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Molecular motion and relaxation below glass transition temperature in poly (methyl methacrylate) studied by positron annihilation

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HIGHLIGHTS

- PMMA was irradiated by ²²Na positron source at room temperature, 225 K and 16 K.
- Irradiation at 225 K and 16 K introduces free radicals and trapped electrons, respectively.
- Ester and main chain methyl group rotations lead to detrapping of accumulated electrons.
- A new method for detection of molecular motion below glass transition is developed.

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ABSTRACT

In this paper, we present the study of local molecular motions in poly (methyl methacrylate) (PMMA) below glass transition temperature by measuring the ortho-positronium (o-Ps) intensity. Two series of experiments were performed: (1) the PMMA sample was irradiated by ²²Na positron source with elongated time at room temperature, 225 K and 16 K, respectively, and positron lifetime spectra were measured as a function of irradiation time and (2) Positron lifetime and Doppler broadening spectra were measured as a function of temperature from 16 to 350 K after positron irradiation at 16 K for more than 350 h. While the o-Ps lifetime always shows no change with elapsed time, decrease and increase of o-Ps intensity I_3 are observed at 225 K and 16 K, which are interpreted as the result of positron irradiation-induced free radicals and trapped electrons, respectively. With temperature increasing from 16 K, there is a continuous drop of I_3 beginning at around 100 K. This is due to some local group movements such as the ester and main chain methyl group rotations, which lead to the detrapping of accumulated electrons. These local motions do not need additional free volume, so we observed no change of the o-Ps lifetime. Some other structural relaxations such as β -relaxation are also observed and discussed.

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1. Introduction

It is believed that molecular motions and their relaxations in polymers below glass transition are closely related to the mechanical properties in their glassy state (Nielsen, 1962). Upon cooling from glass transition temperature, cooperative and long range molecular motion gradually slows down, and the polymer chains are generally thought to be in the frozen state. But in this glassy state, the polymer molecules cannot be regarded as fully immobile. There are still some motions of localized, relatively small sections of the polymer chains, such as movement of some side groups. They are called secondary relaxation, and play a very important role in the mechanical properties of polymers. For

example, the mechanical toughness originates from the chain motions in the glassy state. Therefore, study of the origin of the secondary relaxation is crucial to understand the correlation between the polymer microstructure and its mechanical properties. The free volume theory has been proposed to explain the molecular motion and physical behavior of glassy and liquid states (Fox and Flory, 1951). The mobility of polymer chains is associated with the amount and size of free volume, which is the unoccupied free space between molecules. This is because the free volume provides necessary swept-out space for the movement of polymer chains and segments. From the measurement of free volume, we can obtain information about the polymer chain movements. Therefore, study of the free volume properties in polymers has become a subject of great interest over recent years.

Positron Annihilation Spectroscopy (PAS) has emerged as a powerful technique to study free volume holes in polymers (Hung

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et al., 2010; Liao et al., 2011; Zhang et al., 2012; Zhou et al., 2012; Jean et al., 2013). In porous media such as polymers, positron will combine one electron to form a bound state called positronium (Ps) atom. The Ps atoms prefer to be localized in free volume holes. According to the spin of the electron, the Ps has two states, para-Positronium (p-Ps) and ortho-Positronium (o-Ps). When the o-Ps is trapped at the free volume site, its lifetime is dependent on the free volume hole size. There is a semi-empirical relationship between the average free volume size R and the o-Ps lifetime τ_3 (Tao, 1972; Eldrup et al., 1981; Nakanishi et al., 1988):

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(2\pi \frac{R}{R + \Delta R} \right) \right]^{-1}, \quad (1)$$

The larger the free volume, the longer the o-Ps lifetime and vice versa. A good correlation between τ_3 and free volume hole has been found for hole size up to about a radius of 1 nm. The o-Ps intensity I_3 , on the other hand, contains information about the number of free volume holes. However, the relationship between them is not straightforward and care should be taken to discuss this quantity. There are many factors that affect positronium formation, such as magnetic and chemical quenching, polar groups, electric field and radiation effect. The positron irradiation effect (He et al., 2005; Djourelou et al., 2005; Yu et al., 2006; Zgardzinska et al., 2007; Zaleski et al., 2008; Nahid et al., 2011; Yang et al., 2013, 2014; Kavetsky et al., 2014; Wang et al., 2014) is one of the most common problems, which is unavoidable during the positron annihilation measurements and has been found in various polymers. After long time exposure to positron source, the o-Ps intensity may decrease or increase, while the o-Ps lifetime remains unchanged. Such effect depends on the type of polymers, positron source intensity and also the temperature. In this case, I_3 can no longer be considered to be related to the number of free volume holes.

