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Study on the thermal behavior of a solution-cast liquid–crystalline polymer film by positron-annihilation lifetime spectroscopy

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Abstract

The thermal behavior of a solution-cast liquid–crystalline polymer (LCP) film was extensively studied by positron-annihilation lifetime spectroscopy (PALS). From the positronium (Ps) lifetimes of the first heating process from 40 to 250 °C at a heating rate of 2.5 °C/h, four characteristic temperatures (140, 170, 200, 235 °C) were observed. From a combined investigation with conventional differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), the first three characteristic temperatures were found to correspond to reorientation, glass-transition, and softening temperatures, respectively. The fourth temperature was related to the commencement of crystallization, which was observed above about 235 °C from a decrease in the Ps lifetime. A low-temperature PALS experiment exhibited the γ-transition due to rotation of the phenyl moiety at about −53 °C.

Keywords: Solution-cast LCP film; Thermal behavior; Positron annihilation

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1. Introduction

There have been a variety of reasons for interest in liquid–crystalline polymers (LCPs). Most commercial significance relates to their excellent thermal resistance and thin-wall flow ability, obtained by the injection molding for the precision parts of electronic devices, such as connectors, relays, and bobbins [1]. Recently, a molding process of a LCP film was explored; films that are used for insulating films of multi-layer printed wiring boards or flexible printed circuit board are molded by an extrusion process or tubular process [2]. The low dielectric constant and low losses of the LCP film are especially suitable for high-frequency applications in the future. In addition, these properties are not significantly affected by physicochemical changes in the operation environment, which makes it possible for the LCP film to be an ideal substrate material for high-density printed wiring boards.

It is emphasized, however, that LCP films produced by an extrusion process or a tubular process has a large anisotropy in their substantial orientation nature, resulting in a weak tear strength along the direction perpendicular to the flow direction during molding and film handling. Thus, the film can be easily torn into pieces.

Recently, it was reported that a solution-cast LCP film was successfully developed from a commercial point of view [3]. Due to its essential isotropic nature, the tear strength of the solution-cast LCP film was found to be about one and half times larger than that of films produced by an extrusion process or a tubular process.

However, the physical properties of the solution-cast LCP film are known to be very sensitive to thermal annealing [4]. It is thus desired to investigate the thermal behavior of solution-cast LCP films so as to facilitate their stable fabrication.

Positron-annihilation lifetime spectroscopy (PALS) is well-known as a highly sensitive and non-destructive method to quantitatively measure the size of intermolecular spaces [5]. In polymeric materials, PALS has recently been applied to estimate the free volume from the positronium (Ps, bound state similar to hydrogen) lifetimes (Fig. 1(a)) [6–9]. Positrons injected into a polymer have high energies

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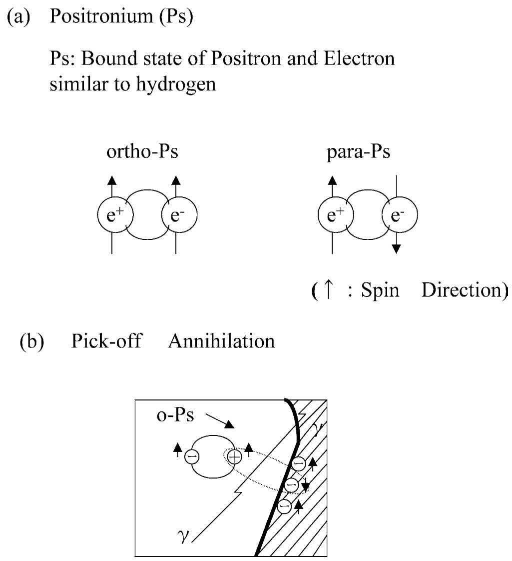


Fig. 1. Schematic illustration of positronium (a) and positronium reactions (b).

