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Characteristics of Ultradrawn Polyethylene Films as a Function of Temperature Estimated by the Positron Annihilation Lifetime Method

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ABSTRACT: Three kinds of mechanical relaxations, the α, β, and λ transitions, of ultradrawn polyethylene films were obtained by dynamic mechanical measurements, and the results were analyzed by positron annihilation. The gels were prepared by crystallization from dilute solutions and were then dried. The dried gel films were stretched by up to a draw ratio of 300 times ($\lambda = 300$). The temperature dependence of the intensity (I_3) of the long-lived component of the orthopositronium (o-Ps) as well as that of the lifetime (λ_3) was observed for undrawn and drawn polyethylene films. For the undrawn film, the peak positions of the γ and β transitions corresponded to the first and second transitions of τ_3. The β dispersion was not observed for the films with $\lambda = 50$ and 300. The second transition of τ_3, corresponding to the β dispersion, was observed for drawn films with $\lambda = 50$ but was not observed for the film with $\lambda = 300$. A histogram of τ_3 for three kinds of specimens showed that the size distribution for the undrawn film ($\lambda = 1$) became broader, and the peak position shifted to a larger value of the lifetime (τ_3) with increasing temperature. This indicates that the free volume holes within the specimen became bigger and had a wider size distribution with increasing temperature and, at the same time, the molecular motion became more active. For the ultradrawn film with $\lambda = 300$, the lifetime distribution at 100 °C showed a much wider and asymmetry profile, and the peak position shifted to a shorter value than those for the other two films with drawing ratios of $\lambda = 1$ and $\lambda = 50$. This indicated poor activity of a large movement (macro-Brownian motion) of amorphous chains. These experimental results justify that the thermal expansion of the film due to an increase in the molecular mobility was almost zero in a given temperature range from 0 to 120 °C and that the storage modulus at 100 °C was higher than 130 GPa.

Introduction

There have been a number of papers concerning the relaxation dispersions, the α, β, and γ transitions associated with several kinds of molecular motions of polyethylene, by measuring the mechanical relaxation,[1−5] dielectric relaxation,[6] and nuclear magnetic relaxation.[7−9] Furthermore, rheooptical techniques have been one of the powerful methods used to investigate the nature of the mechanical loss processes of semicrystalline polymers in connection with the deformation mechanism of the structural units. Stein et al.[10,11] and Kawai et al.[12−14] have studied the deformation mechanism of semicrystalline polymers, e.g., spherulitic polyethylene films, by using dynamic X-ray diffraction and dynamic birefringence techniques.[10−14]

Recently, positron annihilation in polymers has been extensively studied,[15,16] and positron annihilation lifetime spectroscopy (PALS) has been recognized as a useful method for the characterization of polymers.[17−19] The technique employs a positron source (e.g., ^{22}Na) to emit positrons into a sample. After a positron enters a polymer, it is thermalized within a few picoseconds. During this time, most of its energy is transferred to the host, and the positron may form a positronium (Ps: a binding state of a positron and an electron). There are two kinds of Ps: parapositronium (p-Ps), in which the spins of the positron and the electron are antiparallel, has a lifetime of 0.125 ns by self-annihilation in a vacuum; the orthopositronium (o-Ps) has a longer lifetime of 142 ns in a vacuum. In polymers, the o-Ps lifetime is shortened to 1−5 ns, since it is localized in a region of lower electron density, i.e., free volume holes, and undergoes a pick-off annihilation with an electron of the surrounding molecules,[17,18] and the long-lived lifetime is related to the free volume hole size. Since o-Ps has a size like a hydrogen atom, it can only detect free volume holes with diameters larger than 1.85 Å.[20] Therefore, the free volume holes discussed in this paper mean holes that can be detected by o-Ps. Positron annihilation has provided information for the characterization of several kinds of polymers. For example, Liu et al.[19] studied the free volume distribution of polystyrene. They pointed out that the distribution of free volume fraction well fit the theoretical function according to the Shimha−Somcynsky lattice model[21] through a comparison with experimental results obtained by photochromic and fluorescent probes as well as with the Tumbell−Cohen free volume theory.[22,23] PALS has also shown the sensitivity to probe the differences in samples with different molecular weight and dispersity.[24] Although o-Ps cannot probe all of the free volume in the polymer structure, PALS can provide unique information from the viewpoint of intermolecular spaces or free volume holes.[15−24]

Apart from the analysis of polyethylene melt films, the anisotropy of crystal relaxation was investigated as a function of the draw ratio by using undrawn and drawn films with various draw ratios of up to 400-fold.[25,26] The films were prepared by gelation/crystallization from dilute solutions. Young's modulus is higher than 200 GPa, corresponding to the stiffness of steel.

