Free Volume in Poly(*n*-alkylphenylsilane) Probed by Positron Annihilation

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Free volume characteristics in poly(*n*-alkylphenylsilane)s whose *n*-alkyl side-group was changed from methyl to *n*-dodecyl were investigated by positron annihilation technique at room temperature. The average radii of free volume increase in two steps, one is observed with an increase in the length of *n*-alkyl side-groups from methyl to *n*-pentyl, the other from *n*-hexyl to *n*-dodecyl with an interruption between *n*-hexyl and *n*-pentyl. The radius in poly(*n*-hexylphenylsilane) is smaller than that in poly(*n*-pentylphenylsilane). This agrees with the result of the theoretical calculation that *n*-hexyl side chain is entangled leading to suitable packing in the literature.

Keywords: polysilane, positron annihilation, lifetime, free volume

1. Introduction

Organopolysilanes are chain-like polymers with silicon (Si) backbones and two organic substitutes. These polymers show interesting properties, such as intense near-UV absorption [1], high efficient photoluminescence [1], photoconductivity [2–4], non-linear optical effects [5]. These properties arise from the delocalization of Si-Si σ -electrons along the main chains, called σ -conjugated systems [6]. One of the most attractive properties is the high value of hole drift mobility, *ca.* $\mu=10^4$ cm²V⁻¹s⁻¹. The value of mobility in a typical polysilane is two order of magnitude higher than that in conventional side-chain- π -conjugated polymers, e.g. poly-*N*-vinylcarbazole (PVC). It suggests that polysilanes have potentials for application as new electro-optical materials.

The predominant process of charge carrier transport in polysilanes is attributed to the hopping of holes between localized states originated from domain-like subunits along their Si main chain. Hole transport process is affected by molecular weight [7], side-chain [8–9], hopping site energy associated with the length of domain-like subunits in the backbone [7,10–11], and intermolecular distance (free volume) in amorphous materials.

Bässler suggested that the disorder formalism as charge transfer property in amorphous solid is mainly controlled by two factor, the width of Density of States (DOS) of hopping sites and the fluctuation of hopping site distance [12]. Average radius of free volume in polymer can be correlated with the hopping site distance. Thus the characterization of free volume using the positron annihilation lifetime spectroscopy (PALS) is expected to provide an understanding of the charge transport processes in polysilanes.

The structures of poly(di-*n*-alkylphenylsilane)s are carefully investigated because of their high degree of crystallization [13–16]. However, in the measurement of the photoconductivity of these materials, a possibility of selective charge transport through crystal parts confuses the analysis of the charge transport by disorder model. Thus in this study we used poly(*n*-alkylphenylsilane)s which are optimum amorphous polymers.

The positron annihilation techniques have been developed as useful methods to detect micro defects in materials [17]. PALS provides information about the electron density in materials. A positron loses its kinetic energy in materials by inelastic collision and achieves thermal equilibrium (so called thermalization) in much shorter

time (a few pico seconds) as compared to the positron lifetime. After the thermalization it diffuses through the lattice and annihilates with an electron in materials. The annihilation rate reflects the electron density in its immediate microenvironment. Positrons can be trapped by vacancies or defects efficiently and their lifetime becomes longer with decreasing electron density. In amorphous polymers, a large fraction of positron can form a bound state with electron known as positronium (Ps), which is trapped in the free volume. The *o*-Ps (triplet state) lifetime or pick-off annihilation rate reflects the size of the free volume. This is the only way to characterize free volume directly. Therefore, PALS is a powerful technique in detecting the free volume with atomic sizes.

In this study, the dependence of the free volume in poly(*n*-alkylphenylsilane)s on the size of the *n*-alkyl substituent was investigated by changing it from methyl to *n*-dodecyl.