(average energy of around 200 keV in the case of ^{22}Na positron sources), and interact with atoms and molecules until being thermalized in the medium. In most polymers, a fraction of the positrons form Ps atoms after thermalization, which diffuse through the polymer structures until being trapped in intermolecular spaces. A Ps trapped in the intermolecular spaces can exist until it interacts and annihilates electrons from the surroundings. Then, through annihilation, two photons with an energy of 0.511 MeV are emitted in opposite directions. This process is called 'pick-off annihilation', and the time required for this to occur annihilation depends on the size of the space, as schematically illustrated in Fig. 1(b). Hence, the lifetime of Ps in the space is related to the size and, assuming a finite spherical potential, the relation between the lifetime and the radius of the spherical potential has been obtained [10]. Thus, PALS has been recognized to be a useful technique for investigating the free volumes at the nanometer molecular level. By combining this PALS technique with other conventional methods, more detailed characterizations can be achieved in the analysis of polymeric materials. Also, PALS can be applied to study the relaxation process (α, β, γ-transition) of polymeric samples by changing their temperature from low to high. Determinations of the transition points by PALS have been reported to be in good agreement with other methods, like differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and nuclear magnetic resonance (NMR) [11,12].

In this study, the PALS technique was firstly applied to elucidate the thermal behavior of a solution-cast LCP film. Using the characteristics obtained from the data of DSC and DMA, the PALS results are discussed in detail.

2. Experimental

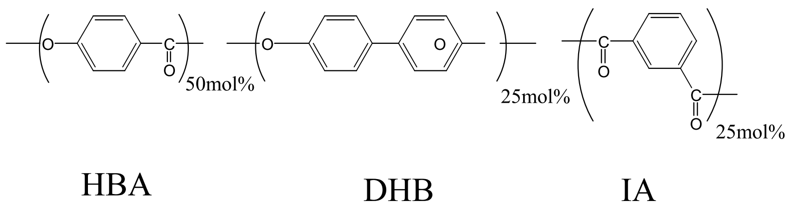
The solution-cast LCP films used in this study were made of copolyesters of *p*-hydroxybenzoic acid (HBA), 4,4′-dihydroxybiphenyl (DHB) and isophthalic acid (IA), having 50/25/25 mol% HBA/DHB/IA. The structures are shown in Fig. 2(a). The copolyesters were synthesized using conventional acidolysis methods described in the literature [13–16]. In order to form solution-cast films, the copolyester was first dissolved in a solvent of *p*-chlorophenol at 120 °C. A solid content in the solution was set up at 10% by weight. The polymer solution, after filtration, was cast on a glass plate in a dust-free environment. To remove the solvents, wet films coated on the glass plate were directly heated on a hot plate at 80 °C for 1 h. The thus-obtained properly dried films that adhered to the glass plate were immersed into water for 48 h to peel off from the glass plate. The films were washed with water and methanol several times to remove any residual solvent, followed by drying at room temperature in a vacuum oven. The as-cast films appeared to be transparent, non-brittle and ranged in thickness around 10 μm.

A positron source was prepared by depositing about 1.1 MBq (30 μCi) of aqueous ^{22}NaCl on a Kapton film of 7 μm thickness and area of 10×10 mm^2, which was then covered with another film of the same size. Finally, the edges of these two films were glued together. The diameter of the source droplet was less than 2 mm. Positrons emitted from ^{22}Na penetrated to the maximum depth of about 1 mm in samples with a density of 10^3 kg/m^3. The positron source was placed between two pieces of folded LCP films. The total thickness of the folded film sample was about 2 mm on one side, which ensured that all of the injected positrons stopped and annihilated inside of the samples.

The PALS experiments were conducted with a conventional fast–fast coincidence system with a time resolution of 0.3 ns full-width at half maximum (FWHM). Gamma-rays with energies of 0.511 MeV (emitted as the result of positron-annihilation) and 1.27 MeV (emitted from the beta-decay of ^{22}Na) were measured by stop and start counters, respectively. The time difference between the two gamma-rays is considered to be the lifetime of the positrons in a sample. The details of the experimental set-up are given elsewhere [6,17].