Due to the above problems, it is somewhat questionable to use the fractional free volume derived from the o-Ps lifetime and its intensity to interpret the experimental result. In many cases, only the o-Ps lifetime result was used to discuss the structural relaxations or phase transitions in polymers. However, only the cooperative and long range molecular motions which cause variation of free volume can be observed by o-Ps lifetime measurements, for example, the glass transition and some other secondary relaxations. In this paper, we show that with careful design of the experiment, it is also possible to get much information about the local molecule movement from the change of the o-Ps intensity. We detected unambiguously the methyl group rotation in PMMA at low temperatures. Such movement cannot be detected from the o-Ps lifetime measurement, because their rotation does not need any additional free volume due to their small size.

2. Experiment

The PMMA sample has a weight-average molecular weight M_w of 2020000. The samples were cut into $10 \times 10 \times 1$ mm³ pieces and were first annealed at 393 K for 2 h to remove any thermal history, then they were kept at room temperature for several days before positron measurements.

A conventional fast–fast coincidence lifetime spectrometer was used to measure the positron lifetime spectra. The ²²Na positron source was sealed in a 7 μ m thick Kapton foil and sandwiched between two identical pieces of samples for the measurement. The intensity of the positron source is 5 μ Ci and 10 μ Ci for room temperature and low temperature measurements, respectively. The source-sample sandwich was attached to the cold finger of a He-cycling refrigerator to measure the temperature dependence of positron lifetimes.

We first studied the positron irradiation effect on PMMA sample. Positron lifetime was measured as a function of elapsed time at room temperature, then the sample was cooled to low temperature of 225 K and 16 K, respectively, and the same experiment was performed. The measurement at 225 K was repeated after heating the irradiated sample at room temperature for 12 h. Before the measurement of radiation effect at 16 K, the sample was heated again to room temperature for more than 48 h. After the sample was kept at 16 K for about 353 h, it was heated to about 350 K at a rate of 1 K/h. During this heating process, the positron lifetime and Doppler broadening spectra were also measured.

3. Results and discussion

All the measured positron lifetime spectra are decomposed into three discrete exponential components using PATFIT computer program (Kirkegaard and Pederson, 1989). Among the three lifetime components, the longest one (τ_3) is attribute to the o-Ps annihilation lifetime in the free volume holes. Therefore in this paper, we will mainly discuss this component. We will first study the positron irradiation effect, then discuss the molecular movements at low temperatures.

3.1. Positron radiation effect on Ps formation

The positron irradiation effect was performed at room temperature by measuring positron lifetime spectra as a function of elapsed time. Fig. 1 shows the variation of both τ_3 and I_3 with time at room temperature in PMMA. We found that both τ_3 and I_3 are not affected by positron irradiation. This means that there is no positron irradiation effect on PMMA at room temperature.

The interesting result is that, after the temperature is decreased to 225 K, we observe the clear decrease of I_3 with time (Fig. 2). The o-Ps lifetime is almost constant at around 1.75 ns, therefore we fixed it to 1.75 ns during the fitting in order to decrease the fluctuation of the data. After positron irradiation for more than 260 h, I_3 decreased from 23.7% to 20.4%. After that, we heated the sample to room temperature and kept for 12 h, then cooled down to 225 K again. The o-Ps intensity I_3 recovers to its initial value of 23.7% at first, and shows decrease again with elapsed time.

Such decrease of o-Ps intensity has been observed by many authors (Peng et al., 1999; Suzuki et al., 2001; Zgardzinska et al., 2007; Zaleski et al., 2008; Nahid et al., 2011). There is a general agreement that the free radicals might be the most probable reason for the decrease of I_3 (Peng et al., 1999; Suzuki et al., 2001;).

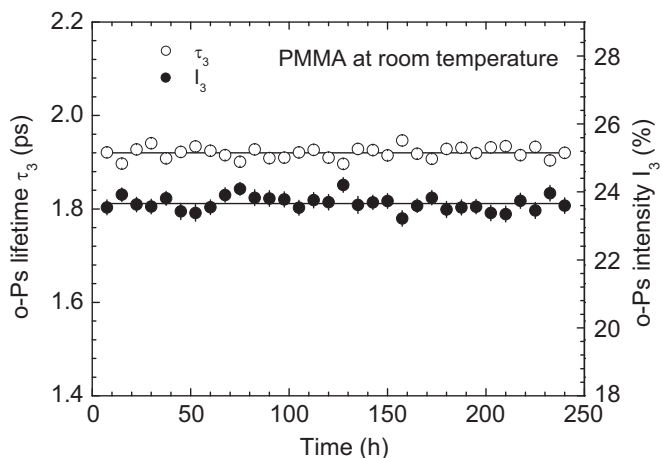


Fig. 1. Positron irradiation effect on the o-Ps lifetime τ_3 and intensity I_3 in PMMA at room temperature.

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