Structural transitions of polyethylene studied by positron annihilation

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Abstract. Two kinds of polyethylene samples, low-density polyethylene and high-density polyethylene, have been studied using positron lifetime measurements in the temperature range from 96 to 370 K. Glass transitions and other secondary transitions are observed and the glass transition temperatures are determined. It has been found that the ortho-positronium lifetime and its intensity are sensitive to the transitions and the number of free-volume holes reaches a minimum near the glass transition temperature T_g. The molecular motions, the structural transitions and the crystallinity effects are discussed in terms of the properties of the free volume.

1. Introduction

Polyethylene is one of the most thoroughly investigated semi-crystalline polymers. However, because of the complex natures of the microstructure and molecular motions in polyethylene, there are still inconsistencies in some aspects of the structural properties, such as the glass transition temperature [1]. In polymers, a small percentage of free-volume distributed in the form of atomic-scale holes plays an important role in many macroscopic properties and structural changes. As the characteristics of positronium (Ps) formation and annihilation depend directly on the free-volume holes, positron annihilation spectroscopy (PAS) has proved to be a sensitive method for studying structural changes and the free-volume of polymers [2, 3]. To our knowledge, only a few positron experiments over a wide temperature range have been carried out on polyethylene [3–5]. In this paper, low-density polyethylene (LDPE) and high-density polyethylene (HDPE), which have different crystallinities, have been studied from 96 to 370 K. From the temperature dependence of the positron lifetime, we obtained some more important structural information for both the LDPE and the HDPE polymers.

2. Experiments

The polyethylene samples, i.e. the LDPE with a density of 0.912 g cm^{-3} and the HDPE with a density of 0.952 g cm^{-3}, were prepared for the positron lifetime measurements. From the densities, the crystallinity is estimated to be 43% for the LDPE and 68% for the HDPE. Before the measurements, the samples were annealed for 2 h at 100 °C in vacuum and then cooled slowly to room temperature.

A 20 μCi ^{22}Na positron source sealed by Ni foil (1 mg cm^{-2}) was placed between two discs of the same sample. Positron lifetime measurements were performed using a conventional fast–fast coincident system with high-efficiency BaF$_2$ detectors. The time resolution of the system was determined to be 235 ps from the prompt curve of a ^{60}Co source. The sample was attached to a cooling head of the liquid-nitrogen cryostat with the temperature controlled better than ±0.5 K. The temperature was varied from 96 to 370 K in intervals of 4–5 K. Half a million counts were collected for each spectrum in about 80 min.

3. Results and discussion

It has been reported that there are three or four lifetime components in the lifetime spectrum of polyethylene [4–7]. In this paper, three positron lifetimes were resolved using the computer program PATFIT [8] and gave more stable results. For both LDPE and HDPE, the shortest-lived component, $\tau_1 = 0.12 \pm 0.01$ ns, is temperature independent and attributed to the annihilation of para-positronium and Ps molecular species. The intermediate-lived component, $\tau_2 = 0.31$–0.36 ns, is assigned to positron annihilation in the defect sites of crystalline regions [6, 9]. The longest-lived component, $\tau_3 = 1.1$–2.8 ns, is attributed to the ortho-positronium (o-Ps) pick-off annihilation in free-volume holes of amorphous regions of the polymer [3, 9].
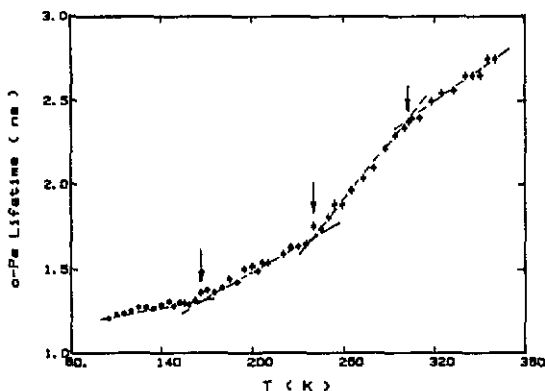

Figure 1. Temperature dependence of the o-Ps lifetime in LDPE.

