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Investigation of thermotropic phase transitions in a triple chain amphiphile forming hexagonal columnar and inverse micellar cubic mesophases: a positron annihilation lifetime study

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Positron annihilation lifetime (PAL) measurements were performed between 25 and 100°C in order to study thermotropic phase transformations in an amphiphilic liquid crystal material with three hydrophobic alkyl chains. The lifetime spectra were separated into three exponential components, the long-lived of which is attributed to *ortho*-positronium (*o*-Ps) annihilation via pick-off processes. The lifetime of *o*-Ps, τ_3, and its relative intensity, I_3, as well as the average positron lifetime, $\tau_{av} \propto I_3 \tau_3$, respond to variations in the structural regularities of the environment. The phase transitions, which have the sequence and temperatures (°C) Cr• 59• Col(H_{II})• 74• Cub(I_{II})• 85• Iso, are well reflected in abrupt changes of τ_3, I_3 and τ_{av}. The *o*-Ps lifetime in the crystalline phase of $\tau_3 = 2.35$ ns may be interpreted as a crystalline packing coefficient of 0.56 or, alternatively, as *o*-Ps confined in vacancy-type crystal imperfections with a volume of 0.132 nm^3. During melting τ_3 increases to 3.05 ns, and this is attributed to the preferential formation of Ps bubbles, with a size of 0.207 nm^3, in mobile, liquid-like regions of hydrophobic alkyl chains. The bubble size remains at this value during the H_{II}–I_{II} transition and increases slightly to 0.216 nm^3 during the transformation to the isotropic liquid phase. I_3 shows variations during all of the phase transitions, which are attributed to changes in the Ps inhibition rate due to electron/positron mobility, and solvation effects varying as a consequence of different degrees of order of the molecular dipoles.

1. Introduction

The use of the positron and in particular its bound state, positronium (Ps), as a probe of physical and chemical properties of condensed matter has been amply demonstrated [1–4]. In molecular materials, the Ps forms either in the so called *para* (antiparallel electron and positron spins: *p*-Ps) or *ortho* (parallel electron and positron spins: *o*-Ps) positronium states with a relative abundance of 1:3 [1]. In vacuum, *p*-Ps has a lifetime of 125 ps and annihilates via 2 γ-photons while *o*-Ps has a lifetime of 142 ns and annihilates via 3 γ-photons. In matter, due to different types of interaction, the *o*-Ps undergoes processes which reduce its lifetime to the low ns range (quenching). Generally, three different lifetimes appear in the positron lifetime spectrum: $\tau_1 = 120$–200 ps due to *p*-Ps annihilation, $\tau_2 = 350$–450 ps due to free positron (not Ps) annihilation and $\tau_3 = 1$–5 ns as result of quenching the long-lived *o*-Ps. The probability of Ps formation (the Ps yield P) is also affected by material properties. Depending on the nature of the material, the relative intensity of the *o*-Ps lifetime component, $I_3 = 3P/4$, may vary between 0 and about 50%.

The unique nature of Ps and its specific interaction with matter may provide information otherwise unavailable via more conventional methods. The relative intensity of the *o*-Ps annihilation channel, I_3, and/or its lifetime, τ_3, can be extremely sensitive to phase transformations [1–4]. Positron annihilation in liquid crystalline materials has been investigated and reviewed by several workers [5–13]. It was found that the magnitude and the nature of the change of τ_3 and I_3 depend on the nature of the transition and materials. A strong correlation between the values of τ_3 and I_3 and the

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degree of molecular order in mesomorphic phases has been observed. The most important feature is the nature of the change in τ_3 across the transition. In some liquid crystalline materials the value of τ_3 increases with the decreasing degree of molecular order, while in others an opposite effect has been observed. From this it has been concluded that τ_3 is sensitive not only to the degree of order, but also to the chemical structure of the material.

From the observation that the changes in τ_3 and I_3 during mesomorphic phase transitions do not correlate well with changes in the (macroscopic) density, it was concluded that the effects seen via the *o*-Ps annihilation are related to local, microscopic properties rather than to the bulk properties of the liquid crystal. This sensitivity to microscopic properties is probably highly related to the dipole character of the molecules which form the mesophases, and the spatial arrangement of dipoles. Although the Ps formation and its interaction is far from being understood completely, the method is used to study thermotropic phase transitions in liquid crystals and phase formation or transitions in lyotropic and micellar systems. In some materials, these investigations have also led to the discovery of novel phases [9, 12]. Progress in understanding the nature of Ps interactions has been gained from the study of micellar formations in several hydrocarbon–water–surfactant systems [10, 12] and new systems of liquid crystals [11, 13].

In this work we use positron annihilation lifetime (PAL) spectroscopy for studying thermotropic phase transitions in the triple chain amphiphilic diol **1** (see figure 1) [14, 15]. Two mesophases were found for this compound: a hexagonal columnar liquid crystalline phase and a cubic mesophase. From the position of the cubic phase in the thermotropic phase sequence, conductivity experiments and miscibility studies, it was concluded that this cubic phase must consist of closed globular inverted micelles, i. e. the hydrogen bonding networks of the polar diol groups are located inside the micelles, surrounded by the liquid-like aliphatic chains. X-ray scattering confirmed a primitive cubic lattice ($Pm3n$ or $P43n$). From the lattice parameter and packing considerations it was proposed that this cubic lattice was built up by eight micelles per unit cell. The special interest in this particular compound arises from the fact that it is the only compound in a homologous series with varying alkyl chain length, which exhibits both the columnar and the micellar cubic thermomesophases. Thus, structural changes at the transition between these two mesophases can be investigated. In the following text, we analyse the PAL spectra, determine the annihilation parameters, discuss their nature and attempt to draw conclusions about the microscopic mechanism causing their changes during the various phase transitions.

