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# Positron annihilation behavior in poly(ethylene)

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**Abstract**

The intensities and lifetimes of positrons annihilating in low and high density poly(ethylene) (LDPE and HDPE) were measured. As expected the orthopositronium (oPs) pick-off lifetime and intensity increases with temperature; the relative values of the intensity are consistent with differential scanning calorimetry (DSC) results. Two other components with shorter lifetimes were deconvoluted from the complex exponential decay profiles. Detailed studies were carried out on quenched and annealed samples of LDPE and HDPE in an attempt to correlate the two shorter components with crystallization; both CsF and plastic scintillators were used. DSC analyses were also carried out. We conclude that the shortest lifetime component is caused by a combination of parapositronium (pPs) decay and the annihilation of free positrons in the crystalline regions and that the second longest lived component can also be associated with crystalline regions especially the crystalline/amorphous boundary. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Positron annihilation; Poly(ethylene); Crystallinity

## 1. Introduction

Positron annihilation has been used extensively to monitor changes in the amorphous component of polymers. Such studies rely on that part of the analysis which relates to the annihilation of the positron in orthopositronium (oPs) by "pick-off" in the time range of 2 to 5 ns. After formation, the oPs atom "seeks" out regions of lower density and becomes "confined" there. The "pick-off" lifetime $t3$ is inversely proportional to the amount of overlap of the wavefunctions of the positron and a local electron. Thus the variation of $t3$ with such variables as temperature, pressure or percent crystallinity gives information about changes in the micro-density of the sample under study. The origin of the shorter lifetime components has not been firmly established. Various possibilities for these short time decays in poly(ethylene) were summarized by Suzuki et al. [1] as: free positron annihilation in less ordered regions between folded chains [2], decay of positrons forming a bound system with molecules [3], decay of Ps trapped at the crystal–amorphous interface [4], decay of a bound positron or a Ps-like system [5].

Suzuki et al. [1] dismiss the possibility of associating the second longest lifetime component with crystallinity. Their argument is based on the fact that this component does not disappear above the polymer melting point. However, in various studies [6–10] it has been shown that the polyethylene melt is not structurally homogeneous. Instead, it comprises several phases of varying density. The most dense of these phases originates in the crystalline structure of the polymer and is very stable even above the melting point, as evidenced by high temperature NMR experiments [6,9,10]. We have now done positron annihilation experiments which indicate that the second longest-lived component in the positron annihilation spectrum can be associated with crystalline regions especially in low density poly(ethylene) (LDPE).

## 2. Experimental

The detection equipment used for the first two studies reported here consists of CsF scintillators coupled to Hamamatsu PMT assemblies H2431. These tubes are characterized by short rise times and amplifications around $10^6$ when operated at $-3$ kV. The voltage supply for our experiments was $-2.91$ kV. The data were collected through a Canberra S100 MCA. The time resolution of our system is 0.0204 ns/channel. The positron source was $^{22}$Na which was sealed between thin Kapton™ foils secured by 3M Kapton™ tape (3M-5413). For the third study the CsF crystals were

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Table 1
Branching characteristics of polyethylene samples

| Sample | Branches per 1000 backbone C's | | | | | |
|---|---|---|---|---|---|---|
| | Isolated methyl | Ethyl | Quaternary ethyl | Butyl | Amyl | > 5C |
| AT 502 | — | 3.9 | 1.9 | 9.0 | 3.5 | 6.2 |
| AT 227R | — | 3.3 | 2.4 | 12.3 | 4.6 | 7.6 |
| Sclair 2907 | 0.2 | 0.4 | — | — | — | 1.35 |

exchanged for plastic scintillators and the voltage was reduced to − 2.21 kV.

In Study 1 (CsF scintillators), one sample of a LDPE was subjected to a temperature cycle in which a return to room temperature was inserted before each increase in temperature. The temperature was increased in steps of 20°C up to 120°C (except the first step, which was an increase of 17°C from 23°C). A vacuum of ~ 0.001 mbar was held at all times. A sample made of layers of Kapton™ film was used to determine the resolution function. Ge metal was used to determine the source correction. Spectra of $1 \times 10^6$ counts were collected and analyzed using the PATFITT-88 program from Riso [11]. The resolution function was determined to be 455 ps in width. Three components could be resolved.

