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Structural transition of polyethylene oxide networks studied by positron annihilation

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ABSTRACT

Positron lifetime spectra have been measured for network polyethylene oxide (PEO) in the temperature range of 120 - 345K. The glass transition and secondary structural transition have been observed and the transition temperatures were determined. The changes of free-volume in amorphous regions and the defect properties in crystalline are discussed.

Introduction

The discovery of conductivity in polyethylene oxide (PEO)-salt complexes has led to an extensive interest to researchers. However, the main disadvantage of using high molecular weight PEO is the high crystallinity, which reduces the ionic conductivity. Attempts to increase ionic conductivity by lowering the molecular weight or the glass transition make the mechanical properties inferior. Therefore, it is very important to find a polymer which has both high ionic conductivity and good mechanical properties. In fact, recent studies have focused attention on the use of polyethylene oxide-containing block copolymers, comb polymers, crosslinked polymers, polymer blends and interpenetrating polymer networks [1] to replace the high molecular weight PEO, so as to obtain the suitable properties of chemistry and physics. In addition the ionic conductivity mainly takes place in the amorphous phase[2], so the study of relation between ionic conductivity and free-volume and the properties of free volume are very interesting.

In this paper, the structural transition of crosslinking PEO has been studied by positron annihilation parameters versus temperature.

EXPERIMENT

The network structure of PEO (the molecular weight is 1540) was prepared by slight crosslinking with trimethylol propane (TMP) after mixing of PEO and tolylene diisocyanate (TDI). A 40 μCi ^{22}Na positron source was placed between two discs of the same samples. Positron

lifetime measurements were performed using a fast-fast coincident system which has a time resolution of 245 ps from the prompt curve of a ^{60}Co source. A million counts were collected for each spectrum in about 60 minutes.

RESULTS and DISCUSSION

All lifetime spectra measured have been well resolved into three lifetime components using the computer program [3] after source correction. The variations of positron annihilation parameters versus temperature (120-345K) are shown in figures 1-4.

1. Free-volume properties

As shown in figure 1 and 2, the changes of the longest component τ_3 and I_3 demonstrate a significant temperature dependence. The glass transition temperature T_g and PEO chains melt temperature (excluding temperature) T_m are determined to be 240 K and 305 K respectively, as shown in figure 1, which are consistent with differential scanning calorimetry (DSC) [4] and also be observed in other polymers [5]. Between T_g and T_m , the size and concentration of free volume increase steeply. It can be explained as follows, when the temperature increases, the long chain segments and molecules all participate in motion owing to thermal activation (i.e., the micro-Brownian motion increases), which leads to increase of I_3 . At the same time, the higher the temperature, the easier the free volume thermal expansion, which results in the drastic increase of τ_3 . After reaching the T_m , τ_3 and I_3 increase slowly. Because the rubbery turns into a real-liquid state, so that the polymer molecules have a relaxation comparable with o-Ps lifetime and a Ps bubble can be formed by Ps, lead to the variation of I_3 and τ_3 not to crucially depend on the expansion of free volume [5-6].

The secondary relaxation at 130 K has also been observed besides T_g and T_m . This is a local non-equilibrium structural relaxation, i.e., time effect [6], because the annealing time of the specimen from room temperature to 120 K before measurement is not long enough for PEO to reach its equilibrium state. Perhaps, it results from crankshaft motion and interior rotation of methyl in benzene ring. Between 150 and 240 K, the size of free volume does not change nearly, but the concentration of free volume holes increases, which indicates that the increase of the local changes motion with increase of temperature mainly gives rise to free volume holes increase. As far as we know, it has not been reported about secondary relaxation.

2. Microstructural changes in crystalline regions

The microstructural changes in crystalline regions is more complex than in amorphous areas. It is clear that crystalline polymers are by no means perfect from a structural viewpoint. The defects which have been found to exist or postulated are as follows: point defects, dislocations and other defects ... [7]. The mechanism of relaxation behavior of semi-crystalline polymers is not very clear. The

relaxation behavior of polyethylene has probably been more widely studied than that any other semi-crystalline polymers, even though it is not completely understood so far [7] . So the relaxation behavior of crystalline regions is much complex. As far as we know, there are not reports about the relaxation behavior of PEO .

According to Authors of [8-10] , we think that the positron annihilation chiefly takes place in crystalline regions , so the positron annihilation parameters τ_2 and I_2 give direct information to the relaxation of crystalline regions .

The microstructural changes in crystalline regions can be analyzed in terms of τ_2 and I_2 of intermediate lifetime component versus the temperature. As shown in figures 3 and 4 , I_2 shows a similar temperature dependence to τ_3 with the exception of initial temperature ranges (120-140K). A peak of τ_2 and valley of I_2 at 130K are observed , this is a γ relaxation in crystalline regions . It is thought that the γ -peak may associated with the local motion of defects [11], such as chain ends , point defects and edge dislocations . They bring about the variations of τ_2 and I_2 . It is very interesting to observe the α relaxation near T_g . It perhaps results from both the motion of folding chains in lamella and twisting of stretching chains . T_g is maybe a phase transition point of crystalline region . Above T_g , I_2 increases with increases of temperature , but τ_2 continuously diminishes , which indicate that the motion of defects owing to thermal activation mainly bring about increase of concentration of their.

Fig.1 The plot of o-Ps lifetime τ_3 vs temperature for PEO

Fig.2 The plot of o-Ps intensity I_3 vs temperature for PEO

Fig.3 The plot of positron lifetime τ_2 vs temperature for PEO

Fig.4 The plot of positron intensity I_2 vs temperature for PEO

REFERENCES

- /1/ N Yak, *Macromol. Sci-phys*, B 30 (3), (1991) 225-243
- /2/ M mincer, C Berthier, W Gorecki, *J. phys*, 45 (1984) 739
- /3/ P Kirkegard, M Eldrup, O Mogensen and N Petersen, *Comp.phys.Commun* 23 (1981) 307
- /4/ Watanabe Masayoshi, Itoh Masashi, Sanui Kohei and Ogat Naoya, *Macromolecules* 20 (1987) 569-573
- /5/ Y C Jean *Microchem J*, 42 (1990) 72
- /6/ D lin and S J Wang, *J. Phys. Condensed Matter* 4 (1992) 3331-3336
- /7/ Young Robert J, "Introduction to Polymers ", (1981) London
- /8/ A V Goldanskii, V A Onishuk, and V P SHantarovich, *Phys. Stat. Sol. (a)* 102 (1987) 559
- /9/ A Chandrashekara , V Sreeramalu, H R Sreepad, V Ravindrachary , C Ranganathaiah ,and S Gopal, *Phys . Stat. Sol.(a)* 125 (1991) 509
- /10/ PKindl and G Reiter , *Phys . Stat. Sol. (a)*. 104 (1987) 707
- /11/ I M Ward, " Mechanical Properties of Solid Polymers ", Wiley-Interscience , 2nd. Ed