The whole sandwich package, prepared as mentioned above, was thermally treated in two steps under the PALS conduct. At the beginning, in a relatively low-temperature region, the samples were fast cooled to −243 °C, and then heated to 37 °C at a rate of 5 °C/h using a cooling system (CW303, Iwatani Co. Ltd). The system had a temperature control device for an automatic measurement, and samples held in the system were under a vacuum. Secondly, in the relatively high-temperature region the samples were heated and cooled between 40 and 250 °C at a rate of 2.5 °C/h. During the high-temperature experiment, nitrogen gas was flowed continuously in order to avoid oxidation. PALS

(a) Chemical structure of the copolyester used in this study



(b) Chemical structure of HIQ copolymer

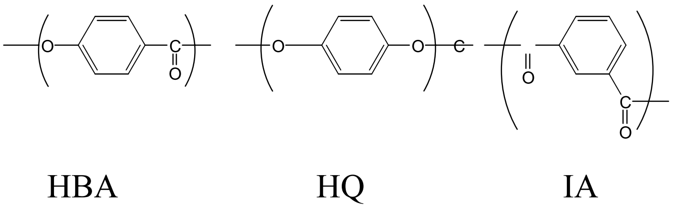


Fig. 2. Chemical structures of the copolyester used in this study (a) and HIQ (b).

spectra were recorded every hour, and 2 h for the low-and high-temperature experiments, respectively, resulting in statistics of about 1.5 million events. All of the spectra were resolved into three components using a positron-annihilation lifetime fitting program (PATFIT) without a source correction [18]. The longest-lived component with a lifetime of τ_3, and corresponding intensity of I_3, was attributed to the pick-off annihilation of *o*-Ps atoms. DSC measurements (Shimazu DSC-50) were performed at heating and cooling rates from 0.5 to 10 °C/min without making any distinction of the coating direction and its perpendicular direction. DMA measurements at a frequency of 10 Hz (TA Instrument DMA 2980 dynamic mechanical analyzer) were conducted while distinguishing the cast-coating direction and its perpendicular direction in the LCP solution-cast film at heating and cooling rates from 0.5 to 10 °C/min.

3. Results and discussion

A class of LCP materials, designated as HIQ (shown in Fig. 2(b)), which can be a solution cast into an isotropic film, has been reported by Cantrell et al. and Morisato et al. [19, 20]. This type material yields transparent films that are amorphous and isotropic, as formed by appropriate solvent casting techniques; however, thermal annealing above the glass-transition temperatures leads to a mesogenic texture, while simultaneously developing some level of crystallinity. The chemical structure shown in Fig. 2(a) and (b) implies that our recently developed material, HBA/DHB/IA, used in this study exhibits a similar thermal behavior to that of the above-mentioned HIQ [4,19,20]. Because these two types of solution-cast LCP films show irreversible behaviors by thermal annealing above the glass-transition temperatures, the as-cast film in the present study was carefully treated below the glass-transition temperatures while drying the solvent.

The temperature dependencies of the *ortho*-Ps lifetime (τ_3) and corresponding intensity (I_3) of the as-cast film in the low-temperature range from −243 to 37 °C at a heating rate of 5 °C/h are, respectively, shown in Fig. 3(a) and (b). While the intensities increase monotonously with temperature, τ_3 indicated that the expansion rate abruptly changed at −53 °C. By examining a series of aromatic polyesters of different compositions, a transition at around −50 °C was found to be γ-transition originated from the rotation of the phenyl moiety in the aromatic polyester [21–23]. The abrupt change of the expansion rate in Fig. 3(a) is therefore considered to be the γ-transition. From this result, the polymer chain structure can easily expand above the γ-transition.

The temperature dependencies of τ_3 and I_3 of the as-cast film over the high-temperature range from 40 to 250 °C at a heating and cooling rate of 2.5 °C/h are, respectively, shown in Fig. 4(a) and (b). Some distinctive temperatures (140,

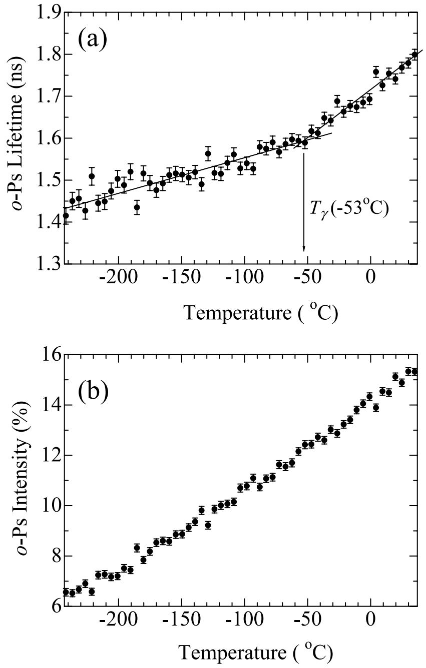


Fig. 3. Temperature dependencies of the *ortho*-positronium lifetime, τ_3, (a) and the intensity, I_3, (b) of the as-cast film in the low-temperature range from −243 to 37 °C at a heating rate of 5 °C/h.

