



Free volume behavior in spincast thin film of polystyrene by energy variable positron annihilation lifetime spectroscopy

S. Ata^a, M. Muramatsu^{a,b}, J. Takeda^a, T. Ohdaira^a, R. Suzuki^b, K. Ito^b, Y. Kobayashi^b, T. Ougizawa^{a,*}

^a Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

^b National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

Article history:

Received 2 February 2009

Received in revised form

21 April 2009

Accepted 26 April 2009

Available online 6 May 2009

Keywords:

Polystyrene thin film

Free volume

Positron annihilation lifetime spectroscopy

ABSTRACT

Free volume behavior in polystyrene thin films with thickness ranging from 22 to 1200 nm on silicon substrates was studied by energy variable positron annihilation lifetime spectroscopy (EVPALS). The films were prepared by spincasting from toluene solutions of 0.5–5.0 wt% polystyrene with $M_w = 1\,090\,000$ g/mol. Distinct deviations from bulk polystyrene in thermal expansion of the free volume holes and the glass transition temperature associated with free volume behavior were observed for the thinnest film with 22 nm thickness, indicating its exclusively high chain mobility. Comparison of the polystyrene concentration in the precursor solution around the overlap concentration suggests that the high chain mobility is due to less entangled chains caused by rapid removal of the solvent from the diluted solution in order to prepare very thin film.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Recent investigations on spincast ultrathin polymer films on substrates have revealed various results in the thermodynamic properties [1–5]. Based on experimental results obtained by advanced techniques such as quasi-elastic neutron scattering [6,7], lateral force microscopy [8,9], dielectric relaxation [10,11], ellipsometry [2,12–14] etc. important roles played by the film surface and film-substrate interaction have been suggested and emphasized. For example, frequently observed depression of relaxation temperature in polymer films thinner than the corresponding coil size has been related to the chain end-groups with higher degree of freedom at the film surface. However, conflicting experimental data have been often reported for the same polymer with similar thicknesses, and it is likely that not only film thickness but also spincasting conditions have an important effect on the nanoscopic structure of polymeric ultrathin films.

One can probe free volume holes with nanometer size, which influence the molecular motions and thermodynamic properties of polymer thin films, with energy variable positron annihilation lifetime spectroscopy (EVPALS) [15,16]. Application of this technique relies on the fact that some of the positrons implanted into a polymer combine with an electron to form the hydrogen-like bound state, positronium (Ps). In polymers there exist three states of positrons

characterized by lifetimes τ_1, τ_2, τ_3 : spin antiparallel *para*-positronium (*p*-Ps) with $\tau_1 \sim 125$ ps, a free positron with $\tau_2 \sim 450$ ps and spin parallel *ortho*-positronium (*o*-Ps) with $\tau_3 \sim 1$ –10 ns. The longest-lived component is of particular importance to the polymer studies, because the lifetime τ_3 is related to the average free volume hole size [17–19]. The relationship between τ_3 and average radius r [nm] of free volume holes in spherical approximation is given by the Tao-Eldrup model as:

$$\frac{1}{\tau_3} = 2 \left[1 - \frac{r}{r_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi r}{r_0} \right) \right] \quad (1)$$

where $r_0 = r + \Delta r$ and $\Delta r = 0.166$ nm is the thickness of the homogenous electron layer in which the positron in *o*-Ps annihilates via the so-called pick-off process [20]. Free volume size V_f in nm^3 is calculated as:

$$V_f = 4\pi r^3 / 3 \quad (2)$$

The advantage of EVPALS over most other techniques is that one can probe thin films with varying thicknesses nondestructively by tuning incident positron energy so that all the positrons are stopped inside the film and annihilated therein. Implantation depth distribution $P(z)$ of positrons with energy E [keV] inside the polymer is expressed by the Makhovian equation [21]:

$$P(z) = \frac{d \left[\exp(-z/z_0)^2 \right]}{dz} \quad (3)$$

* Corresponding author. Tel./fax: +81 3 5734 2423.