In Studies 2 and 3, four samples were compared: quenched LDPE, quenched high density poly(ethylene) (HDPE), annealed LDPE, and annealed HDPE. Annealing was done by pressing samples on a hot press between layers of thick aluminium foil at 170°C. The entire package was then transferred to an oven at 180°C and cooled at 5°/h [12–14] to room temperature. Quenching was achieved by simply placing the samples coming from the 170°C press in a water bath. Positron annihilation spectra were accumulated to $6 \times 10^6$ counts and analyzed using the PATFITT-88 program. Ge metal was used to determine the resolution function. The experiments were done at various temperatures ranging from room temperature to 140°C and the samples were in the oven for different times, depending on the temperature profile being used. Three components could be resolved.

A differential scanning calorimetry (DSC) analysis was also done on the materials used in these studies. Each sample was scanned twice. Measured values of heat of

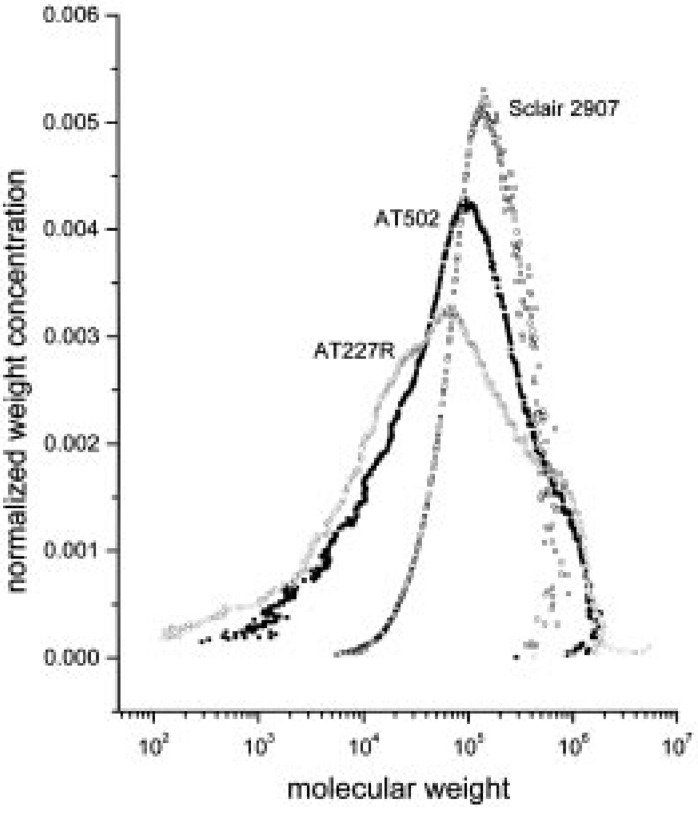

Fig. 1. Normalized molecular weight distributions of AT502, AT227R and Sclair 2907.

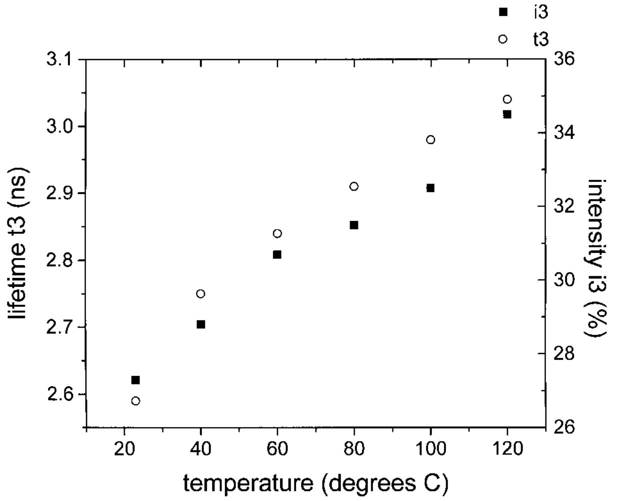

Fig. 2. The lifetime and intensity of the longest component in LDPE as a function of temperature. For errors, see Table 3.

