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Polymer 42 (2001) 5381–5388

polymer

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# The local free volume in metallocene-catalysed poly(α-olefin)s: a positron lifetime study

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Received 31 August 2000; accepted 24 November 2000

**Abstract**

Positron lifetime measurements are reported for linear poly(α-olefin)s from polypropylene to poly-1-eicosene polymerised using zirconocene catalyst. For comparison a low density polyethylene was also studied. Four lifetimes are resolved, the longest of them ($\tau_4$) is attributed to *o*-Ps annihilation from free-volume holes in the amorphous phase and is used to estimate the mean volume of these holes. It is observed that the hole size increases with increasing separation between the measuring temperature ($T = 300$ K) and the glass transition temperature $T_g$, estimated with differential scanning calorimetry. Among the poly(α-olefin)s the average hole volume is the largest in poly-1-dodecene (0.205 nm$^3$, $T_g = 166$ K) and the lowest in polypropylene (0.117 nm$^3$, $T_g = 262$ K). A method for estimation of the glass transition temperature $T_g$ from the experimental hold volumes is proposed. From comparison of amorphous and crystalline densities the fractional free volume was calculated. From this the number of holes was estimated to be 0.5–0.9 nm$^{-3}$. The effect of exposure of the polymers to positron radiation from the source on the *o*-Ps annihilation parameters was also studied. While lower poly(α-olefin)s show a more or less pronounced exponential decrease of the *o*-Ps intensity $I_4$ as a function of time, a slight increase is observed in higher poly(α-olefin)s. Possible reasons for this behaviour are discussed. © 2001 Published by Elsevier Science Ltd.

*Keywords*: Poly(α-olefin)s; Free volume; Positron annihilation

## 1. Introduction

Many of the application-based macroscopic properties of polymers depend crucially on the microstructure of the subnanometer local free-volume holes that arise as a consequence of the irregular molecular packing in these materials [1–4]. The appearance of holes lowers the density of the amorphous polymer by about 10% compared with the crystalline state of the same material. Although the concept of free volume in polymers has been known for almost half of a century, only a limited amount of experimental data has been reported. This is mainly due to a lack of suitable probes for open volumes of molecular dimensions. Positron annihilation is a well-established technique for studying atomic and subnanometer-size voids in solids [5,6]. It has also been developed to be, probably, the most successful technique for studying local free volumes in polymers [6–16].

Positrons emitted from radioactive sources (e.g. $^{22}$Na) into the polymeric matrix become thermalised and may annihilate with an electron, or form positronium (Ps) — a hydrogen-like bound state [6]. While *para*-positronium (*p*-Ps) decays quickly via self-annihilation, the long-lived species *ortho*-positronium (*o*-Ps) undergoes pick-off annihilation during collision with molecules. *o*-Ps annihilates preferentially in regions of low atomic density (i.e. a “hole”). Its lifetime reflects very sensitively local free volumes of typical size 0.3–1 nm [7–13].

In this work we study the free volume in various poly(α-olefin)s which were polymerised with a metallocene catalyst. This catalyst delivers polymers of high isotacticity and small polydispersity. Positron lifetime spectra of high total count and good time resolution are analysed using both the discrete-term analysis (routine LIFSPECFIT [17]) and the routine MELT (maximum entropy for lifetime analysis [18,19]) which assumes a continuous lifetime distribution. From the lifetime parameters we assess size and number of

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PII: S0032-3861(00)00890-9

free-volume holes in the amorphous phase and discuss their properties in relation to the glass transition temperature. This work is thought also as a basis for the investigation of α-olefin copolymers planned for the future.

## 2. Experimental

Linear poly(α-olefin)s, $(-CH_2-CHR-)_n$ with $R = (-CH_2)_NH$, were polymerised using metallocene catalyst ($Et[Ind]_2ZrCl_2$/methylaluminoxane). Details of the synthesis and characterisation of these polymers (molecular weight, molecular weight distribution, $^{13}C$ NMR spectra, differential scanning calorimetry (DSC) glass transition and melting temperatures) can be found in a previous paper [20]. In contrast to heterogeneous Ziegler–Natta catalysts homogeneous metallocene catalysts have only one kind of active site and produce polymers with a narrow molecular weight distribution. The total number of carbon atoms in the chemical repeating unit of the polymers under investigation, $N_c = N + 2$ ($N$ is the number of methylene groups), is 3 (polypropylene, PP), 4 (poly-1-butene), 12 (poly-1-dodecene), 16 (poly-1-hexadecene), 18 (poly-1-octadecene), and 20 (poly-1-eicosene). The weight-average molecular weight $M_w$ varied from 29 to 70 kg/mol with the exception of polypropylene (128 kg/mol). The ratio of weight- to number-average molecular weights (the polydispersity $D$) varied from 1.5 to 2.2. The melting points and glass transition temperatures were determined using DSC (see Fig. 5). For comparison a commercial low density polyethylene ($N_c = 2$, PE) having approximately the same crystallinity as the polypropene (≈40% from DSC) was also studied. This PE was already investigated in detail previously [21].