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The activation energy associated with α dispersion for the ultradrawn films was estimated on the basis of master curves obtained from temperature−frequency superposition and temperature−time superposition. Each superposition was realized by a combination of horizontal and vertical shifts, resulting in apparent master curves. The α dispersion estimated by temperature−frequency superposition was classified into several components. Among them, the activation energy associated with α_1 relaxation decreases as the draw ratio increases, but the value levels off when the draw ratio is beyond 100. On the other hand, the component of the α_2 relaxation decreases with increasing the draw ratio and becomes zero at a draw ratio of 400.[25] This means that the α_2 relaxation could not be observed, since the external excitation was parallel to the *c*-axis. The crystal dispersion was also investigated by the temperature−time superposition obtained by stress relaxation measurements in the time range from 2 to 10^4 s.[26] The measurements were carried out for specimens with three kinds of molecular weight (10^6, 3×10^6, and 6×10^6). The activation energies associated with the α_1 and α_2 mechanisms obtained by Arrhenius plots became lower with increasing draw ratio. This tendency was in good agreement with that obtained by the dynamic measurement, indicating that the molecular orientation is correlated with the activation energies associated with the α_1 and α_2 mechanisms. However, the activation energies are almost independent of the given molecular weights (10^6−6×10^6).

Here, we must emphasize the difficulty in estimating the β and γ dispersions of ultradrawn films with high crystallinity, >90%, and high molecular orientation by using dynamic mechanical measurements. Namely, the β and γ dispersion peaks associated with the amorphous relaxations showed a very low magnitude compared with those for melt-crystallized films. Accordingly, only the α dispersion has been analyzed by dynamic mechanical and stress relaxation measurements.[25,26] In this paper, the focus is concentrated on an analysis of the β and γ transitions of ultradrawn polyethylene films by using positron annihilation, since no measurement has ever been made for ultradrawn polyethylene. Actually, positron annihilation has been adopted as a useful technique to analyze the β and γ relaxation of polyethylene. The analysis in this paper is pursued in comparison with results obtained by using dynamic mechanical measurements.

Experimental Section

A. Sample Preparation. The samples used in this experiment were UHMWPE (Hercules 1900/90189) with a viscosity-average molecular weight ($\bar{M}_v$) of 6×10^6. The solvent was decalin. The chosen concentration of UHMWPE was 0.4 g/100 mL,[27,28] which is the optimum concentration ensuring the greatest draw ratio of UHMWPE films with $\bar{M}_v = 6 \times 10^6$.[26−28] Decalin solutions were prepared by heating a well-blended polymer−solvent mixture at 135 °C for 40 min under nitrogen. The solution was stabilized with 3% w/w of an antioxidant (di-*tert*-butyl-*p*-cresol) against UHMWPE. The hot homogenized solution was quenched to room temperature by pouring it into an aluminum tray, thus generating a gel. The decalin was allowed to evaporate from the gels under ambient conditions. The resulting dry gel film was vacuum-dried for 1 day to remove any residual trace of decalin and then elongated up to 300 times at 135 °C under nitrogen. The detailed method has been described elsewhere.[27,28]

B. Measurements. 1. Positron Annihilation. Positron annihilation experiments were conducted with a conventional fast−fast coincidence system having a time resolution of 300 ps full width at half-maximum (fwhm). The time spectrometer was composed of two plastic scintillation detectors (40 mm diameter × 40 mm Pilot-U mounted on a Hamamatsu H1949 photomultiplier), two differential constant fraction discriminators (ORTEC 583) (one for start signals from 1.27 MeV γ-rays and the other one for stop signals from 0.511 MeV annihilation γ-rays), a time-to-amplitude converter (ORTEC 4570), and a multichannel analyzer with a 1024 conversion gain (SEIKO 7800). The data taking was controlled by a personal computer (NEC-PC).

Table 1. Characteristics of the UHMWPE Gel Films

specimen	Young's modulus (GPa)	crystallinity (%)	melting point (°C)	orientation factor
$\lambda = 1$	5	84	140	
$\lambda = 50$	25−30	87−90	147	0.994−0.996
$\lambda = 300$	151−202	95−96	155	0.999

A position source was prepared by depositing ca. 1.1 MBq (30 μCi) of aqueous ^{22}NaCl on a Kapton foil of 7 μm thickness and 10 × 10 mm area. After drying, the foil was covered with the same size of foil, and the edges were glued with epoxy resin. The source was further sealed in a 3 μm Mylar foil and then sandwiched by two identical samples for positron annihilation measurements. The diameter of the spot of the ^{22}Na source was ca. 2 mm.