For LDPE, the variations in the longest-lived component demonstrate a significant temperature dependence. From figure 1, the curve of the o-Ps lifetime versus temperature, which mainly indicates the expansion of free-volume holes [2, 5], can be approximated by neighbouring lines; thus three inflection points can be found at 160, 240 and 305 K, corresponding to the structural transitions in the amorphous regions. The inflection point at 160 K is identified as the γ-transition related to the small segment motions of polyethylene molecules, e.g. crankshaft motion [4, 5]. As a rotation of small parts of the molecules containing several carbon–carbon links [10], crankshaft motion is possible even far below the glass transition temperature. We assign the inflection point at 240 K to the result of the β-transition and glass transition. The glass transition temperature T_g of LDPE is determined to be 240 K. The glass transition is characterized by the onset of micro-Brownian motion of macromolecules.

For the highly branched molecules of LDPE, cooperative motion of large segments can be accompanied by the motion of branch points that lead to the so-called β-transition. Generally, the duration of measurement in positron lifetime spectroscopy at each temperature is over an hour, while by DSC it is less than a minute. At temperature below and near T_g, the long-time relaxation process may affect significantly the molecular structure of polymer, and in particular the relaxation of molecular chains. So T_g determined from the o-Ps lifetime is often a few kelvins lower than T_g measured by DSC experiment [2, 3] but should be closer to the actual T_g (at an infinite time of relaxation). The inflection point at 305 K, known as the excluding temperature T_e [2], is probably due to the thermal density fluctuation effect [11], which can also be observed in other polymers [12]. At temperatures above T_e, the polymer molecules have a relaxation time comparable with the o-Ps lifetime, and a Ps bubble (a new space created by Ps) can be formed, so that the variation in the o-Ps lifetime does not crucially depend on the expansion of free volume. Therefore, the dramatic increase in τ_3 with increasing temperature slows down at 305 K.
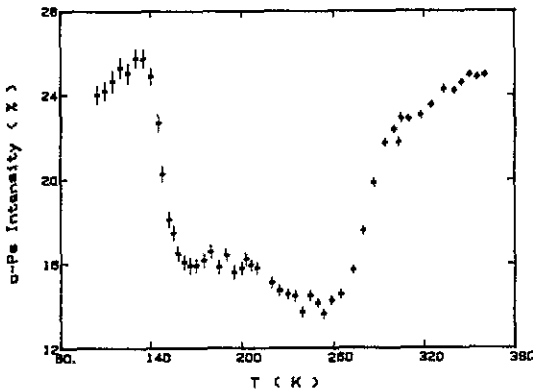

Figure 2. Temperature dependence of the o-Ps intensity in LDPE.

The o-Ps intensity I_3 in the LDPE sample as shown in figure 2 demonstrates an interesting temperature dependence. However, the obvious increase in I_3 in the initial temperature range from 96 to 120 K is not caused by thermal expansion but is due to a time effect. This time effect results from structural relaxation [4] because the annealing time of the sample from room temperature to 96 K before measurement is not long enough for LDPE to reach its equilibrium state. Since the o-Ps intensity is a relative quantity representing the number or concentration of free-volume holes [2, 5], a larger value of I_3 means that LDPE in the equilibrium state at temperatures below γ-transition temperature region contains a high concentration of free-volume holes, although the average size of these holes is very small. In temperature range from 140 to 160 K, the o-Ps intensity has a steep decrease while the o-Ps lifetime is nearly constant. This also gives evidence of the existence of a structural transition, namely the γ-transition mentioned earlier, in which process the number of free-volume holes decreases rapidly. it is well known that, below the glass transition temperature T_g, the rearrangement of polyethylene molecules is impossible; thus the observed remarkable decrease in the free-volume concentration can be explained as the result of the limited local motions of small segments. For example, the crankshaft motion of the polyethylene molecule during the γ-transition will lead to the occupation of a fraction

of free-volume holes available for Ps formation. It may be deduced from our result shown in figure 2 that the crankshaft motion occurs mainly in the temperature region from 140 to 160 K in LDPE.