The positron lifetime experiments were carried out at room temperature using a fast–fast coincidence system [5,6] with a time resolution of 235 ps (full width at half maximum, FWHM, of a gaussian resolution function) and a channel width of 12.5 ps. The specimens were platelets of $8 \times 8\ mm^2$ in area and 1.5 mm in thickness. For each experiment, two identical samples were sandwiched around a $5 \times 10^6$ Bq positron source ($^{22}Na$), prepared by evaporating carrier-free $^{22}NaCl$ solution on a Kapton foil of 8 μm thickness. Well-annealed aluminium platelets ($\tau = 162$ ps) were studied as a reference material for estimating the resolution FWHM and the positron source correction. Thirty-five measurements, each lasting 1200 s, were performed for each of the specimens. In a preliminary inspection the time-zero of each 1200 s spectra was determined. The counts of those spectra where the time-zero did not differ by more than one channel were summed to a final spectrum which contained a total number of $\sim 25 \times 10^6$ coincidence counts. For the final analysis the content of every four channels were summed up to obtain the coincidence count for one 50 ps channel. The procedure described delivers spectra of very good statistical accuracy, high time resolution and small influences due to possible spectrum drifts.

## 3. Data analysis and results

The positron lifetime spectrum is conventionally described by a sum of discrete exponentials [6]

$$s(t) = \sum (I_i/\tau_i)\exp[-(t/\tau_i)], \tag{1}$$

each having a characteristic positron lifetime of $\tau_i$ with a relative intensity of $I_i$, $\sum I_i = 1$. Assuming that the positron lifetimes $\tau$ follow a distribution, the lifetime spectrum may be described by a continuous decay form [18,19]:

$$s(t) = \int_0^\infty I(\tau)(1/\tau)\exp(-t/\tau)\mathrm{d}\tau \tag{2}$$

where $\int I(\tau)\mathrm{d}\tau = 1$. The observed spectrum may be expressed by:

$$y(t) = R(t)^*(N_t s(t) + B) \tag{3}$$

where $^*$ denotes a convolution of the decay integral with the resolution function $R(t)$ (a gaussian), and $B$ and $N_t$ are the background and the total count of the spectrum, respectively.

For the discrete-term analysis we used the routine LIFSPECFIT [17]. In this routine the model function (1) together with Eq. (3) is least-squares fitted to the experimental data points. From the fit the characteristic lifetimes $\tau_i$ and their intensities $I_i$ are obtained. The routine MELT [18,19] inverts the lifetime spectrum into a continuous lifetime distribution $I(\tau)$ (Eq. (2)) using a quantified maximum entropy method. The parameters of the analysis were chosen as in a previous paper [22].

The positron lifetime distribution $I(\tau)$ obtained from the MELT analysis of the lifetime spectra for poly-1-butene ($N_c = 4$) and poly-1-dodecene ($N_c = 12$) are shown in Fig. 1 as examples. The lifetime distribution exhibits four well-separated peaks. The characteristic lifetime $\tau_i$ of each peak is calculated from its mass centre and its intensity $I_i$ from the relative area below the corresponding peak. The two lower peaks have mass centres at $\tau_1 \approx 160$ ps and $\tau_2 \approx 360$ ps. These lifetimes are well known and come from $p$-Ps self-annihilation and free positron (not Ps) annihilation [6–13].

The third ($\tau_3 \approx 1$ ns) and fourth ($\tau_4 \approx 2.2$–3 ns) lifetime peaks are attributed to $o$-Ps annihilation. In vacuum, $o$-Ps lives 142 ns and decays via emission of three γ-photons [6]. In matter, so-called pick-off annihilation occurs, in which the positron of the Ps annihilates with an electron of opposite spin to its bound partner during a collision with a molecule. The result is the emission of two 0.51 MeV γ-photons rather than three and a much reduced $o$-Ps lifetime that depends on the frequency of collisions. In the presence of a sufficient concentration of small cavities in the sample, the Ps density is largely confined within these open volumes and

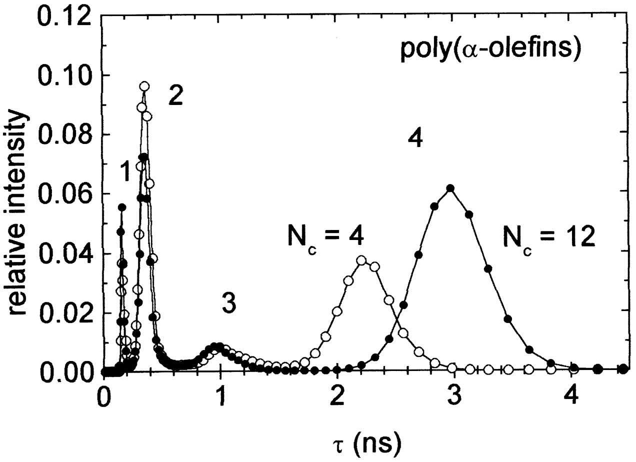

Fig. 1. Positron lifetime distribution $I(\tau)$ analysed with the MELT routine from the lifetime spectra of poly-1-butene ($N_c = 4$) and poly-1-dodecene ($N_c = 12$).