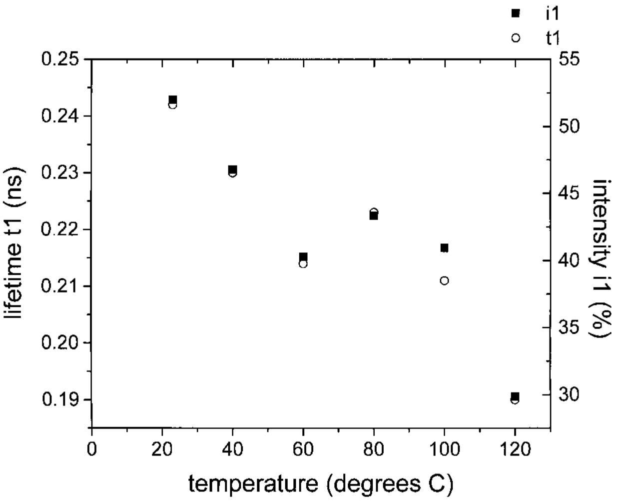

Fig. 4. The lifetime and intensity of the shortest component in LDPE as a function of temperature. For errors, see Table 3.

fusion (cal/g), onset of melting (°C) and maximum melting temperature (°C) were respectively as follows: annealed LDPE (29,25; 111,110; 119,117), quenched LDPE (26,28; 108,110; 118,118), annealed HDPE (56,49; 131,126; 139,134) and quenched HDPE (43,49; 125,126; 134,135).

Study 3 was a repeat of Study 2 but with plastic scintillators instead of CsF. There were several advantages to this including no backscattering which permitted the photomultiplier tubes and source to be better aligned. This improved the count rate, thereby reducing the time the sample spent at any given temperature. The FWHM was much smaller, 214 ps compared to 400 ps, which should give more reliable results for the shorter lifetime component(s). The results from Study 2, in which the experiments were done with CsF crystals with the stop PMT centered underneath the sample and the start PMT displaced halfway from the centre above the sample, were used to support the more accurate Study 3 and allow for firmer conclusions.

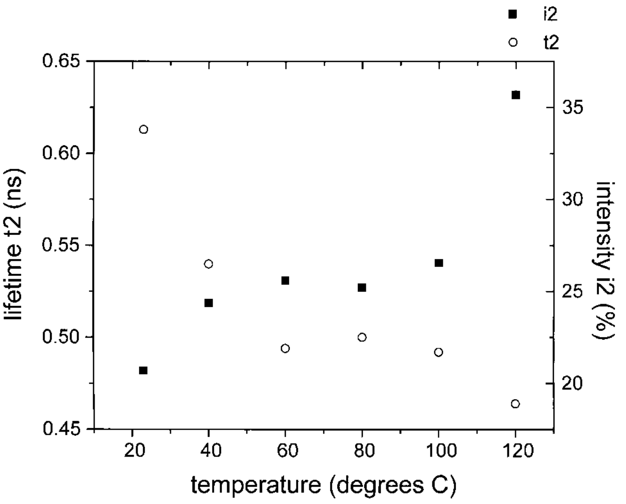

Fig. 3. The lifetime and intensity of the medium component in LDPE as a function of temperature. For errors, see Table 3.

The polymer samples were pressed disks with a 3.6 cm diameter and a 2.0 mm thickness. The thickness range was calculated from the formula provided by Tabata and coworkers [15]; these samples were just thick enough for positron annihilation experiments. Table 1 lists the branching characteristics of the poly(ethylene) samples. These were determined by $^{13}$C NMR analyses. The molecular weight distributions of the LDPEs, measured by high temperature size exclusion chromatography in 1,2,4-trichlorobenzene solution [16], are shown in Fig. 1.

The effect of irradiation on various polymers has been studied by Welander and Maurer [17] who found that the intensity *i*3 decreases with the total amount of radiation but that the effect was less at higher temperatures. Suzuki et al. [1] studied the effect of irradiation on poly(propylene) (PP) and found that it was more severe in air than in vacuum. To check how sensitive our polymers are, a sample of LDPE (AT227R) was subjected to 16 h of radiation with our strongest source (111 μCi) at room temperature under a vacuum of 0.02 mbar. New spectra were started each hour. There was no change in the parameters over the time studied. In contrast, a sample of a CIL 502/15% PP blend subjected to irradiation at room temperature in various experiments spaced over several days showed clear signs of damage.