During the measurement, samples were kept in a vacuum cell, in which their temperature was controlled. Spectra were recorded every hour, and about 1−2 million events were stored in each spectrum. Thus, a positron annihilation spectrum with sufficient statistics to decompose the orthopositron (o-Ps) component was obtained.

2. Viscoelastic Measurements. The dynamic tensile modulus of the complex was measured at 10 Hz over the temperature range from −150 to 150 °C by using a viscoelastic spectrometer (VES-F) obtained from Iwamoto Machine Co. Ltd. The length of the specimen between the jaws was 40 mm, and the width was about 1.5 mm. During measurements, the specimen was subjected to a static tensile strain in order to place the sample in tension during axial sinusoidal oscillation. The complex dynamic modulus was measured by imposing a small dynamic strain (0.05−0.25%) to ensure a linear viscoelastic behavior of the specimen.[25]

3. Sample Characterizations. The second-order orientation factors of the *c*-axes for the ultradrawn films were estimated from the orientation distribution functions of the reciprocal lattice vectors of the (002) plane. X-ray measurements were carried out using a 12 kW rotating anode X-ray generator (RDA-rA). To check the validity of the values of the *c*-axes, the orientation factor of the *c*-axis was also estimated from the factors of the (110) and (200) planes by Wilchinskey's equation.[29] The factors of the *c*-axis obtained by the two methods were in good agreement.

The crystallinity was calculated from the density, which was measured by a pycnometer in chlorobenzene−toluene as a medium, using 1.000 and 0.864 g/cm^3 as densities of the crystal and amorphous phases.[30] The melting point was estimated by a Rigaku Thermoflex TG8110 apparatus with the TG-DSC mode at a heating rate of 5 °C/mm. Specimens, weighing 5 mg each, were placed in a standard aluminum sample pan.

Young's modulus was measured on an Instron tensile testing machine at a cross-head speed of 2 mm/min at room temperature. The initial dimensions of the specimens were 60 mm in length and 2 mm in width. The distance between two chucks was 40 mm.

Table 1 summarizes the crystallinity, the melting point, Young's modulus, and the second-order orientation factor of the *c*-axis. Characterizations were carried out for more than 10 specimens with the same draw ratio; the most probable data are listed. With increasing draw ratio, the crystallinity increased. At $\gamma = 300$, the crystallinity was more than 95%. Such a high value has never been obtained by drawing melt polyethylene films. The second-order orientation factor (FC) characterizes the orientation distribution of the *c*-axis, with a

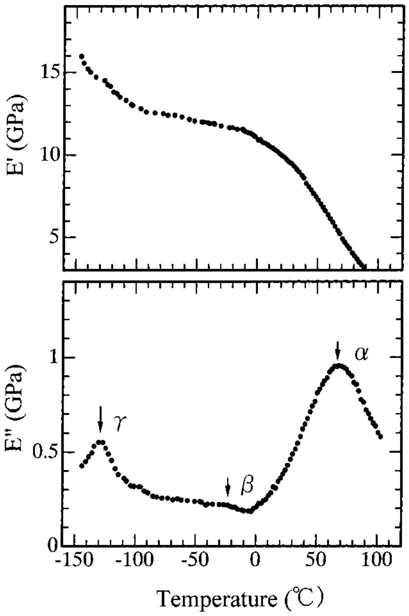

Figure 1. Temperature dependence of the storage and loss moduli for an undrawn polyethylene film measured at 10 Hz.

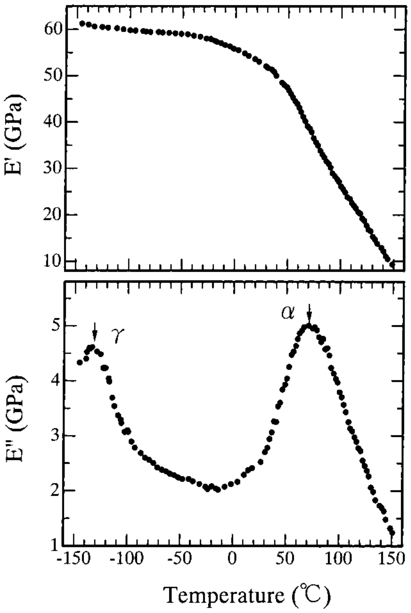

Figure 2. Temperature dependence of the storage and loss moduli for a drawn polyethylene film with $\lambda = 50$ measured at 10 Hz.

variation of between $-^1/_2$ and 1.[31] For a random orientation FC is 0, while for complete orientation parallel and perpendicular to the drawing direction FC is 1 and $-^1/_2$, respectively. The value was close to unity at $\gamma = 300$, indicating almost perfect orientation of the *c*-axis with respect to the stretching direction. Young's modulus reached 200 GPa. This value, which is similar to Young's modulus of steel, is close to the crystal lattice modulus in the chain direction,[32] corresponding to the ultimate goal of polyethylene materials.