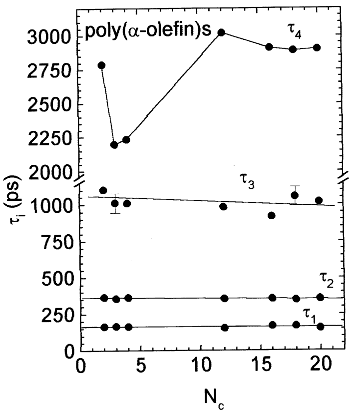

Fig. 2. Characteristic positron lifetimes $\tau_i$ in poly(α-olefin)s obtained form the MELT analysis as a function of the number of carbons in the chemical unit $N_c$.

their extent is reflected in the *o*-Ps pick-off lifetimes being in the nanosecond-range [7–13]. From this it follows that the *o*-Ps lifetimes respond to material properties (holes size, packing density) while the *p*-Ps and the free positron annihilation do not or do so only weakly. As observed in Fig. 1, the fourth peak of the lifetime distribution shifts from $\tau_4 =$ 2.2 ns in poly-1-butene to 3 ns in poly-1-dodecene. This lifetime can be attributed to the *o*-Ps pick-off annihilations at local free volumes (holes) in the amorphous phase. As can be clearly seen, the hole size increases when going from poly-1-butene to poly-1-dodecene.

The nature of third component of ~1 ns is not entirely clear. For semicrystalline polymers, the most natural explanation is that this component comes from *o*-Ps pick-off annihilation within the crystalline regions which are more densely packed than the amorphous phase [21–23]. There are several arguments in favour of this interpretation. As shown by Serna et al. [24], the intensity of the third lifetime component increases while the intensity of the fourth lifetime component decreases with increasing crystallinity of PE. We have studied PE of widely varying crystallinity and found a similar behaviour of the *o*-Ps intensities. As recently shown [21], $\tau_3$ increases between 80 and 300 K as expected from the thermal expansion of the PE crystal unit cell. In the following we will attribute the $\tau_3$ lifetime to *o*-Ps pick-off annihilations from the crystalline phase of the poly(α-olefin)s.

The behaviour of the four lifetimes $\tau_i$, the average positron lifetime $\tau_{av}$ and the *o*-Ps intensities $I_3$ and $I_4$ are shown in Figs. 2 and 3. The average positron lifetime, defined as mass centre of the lifetime spectrum $s(t)$, $\tau_{av} = \int ts(t)\mathrm{d}t$, is an integral and model independent parameter. It is related to the parameters of the individual components via $\tau_{av} = \sum \tau_i I_i$. The characteristic lifetimes of the two lower peaks in the MELT lifetime distribution, $\tau_1$ and $\tau_2$, do not depend on the number of carbons $N_c$: $\tau_1 = (162 \pm 7)$ ps and $\tau_2 =$ $(356 \pm 9)$ ps. $\tau_3$ has an average value of 1000 ps but shows stronger fluctuations between 900 and 1100 ps (statistical error: ±65 ps). The intensities of these lifetimes show random fluctuations in the range $I_1 = 15$–22%, $I_2 =$ 40–58% and $I_3 = 5$–8%.

The longer *o*-Ps lifetime $\tau_4$ shows a remarkable dependence on the number of carbons $N_c$ (Fig. 2). $\tau_4$ decreases from 2780 to 2200 ps when going from PE to PP. These lifetimes agree with findings in the literature for PE [21,23–27] and PP [28–31]. A slight increase of $\tau_4$ to 2285 ps for poly-1-butene is followed by a rapid rise to 3020 ps for poly-1-dodecene. After that a slight decrease

