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Positron annihilation lifetime and gas permeation studies of energetic ion-irradiated polycarbonate membranes

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Abstract

The polycarbonate membranes of 40–50 μm thicknesses were prepared by the solution cast method. These films were irradiated by a 60 MeV, C^{5+} ion beam with the fluence of 5×10^6, 4×10^8 and 1×10^{12} ions cm^{-2}. The ion beam effects were studied by the positron annihilation lifetime technique. The *ortho*-positronium (*o*-Ps) lifetime shows an increase with the ion dose 5×10^6, 4×10^8 ions cm^{-2}. For the films irradiated to the fluence of 1×10^{12} ions cm^{-2}, the *o*-Ps lifetime falls to the lower value. The results are interpreted in terms of change in the free volume. The gas permeability measurements also indicate an increase in the free volume in the samples irradiated upto the fluence of the 4×10^8 ions cm^{-2}.

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1. Introduction

When an energetic particle passes through polymeric material, it loses energy by two main processes, namely, by interacting with target nuclei and by interacting with target electrons. The former process is called nuclear stopping and the later electronic stopping. The outcomes of the ion irradiation on the polymeric material include electronic excitations, phonons, ionization, ion pair formation, radical formation and chain scission. Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less-abundant heavier molecular species which are scission products from the pendant side groups and chain-end segments and their reaction products. Cross-linking occurs when two free dangling ion or radical pairs unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite. The magnitude of the scission and cross-linking depends largely upon the energy loss mechanism. The nuclear stopping is considered to be responsible for scission and the electronic stopping for cross-linking,

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although both processes can cause cross-linking as well as scission. The property changes in the polymers are determined by the magnitude of cross-linking and scission (Cowie, 1973).

The ion path in a polymeric material, called latent tracks, is described by a cylindrical trajectory. The trajectory has a physical core (the approximate limiting distance from the particle trajectory at which electronic excitation occurs initially). The core is surrounded by a halo (the outer most cylindrical boundary of secondary electrons, called δ-rays, released along the path of swift heavy ion (SHI) which have broad energy spectrum and cause ionization on their own) (Magee and Chatterjee, 1997). Another distance, which lies between physical core and penumbra, is called chemical radius, which defines a range where chemical reactions occur. The chemical radius is thus determined by the diffusion and reaction rates of active chemical species such as radicals, cations, anions, electrons and other activated chemical species. Shapes and sizes of track entities are first defined and then followed by the formation of active chemical species, diffusion and their interaction via chemical and coulombic forces. Some chemical species recombine and neutralize in a dense chemical sea, some diffuse out to the halo region and mix up with the species induced by the δ-rays. Most of the chemical reactions, cross-linking and scission take place near r_c where concentration of radicals and ion pairs is high due to slow migration of radicals. The radii of core and halo depend on energy per nucleon. These are of the order of 1–10 nm and 100–1000 nm, respectively (Trautmann, 1998).

The damage caused by the passage of energetic ion modifies the free volume properties of the polymeric material. The concept of free volume has significant importance for the gas permeation properties of polymeric membranes as well as for other related subjects of polymer science.

The relationship between the chemical structure and the permeation properties are not straightforward and the development of a suitable glassy polymeric membrane for a given application is still to a large extent empirical. Sometimes a minor change in the chemical structure may also affect the gas transport properties tremendously. However, while considering gas transport data obtained on polymers with various structures, it has been shown that the greater the free volume content or the fractional free volume (FFV), the greater the permeability coefficient P. A linear relationship between $\ln P$ and $(\mathrm{FFV})^{-1}$ has been reported (Mohr et al., 1991; McHattie et al., 1991). Similar trends have been reported for the diffusion coefficient (Maeda and Paul, 1987).

The effect of chemical structural variations in various glassy polymers on gas transport has been investigated in many studies (Toi et al., 1995). In addition to the free volume content (related to the chain packing), the gas transport parameters have been shown to be influenced by the chain rigidity (or flexibility), the segmental mobility, the interchain distance, and the chain interactions.

For gas separation applications, a polymer should have both high permeability and high permselectvity. In typical polymer materials, higher permeabilities are usually connected with lower permselectivities, and vice versa (Fried Joel, 1999). In order to achieve good membrane performance, the polymer should ideally possess two particular characteristics: a high fractional free volume and a narrow free volume distribution. This can be achieved in two ways: (a) chemically modifying during synthesis, using polymer structure–properties relationship, and (b) physically improving the membrane structure, for example, by ion irradiation. In the present study, the improvement in the gas separation properties of membranes is attempted through SHI bombardment.

The positron annihilation lifetime (PAL) spectroscopy is capable of probing free volumes directly. The atomic scale free volume holes are detected on the basis that the positronium (Ps) atoms are formed and localized in the free volume holes (Shrader and Jean, 1988). The orthopositronium (o-Ps) lifetime has a strong correlation with the size of the free volume. The annihilation of o-Ps in the spherical free volume hole is described by simple quantum mechanical model of spherical potential well with an electron layer thickness of ΔR. The semi-empirical relation between radius of the free volume hole R and o-Ps lifetime is given by

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right)^{-1}, \quad (1)$$

where $R_0 = R + \Delta R$ and $\Delta R = 1.66$ Å. ΔR has been determined by fitting the experimental values of τ_3 obtained for the materials with known hole size (Nakanishi et al., 1988).

2. Experimental

2.1. Membrane preparation

The polycarbonate (PC) used for the present study is a glassy polymer, which contains a bisphenol-A residue. The bisphenol-A moiety provides the necessary backbone rigidity. The 40–50 μm thick membranes were prepared by solution cast method. The material was dissolved in dichloromethane (CH_2Cl_2) and a 5% solution was prepared. The solution was then put into flat-bottomed Petri dishes floating on mercury. The solvent was allowed to evaporate slowly over a period of 10–12 h. The films so obtained were peeled off and dried in vacuum at 60 °C for 24 h in order to ensure the removal of the solvent.