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EFFECT OF POLYMERIZATION DEGREE ON MICROSTRUCTURE OF POLYETHYLENE GLYCOL STUDIED BY POSITRON ANNIHILATION*

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ABSTRACT

Positron lifetimes in polyethylene glycol (PEG) polymer have been measured as a function of polymerization degree N (N = 25 - 500). It is observed that all the positron parameters are strongly dependent on N when $N \leqslant 250$, and then tend to constant levels when $N \geqslant 250$. The variations of the longest-lived component (I_3, τ_3) show that the size of free-volume holes has a minimum at $N = 100$ and the hole concentration decreases with N. These trends may be due to the variations in crystallinity, the chain ends, entanglements and the Van der Waals interaction between segments. The variations of the second component (I_2, τ_2) with N reflect the changes of defect properties in crystalline regions of PEG.

Keywords: Potitron annihilation Polyethylene glycol Free-volume hole Defect

1 INTRODUCTION

The polymerization degree N, as a fundamental parameter, essentially influences some macroscopic properties of polymers, e.g., the glass transition temperature T_g and the viscoelastic properties[1]. From the viewpoint of structure-property relation, the effect of polymerization degree on the morphology and defects of polymers should be attracted much more attention.

In amorphous regions of polymers, a small percentage of free-volume distributed in form of atomic-scale hole plays an important role in many physical processes, such as glass transition[2,3], physical aging and pressure response[4]. Positron Annihilation Spectroscopy (PAS) has been developed to be a sensitive method to probe the changes of microstructure and free-volume holes in polymers[2], due to the fact that positronium (Ps) atoms are preferentially localized and annihilate in the free-volume holes. However, for the complex microstructure and interaction between monomers

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in polymers, there were still inconsistences in the effect of N on the free-volume properties[5,6]. In this work we present the results of positron lifetime measurement on PEG as a function of N (N = 25—500). These results are combined with parameters derived from Wide-Angle X-ray Scattering (WAXS) measurement.

2 EXPERIMENT

The samples of polyethylene glycol (PEG) are commercially manufactured with a mean polymerization degree N = 25, 50, 100, 150, 250 and 500 respectively. Their chemical composition is $HO-(CH_2-O-CH_2)_N-OH$ and their crystallinities X_c and crystallite sizes were measured by WAXS[7] as shown in Table 1. All the samples were prepared under a constant pressure of 8 MPa within 10 min and had a thickness of 2 mm and a diameter of 10 mm. The positron source was 555 kBq ^{22}Na deposited on Al foil (1 mg cm^{-2}) and it was inserted between two identical samples.

Table 1

The variations of crystallinity X_c with N for PEG

N	25	50	100	150	250	500
X_c / %	63.9	79.7	81.7	82.1	82.3	76.5

The positron lifetime measurements were performed using a conventional fast-fast coincident system at room temperature 296 ± 1.0 K. The time resolution of the system was determined to be 273 ps from the prompt curve of ^{60}Co source. An area of 10^6 counts was collected for each spectrum in about 1 h.

3 RESULTS AND DISCUSSION

Three positron lifetimes are resolved for each spectrum by using program PATFIT[8], where a source correction of 7 % for Al foil is subtracted, and the variance of fit is less than 1.15. The results are shown in Figs.1—3.

3.1 Free—volume properties

The third lifetime (τ_3 = 1.8—2.3 ns) is attributed to ortho-Positronium (o-Ps)