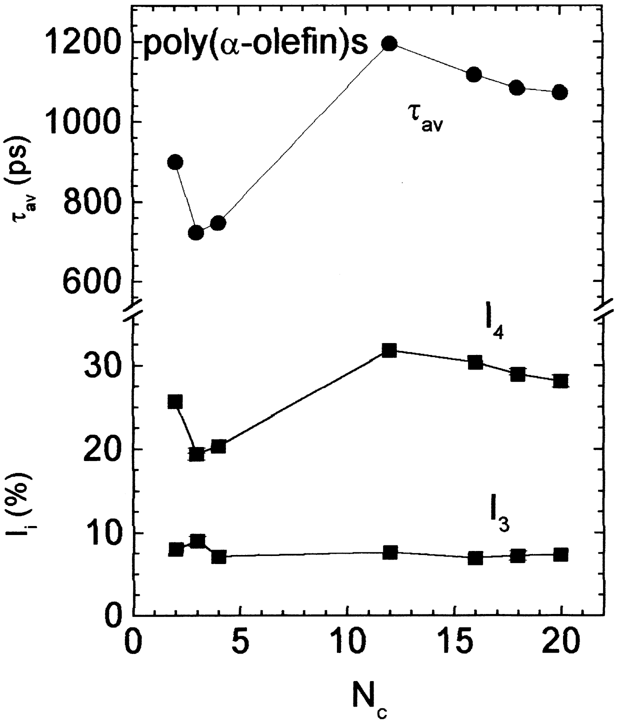

Fig. 3. The average positron lifetime $\tau_{av}$ and the intensities of the *o*-Ps components $I_3$ and $I_4$ in poly(α-olefin)s as function of the number of carbons in the chemical unit $N_c$.

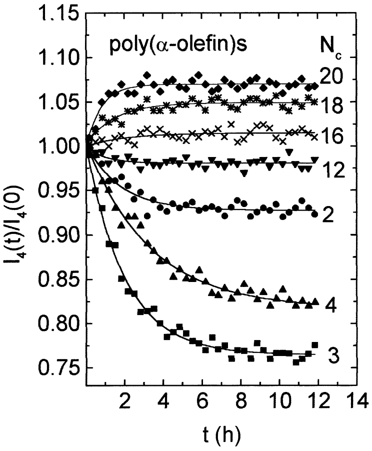

Fig. 4. The intensity $I_4(t)$ of the *o*-Ps lifetime $\tau_4$ normalised to initial value $I_4(0)$ as function of the exposure time *t* of the poly(α-olefin) samples to radiation from the positron source. Each of the measurements lasted 1200 s. The results were obtained via a constrained four-discrete term analysis (LIFSPECFIT) with fixed lifetimes. The lines are due to least-square fits of decreasing or increasing exponential function through the data points.

with increasing $N_c$ follows. The intensity of the lifetime component attributed to *o*-Ps annihilation in the amorphous phase, $I_4$, varies analogously to the lifetime $\tau_4$ (Fig. 3). $I_4$ mirrors the *o*-Ps yield in the amorphous phase which may be related to the size of local open volumes in which Ps is formed [32]. Due to the large value of $\tau_4$ the behaviour of $\tau_{av}$ is dominated by the term $I_4\tau_4$. The results of the MELT analysis agree within the statistical errors with the results from a four-discrete term LIFSPECFIT fit (not shown).

It is well known that radiation-induced changes occur in polymers as a result of prolonged exposure to the $^{22}$Na positron source. For PE [21,26,30], PP [30,31] and other polymers [33,34] it was observed that the *o*-Ps intensity may decrease while the corresponding lifetime remains constant. We observed the same effect in our experiments. The lower three of the four lifetime components did not show any observable change with the exposure time. In Fig. 4 the intensity $I_4$ of the fourth (*o*-Ps) lifetime is shown as a function of the measuring time, i.e. the time during which the samples was exposed to the radiation from the positron source. For getting parameters of sufficient statistical accuracy from spectra taken over a period of only 1200 s we used the discrete term routine LIFSPECFIT and during the fits constrained the lifetimes $\tau_1$ and $\tau_2$ to their average values. As observed in Fig. 4, the intensity $I_4$ in most of the samples shows a more or less pronounced decrease, but in some samples an increase is shown. No variations of $\tau_3$ and $\tau_4$ with time were observed. The behaviour of $I_4$ may be fitted by a decreasing (or increasing) exponential function $I(t)/I(0) = 1 \pm [\Delta I/I(0)][\exp(-t/t_r) - 1]$ where $\Delta I = |I(t = 0) - I(t \rightarrow \infty)|$ denotes the maximum variation if the intensity. (In the following we omit the index "4".) The time constant $t_r$ of the processes have values in the range $t_r = 1.7$–$3.3$ h for poly(α-olefin)s of $N_c = 2$, 3 and 4, but values of $t_r = 0.8$–$1.4$ h for higher poly(α-olefin)s. The decrease in the *o*-Ps intensity is frequently observed and attributed to electrical field effect as a consequence of electron annihilation [33], or to electron/positron trapping by free radicals or other traps formed during irradiation [20,26,35,36]. These effects can inhibit Ps formation [6].