## 3. Results and discussion

### 3.1. Study 1

The results for the positron annihilation experiment on LDPE CIL502 are shown in Figs. 2–4. As expected, *t*3, the oPs pick-off lifetime, increases with temperature, as does the corresponding intensity, *i*3 (Fig. 2). Both *t*2 and *t*1

Table 2
Room temperature data from the temperature cycle study

| Line number | Previous temp. (°C) | $t1$ (ns) | $t2$ (ns) | $t3$ (ns) | $i1$ (%) | $i2$ (%) | $i3$ (%) | $\chi 2$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 23 | 0.244 | 0.610 | 2.57 | 52.2 | 20.3 | 27.5 | 1.15 |
| 2 | 40 | 0.243 | 0.620 | 2.62 | 52.1 | 20.9 | 27.0 | 1.44 |
| 3 | 40 | 0.240 | 0.621 | 2.60 | 52.1 | 20.6 | 27.3 | 1.14 |
| 4 | 60 | 0.225 | 0.530 | 2.54 | 46.0 | 26.0 | 28.0 | 1.25 |
| 5 | 60 | 0.242 | 0.600 | 2.58 | 51.5 | 21.1 | 27.4 | 1.43 |
| 6 | 80 | 0.229 | 0.540 | 2.58 | 47.1 | 25.0 | 27.9 | 1.29 |
| 7 | 100 | 0.223 | 0.530 | 2.59 | 45.6 | 26.7 | 27.8 | 1.30 |
| 8 | 100 | 0.224 | 0.529 | 2.58 | 45.9 | 26.1 | 28.0 | 1.14 |
| 9 | 120 | 0.227 | 0.540 | 2.60 | 46.6 | 27.0 | 26.4 | 1.32 |
| 10 | 120 | 0.246 | 0.610 | 2.62 | 52.7 | 21.2 | 26.1 | 2.11 |
| Average | | 0.23 | 0.57 | 2.59 | 49.2 | 23.5 | 27.3 | |
| St. dev. | | 0.01 | 0.04 | 0.02 | 3.1 | 2.9 | 0.7 | |

decrease, $i1$ decreases, $i2$ is approximately constant below the melting point, but increases at about 120°C indicating that the melting process has started, but there are no dramatic changes below the melting region for either $i1$ or $i2$.

The room temperature data collected in between the temperature increases are summarized in Table 2; the elevated temperature data are given in Table 3. The averages in Table 2 have been calculated over all the room temperature data. In Figs. 2–4 and Table 3, however, the averages used for the room temperature data have been calculated using only the data in lines 1–3 and 5 in Table 2. This acknowledges that there is a clear change in the parameter values after the sample has been heated to 80°C. Only the data in lines 4 and 10 do not fit this trend.

The shortest lifetime component in our experiments is a combination of parapositronium (pPs) decay and a mode of free positron decay. From evidence in the literature, the parameters associated with pPs are not affected by temperature [2]. Hence, changes in $t1$ and $i1$ are a result of free positron decay. Thus, if either the first or the second component is because of annihilation in the crystalline regions, then the decrease in the lifetime suggests that the sample melted and partially recrystallized under the conditions of this experiment. In view of the fact that $i1$ decreases with temperature, it is plausible that this component contains information about the crystalline regions, while the second component originates in crystalline/amorphous boundary layers. The latter contention would be consistent with an increase in $i2$ around the melting point. More evidence is required to confirm this idea. Also the source of the second component could well be multifold and originate due to $e+$ annihilation in the amorphous regions as well.

### 3.2. Studies 2 and 3

Quenched and annealed samples of both LDPE AT277R (AT Plastics, Brampton, Ontario) and an HDPE, Sclair 2907 (Novacor Chemicals, Calgary, Alberta), were made to study the effect of temperature in more detail. DSC results showed that the annealed LDPE was 15% more crystalline than its quenched version. The difference in crystallinity was 28% in the case of the HDPE.

The positron annihilation experiments were set up to monitor the signal as a function of temperature as well as time. To do this, the temperature profiles were as follows: (1) 23°C, 80°C, 110°C, 140°C; (2) 80°C, 110°C, 140°C; (3) 110°C, 140°C; (4) 140°C. Profile 1 was therefore our long time exposure, profile 4 gave the shortest time exposure. The samples were not cooled between temperature increases and the vacuum at all times was 0.02 mbar. The resulting lifetimes and intensities showed no change with time. Therefore, only the averaged results were used. The results for Study 3 are shown in Figs. 5–7.