Results and Discussion

Figure 1 shows the temperature dependence of the storage modulus (E') and the loss modulus (E'') at a frequency of 10 Hz for the undrawn film ($\gamma = 1$), and Figures 2 and 3 show that for the drawn films with $\gamma = 50$ and 300, respectively. As already reported,[33] the loss modulus for the undrawn film has α, β, and γ relaxations. On the other hand, the loss modulus for the drawn films with $\gamma = 50$ and 300, whose crystallinities are higher than 87%, has α and γ relaxations, while no β relaxation peak has been observed. The measurements shown in Figures 1−3 were carried out to determine the approximate peak magnitude of several kinds of relaxation processes. The mechanical relaxation of the ultradrawn films had already been investigated for the α dispersion on the basis of master curves obtained from the temperature−frequency superposition and the temperature−time superposition in previous papers.[25,26] The analysis was conducted on the basis of activation energies obtained by logarithm plots of the horizontal shift factors against the reciprocal absolute temperature. Although the activation energy associated with the α_1 relaxation decreases as the draw ratio increases, the value leveled off when the draw ratio was beyond 100. On the other hand, the component of the α_2 relaxation decreased with increasing the draw ratio and became zero at a draw ratio of 400. This means that α_2 relaxation could not be observed when the external excitation was parallel to the *c*-axis. The same treatment was successful in estimating the β and γ relaxations.[34] The activation energy of the β relaxation measured for a specimen with a crystallinity of <50% was 114−115 kJ/mol. These values were similar to those of the α_1 relaxation already reported.[25] For the γ relaxation mechanisms measured for specimens with a crystallinity of <87%, there exist two mechanisms, γ_1 and γ_2, whose activation energies are 9−11 and 23−25 kJ/mol, respectively. The values were independent of the molecular orientation and crystallinity.[34]

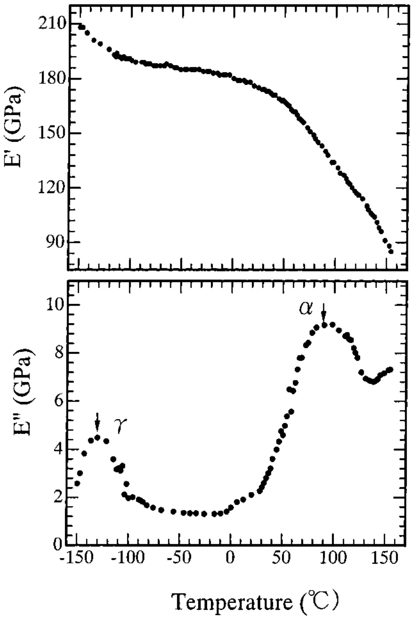

Figure 3. Temperature dependence of the storage and loss moduli for a drawn polyethylene film with $\lambda = 300$ measured at 10 Hz.

However, we must emphasize that the temperature−frequency superposition at a low temperature of <−10 °C was impossible for these specimens with crystallinity >87%. As can be seen in Figures 1−3, the peak magnitude of the α dispersion is much lower than that of the α dispersion. Furthermore, the magnitude of the γ peak was also confirmed to be much lower than that of melt-crystallized films.

To describe the dispersions of ultradrawn polyethylene films with crystallinity >95%, positron annihilation

Table 2. Lifetime and Intensity of o-Ps for UHMWPE Gel Films at Room Temperature

specimen	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
$\lambda = 1$	1.072 ± 0.159	4.61 ± 0.40	2.445 ± 0.037	14.62 ± 0.65
$\lambda = 50$	1.118 ± 0.228	5.81 ± 0.91	2.354 ± 0.138	8.50 ± 1.53
$\lambda = 300$	1.361 ± 0.140	7.69 ± 0.87	2.953 ± 0.415	3.17 ± 1.16

is adopted in this paper, since it is well-known that an increase in the free volume holes can be clearly estimated by positron annihilation.[15] Actually, positron annihilation is one of the useful techniques used to investigate the relaxation characteristics of polymers. Positrons emitted from ^{22}Na induce a radiation effect on polymer samples, and electrons are excited from the constituent atoms. These electrons are trapped in a shallow potential, which is formed at a low temperature far below the glass temperature (T_g). The increase in these trapped electrons is observed as the intensity (I_3) of the long-lived component of orthopositronium (o-Ps) increases.