Our results for poly(α-olefin)s shown an interesting variation of the maximum *o*-Ps intensity variation $\Delta I/I(0)$ as a function of glass transition temperature $T_g$. $\Delta I(t)$ decreases but its saturation level increases the more $T_g$ is below the temperature of measurement (300 K), i.e. when going from PP ($T_g = 265$ K) via poly-1-butene (257 K) and PE (195 K) to poly-1-dodecene (166 K, see the next section). Similar effects were also observed in the literature [30,35,36]. The decrease in the *o*-Ps intensity in PP due to its exposure to the positron source, for example, disappears (or can be recovered) at 373 K [30]. Obviously, this leads to an "annealing" of the positron radiation effects. From this behaviour it was concluded [30] that structural damage in the polymer such as cross-linking or chain scission is unlikely to cause the observed change in the *o*-Ps intensity. The *o*-Ps intensity in the higher poly(α-olefin)s ($N_c \geq 16$) increases slightly. The relative maximum of the increase, $\Delta I/I(0)$, grows with increasing $N_c$.

The intensity of the *o*-Ps annihilation is related to the Ps yield *P* via $I_{o\text{-Ps}} = 3P/4$. The Ps formation is a very complex phenomenon which is affected by various processes. When a fast positron penetrates a polymer, it loses its energy by ionisation and excitation of molecules. The thermalised positron may react with a free electron formed in the last part of the ionisation path to form Ps (spur model, see Mogensen [6]). This process competes mainly with the recombination of ionised molecules with free electrons, and with the trapping of free electrons and/or positrons by scavengers. Therefore, ionisations and excitation energies, electron/positron mobilities and binding energies are important factors affecting *P*.

Recently it was observed that in poly(methyl methacrylate) the *o*-Ps intensity increased, at temperature <150 K, with the duration of radiation [35,36]. Based on the spur model [6] this increase was explained by the accumulation of shallowly trapped electrons (which are created due to irradiation from the positron source) in the spur with which the positron may combine to form Ps. In the temperature range between 150 and 220 K and *o*-Ps intensity decreased with duration of irradiation. The decrease was attributed to a release of weakly bound electrons by the thermal activation of molecules and the recombination of free electrons with reactive species (cations and radicals containing nonsaturated bonds). A new increase of the *o*-Ps intensity above 220 K was explained by a decrease in the concentration of reactive species due to their increased mobility. Adopting this type of interpretation to our experiments the observed decrease of $I_4$ with irradiation time in PP ($T_g = 262$ K) could be attributed to trapping of spur electrons by reactive species. All of the other poly(α-olefin)s have a lower glass transition temperature $T_g$ resulting in increasing molecular mobility at 300 K ($T_g$) and, due to this, a decreasing lifetime of reactive species. Thus the fraction of trapped free electrons which are not available for Ps formation (and the magnitude of $\Delta I/I(0)$) decreases with decreasing $T_g$. The high molecular mobility in higher poly(α-olefin)s ($N_c \geq 16$) may lead to an additional thermal activated release of spur electrons from deeper traps and in that way to an additional increase in the Ps formation rate.

The observation that the intensity $I_4$ but not the lifetime $\tau_4$ changes with the exposure duration of the polymer to the positron source, indicates that only the Ps yield, not Ps reactions, are affected by the irradiation. This is a necessary assumption for estimating the size of local free volumes from positron lifetime data. The decrease in $I_4(t)$ during the total duration of the measurement (12 h) means that the (integrated) intensities shown in Fig. 3 are more or less smaller than their initial values $I_4(0)$. The most pronounced decrease occurs in PP (from 22.8 to 17.4%, integrated 19.0%, Fig. 3) and in poly-1-butene (from 21.7 to 17.9%, integrated 19.4%). In all of the other samples under investigation this effect is very small.

## 4. Discussion

The poly(α-olefin)s $(-CH_2-CHR-)_n$ with $R = (-CH_2)_N H$ under study ($N_c = N + 2 = 2, \ldots, 20$) form a class of semicrystalline homopolymers, the length of the side chain within the chemical repeating unit increases with increasing $N$. Melting ($T_m$) and glass transition temperatures ($T_g$) estimated from DSC measurements are shown in Fig. 5. For higher poly(α-olefin)s ($N_c \geq 10$) two melting peaks are observed in DSC runs which may be attributed to different crystalline phases formed by both the main chains and the longer side chains (see Ref. [20]). For $N_c \geq 16$ the glass transition could not be observed in the DSC runs due to the crystallinity of these poly(α-olefin)s. Therefore, another method described later is used to estimate $T_g$ of these polymers. The glass transition of PE, $T_g = 195$ K, was taken from our temperature dependent positron lifetime measurements published previously [21].

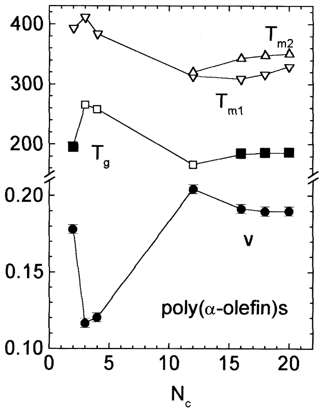

Fig. 5. The size of the free-volume holes $v$, the glass transition temperature $T_g$ and the melting temperatures $T_{m1}$ and $T_{m2}$ as function the number of carbons $N_c$ in poly(α-olefin)s. The filled squares are $T_g$'s from positron experiments (see text), all of the other $T_g$'s and the $T_m$'s come from DSC measurements.