Above 165 K, the o-Ps intensity I_3 shows little increase and forms a shallow valley in the vicinity of 165 K and then reduces slowly with increasing temperature until 250 K. Accordingly, the variations in o-Ps intensity exhibit a sharp minimum about 250 K which agrees well with reported work [5], as well as a secondary minimum at about 165 K which is less obvious and only observed in our work. From the dramatic changes in I_3, we conclude that the number of free-volume holes in LDPE varies sensitively with molecular motions and reaches its minimum during the glass transition. Above 250 K, the pronounced rise in o-Ps intensity which is observed shows that a large number of free-volume holes have been produced in the thermal expansion process of the post-glass-transition stage. According to the motion modes of molecular segments, the thermal expansion process can be divided into two stages [13] by the glass transition, i.e. the pre-glass-transition stage just below T_g and the post-glass-transition stage above T_g. In the former stage, the thermal expansion mechanism is mainly to enlarge the intermolecular space without the rearrangement of chains. Therefore, the average free-volume hole size increases constantly but the number of the holes is gradually reduced by the motions of thermally activated segments. In the later stage, the short-range diffusional motions of the LDPE molecules enable some of the large segments to alter the intermolecular arrangement, so that new free-volume holes with the same average size have been successively introduced in [13], corresponding to the rapid increase in o-Ps intensity above 250 K. From the discussion above, the I_3 minimum is explained as a result of the glass transition and may be expected to indicate the existence of intermolecular rearrangement in the LDPE.
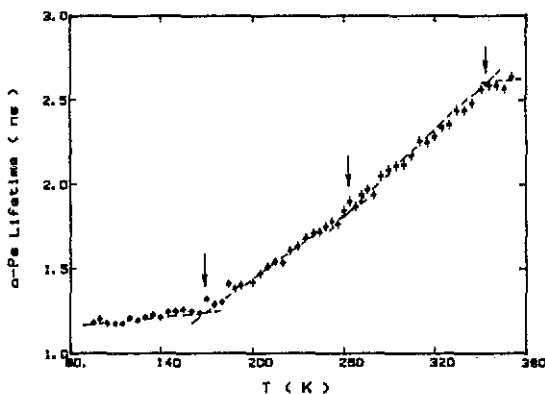

Figure 3. Temperature dependence of the o-Ps lifetime in HDPE.

In comparison with LDPE, HDPE has a much higher crystallinity because the molecules of HDPE are linear or less branched. From the results shown in figures 3 and 4, similar features have been found for HDPE in the same temperature range. This implies that the same structural changes exist in HDPE. The variations in o-Ps lifetime also show three inflection points at 165, 256 and 360 K.

As shown in figure 3, the γ-transition at 165 K is as clear as in the LDPE. This implies that the crystallinity has no obvious effect on the γ-transition characterized
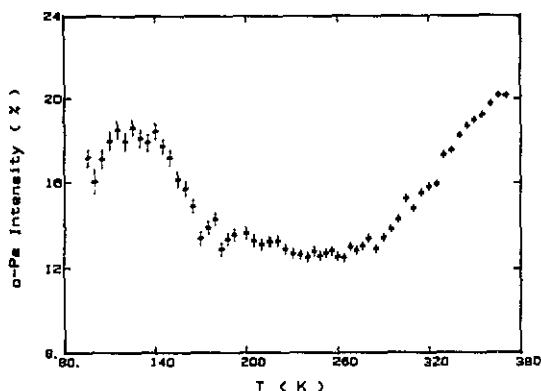
Figure 4. Temperature dependence of the o-Ps intensity in HDPE.

by crankshaft motion. The transition at 256 K is more possibly assigned to the glass transition of HDPE since the β-transition is almost missing in the highly linear HDPE. However, this inflection point of the glass transition is not so noticeable as that for LDPE. Apparently, the glass transition in HDPE is weakened because the existence of a large number of microcrystalline regions has imposed restrictions on the thermal expansion of free volume in the amorphous regions. In other words, the micro-Brownian motion of large molecular segments in the amorphous regions is partly restricted by the microcrystalline regions. T_g for the HDPE is higher than that for LDPE, showing that a higher activation energy is needed for the glass transition of HDPE. Additionally, the effect of thermal density fluctuation for HDPE is demonstrated as the highest inflection point at 360 K.

On the other hand, the variations in o-Ps intensity for HDPE show a similar temperature dependence to LDPE with a minimum near T_g and a secondary minimum near the γ-transition temperature. Nevertheless, owing to the higher crystallinity in HDPE, the o-Ps intensity of HDPE is less than that of LDPE. Again this further supports the opinion that Ps formation depends on the free-volume holes. The I_3 minimum valley of HDPE is not so sharp as that of LDPE, also giving evidence of the weakening of glass transition in HDPE.

Acknowledgment

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