In polyethylene, the positron lifetime spectra can be resolved into three or four components. Following the four-component analysis, the third long-lived positronium lifetime, τ_3 (~1.0 ns), was generally due to o-Ps annihilation in the free volume holes located at the boundary between crystallites and amorphous region, and the fourth component, τ_4 (~2.8 ns), resulted from o-Ps annihilation in free volume holes within the amorphous region.[35] The positron lifetime spectra in the UHMWPE films with different drawing ratios of $\lambda = 1$, 50, and 300 at room temperature were resolved into four components when the first lifetime was fixed to be 125 ps. The results are listed in Table 2. It is seen that the intensity of the third component increases with increasing drawing ratio, while the intensity decreases for the fourth component. The total intensity of two long-lived components also decreases with increasing λ because of an increase in the crystallinity. As listed in Table 2, I_4 for a film with $\lambda = 300$ at room temperature is very low because of high crystallinity. Furthermore, at low temperature, the lifetime of the fourth component is close to the third component. This indicates the difficulty in decomposing all of the positron lifetime spectra into four components. Accordingly, the positron spectra in this paper was resolved into three components to compare the characteristics of the o-Ps parameters among the three specimens over a wide temperature range from −240 to 100 °C.

Figures 4−6 show the variations of the o-Ps intensity (I_3) and its lifetime (τ_3) in films with $\lambda = 1$, 50, and 300 as a function of temperature. It is seen that the o-Ps intensity increases as a function of temperature up to −130 °C. The increase in the o-Ps intensity (I_3) has been proved to be due to the positron irradiation effect on a polymer at low temperature.[36,37] The secondary electrons escaped from the positron spur could be easily tapped in shallow potentials formed between the polymer chains when the motions of the molecular chains and groups are frozen at low temperature. Because of an increase in the trapped electrons with increasing positron irradiation time (experimental time), the probability of Ps formation would become larger. This tendency has been confirmed for other samples.[38] It has been found that visible light[36,37] and the activation of the molecular chain and group motion could bleach the trapped electrons with increasing temperature,[38] and consequently, the o-Ps intensity would be greatly reduced. Accordingly, positron annihilation can detect the motion of polymer chains and groups at low temperature by the variation of the o-Ps intensity.

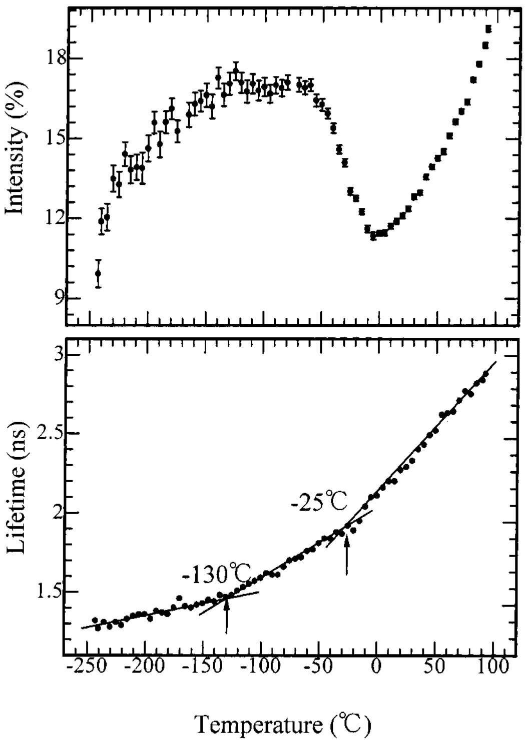

Figure 4. Intensity (I_3) and lifetime (τ_3) of the long-lived component of the orthopositronium (o-Ps) as a function of temperature for an undrawn polyethylene film.

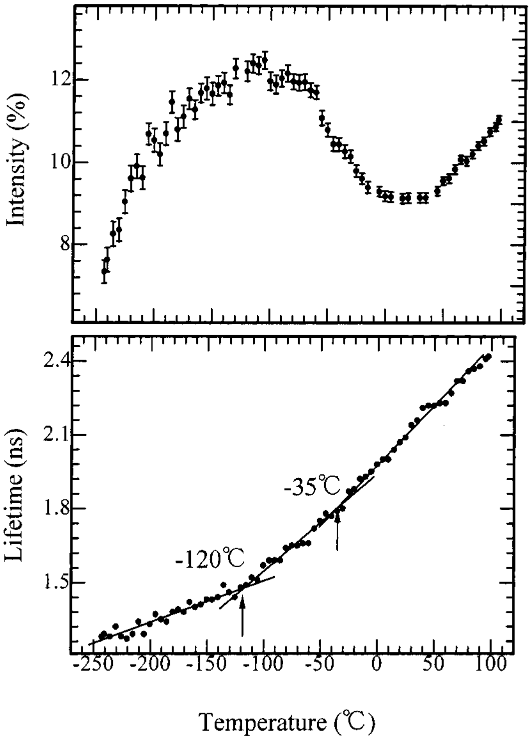

Figure 5. Intensity (I_3) and lifetime (τ_3) of the long-lived component of the orthopositronium (o-Ps) as a function of temperature for a drawn polyethylene film with $\lambda = 50$.