The size of the open spaces seen by the *o*-Ps probe may be described either via a packing coefficient or as a mean local hole size. The first model provides a good description for the *o*-Ps pick-off annihilation in molecular crystals [7,8,11]. As published by Lightbody et al. [11], the *o*-Ps pick-off lifetime $\tau_{po}$ (given in ns) in hydrocarbon molecular crystals shows a linear dependence on the known crystal packing coefficient $C$. Through a least-square fit of this linear dependence one may derive an empirical relation involving the *o*-Ps lifetime and $C$ defined as the volume occupied by a molecule (the van der Waals volume) divided by the total volume per molecule

$$\tau_{po} = 7.92 - 9.616C. \tag{4}$$

The van der Waals volume of the $CH_2$ group is 0.017 nm$^3$ (Bondi [37,38], see also the tabulated values collected by van Krevelen [39]). Crystalline PE has an orthorhombic unit cell with parameters $a = 0.740$ nm, $b = 0.494$ nm and $c = 0.255$ nm at 300 K [40]. From this a total volume per $CH_2$ group at room temperature of $(a \times b \times c)/4 = 0.0233$ nm$^3$ follows, resulting in a packing coefficient of $C = 0.017/0.0233 = 0.73$. From the third lifetime in the poly(α-olefin)s, $\tau_3 \sim 1$ ns, a packing coefficient of 0.72 is estimated using Eq. (4). Its agreement with the theoretical value may support the idea that $\tau_3$ reflects the *o*-Ps pick-off annihilation in crystallites of semicrystalline polymers.

The concept of local holes is more suitable for the description of the *o*-Ps pick-off annihilation in amorphous materials. This simple model assumes that the Ps annihilates from an infinite square well potential where the Ps wave function has a finite penetration depth $\delta r$ into the material surrounding the potential well. If the radius of the square well is $r$, it follows from elementary quantum mechanics that the observed *o*-Ps pick off lifetime can be related to the radius of the hole (same size as the potential well) as [9,10,12,13]

$$\tau_{po} = 0.5\ \text{ns}\left[1 - \frac{r}{r + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r}{r + \delta r}\right)\right]^{-1}. \tag{5}$$

The prefactor of 0.5 ns is the spin-averaged Ps annihilation lifetime which is also observed in very densely packed molecular crystals [11]. The term in the brackets is the fraction $G$ of localised Ps density which overlaps with the electron layer at the inner surface of the hole, $\tau_{po} = 0.5\ \text{ns}/G \approx 1$–$10$ ns, $G \approx 0.05$–$0.5$. A value $\delta r = 0.166$ nm is obtained by fitting Eq. (5) to observed *o*-Ps lifetimes in porous materials of known mean hole radii [10,12].

In Fig. 5 the (mean) volume of holes estimated from the lifetime $\tau_4$ using Eq. (5) and $v = 4\pi r^3/3$ is shown as a function of the number of carbons in the chemical unit, $N_c$, together with $T_g$ and the two melting temperatures $T_{m1}$ and $T_{m2}$. The hole size decreases from $r = 0.349(\pm 0.002)$ nm/$v = 0.178(\pm 0.003)$ nm$^3$ in PE to $r = 0.303$ nm/$v = 0.117$ nm$^3$ in PP. It has its maximum in poly-1-dodecene: $r = 0.365$ nm/$v = 0.204$ nm$^3$. As can be observed, the free-volume holes size correlates well with glass transition temperature: the higher the $T_g$ the lower the $v$.

As mentioned previously, $T_g$ could not be estimated from DSC runs for higher ($N_c \geq 16$) poly(α-olefin)s. Therefore, we estimated the $T_g$'s of these polymers from the positron data in the following way. The variation of the free-volume hole size $v$ in the rubbery phase of amorphous polymers with the temperature $T$ may be described by the relation

$$v(T) = v_g + e_{h,r}(T - T_g) \text{ for } T > T_g. \tag{6}$$

Here $v_g$ is the hole volume at $T_g$ and $e_{h,r} = dv/dT(T > T_g)$ denotes the thermal expansivity of the hole volume. Recently, several authors [41–43] showed that $v_g$ increases linearly with $T_g$, $v_g = aT_g$. This relation indicates that for high-$T_g$ polymers a larger hole is required to pass from the glassy into the rubbery state. A typical slope of $a = 3.27 \times 10^{-4}$ nm$^3$/K has been estimated [43]. From Eq. (6) follows