E-mail address: tougizaw@o.cc.titech.ac.jp (T. Ougizawa).

with

$$z_0 = \frac{80 E^{1.6}}{\sqrt{\pi} \rho} \quad (4)$$

Here z [nm] and ρ [g/cm³] are the positron implantation depth and film density, respectively. The mean implantation depth Z_m is given by:

$$Z_m = \frac{\sqrt{\pi}}{2} z_0 \quad (5)$$

Thus for example at $E = 0.4$ keV $Z_m = 8.8$ nm and at $E = 4.0$ keV $Z_m = 350$ nm. The distributions of implanted positrons at these two energies are shown for $\rho = 1.05$ g/cm³ in Fig. 1.

In this investigation, we apply EVPALS to spincast polystyrene films with thickness ranging from 22 to 1200 nm to study the effect of not only film thickness but also spincasting conditions on free volume. There was some discrepancy in previous EVPALS studies of thin polystyrene films, where no detailed information other than thickness and molecular weight was provided on the samples [22–24].

2. Experimental

2.1. Sample preparation

Thin films of polystyrene (TOSOH, $M_w = 1090000$ g/mol, $M_w/M_n = 1.03$) with thickness ranging from 22 to 1200 nm were prepared by spincasting of toluene solutions onto clean silicon wafers and subsequent annealing at 120 °C for 24 h under vacuum. Prior to spincasting, native oxide on the silicon wafers had been removed by treatment of the surface with 1.0 wt% HF solution. To control the film thickness, polystyrene concentration in the precursor solution and revolution rate at spincasting were varied from 0.5 to 5.0 wt% and from 500 to 2000 rpm, respectively. Film thickness was measured with a spectroscopic ellipsometer (Otuka Electronics CO.,LTD.; FE5000S). Thickness of the prepared films, polystyrene concentration in the precursor solution and revolution rate at the spincasting are listed in Table 1.

2.2. Positron lifetime measurements

EVPALS was carried out by utilizing the intense pulsed-positron beam at the National Institute of Advanced Industrial Science and

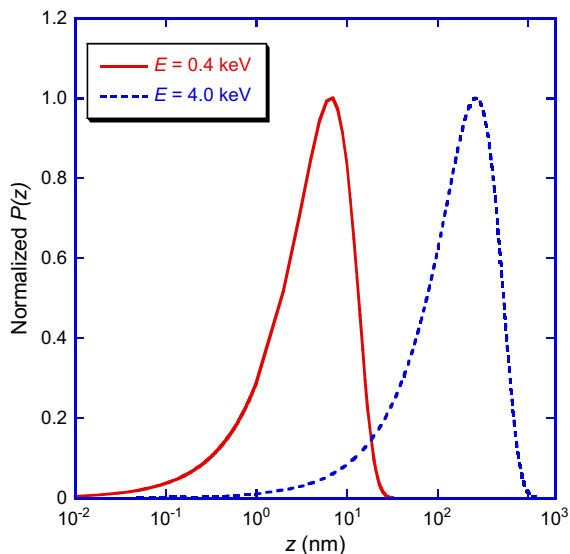


Fig. 1. Normalized probability functions of positron implantation depth at $E = 0.4$ keV and 4.0 keV for a density of $\rho = 1.05$ g/cm³.

Table 1

Spincast polystyrene thin film samples and their preparation conditions. C: polystyrene concentration in the precursor solutions. R: revolution rate at spincasting. E: incident positron energy. Z_m : mean implantation depth of positrons.

ID	Thickness (nm)	C (wt%)	R (rpm)	E (keV)	Z_m (nm)
A	1200	5.0	500	4.0	350
B	156	2.0	2000	1.5	73
C	56	1.0	2000	0.8	27
D	22	0.50	2000	0.4	8.8

Technology in Tsukuba, Japan. Positrons generated with a linear accelerator were converted to a DC beam from which positron pulses with a time spread of about 100 ps were produced by chopping and bunching. Lifetime spectra were recorded by determining the time interval between the timing signal from the pulsing system and the detection of an annihilation γ -ray by a BaF₂ scintillation detector, as detailed elsewhere [25]. Positron lifetime was measured under a vacuum of 10⁻⁶ Pa with increasing temperature from 25 to 180 °C. The observed positron lifetime data were fitted to a sum of three exponentially decaying components convoluted with a Gaussian resolution function to estimate the longest-lived lifetime τ_3 [ns] due to the pick-off annihilation of *o*-Ps. From τ_3 , free volume hole size V_f [nm³] was evaluated based on Eqs. (1) and (2) [18]. Depending on film thickness, positron incident energy E was varied from 0.4 to 4.0 keV, so that the film is entirely probed along depth. The incident energy and corresponding mean positron implantation depth are included in Table 1.