As can be seen in Figure 4a, I_3 for the undrawn film becomes maximum at around −130 °C and begins to decrease with increasing temperature. I_3 attains to a minimum at about −10 °C. I_3 again increases beyond

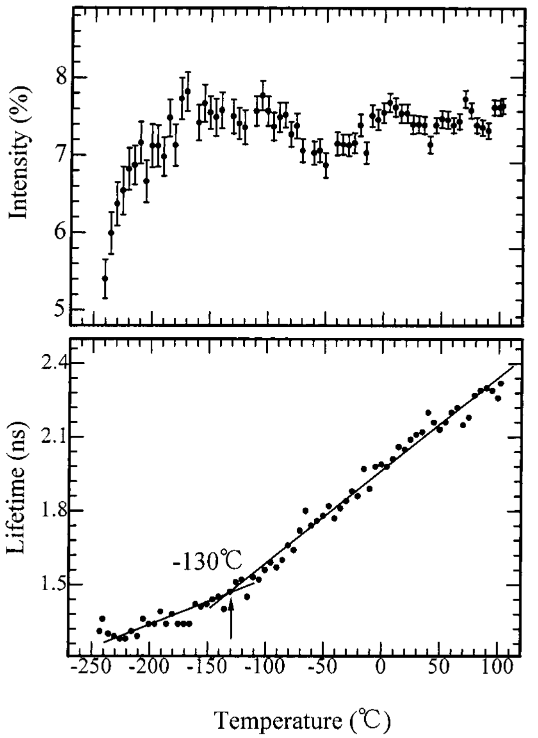

Figure 6. Intensity (I_3) and lifetime (τ_3) of the long-lived component of the orthopositronium (o-Ps) as a function of temperature for a drawn polyethylene film with $\lambda = 300$.

−10 °C. As discussed before, this is due to an apparent increase in the number of holes detected by positron annihilation because of the thermal expansion of the holes at elevated temperatures. The very small holes, which cannot be detected by positron annihilation, can be detected by an increase in the size by thermal expansion. In any case, it turns out that the β dispersion corresponds to the minimum point of I_3 and the γ dispersion, approximately the starting point of the decrease in I_3. Actually, the β dispersion estimated by a dynamic mechanical measurement appeared as a small indistinct peak at around −25 °C, while the γ dispersion appeared as a peak at around −130 °C.

In accordance with Suzuki et al.,[39] the minimum temperature of I_3 is due to the fact that the local motion causes a large (macro-Brownian) movement of the polymer chains in the amorphous phase. Accordingly, most of the shallow potentials may be smeared out by the movement; the trapped electrons may then also disappear. If this is the case, the molecular motion at low temperatures affects the trapped electrons in a shallow potential, and consequently, the variation in I_3 is closely related to the relaxation temperature as a secondary effect.

The lifetime (τ_3) is well-known to be related to the hole size by using Tao's equation.[15] The longer is τ_3, the bigger is the hole size in a polymer solid. As shown in Figure 4b, there exist two transitions of τ_3 for an undrawn film. The first transition at around −130 °C corresponds to the glass transition (γ relaxation), and the second transition at −25 °C corresponds to the β relaxation. Hence, it is obvious that the two transitions of τ_3 are in good correlation with the mechanical dispersion peaks, the β and γ relaxations.

Accordingly, −130 and −25 °C were considered to be the temperatures corresponding to the local mode relaxation of polyethylene having two different effects on the trapped electron, respectively. The former is the commencement to remove trapped electrons from a shallow potential due to the rapid trans−gauche transition of the central C−C bond of a short segment (e.g., three to four CH_2). The latter is the contribution to the elimination of the shallow potential due to the motion of the polymer chains.

