the structural change, the lifetimes shown in the following sections are restricted to the lifetimes of o-Ps. The lifetimes were also analyzed using the CONTIN program in addition to the PAFIT program to ensure the validity of the four-component analysis. Many of the lifetime spectra were confirmed to be comprised of four components; however, some spectra were decomposed into only 3 components. The number of acquired data points for each spectrum was in the range of 2 million to 3 million throughout the experiments, which might not be adequate for CONTIN. However, the longest lifetimes analyzed using CONTIN were found to well coincide with the fourth component of the PATFIT analysis. The temperature dependencies of the lifetimes of o-Ps are shown in Figure 2. A slight increase of $\tau_3$ and an evident increase of $\tau_4$ were observed between room temperature (ca. 22 ºC) and 300 ºC, which is consistent with the results of Drubek [3], whereas no significant differences were found for $I_3$ and $I_4$. These results indicate that the volume expansion of PTFE below the melting point is mainly due to the expansion of the amorphous region. In contrast, significant increases of $\tau_3$ and $\tau_4$ were observed at 335 ºC and 330 ºC, respectively. The increase of $\tau_4$ occurred at a lower temperature than that of $\tau_3$, implying that the volume expansion of the amorphous region was followed by the expansion of the crystal region. Taking into account the observation that the increase of $\tau_3$ and $\tau_4$ above the melting point are small and moderate, respectively, these abrupt changes in $\tau_3$ and $\tau_4$ would suggest the formation of positronium bubbles because the binding energy of the polymer chain is reduced greatly above the melting point and Ps is able to form a bubble by overcoming the tension of surrounding polymer chains in liquid. Above 335 ºC, $\tau_4$ increased gradually, whereas $\tau_3$ remained almost constant, suggesting that the volume expansion is primarily due to the expansion of the amorphous region above the melting point. Based on these results, it can be deduced that at melting of homo PTFE, the relaxation of amorphous region initiates volume expansion of the amorphous region and peeling of the crystal surface that retains crystallinity [2]. Two perspectives exist regarding the annihilation of o-Ps in the crystal region: annihilation inside of the crystal and annihilation on the surface of the crystal. If the former is true, then the volume expansion of the crystal region indeed occurred, and the Ps bubble also formed inside of the crystal. If the latter is true, then the Ps bubble was formed on the surface, and the inter-chain distance in crystal region was not significantly changed. This issue will be discussed again in a later section. Regarding the relative intensities, both $I_3$ and $I_4$ changed abruptly at 335 ºC; however, the following behavior contradicted each other, i.e., $I_4$ kept increasing after jumping, while $I_3$ slightly decreased after dropping. This behavior occurred because the volume fraction corresponding to the amorphous region increased and a number of positrons formed positronium here, with the help of an increase in the number of lower energy electrons, as shown in the next section, resulting in the decrease of positronium formation in the crystal region.

![Figure 2](image-url). Temperature dependencies of lifetime and relative intensity of homo PTFE.
3.2.2. Doppler Broadening Measurements. Doppler broadened spectra were also measured at several temperatures, and the representative ones are shown in Figure 3, where the dotted, solid, and dashed lines were obtained at 24 °C, 300 °C, and 340 °C, respectively. The peaking process was mild in the range from 24 °C to 300 °C. Drastic peaking was observed at 340 °C, but no additional peaking was observed above 340 °C. This remarkable change was due to melting. To investigate the significant peaking process in detail, the spectra observed at 24 °C and 340 °C were decomposed into three Gaussians distributions of different energy spreads, representing the annihilations with core electrons, valence electrons and lower energy electrons relating to thermal radicals. The three Gaussians were characterized by the energy spreads of 3.38 keV, 1.95 keV and 0.918 keV, which were determined via fitting. Taking into account that the energy spread for the peak of Cs-137 (662 keV) was 0.845 keV, the obtained lowest energy spread is found to be close to the intrinsic energy spread due to the instrument. The fitted results are shown in Figure 4. The upper figures are the raw data (open circles) and fitted curves (solid line). The proportion of the distribution characterized by the highest energy spread to the whole distribution was the lowest and quite similar between the two spectra. The major annihilation at 24 °C was characterized by the medium energy spread (1.95 keV), and the lowest energy spread was dominant at 340 °C. The increase of the lowest energy spread component means the increase of free annihilation with low energy electrons in addition to the annihilation of \( \alpha \)-Ps in the amorphous region. The increase of the number of low energy electrons, whose energy levels are almost equivalent to thermal electrons, would be useful to reprocess the materials. The intensity ratio of the lowest energy spread to the medium energy spread was 0.17 for the data of 24 °C, whereas the same ratio for 340 °C was 1.59. The annihilation rate with the lowest energy electron increased approximately 9 times at 340 °C versus 24 °C. The ratio of \( I_4 \) to \( I_3 \) in PALS was changed from 1.26 to 3.72 (3 times), but total annihilation ratio of \( \alpha \)-Ps, increased 1.7 times from 24 °C to 340 °C. Thus the low energy electron was increased in amorphous region and the formation rate of positronium in there increased approximately 2.4 times. These indicate that annihilation process of positron and formation of \( \alpha \)-Ps are greatly influenced by melting.