170, 200 °C) were observed in the temperature dependency of τ_3 only for the heating process in the high-temperature range (Fig. 4(a)).

Fig. 4(a) shows that τ_3 started a sharp decrease at 140 °C (T_r), which indicates that the free volume started to shrink at this temperature. To elucidate the origin of this drastic change, a DSC measurement of the as-cast film at a heating rate of 10 °C/min was also performed. As shown in Fig. 5, a shallow exothermic peak at around 120–140 °C could be observed in the diagram, indicating that the transition at 140 °C (T_r) should be regarded as being a reorientation process of the molecule due to the crystallization of an unstable amorphous region that occurred during solvent evaporation.

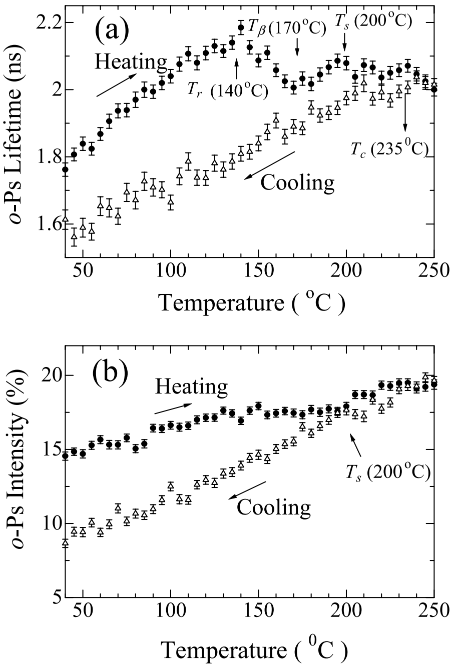


Fig. 4. Temperature dependencies of the *ortho*-positronium lifetime, τ_3 (a), and intensity, I_3 (b), of the as-cast film over the high temperature range from 40 to 250 °C at heating and cooling rates of 2.5 °C/h.

Secondly the lifetime (τ_3) stopped decreasing at the characteristic 170 °C (T_β) in the heating process, and started increasing again. The DSC thermogram shown in Fig. 5 clearly sets forth that the T_β transition corresponds to the glass-transition of the copolyester.

Finally, τ_3 stopped increasing again at 200 °C (T_s) in the heating process, and remained almost constant, or exhibited a slight decrease. To clarify the origin of the subtle change, the DMA measurement shown in Fig. 6 was also conducted. The elastic modulus drastically decreased at around T_s. Thus, the combined results of the *o*-Ps lifetime with the DMA measurement gave an indication that the transition at T_s should be considered to be the softening point.

In our previous presentation [3], we reported that some level of crystallinity can easily be developed in the LCP used in this study at temperatures higher than 300 °C within 1 h. The crystallization can proceed even at a low temperature, like 200 °C, at which the speed is expected to be very slow. It is possible to detect the crystallization by PALS, since the crystallization affects both τ_3 and I_3. Fig. 4(b) shows that I_3 at room temperature was reduced after the annealing process, which indicates a reduction in the number of free-volume holes available for Ps formation. This is a direct result of the crystallization or/and annealing effect that occurred during heating at a higher temperature than the softening point.

Fig. 4(a) shows the heating process above T_s, which shows a constant value of τ_3 from T_s to 235 °C; this indicates that Ps is annihilating in a very soft state, like rubber. Above 235 °C, τ_3 starts decreasing; this suggests a shrinking of the intermolecular space in the amorphous region, i.e. the commencement of crystallization.