In Figures 4−6, it may be noted that the decrease in I_3 tends to be smaller with increasing draw ratio. This indicates that both the trapping site of electrons and the amorphous regions for the trapping site of positrons decreased because of an increase in crystallinity. Especially, for a specimen ($\lambda = 300$) with crystallinity >95% (see Figure 6), I_3 with weak magnitude tends to increase slightly in the temperature range from −50 to 100 °C, indicating a very slight increase in the number of free volume holes. Such a phenomenon is due to the fact that the large amounts of crystallites with perfect orientation with respect to the stretching direction suppressed the thermal expansion of the holes detected by positron annihilation and that most of the holes were maintained at such a small size that they could not be detected. In other words, the thermal expansion of the holes is less pronounced in comparison with the other two specimens, since large crystallites with a stable state, even at 100 °C, suppress the active motion of molecular chains.[41]

The second transition of τ_3 is not observed for those specimens with $\lambda = 300$. Of course, this is due to the poor mobility of amorphous chains as well as the high crystallinity of the ultradrawn films (see Table 1). Such an unusual phenomenon has never been reported for any kind of polyethylene. This justifies the high modules of ultradrawn polyethylene with $\lambda = 300$. In Figure 3, the β relaxation also cannot be observed using a dynamic mechanical measurement. However, the variation of I_3 as a function of the temperature in Figure 6 produces a shallow "V" shape with a minimum of I_3 at about −45 °C. The result can be interpreted in terms of viewpoints of complete bleaching of the trapped electrons due to the activation of β relaxation and an increase in the detectable holes by o-Ps with increasing temperature. Therefore, PALS is a useful tool to detect some weak motion of polymer groups and chains at low temperature.

Figure 7a,b shows histograms of the o-Ps lifetime distributions as a function of temperature for a film with $\lambda = 1$ and 300, and Figure 7c shows the o-Ps lifetime distributions at 100 °C for films with drawing ratios of $\lambda = 1$, 50, and 300. The positron lifetime distributions were calculated by using the maximum entropy for a lifetime analysis (MELT).[40] The horizontal scale is also given as the radius of the mean free volume holes calculated by Tao's equation.[15] The relative o-Ps intensities at $\lambda = 1$ were calculated for the spectra measured at −240, −120, −25, 25, and 100 °C, and those at $\lambda =$ 300 were calculated for the spectra measured at −240, −25, 25, and 100 °C. The sharp intensity distribution indicates a distribution of holes with a relatively uniform size. As can be seen in Figure 7a,b, the size distribution for films with $\lambda = 1$ and 300 becomes broader, and the peak position shifts to a larger value of the lifetime (τ_3) with increasing temperature. This indicates that the free volume holes within the specimen become bigger and have a wider size distribution with increasing temperature, and at the same moment the molecular motion becomes more active. The same

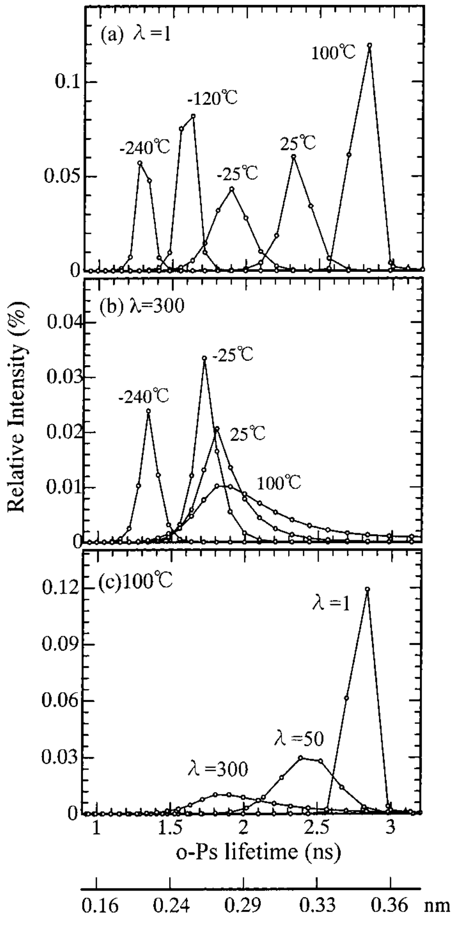

Figure 7. Histograms of the lifetime distribution for polyethylene films with $\lambda = 1$, 50, and 300 measured at the indicated temperature.

tendency is found for a drawn film with $\lambda = 50$, which was not plotted in this paper. The temperature dependence of the o-Ps lifetime distribution is accepted to be due to thermal expansion of the specimen, which is related to an increase in the molecular mobility.

In Figure 7c, it is of interest to consider that the free volume distribution becomes wider and wider and that the peak position shifts to a shorter value with increasing the drawing ratio. For an ultradrawn film with $\lambda =$ 300, the lifetime distribution at 100 °C shows a much wider and asymmetry profile, and the peak position shifts to a shorter value than those for the other two films with drawing ratios of $\lambda = 1$ and $\lambda = 50$. Our measurements indicated that although the free volume holes became smaller with increasing λ, some relatively larger holes still existed in the amorphous region, which resulted in a wider and asymmetry o-Ps lifetime distribution in a film with $\lambda = 300$. Another possibility is that the shape of the free volume hole has been stretched in the stretching direction under elongation. In any case, the small size of the free volume hole in the film with $\lambda = 300$ indicated the extremely poor activity of a large movement of amorphous chains, even at temperatures beyond the β dispersion in this sample.