Below the temperatures of the melting region the annealed samples show a suppressed value of $i3$ when compared to the corresponding quenched samples (see Fig. 5). This is especially clear in the HDPE data. At 140°C the manner of cooling of the samples is no longer distinguishable for the longest-lived component. At the lower temperatures (below 140°C) the amorphous component is smaller in the HDPE than in the LDPE. This agrees with the DSC data.

The $t3$ lifetimes in both quenched polyethylenes and the annealed LDPE are the same and increase with temperature

Table 3
Data for temperature cycle study at elevated temperatures

| Temperature (°C) | $t1$ (ns) | $t2$ | $t3$ | $i1$ (%) | $i2$ | $i3$ | $\chi^2$ |
|---|---|---|---|---|---|---|---|
| 23 | 0.242 | 0.613 | 2.59 | 52.0 | 20.7 | 27.3 | —[a] |
| 40 | 0.230 | 0.540 | 2.75 | 46.8 | 24.4 | 28.8 | 1.22 |
| 60 | 0.214 | 0.479 | 2.84 | 40.3 | 29.0 | 30.7 | 1.06 |
| 80 | 0.223 | 0.500 | 2.91 | 43.3 | 25.2 | 31.5 | 1.30 |
| 100 | 0.211 | 0.492 | 2.98 | 40.9 | 26.6 | 32.5 | 1.22 |
| 120 | 0.190 | 0.464 | 3.04 | 29.9 | 35.7 | 34.5 | 1.10 |
| Typical error | 0.006 | 0.02 | 0.01 | 2.0 | 2.0 | 0.2 | |

[a] See text for origin of these room temperature data.

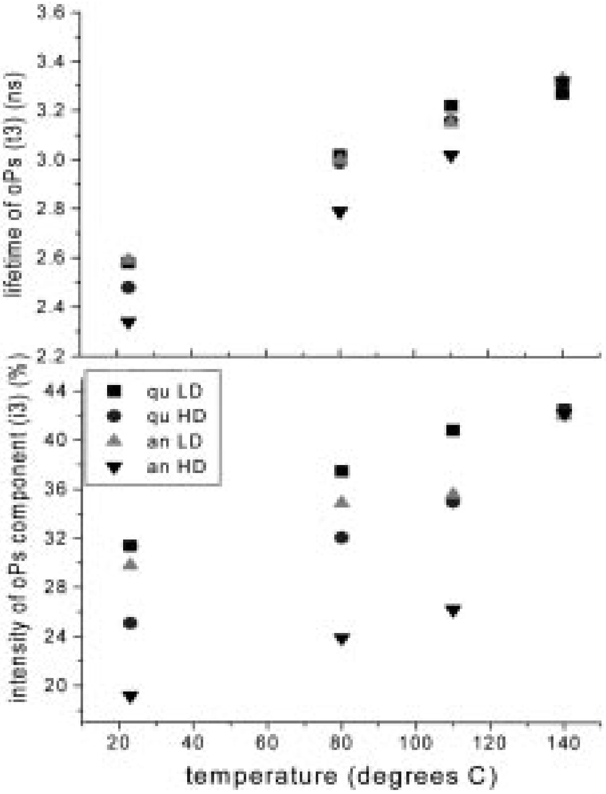

Fig. 5. The lifetime and intensity of the shortest lifetime component in LDPE and HDPE as a function of temperature and morphology. Data obtained with plastic scintillators. qu = quenched, an = annealed, LD = AT227R LDPE, HD = Sclair 2907 HDPE.

in a manner producing a slightly convex curve. The annealed HDPE, however, shows a slightly shorter lifetime at temperatures below melting and the increase of *t*3 with increase in temperature is linear. The free volume in the annealed HDPE therefore increases more slowly with temperature than in the other samples. The trends emerging from these experiments (Fig. 5) were the same as those obtained with the CsF crystals, but the absolute values were different.