3. Results and discussion

Fig. 2 shows the temperature dependence of free volume hole size V_f derived from *o*-Ps lifetime τ_3 for the 1200 nm thick polystyrene film. With increasing temperature, V_f increases from 0.10 to 0.20 nm³ due to thermal expansion, similarly to bulk polystyrene [18]. Onset of the micro-Brownian motion of the polymer chains is clearly visible as an abrupt change in the slope of V_f around 100 °C. The concept of glass transition, that the movement of the center of gravity in polymer chains is frozen, may not be applicable to thin films as is. For this reason we regard the characteristic temperature in Fig. 2 as the glass transition temperature specifically associated with free volume behavior ($T_{g,f}$). We also note that V_f depends less on temperature above 180 °C. At sufficiently high temperatures, the

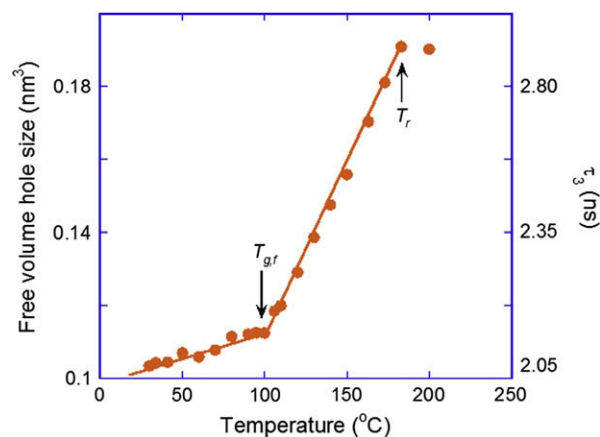


Fig. 2. Change of free volume hole size with temperature in polystyrene film with 1200 nm thickness derived from the *o*-Ps lifetime measured at a positron incident energy of 4.0 keV. The glass transition temperature associated with free volume behavior ($T_{g,f}$) was determined as an intersect point of two straight lines obtained by least squares fitting.

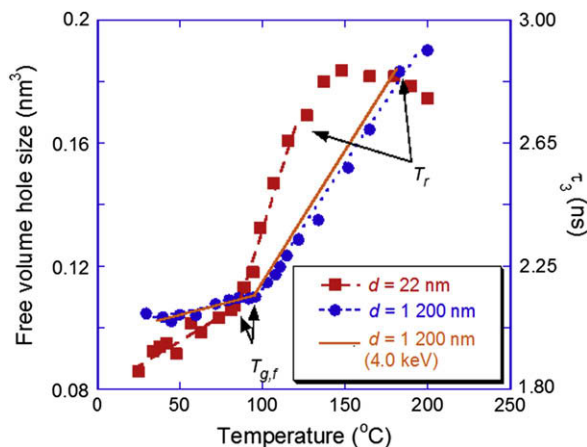


Fig. 3. Change of free volume hole size with temperature in polystyrene film with 22 nm thickness derived from the *o*-Ps lifetime measured at a positron incident energy of 0.4 keV. Also the data of polystyrene film with 1200 nm thickness measured at a positron incident energy of 0.4 keV are included. The solid line indicates the data for the 1200 nm thick film at $E = 4.0$ keV in Fig. 2. The glass transition temperatures associated with free volume behavior ($T_{g,f}$) are 84 and 100 °C for 22 nm and 1200 nm thick films, respectively.

cohesive force of polymer chain becomes weak, and then it cannot make resistance for energy of Ps. This enables Ps to dig a hole called a bubble around itself above a characteristic temperature (T_r) [26]. Our data suggest that this characteristic temperature for Ps bubble formation is around $T_r = 180$ °C in the 1200 nm thick polystyrene.