3.3. X-ray Diffraction (XRD).
XRD pattern obtained at 27.5 °C is shown in Figure 5. The peaks could be assigned to each reflection plane. With increasing temperature, many peaks disappeared, except the (100), (110), (200) plane peaks; these peaks were shifted toward lower angles. The temperature dependence of the diffraction peak angle for the (100) plane is shown in Figure 6. The peak shifted linearly from 18.1° to 17.5° with the increase of temperature from 27.5 °C to 326.5 °C and then decreased without shifting above the melting point. The lattice constants for the angles of 18.1° and 17.5° are 4.90 Å and 5.07 Å, respectively. To investigate the structural change of the crystal region with the increase of temperature, the crystallinity was defined as the ratio of the peak area to whole area for the (100) plane peak. The peak area was calculated by subtracting the background, which was evaluated by fitting a combination of a Lorentzian, an exponential and a constant, over the whole background area. The obtained crystallinity was approximately 90.5 % for the data of 27.5 °C. The evaluated crystallinity was quite high compared to the one evaluated using DSC. This difference is due to the reduced background, as shown in Figure 5 and is most likely a property of the semi-crystalline polymer. A detailed description regarding the differences of crystallinity among the evaluation methods is found elsewhere [4].

3.4. Comparison of the PALS and XRD
In PALS, the significant increase of τ₃ from 1.64 ns to 2.15 ns was observed at 335 °C, following a mild increase from room temperature. In XRD, a gradual decrease of the (100) peak angle (2θ) was observed up to 330 °C; however, the crystallinity remained nearly constant at approximately 88 % for temperatures increasing from room temperature to the melting point and then decreased below 80 % above the melting point. Note that the crystallinity remained at a high percentage for temperatures above the melting point.

Figure 5. XRD pattern at 27.5 °C

Figure 6. Temperature dependent X-ray diffraction from the (100) plane. Each curve for temperatures above 27.5 °C is shifted upward in proportion to the temperature increase.

Figure 7. Temperature dependence of the inter-chain distance evaluated via XRD and the diameter of FVH based on τ₃ of PALS.
no shift of the peak was observed for temperatures above 330 °C. The lifetime of o-Ps is correlated with the size of the space, i.e., the so-called free volume hole (FVH), through the Tao-Eldrup equation with the interaction range of 0.166 nm, where a positron of trapped o-Ps in FVH annihilates with an electron. The temperature dependences of the evaluated diameter of FVH and the lattice constant calculated from the peak angle of the (100) plane are shown in Figure 7. The trends of the diameter of FVH and the lattice constant are found to be similar to each other up to 330 °C, indicating that a part of o-Ps indeed remained in/on crystal region. At melting, if the crystal structure retained hexagonal form and the lattice constant expanded from approximately 5 Å to 6 Å based on the result of PALS, the corresponding diffraction peak would appear at 14.8 degrees. However, no such peak shift was observed. Thus, the drastic increase of $\tau_3$ was confirmed to be marginal with respect to an expansion of the crystal region and that the lifetime was due to the annihilation of o-Ps on the surface of the crystal region after forming the Ps bubble. It is unclear whether o-Ps was formed on the surface of crystal region or formed inside of it and leached from there; however, the dominant annihilation of o-Ps occurs on the surface of the crystal. It is remarkable that the evaluated inter-chain distances in the crystal region using PAS and XRD were very close to each other, despite the fact that o-Ps was not fully confined in the FVH but was trapped on the surface and the fact that the interaction length in Tao-Eldrup equation was the usual 0.166 nm.

4. Summary
The melting process of PTFE was investigated by PAS and XRD. Several diffraction peaks were observed in XRD at room temperature. The peaks corresponding to higher Miller indices disappeared with the increase of temperature; however, the peaks having lower Miller indices, such as (100), remained, and the peak shifts toward lower angle were observed with increase of temperature up to melting point, indicating the expansion of the crystal region. Successive peak shifting and the appearance of new peaks were not observed above the melting point. Based on the behavior of $\tau_3$ and $\tau_4$ in PAS for temperatures up to the melting point, volume expansion progressed both in the crystal region and in the amorphous region (the latter being dominant), and then the relaxation in the amorphous region at melting initiated volume expansion of the amorphous region while retaining the crystallinity in the crystal region. A remarkable increase and the following successive increase of $\tau_4$ were observed at and above the melting point, respectively, indicating the formation of a Ps bubble in the amorphous region and the volume expansion of the amorphous region above the melting point. A significant increase of $\tau_3$ was also observed at the melting point, but no successive increase was observed above the melting point. Taking into account the results of XRD above the melting point, this significant increase was certainly due to the formation of Ps bubble, indicating the annihilation of o-Ps on the surface of crystal. Based on these results, the melting process is initiated by the relaxation in the amorphous region, and then volume expansion starts together with peeling off the crystal surface. The decomposition of the Doppler broadened annihilation photopeak into three components of different energy spreads revealed a remarkable increase of the number of lower energy electrons at melting; the increase in the number of such electrons was found to have great influences on the formation process of o-Ps and the annihilation processes of positrons and o-Ps. Such information is useful for reprocessing PTFE.

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