$$T_g = A + Bv, \quad B = dT_g/dv = 1/(a - e_{h,r}). \tag{7}$$

for a group of polymers having the same values of $A$, $e_{h,r}$ and $a$. The hole volumes $v$ are measured at a constant temperature $T > T_g$. Using the hole volumes of PP, poly-1-butene and poly-1-dodecene, one obtains from a plot of $T_g$ (obtained from DSC measurements) versus $v$ the constant $A = 388.5$ K and the slope $B = -1074.43$ K/nm$^3$. Using this values, we estimated from Eq. (7) $T_g$'s of 183, 185 and 185 K for poly-1-hexadecene, poly-1-octadecene and poly-1-eicosene. These values are shown in Fig. 5 as open squares. From Eq. (7) one may also estimate the hole volume of a polymer having a $T_g$ of 300 K. One obtains $v(300\text{ K}) = v_g = 0.0854$ nm$^3$. From the value of $B$ the slopes $dv/dT_g = 1/B = -9.307 \times 10^{-4}$ nm$^3$/K, and $e_{h,r} = 12.58 \times 10^{-4}$ nm$^3$/K follow. With these values one may estimate the corresponding coefficient of thermal expansion of holes, $\alpha_{h,r} = (1/v_g)dv/dT = e_{h,r}/v_g(T > T_g)$, and obtains $\alpha_{h,r} = 14.7 \times 10^{-3}$ K$^{-1}$. These values of $v_g$ and $\alpha_{h,r}$ are in the same range but somewhat different from those determined previously for low density polyethylene from thermal expansion experiments [21], $v_g = 0.062$ nm$^3$ and $\alpha_{h,r} = 18.1 \times 10^{-3}$ K$^{-1}$ ($T_g = 195$ K). The difference in $v_g$ corresponds to the relation $v_g = aT_g$ (with $a = 2.8$–$3.2 \times 10^{-4}$ nm$^3$/K) used above.

Unfortunately, there is no direct way to estimate the number density of holes, $N_h$, and the fractional hole volume, $h$, only from positron lifetime data. Dlubek et al. [21] and other authors [44] have recently discussed the relation between the thermal coefficient of expansion of the macroscopic and the hole volume and estimated $N_h$ and $h$ from this relation. Similar to previous work [21], we assume that the total volume of an amorphous polymer $V_a$ may be subdivided into the volume formed by the holes, $V_h$, and into a hypothetical occupied volume $V_{occ}$, $V_a = V_h + V_{occ}$. In semicrystalline polymers, the specific occupied volume may be approximated by the specific volume of the crystalline phase [39], $V_c$. It represents the most dense packing of a given polymer and is composed of the actually occupied volume — the van der Waals-volume [37,39] — and a free volume which may be called interstitial free volume. The interstitial free volume is the supplement of the crystalline packing density to 100%. Following this line, the total hole volume may be considered as an excess free volume which appears in addition to the occupied (crystalline) volume due to the structural disorder in amorphous polymers. The disorder has a dynamical behaviour above the glass transition $T_g$, and is frozen-in below $T_g$. From the definition of the free volume, $V_h = V_a - V_{occ} = V_a - V_c$, a fractional free volume $h$ of

$$h = (V_a - V_c)/V_a = 1 - \rho_a/\rho_c \tag{9}$$

follows for a given temperature, where $V_a = 1/\rho_a$ and $V_c = 1/\rho_c$ denote the specific volume and $\rho_a$ and $\rho_c$ the mass density of the polymer in the amorphous (either glassy or rubbery) phase and in the crystalline phase [21]. With $\rho_a = 0.85$ g/cm$^3$, $\rho_c = 1.00$ g/cm$^3$ for PE [39,40] we obtain $h = 15.0\%$ at room temperature. With the hole volume of $v_a(300\text{ K}) = 0.178$ nm$^3$ and from the relation

$$h(T) = N_h(T)v_a(T) \tag{10}$$

a number of holes of $N_h(300\text{ K}) = 0.84 \times 10^{27}$ m$^{-3}$, i.e. 0.84 nm$^{-3}$, follows. The corresponding values for PP, poly-1-butene and poly-1-octadecene estimated from the density data collected by van Krevelen [39] are collected in Table 1. The number densities of the holes agrees well with $N_h(T_g) = 0.73$ nm$^{-3}$ (PE) and $N_h(T_g) = 0.36$ nm$^{-3}$ (PTFE) estimated recently from comparison of the thermal