Fig. 3 shows the variation of V_f in the 22 nm thick film with temperature. The behavior of V_f is obviously different from one of the 1200 nm thick film; at low temperatures, it is smaller and at high temperatures below 160 °C, it is substantially larger. Moreover, T_r shifted down to 120 °C and the thermal expansion rate of V_f dramatically increases below T_r . Figs. 4 and 5 show $T_{g,f}$, T_r and coefficients of thermal expansion (CTE's) of V_f for all the films measured in this work, respectively. Clear deviations from bulk polystyrene occur only for the thinnest 22 nm thick film, where $T_{g,f}$ and T_r are depressed by 16 °C and 70 °C, respectively, and CTE's increase up to 3 times in comparison with the thicker films.

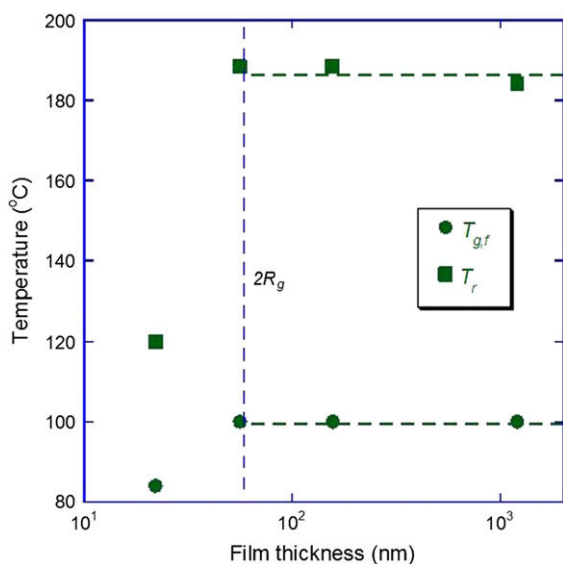


Fig. 4. Film thickness dependence of the glass transition temperature associated with free volume behavior ($T_{g,f}$) and characteristic temperature of Ps bubble formation (T_r) in polystyrene film.

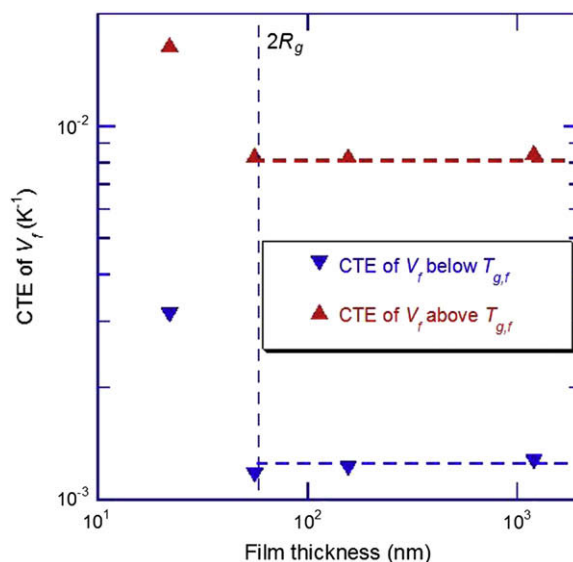


Fig. 5. Film thickness dependence of coefficient of thermal expansion (CTE) in polystyrene film. ▼: CTE below $T_{g,f}$, ▲: CTE above $T_{g,f}$.

It has been discussed that the peculiarity of ultrathin polymer films appeared, when their thickness became smaller than $2R_g$. Here R_g is the characteristic radius of gyration and is given by the following relation [27].

$$\langle R_g^2 \rangle^{1/2} = \sqrt{\frac{Nb^2}{6}} \quad (6)$$

Here N and b are the number of Kuhn monomers and their effective bond length, respectively. The peculiarity of ultrathin films such as depression of $T_{g,f}$ is often attributed to the enhanced chain motions in a region of the order of the corresponding coil size due to the enrichment of chain end-groups at the film surface. For polystyrene with $M_w = 1\,090\,000$ g/mol $N = 1514$ and $b = 1.8$ nm so that $\langle R_g \rangle^{1/2}$ is about 30 nm. Hence among the present samples, only the film with 22 nm thickness was relatively thinner than $2R_g$ and our results appear to be consistent with the above argument based on film thickness.