According to previous papers,[41] the crystal lattice modulus of polyethylene measured for ultradrawn films with $\lambda = 300$ by X-ray diffraction was 211−222 GPa, which is independent of the temperature in the range 20−140 °C. The crystallinity measured by the Ruland method[42,43] decreased from 97% at 20 °C to 80% at 100 °C. Hence, it was concluded that the increase in the amorphous content with temperature causes a decrease in the storage modulus (E'). Namely, E' for ultradrawn films with the $\lambda = 400$ decreased from 216 GPa at 20 °C to 160 GPa at 100 °C. The high value of E' at 100 °C is surely due to the poor mobility of the amorphous chains. The result supports the histograms in Figure 7c and no appearance of the second transition of τ_3 in Figure 6b. Namely, the free volume distribution in the amorphous phase and the number of holes measured for the film with $\lambda = 300$ are less sensitive to elevated temperature, compared with the temperature dependence of the other two films. This behavior supports that E' maintains a modulus higher than 140 GPa at 100 °C, as shown in Figure 3.

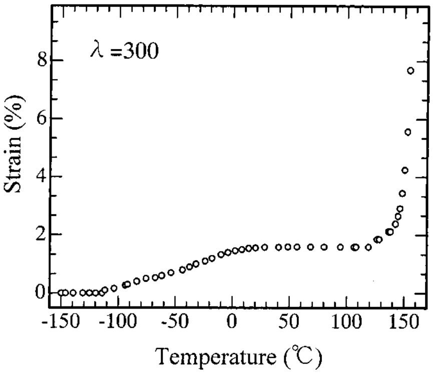

Figure 8. Temperature dependence of strain for a polyethylene film with $\lambda = 300$ under a constant stress of 5 MPa. The reference temperature was set at −150 °C.

Figure 8 shows the temperature dependence of the strain of a specimen with $\lambda = 300$ under a constant stress of 3.5 MPa. The reference temperature was set at −150 °C. The strain is almost constant at temperatures <−115 °C and tends to increase slightly up to 0 °C. The increase is associated with the mobility of the amorphous chains beyond the glass transition. The strain is almost constant at 0−120 °C. This indicates that the size distribution of the free volume holes is closely related to the thermal expansion of the specimen due to an increase in the molecular mobility. The drastic increase in strain tends to occur beyond 135 °C. Interestingly, this temperature, which is higher than the α transition, is the best one for ensuring the greatest elongation up to $\lambda = 300$.

Through a series of experiments, it may be concluded that positron annihilation plays an important role to analyze the β and γ dispersions for ultradrawn films with crystallinity >95%, since the superposition of E' and E'' at low temperatures < 0 °C is essentially very difficult for the films.

Conclusion

Two kinds of dispersions, the β and γ transitions, of ultradrawn polyethylene films were analyzed by positron annihilation. The specimens were prepared by gelation/crystallization from dilute solutions. The films were stretched by up to 300 times. The temperature dependence of the intensity (I_3) of the long-lived component of the orthopositronium (o-Ps) as well as that of the lifetime (τ_3) were in fairly good agreement with the mechanical dispersions. For the undrawn film, the peak positions of the β and γ transitions obtained by dynamic mechanical measurements correspond to the first and second transitions of τ_3. The β dispersion was not observed for the drawn films with $\lambda = 50$ and 300. The second transition of τ_3, corresponding to the β dispersion, was observed for the film with $\lambda = 50$, but not for the specimen with $\lambda = 300$. No appearance of the second transition for the specimen with $\lambda = 300$ is an unusual phenomenon for polyethylene films. This is due to crystallinity higher than 95% and a poor mobility of amorphous chains. The increasing degree of I_3 with temperature was much smaller compared with that of the other two specimens, and the average value of intensity I_3 at 100 °C was lower than that observed at 25 °C for the film with $\lambda = 50$. This indicated that the number of free volume holes at 100 °C was much fewer than those for the film with $\lambda = 50$ at 25 °C and that their average size was also smaller. Such unusual phenomena justify the experimental results that thermal expansion of the specimen due to an increase in the molecular mobility is almost zero in the temperature range from 0 to 120 °C, and consequently, the storage modulus is higher than 130 GPa at 100 °C.

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