During the cooling process, τ_3 showed relatively smaller values than those shown during the heating process. It was pointed out that the size of the free volume was reduced due to two possible processes: (1) crystallization by thermal annealing above the crystallization temperature; (2) an annealing effect of irregular intermolecular spaces induced by heating above the softening temperature. Accordingly, assuming a finite spherical potential, the radius of the free volume hole at room temperature before and after thermal annealing were estimated from τ_3 (Table 1). The evaluated values indicate that the difference in the radius free volume hole before and after thermal annealing was 5.8%. According to the literature [24], the gas permeability changes about one order of magnitude if the variation in the free volume hole radius is just as several percent. On the

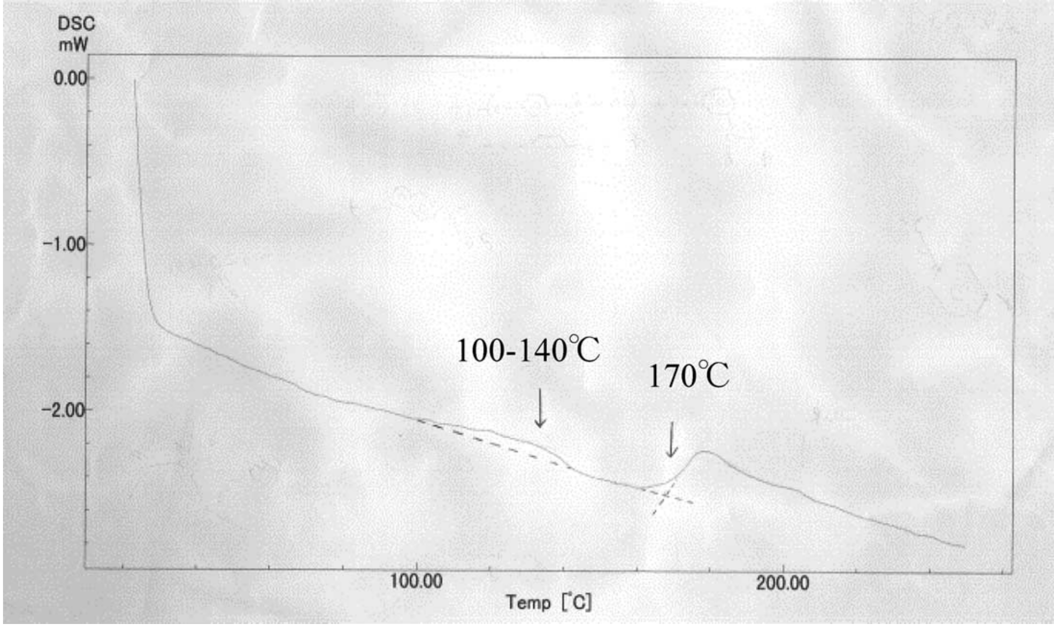


Fig. 5. DSC thermogram of the as-cast film during the first heating process at a rate of 10 °C/min.

other hand, in the analogous case of the LCP solution-cast film (HIQ) [4] it is reported that about one order magnitude decrease in the gas (oxygen) permeability before and after heat treatment. Therefore, it might be suggested that a reduction in the size of the free volume could lead more dominantly to a dramatic decrease in the gas permeability reported in the solution-cast LCP film after thermal annealing [4] than a reduction of the number of the free volume.

While in Fig. 4(b) the above-mentioned T_r and T_β cannot be read clearly from the temperature dependencies of I_3, only T_s can be read easily in the figure. I_3 is related to the amount of intermolecular spaces in the polymer; in the case of the LCP film, the reorientation and glass-transition