From these results (Fig. 5) it is quite clear that annealed HDPE has the lowest proportion of long lifetime component, i.e. it is the least amorphous. This is consistent with the DSC data, which showed it to be the most crystalline. The regions of low microdensity in the amorphous parts of the annealed HDPE are also smaller, as can be seen from lower values of *t*3 below the melting point. From this data set, the quenched HDPE appears to be slightly more crystalline than the annealed LDPE. This is consistent with the DSC data which show, as expected, that the heat of fusion for the HDPE is much higher than for the LDPE. However, the differences in *i*3 are not proportional to the differences in the heat of fusion. There is a large difference in heat of fusion between the LDPE and HDPE, with a much smaller difference between the quenched and annealed versions of each polymer. The difference in *i*3 between the quenched and annealed version of HDPE is much larger than one would expect based on the difference between the two annealed polymers and the DSC results.

Table 4
The crystalline component of *i*1

| Sample | 23°C | 80°C | 110°C | 140°C |
|---|---|---|---|---|
| Qu. LDPE | 23.4 | 16.0 | 11.3 | 12.3 |
| Qu. HDPE | 17.8 | 25.7 | 25.1 | 10.4 |
| Ann. LDPE | 29.5 | 19.4 | 16.7 | 10.4 |
| Ann. HDPE | 41.8 | 41.8 | 41.5 | 10.7 |

For the second component (Fig. 6) it was found that for the LDPE *t*2 decreased up to the melting point range, then increased. The annealed HDPE does the opposite: *t*2 increases from a much higher value up to the melting point range, then decreases; the quenched HDPE shows a slight increase with increase in temperature. At 140°C the values of *t*2 cluster; there is no memory of the various heat treatments. *i*2 remains fairly constant (with the exception of the spurious value for quenched HDPE at 23°C which can be ignored based on the CsF results). The only possible exception is the annealed HDPE for which values of *i*2 are below the values for the quenched HDPE and fall slightly then increase as the temperature in increased. The increase in

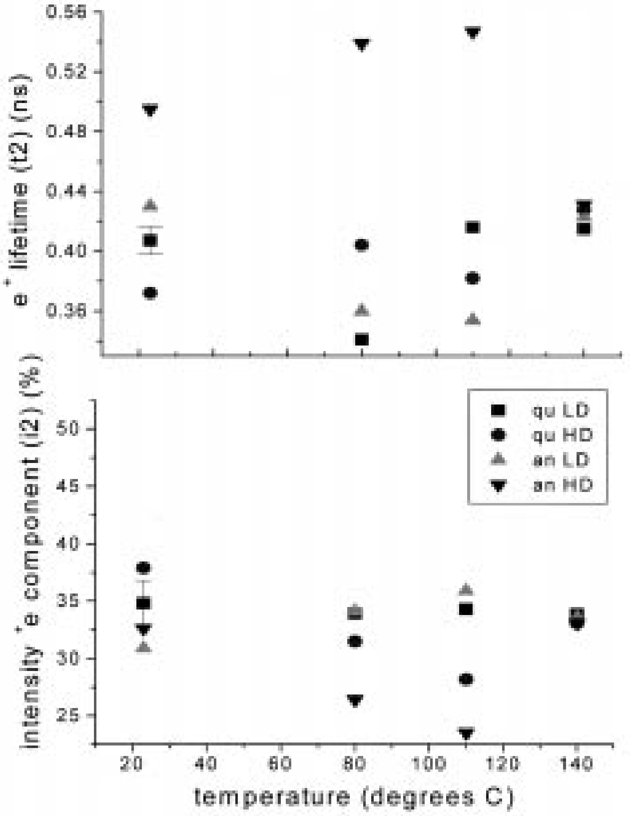

Fig. 6. The lifetime and intensity of the medium lifetime component in LDPE and HDPE as a function of temperature and morphology. Data obtained with plastic scintillators. Labels as in Fig. 5.