Kajiyama et al. [28] studied visco-elastic characteristics of surface in polystyrene films by lateral force microscopy. They revealed that T_g at the surface up to a few tenths nanometers depth in polystyrene with $M_w = 10^6$ g/mol was about 30 °C lower than one of bulk polystyrene regardless of overall film thickness. Based on molecular weight dependence of T_g , these authors concluded that depression in T_g is due to the higher degree of freedom of the chain end-groups at the surface. We probed the free volume at a near surface region of the 1200 nm thick film with the positrons of $E = 0.4$ keV, for which the mean implantation depth is approximately 8.8 nm (Table 1). As seen in Fig. 3, the behavior of V_f at each temperature agrees well with that probed with the positrons of $E = 4.0$ keV. This suggests that the surface effect is not influential at depths around 8.8 nm from the surface in thick film and the effect plays an important role in the region less than 8.8 nm. Hence beneath the surface of this film with $T_{g,f}$ dropped by about 30 °C is a layer with the same free volume as bulk polystyrene. On the other hand, beneath the surface of the 22 nm thick film is a layer with $T_{g,f}$ suppressed by about 16 °C and free volume three times more expandable than bulk polystyrene.

Apart from the surface effect, the segmental mobility increased in a polymer with less entangled chains. It is predicted that the density of the chain entanglements in a spincast film may be related to

polymer concentration of the precursor solution comparable to overlap concentration (C^*), which is the boundary concentration separating the regimes of isolated and overlapped chains in a solvent. We determined the overlap concentration of toluene solution of polystyrene used in this study to be 0.50 wt% by viscosity measurements [29]. At a concentration above C^* the chains are well entangled in the solution. As the concentration decreases, the molecular coil from a polymer chain becomes isolated at C^* [30]. Hence the films spincast from solutions more concentrated than C^* may consist of entangled chains, whereas those from diluted solutions at high revolution rates in the spincast are supposed to be less entangled. The polystyrene concentrations in the precursor solutions of the 56, 156 and 1200 nm thick films are much higher than 0.50 wt%, so that all of them have entangled chains and properties similar to bulk polystyrene. On the other hand, the polystyrene concentration of the precursor solution to prepare the film with 22 nm thickness is 0.50 wt% and comparable to C^* . Rapid elimination of the solvent during spincasting of this film leaves less entangled chains, which may be responsible for its peculiar behavior. It may be that one cannot make the thin film with less $2R_g$ thickness, which has the same entanglement density as bulk state, namely the entanglement density in thin films with less $2R_g$ thickness should be less than that of polymer bulk regardless of how to make. Also it should be emphasized that depressed $T_{g,f}$, T_f and distinctively expandable free volume observed in this work can be explained well by the less entangled chains of the film.

So far thermodynamic properties of ultrathin polymer films have been discussed with respect to film thickness, referring to the effects of the film surface and film–substrate interaction. As far as ultrathin films are prepared by spincasting, use of diluted solutions is inevitable. This necessarily reduces the interchain entanglements and increases the chain mobility. It is not surprising that peculiarity appears for ultrathin films prepared from solutions diluted to a concentration as low as the overlap concentration. We believe that to fully understand the peculiar behavior of ultrathin polymer films it is necessary to take account of chain entanglements in more detail in addition to the effects of the film surface and film–substrate interaction.

4. Conclusions

Temperature dependence of the free volume hole size for spincast polystyrene films with thickness ranging from 22 to 1200 nm has been examined by energy variable positron annihilation lifetime spectroscopy (EVPALS). Distinct deviations from bulk polystyrene in, among others, coefficients of thermal expansion of the free volume and the glass transition temperature specifically associated with free volume behavior were observed for the thinnest film with 22 nm thickness, indicating its exclusively high chain

mobility. The peculiarity is not attributable to the surface effect because no such deviations from bulk polystyrene were observed for the 1200 nm thick film when probed with the positrons of 0.4 keV having a mean implantation depth of 8.8 nm. As the film with 22 nm thickness was prepared from a precursor solution with concentration comparable to the overlap concentration, the peculiarity likely originates from the untangled chains caused by rapid removal of the solvent. To fully understand the peculiar behavior of ultrathin polymer films it is necessary to take account of chain entanglements in more detail in addition to the effects of the film surface and film–substrate interaction, because use of spincasting for the preparation of ultrathin films from diluted solutions inevitably reduces the interchain entanglements.