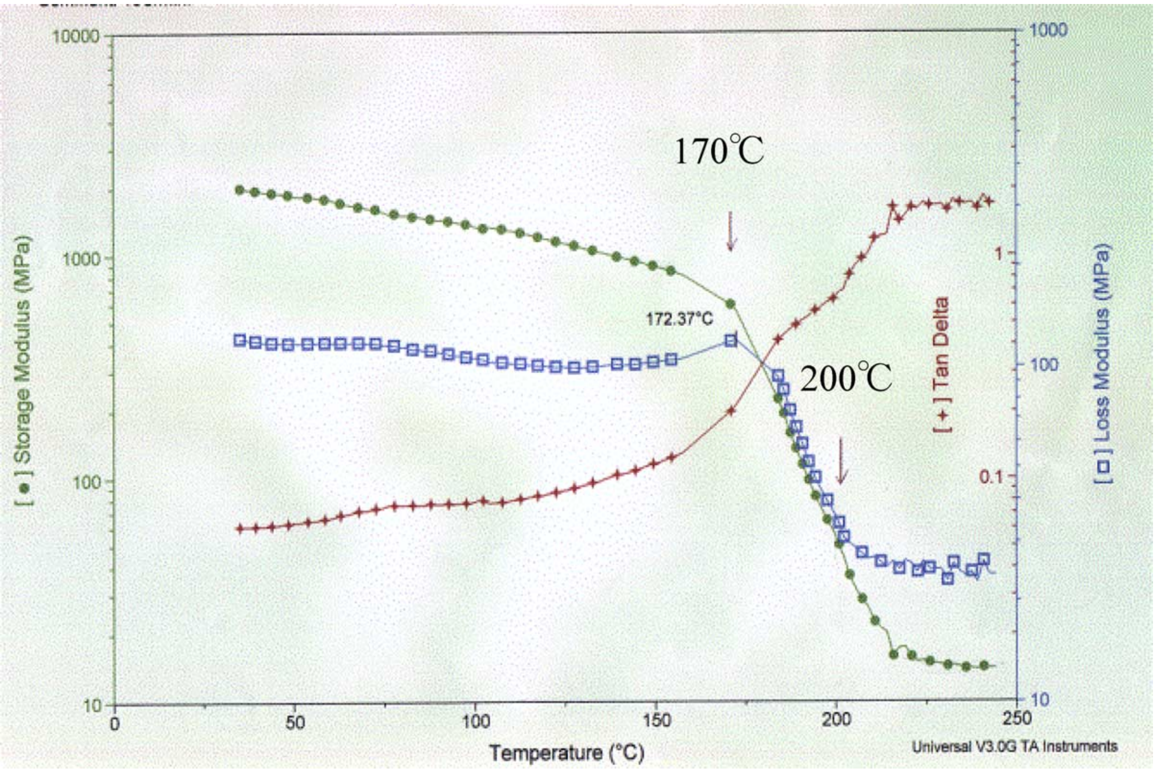


Fig. 6. DMA data of the as-cast film on the first heating process at a rate of 10 °C/min at a frequency of 10 Hz.

Table 1
Radius of the free volume at room temperature before and after thermal annealing, calculated from the *o*-Ps lifetime (τ_3) by a finite spherical approximation

	o-Ps lifetime τ_3 (ns)	Radius of the free volume (nm)
As-cast film	1.76	0.262
After annealing at 250 °C	1.62	0.247

temperature do not affect these space structures. At around T_s (200 °C), the intensities (I_3) in the heating and cooling processes coincide with each other; at temperatures higher than 200 °C, I_3 follows approximately the same temperature dependence for the heating and cooling processes, suggesting that the copolyester in this temperature range takes a rubber state, and therefore its film becomes soft.

4. Conclusion

The thermal behavior of a solution-cast LCP film was extensively investigated by PALS. The *o*-Ps lifetime (τ_3) during the first heating process at an increasing rate 2.5 °C/h indicated that four characteristic temperatures (140, 170, 200, 235 °C) were observed in the temperature range from 40 to 250 °C. By a combined investigation with conventional DSC and DMA methods, the first three characteristic temperatures were found to correspond to reorientation, glass-transition, and softening point, respectively. The decreasing τ_3 above 235 °C showed the commencement of crystallization, which is difficult to detect by the standard methods, like DSC and DMA.

Furthermore, as estimated from τ_3, the difference between the free-volume hole radius in the as-cast LCP film before and after thermal annealing is 5.8%. The difference corresponds to about one order of magnitude in the gas permeability in the film. The current results are consistent with previously reported gas permeability results in a solution-cast LCP film [4,19,20]. From the low-temperature PALS experiment, τ_3 indicated a relaxation temperature at -53 °C, which can be assigned to the γ-transition that originated from the rotation of the phenyl moiety in the aromatic polyester.

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