2. Experimental and Data Analysis

n-Alkylphenyldichlorosilanes were synthesized by the reaction of phenylmagnesium bromide with the commercially available *n*-alkyltrichlorosilanes. In a typical reaction a phenylmagnesium bromide solution was prepared from Mg and bromobenzene in diethyl ether. The Grignard solution was syringed into *n*-alkyltrichlorosilane in diethyl ether under intensive stirring. After stirring overnight each monomer was distilled under vacuum to give pure *n*-alkylphenyldichlorosilane. NMR identification of these monomers was carried out by JEOL EX-270 NMR spectrometer at 270 MHz. Polymerization was carried out by the conventional sodium condensation method from each monomer. The monomer was added into a reaction vessel and mixed with sodium in toluene for 4-6 hours at 398 K in Ar atmosphere [1]. Obtained polymers were precipitated using isopropyl alcohol after filtration to roughly remove NaCl, and the precipitates were dried under vacuum, respectively. Toluene solution of the polymer was washed by water, and precipitated with tetrahydrofuran-isopropyl alcohol mixture. The molecular weight distributions in these polymers were also measured with a Shimadzu C-R3A gel permeation chromatography (GPC) system with polystyrene calibration standards.

Figure 1. Molecular structure of poly(*n*-alkylphenylsilane).

$$R = \text{CH}_3(\text{CH}_2)_m \quad (m=0-11)$$

Thermal analysis with a Shimadzu DSC-60 differential scanning calorimeter (DSC) was carried out to collect information about the phase transition and enthalpy of each sample. Density of amorphous solid polysilane is also measured by the specific gravity method.

The ^{22}Na positron source ($< 7.4 \times 10^5$ Bq) in Kapton foil was sandwiched between the samples in holders. The apparatus consisted of two BaF_2 scintillation counters coupled to photomultipliers, for detecting 1.28 MeV γ -rays as start signals and the 511 keV annihilation γ -rays as stop signals. Timing signal was produced by a constant fraction discriminator and the difference in the timing was measured by a time-pulse height converter using appropriate delay. Data were accumulated over 1×10^6 counts [18]. The resolution was evaluated as 270 ps. This measurement was carried out at room temperature.

Data analysis was carried out using PATFIT program [19]. The positron lifetime and correlating intensity were evaluated. A source component 382 ps (5 %) obtained by analyzing a super pure aluminum spectrum was used for source correction. In order to evaluate free volume hole size, a semi-empirical equation between *o*-Ps lifetime and hole radius that is considered to be a spherical wall with infinite potential barrier was used which is given in the followings,

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

where τ_3 is *o*-Ps pick-off lifetime (ns), R the radius of free volume hole (nm), $R + \Delta R$ the radius of the hypothetical spherical wall where Ps exist, and ΔR the homogeneous electron layer thickness which is the empirical parameter of 0.166 nm fitted from *o*-Ps lifetime measurement of known cavity size

[22].

3. Results and Discussion

Table 1 summarizes the weight average molecular weight, the molecular weight distribution, and the density of poly(*n*-alkylphenylsilane)s respectively.

Table 1. Molecular weight (M_w), its distribution, and density of poly(*n*-alkylphenylsilane)s

entry	M_n	M_w/M_n	density (gcm^{-3})
poly(methylphenylsilane)	3.2×10^4	2.38	1.18
poly(ethylphenylsilane)	3.4×10^6	2.18	1.13
poly(<i>n</i> -propylphenylsilane)	5.2×10^2	1.06	1.09
poly(<i>n</i> -butylphenylsilane)	2.0×10^3	1.42	1.06
poly(<i>n</i> -pentylphenylsilane)	1.7×10^6	2.00	1.02
Poly(<i>n</i> -hexylphenylsilane)	1.5×10^6	1.59	1.02
Poly(<i>n</i> -heptylphenylsilane)	1.3×10^3	1.68	1.01
Poly(<i>n</i> -octylphenylsilane)	1.2×10^6	2.26	1.01
Poly(<i>n</i> -decylphenylsilane)	8.8×10^5	2.26	0.990
Poly(<i>n</i> -dodecylphenylsilane)	4.2×10^5	3.35	0.994

The molecular structures of poly(*n*-alkylphenylsilane)s are shown in Fig. 1. PALS data were resolved into three components. The shortest lifetime component (τ_1) of ~190-230 ps is ascribed to *p*-Ps (singlet state) along with other short-lived components, an intermediate component (τ_2) of ~580-780 ps is ascribed to free positron, and the longest component (τ_3) of a few ns is ascribed to *o*-Ps pick-off annihilation which provides information on free volume.