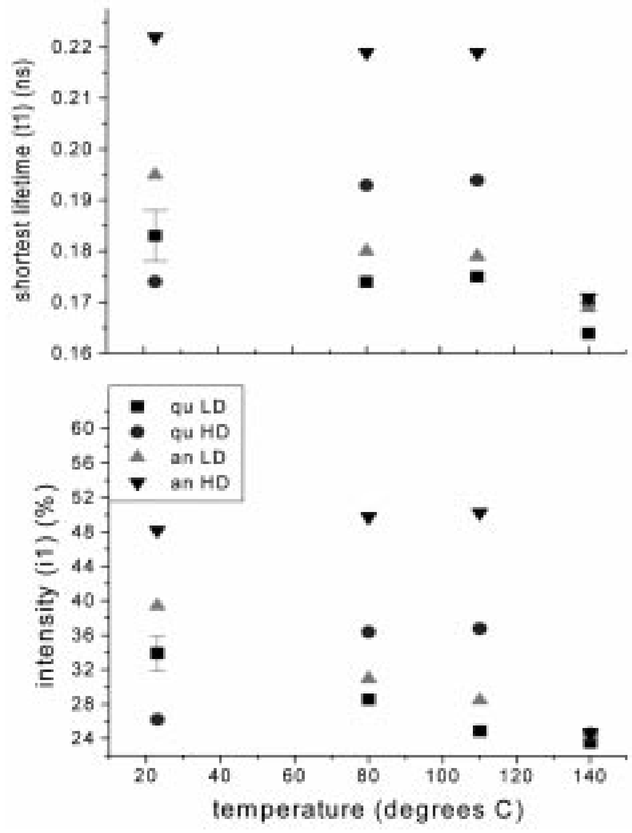

Fig. 7. The lifetime and intensity of the longest lifetime component in LDPE and HDPE as a function of temperature and morphology. Data obtained with plastic scintillators. Labels as in Fig. 5.

*t*2 below 110°C for the annealed HDPE and the decrease in *i*2 may be attributed to a perfection of order in the crystalline regions of the polymer combined with expansion due to an increase in temperature. Apparently, the segmental motions in the HDPE are not sufficient to cause the crystal regions to break up until the onset of melting at ~ 130°C.

Both the lifetime and intensity of the shortest component for the LDPE (Fig. 7) decrease as the temperature is increased. Again melting and recrystallization is suggested. The results for the HDPE again show a marked difference between the quenched and annealed samples and show that the decreases in *t*1 and *i*1 are delayed to nearer the melting point. *t*1 and *i*1 are constant for the annealed HDPE for lower temperatures; for the quenched HDPE *t*1 and *i*1 first increase, then plateau and then decrease.

Finally we note that at 140°C these samples are no longer distinguishable in terms of all three positron annihilation components.

## 4. Conclusions

From these results, we can conclude that the interpretation of Stevens and Lichtenberger [2] is quite plausible. This would mean that *t*1 and *i*1 are caused by pPs decay and annihilation of free positrons in the crystalline regions of the polymer. The pPs part would be equal to 1/3 the intensity of *i*3 with the remainder of *i*1 being a result of free positrons decaying in remnant crystalline regions. The decrease in *t*1 and *i*1 with temperature could then be explained by the melting of the crystalline regions. The percentages due to free positron decay after subtracting the pPs component are shown in Table 4.

In annealed HDPE the crystalline structure is relatively stable until the polymer is very close to the peak melting point. The amount of crystalline material in the annealed polymers for each class is higher than in the quenched versions. This trend is consistent with the DSC results although the degree to which they differ is not the same. It is generally believed that pPs has a lifetime of 125 ps. Our data shows that *t*1 after melting is about 164 ps. The difference between these two values is because of the crystalline remnant. Also note that even at 140°C, there is around 10% of very tight, pseudo-crystalline material left in all samples.

*t*2 decreases at first because relatively tight material from the crystalline regions is added, while the looser regions become part of the amorphous component. Above the melting point range, the whole structure loosens up resulting in an increase in *t*2. In annealed HDPE, *t*2 increases with temperature as a result of expansion because no crystalline material is added; the crystals are too stable to be affected below the melting point range. However, above the melting point range, the structure collapses; the crystalline/amorphous boundary layer content increases and *t*2 decreases and *i*2 increases. The amount of this crystalline/amorphous boundary layer material does not vary much with temperature below the melting range in the LDPEs and the quenched and annealed versions have about equal amounts. In the HDPEs, the quenched version has more interstitial material than the annealed material. This is as would be expected. The amount decreases with increasing temperature as part of it becomes truly amorphous with no compensation from the crystalline regions.

Finally, the third component is entirely consistent with the behavior of amorphous material under a temperature increase. The relative amounts of *i*3 in the different samples are consistent with the DSC results. *t*3 increases more slowly in the annealed HDPE than in any of the other samples. Thus, not only is the crystalline component of this polymer very stable, but the amorphous regions are stiffer than in the quenched HDPE and LDPEs.

## Acknowledgements

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