Table 1
Mass density of the amorphous and crystalline phase (from van Krevelen [39]), $\rho_a$ and $\rho_c$, the glass transition temperature $T_g$ (see text), the fractional free (hole) volume $h$, the mean volume of holes, $v$ and the number density of holes, $N_h$, in various poly(α-olefin)s

| Polymer | $\rho_a$ (g/cm$^3$) | $\rho_c$ (g/cm$^3$) | $T_g$ (K) | $h$ (%) | $v$ (nm$^3$) | $N_h$ (nm$^{-3}$) |
|---|---|---|---|---|---|---|
| Polyethylene | 0.85 | 1.00 | 195 | 15.0 | 0.178 | 0.84 |
| Polypropylene | 0.85 | 0.95 | 265 | 10.5 | 0.117 | 0.90 |
| Poly-1-butene | 0.86 | 0.95 | 257 | 9.4 | 0.120 | 0.78 |
| Poly-1-octadecene | 0.86 | 0.95 | 182 | 9.4 | 0.190 | 0.50 |

coefficient of expansion of the macroscopic volume with that of the hole volume at $T_g$ (195 K) [21]. In this study and in other works [43,45,46] it was also concluded that $N_h$ is approximately independent of the temperature, $N_h(T) \approx N_h(T_g)$. From the comparison of positron lifetime results and mass density measurements in polycarbonate, Jordan and Koros [47] have estimated a number of holes of 0.4 $nm^{-3}$. From similar experiments at $T = 300$ K values of $N_h = 1\ nm^{-3}$ for a cross-linked polymer system [48] and of $N_h = 0.7\ nm^{-3}$ for ethylene–vinyl acetate copolymers [49] have been found. Recently, from the comparison with PVT experiments, hole numbers of $0.23–0.65 \times 10^{21}\ g^{-1}$ were estimated for a larger series of polymers [44]. From further data published in the literature [45,46,50], $N_h = 0.5–1\ nm^{-3}$ may be estimated.

The intensity $I_4$ of the *o*-Ps lifetime $\tau_4$ (Fig. 3) varies qualitatively in the same way as $\tau_4$ (Fig. 2) and the hole volume $v$ (Fig. 5). In the literature [34] it is very often assumed that the intensity of the *o*-Ps lifetime component behaves proportional to the number density of free-volume holes, $N_h$. If we, however, compare $I_4$ with our previous estimates the opposite behaviour is observed.

It was shown that Ps may be formed in perfect organic crystals [51], but with increasing number of open-volume defects $I_{o\text{-Ps}}$ usually increases. Thus, $N_h$ may be one of the factors controlling the Ps formation. On the other hand, many authors observed no correlation between $I_{o\text{-Ps}}$ and $N_h$ [43,45,46,48–50] which indicates that other factors affect the *o*-Ps yield $I_{o\text{-Ps}}$ more strongly than $N_h$ does. Ito [32] has shown that for the same family of polymers $I_{o\text{-Ps}}$ increases with $\tau_{o\text{-Ps}}$. From theoretical considerations with respect to the role of ($e^-$, $e^+$, Ps) energy levels and hole sizes in Ps formation he concluded that, due to the energy gain, larger holes promote Ps formation. Owing to their same chemical nature, this effect probably controls the Ps formation in poly(α-olefin)s and leads to the parallel variation of $I_4$ with $\tau_4$.

## 5. Conclusions

In positron lifetime spectra of poly(α-olefin)s four different lifetimes appear when analysed with the routine MELT which assumes continuous lifetime distributions. The longest lifetime, $\tau_4 = 2.2–3$ ns, is attributed to *o*-Ps annihilation from free-volume holes in the amorphous phase of the polymers. The medium lifetime time, $\tau_3 \sim 1$ ns, is attributed to *o*-Ps annihilation from the interstitial region of the crystalline phase.

It was found that the size of free-volume holes, as calculated from the lifetime $\tau_4$, increases with increasing separation between the measuring temperature ($T = 300$ K) and the glass transition temperature $T_g$. Among the poly(α-olefin)s the average hole volume is the largest in poly-1-dodecene (0.205 $nm^3$, $T_g = 166$ K) and the lowest in polypropylene (0.117 $nm^3$, $T_g = 265$ K). From comparison of amorphous and crystalline densities the number of holes $N_h$ was estimated to be 0.5–0.9 $nm^{-3}$.

The exposure of the polymers to positron radiation from the source effects the *o*-Ps annihilation. While the *o*-Ps lifetime is not changed, the relative intensity of this lifetime component varies exponentially with increasing exposure time. It decreases for poly(α-olefin)s with $N_c = 2$, 3 and 4, but increases for $N_c = 16–20$. Possible reasons for this behaviour are discussed in terms of trapping and releasing of spur electrons by reactive species.

## Acknowledgements

The authors wish to thank A. Shukla (Geneva) and P. Hautojärvi (Helsinki) for supplying the PC versions of the routines MELT and LIFSPECTFIT. This work was carried out with the support of the Commission of the European Community through the program “LEONARDO DA VINCI”. Financial support from the EPSRC, UK is gratefully acknowledged. One of the authors (G.D.) would like to thank the Benjamin Maeaker Foundation (University of Bristol) for the award of the foundation’s visiting professorship.

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