References

- [1] Reiter G. *Macromolecules* 1994;27(11):3046–52.
- [2] Keddie JL, Jones RAL, Cory RA. *Europhys Lett* 1994;27:59.
- [3] Huang Y, Paul DR. *Polymer* 2004;45(25):8377–93.
- [4] Forrest JA, Dalnoki-Veress K. *Adv Colloid Interface Sci* 2001;94:167–96.
- [5] Lenhart JL, Wu WL. *Langmuir* 2003;19(11):4863–5.
- [6] Soles CL, Douglas JF, Wu WL. *J Polym Sci B* 2004;42(17):3218–34.
- [7] Soles CL, Douglas JF, Wu WL, Dimeo RM. *Macromolecules* 2003;36(2):373–9.
- [8] Jun F, Binyao L, Yanchun H. *J Chem Phys* 2005;123(6):064713.
- [9] Cyganik P, Budkowski A, Raczowska J, Postawa Z. *Surf Sci* 2002;507–510:700–6.
- [10] Fukao K, Miyamoto Y. *Europhys Lett* 1999;46:649–54.
- [11] Fukao K, Miyamoto Y. *Phys Rev E* 2000;61(2):1743–54.
- [12] Pham JQ, Green PF. *J Chem Phys* 2002;116(13):5801–6.
- [13] Pham JQ, Green PF. *Macromolecules* 2003;36:1665–9.
- [14] Singh L, Ludovice PJ, Henderson CL. *Thin Solid Films* 2004;449:231–41.
- [15] Wang CL, Kobayashi Y, Togashi H, Hirata K, Suzuki R, Ohdaira T, et al. *J Appl Polym Sci* 2001;76(6):974–80.
- [16] Oka T, Ito K, Muramatsu M, Ohdaira T, Suzuki R, Kobayashi Y. *J Phys Chem B* 2006;110:20172–6.
- [17] Tao SJ. *J Chem Phys* 1972;56:5499–510.
- [18] Hagiwara K, Ougizawa T, Inoue T, Hirata K, Kobayashi Y. *Radiat Phys Chem* 2000;58(5):525–30.
- [19] Muramatsu M, Okura M, Kuboyama K, Ougizawa T, Yamamoto T, Nishimura Y, et al. *Radiat Phys Chem* 2003;68(3–4):561–4.
- [20] Nakanishi N, Jean YC. In: Schrader DM, Jean YC, editors. *Positron and positronium chemistry, studies in physical and theoretical chemistry 57*. Amsterdam: Elsevier; 1988. p. 159.
- [21] Kobayashi Y, Ito K, Oka T, He C, Mohamed HFM, Suzuki R, et al. *Appl Surf Sci* 2008;255:174–8.
- [22] DeMaggio GB, Frieze WE, Gidley DW, Zhu M, Hristov HA, Yee AF. *Phys Rev Lett* 1997;78(8):1524–7.
- [23] Cao H, Yuan JP, Zhang R, Sundar CS, Jean YC, Suzuki R, et al. *Appl Surf Sci* 1999;149(1–4):116–24.
- [24] Algers J, Suzuki R, Ohdaira T, Maurer FHJ. *Polymer* 2004;45(13):4533–9.
- [25] Suzuki R, Kobayashi Y, Mikado T, Ohgaki H, Chiwaki M, Yamazaki T, et al. *Jpn J Appl Phys* 1991;30pt2(3B):532–4.
- [26] Stepanov SV, Byakov VM, Ganguly BN, Gangopadhyay DG, Mukherjee T, Dutta-Roy B. *Physica B* 2002;322(1–2):68–79.
- [27] Rubinstein M, Colby R. *Polymer physics*; 2003; Oxford University Press.
- [28] Kajiyama T, Tanaka K, Takahara A. *Macromol Symp* 2003;192:265–70.
- [29] Turner DT. *Polymer* 1978;19:789.
- [30] Strobl G. *The physics of polymers. third revised and expanded edition*. Berlin, Heidelberg, New York: Springer; 2006.