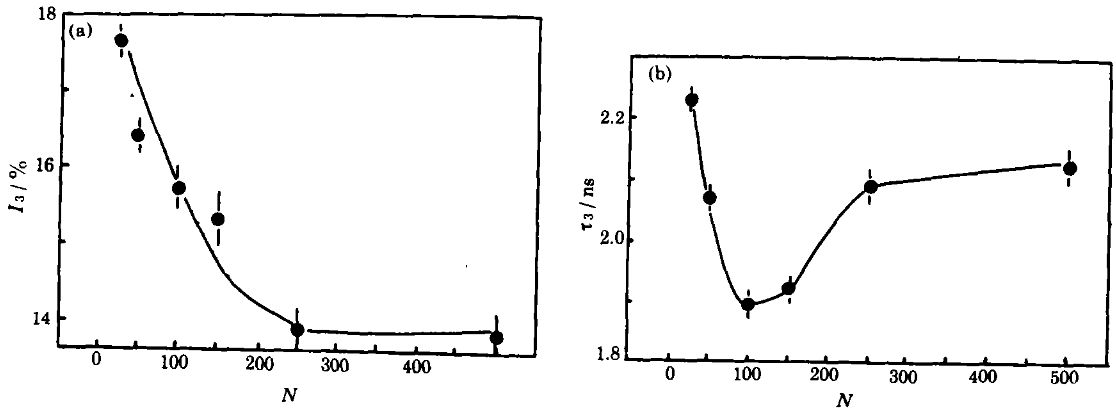

Fig.1 The variations of o—Ps intensity I (a) and lifetime τ_3 (b) with N for PEG

annihilation in free-volume holes of polymers according to the free-volume model[2], the average hole radius is approximately proportional to τ_3, and o-Ps intensity I_3 is directly proportional to hole concentration. In polymers, due to the packing irregularities of segments and the chain ends in amorphous regions, the free-volume holes are formed and provide some exceeded space for the main-chain segmental motions and the molecular adjustments[1]. The variation of I_3 in Fig.1 shows that the hole concentration decreases in the region of $N = 25—250$, and then reaches a lower level when $N \geqslant 250$. This observation arises from the following reasons: 1) The concentration of chain ends is proportional to $1/N$, therefore the concentration of free-volume holes formed due to chain ends decreases with N. At bigger N, this effect is negligible. 2) In polymers, the entanglements play the role of anchorage of segments and can effectively restrict the segmental motion[1]. From the viewpoint of statistics, the number of entanglements along a chain increases with N, which can lead to the decrease of hole concentration. 3) As shown in Table 1, the crystallinity X_c of PEG generally decreases with N during $N = 25—100$ and then tends to a constant, which suggests the weight traction of amorphous regions in total polymer decreases when $N = 25—100$ and reaches a lower level. From this factor the hole concentration is expected to decrease with N.

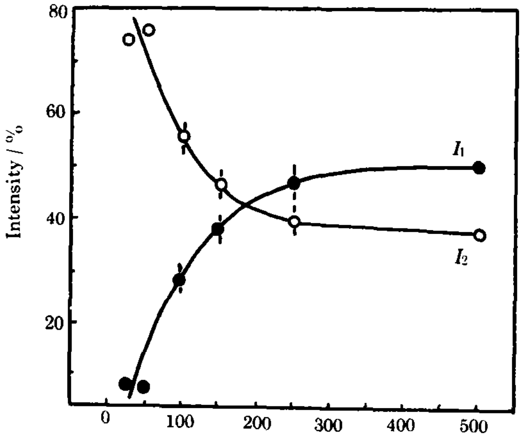

Fig.2 The variations of intensities I_2 and I_1 for PEG

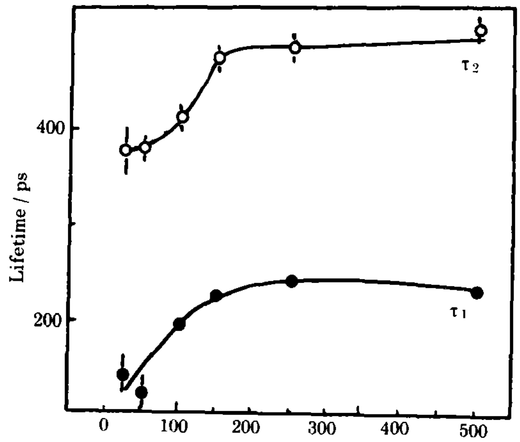

Fig.3 The variations of lifetimes τ_1 and τ_2 for PEG

The variation of o-Ps lifetime τ_3 with N provides the information on local packing structure of amorphous regions. At smaller N (i.e. $N = 25—100$), τ_3 and hole radius dramatically decrease with N, which implies the local packing density becomes larger. When $N \geqslant 100$, τ_3 increases with N and finally becomes a constant. This trend of o-Ps lifetime τ_3 is different from that of polypropylene (PP)[5], where the degree of polymerization is especially large (~ 10^4). The change of hole radius in PEG may be due to the variation of Van der Waals interaction between segments.

3.2 Defect properties in crystalline region

The second component (τ_2 = 0.37— 0.51 ns) is attributed to the defects in crystalline region. These defects are the small voids arising from the thermal perturbation and the irregular arrangement of atoms in the crystallizing process, where the density of electrons is lower than that in crystal lattice. The magnitude of positron lifetime τ_2 shows the average size of defects, while I_2 reflects the concentration of defects according to the positron trapping model[9]. From Fig.2— 3, when N increases upto 250, the concentration of defects in crystalline regions is reduced, but the average size is enhanced. When $N \geqslant 250$, both the concentration and size of defects tend to be constant.

The shortest component (τ_1 = 0.12— 0.24 ns) is due to p-Ps annihilation and positron annihilation in the bulk of crystalline region. In the vacuo, the population ratio between p-Ps and o-Ps atoms should be 1:3, while the experimental result shows $I_1 / I_3 > 1/3$. This observation shows that I_1 includes the contribution of positron annihilation in the crystal lattice.

4 CONCLUSIONS

Positron lifetimes have been measured on six PEG samples as a function of degree of polymerization N (N = 25—500). It is observed that all the positron parameters are strongly dependent on N below N = 250, however, they are irrelevant to N when $N \geqslant$ 250. Below N = 250, the concentration of free-volume holes in PEG decreases with N, which suggests the changes in crystallinity and the number of ends and entanglements of chains. When N increases, the hole size reaches a minimum at N = 100. It may be attributed to the change in the magnitude of Van der Waals interaction between segments. The number of defects in crystalline regions decreases with N, while their average size increases with N. The preaent result shows that positron annihilation spectroscopy is sensitive to probe the defect properties in both amorphous and crystalline regions of polymers.

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