Figure 2. The plots of τ_3 in poly(*n*-alkylphenylsilane)

Figure 3. Average radius of free volume in poly(*n*-alkylphenylsilane).

The values of τ_3 in poly(*n*-alkylphenylsilane)s are plotted in Fig. 2. These values are found to be shorter than the vacuumed lifetime of *o*-Ps. Thus these annihilations can be associated with the pick-off annihilation of *o*-Ps trapped by the free volume. The τ_3 gives information on the average radius of the free volume based on eq. (1), and the calculated values of radius are plotted in Fig. 3. The average radius gradually increases with an increase of *n*-alkyl substitute length, however an interruption of the increase is observed between *n*-pentyl and *n*-hexyl. A steep decrease in the radius is seen between *n*-pentyl and *n*-hexyl. The radius increases again with increasing carbon number from *n*-hexyl to *n*-dodecyl. It was reported that the size of free volume is independence on molecular weight [20]. We observed a continuous increase at the first step from methyl to *n*-pentyl though their molecular weight varied from

Figure 4. Intensity of τ_3 in poly(*n*-alkylphenylsilane)

$\sim 10^4$ to 10^6 , supporting that the radius of the free volume is independent of the molecular weight of the polymers. Thus the molecular weight dependence was neglected in this study. It was also reported that *n*-hexyl side chains in poly(di-*n*-hexylsilane)s are slightly tilted to minimize intermolecular sterical interactions [21]. In spite of the difference of side chains between poly(*n*-alkylphenylsilane) and poly(di-*n*-alkylsilane), it can be surmised that longer *n*-alkyl side groups than *n*-hexyl are tilted.

Intensity (I_3) of the longest component (τ_3) is shown in Fig. 4. With an increase in the length of *n*-alkyl side groups, the number of free volumes decreases, and reaches minimum value (10 %) in poly(*n*-butylphenylsilane). And it increases to approach a constant value around 25% for the alkyl chains longer than *n*-hexyl. This might be related to solid state structure of the polysilanes. However it is uncertain at the moment. Small and broad thermal absorptions are often observed between 173K and 473 K by the DSC measurement.

Figure 5. DSC thermograms of poly(*n*-alkylphenylsilane)s

DSC thermograms were shown in Fig. 5. It is guessed that these small peaks are attributed to the thermal motion of the *n*-alkyl side chains, not to the conformational change of the polymer backbones.

Assuming that the intensity (I_3) gives the number of free volumes per unit volume, we can compute the free volume fraction i.e. the ratio of the free volume to the total volume of polymer in the following way,

$$f_v = \bar{C} \cdot I_3 \cdot \bar{V} \quad (2)$$

where $\bar{V}$ is the average free volume, $\bar{C}$ is a constant (here $\bar{C}=1$ for relative comparison). The calculated value of f_v are shown in Fig. 6.

Figure 6. The ratio of the free volume to the total volume (●), and inverse of density (▼) of poly(*n*-alkylphenylsilane)s.

It can be seen that the free volume fraction increases with an increase in the *n*-alkyl side chain length. The specific volume data (inverse of density) also shows a similar trend. The value of f_v actually reflects the specific volume data in the present system.

4. Conclusion

Poly(*n*-alkylphenylsilane)s with *n*-alkyl side chains from methyl to *n*-dodecyl were synthesized. Free volume characteristics in these polysilanes were investigated by the positron annihilation technique. The average radius of the free volume increases in two stages, from methyl to *n*-pentyl, and, from *n*-hexyl to *n*-dodecyl with a break between *n*-pentyl and *n*-hexyl. This experimental

results support a reported theoretical calculation meaning that higher *n*-alkyl side chains are entangled leading to better packing. The results also suggest that *n*-hexyl group has the most compact packing due to a special intermolecular attraction. The ratio of the free volume to the total volume of polymers actually reflects the specific volume data in the present system.

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