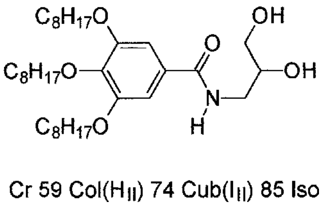
Cr 59 Col(H$_{II}$) 74 Cub(I$_{II}$) 85 Iso

Figure 1. Structure and transition temperatures (°C) of the racemic triple chain amphiphile **1** [15], Cr = crystalline solid, Col(H$_{II}$) = inverted hexagonal columnar phase, Cub(I$_{II}$) = inverted micellar cubic phase, Iso = isotropic liquid.

2. Experimental

The compound **1** was synthesized and purified according to ref. [15]. The structure and the phase transition temperatures are shown in figure 1. Positrons are derived from radioactive sources such as ^{22}Na. The fast positrons penetrating a polymer sample are slowed down to thermal energies within ~1 ps mainly by ionization and excitation of molecules [1, 2]. The positron implantation profile is a decreasing exponential function with a typical maximum range (99% positron absorption) of ~1 mm in materials of 1 $\mathrm{g\,cm^{-3}}$ density. The thermalized positron migrates through the material with a typical mean distance of 100 nm, and finally annihilates with an electron resulting in the emission of two 0.51 MeV γ-photons. The ^{22}Na nucleus emits a 1.28 MeV γ-ray simultaneously (within a few ps) with the positron. The positron lifetime is determined from the time delay between the emission of the birth gamma (1.28 MeV) and one of the 0.51 MeV annihilation quanta. In this experiment, a positron source with an activity of 30×10^5 Bq was used, made by evaporating carrier-free ^{22}NaCl solution on a Kapton film 8 μm thick.

Positron lifetime measurements [1, 2] were carried out using a fast–fast coincidence system with a channel width of 12.63 ps. For the final spectrum analysis, the contents of every six channels were summed-up to give the coincidence rate in one 75.78 ps channel. First, the positron source was sandwiched with the crystalline powder of **1** using a thickness of 1.5 mm on each side of the source, and an area of $10 \times 10\,\mathrm{mm}^2$. The sandwich was wrapped in Al foil 0.3 mm thick and placed in a small copper container. This container, together with a thermocouple, was placed in a holder equipped with a resistivity heater. The measurements were performed in air at temperatures in the range 25 to 100°C. Wrapping the sample in Al foil should have reduced air circulation and prevented contamination of the material with atmospheric water vapour. Compound **1** was first examined as the crystalline powder obtained after chromatographic purification [15]. Following this, it was heated to 55°C and measurements made at this temperature. The sample was then cooled to 25°C and again measurements were made. The temperature run following this first treatment was started at 40°C and finished at 100°C. The temperature was controlled throughout by a Eurotherm programmable temperature controller. The absolute temperature accuracy in the measuring chamber was ±1°C, and the temperature fluctuations within one series of measurements were within ±0.5°C. The sample was allowed to reach equilibrium at each new temperature over a period of 2 h, before the corresponding measurement, which lasted 10 h, was started.

Twenty measurements, each lasting 30 min, were taken at each temperature. The time-zero of each 30 min-spectrum was determined from a preliminary inspection, before the counts of the spectra were summed to a final spectrum containing a total number of $\sim 1 \times 10^6$ coincidence counts. The source correction and width of the time resolution function (assumed to be a Gaussian) was estimated to be 260 ps (FWHM) from measurements of an Al reference spectrum ($\tau_{Al} = 162$ ps).

While the lifetime of an individual positron may vary between 0 and ∞, the lifetime spectrum of an ensemble of positrons annihilating from a unitary state is a single exponential $\exp(-t/\tau)$. τ denotes the mean lifetime of the positrons which responds inversely to the electron density at the positron site [1–4]. For the analysis of the lifetime spectra, we applied the conventional discrete-term analysis using the routine LIFSPECFIT [16]. In this analysis procedure the positron lifetime spectrum is assumed to be represented by a sum of negative exponentials

$$s(t) = \sum (I_i/\tau_i) \exp(-t/\tau_i) \qquad (1)$$

where τ_i is the lifetime of component i, and I_i denotes the intensity of the corresponding component, normalised to $\Sigma I_i = 1$ $(i = 1\text{–}3)$. Following subtraction of source annihilation components (380 ps/4%—NaCl and Kapton cover, and 2500 ps/0.4%—surface effects) the routine LIFSPECFIT convolutes equation (1) with the resolution function and estimates, from a non-linear least squares fit of the model function to the experimental spectrum, the parameters τ_i and I_i, the background per channel, the width of the Gaussian resolution function and the time-zero of the spectrum. Two typical PAL spectra for the crystalline and liquid crystalline states of compound **1** are shown in figure 2. Three components are resolved in the lifetime spectra with lifetimes of $\tau_1 = 180\text{–}240$ ps, $\tau_2 = 380\text{–}440$ ps, and $\tau_3 = 2\text{–}3$ ns.

3. Results

The three resolved components in the analysed spectra are well known and correspond to the three general annihilation channels: p-Ps (τ_1), free positrons (τ_2) and o-Ps (τ_3) [1–10]. Due to the short lifetimes of p-Ps and free positrons, only the o-Ps lifetime τ_3 and its intensity I_3 respond clearly to the material properties (figure 2). The lifetime parameters I_3 and τ_3 are shown in figure 3 (a), and the average positron lifetime τ_{av} together with the parameter $I_3\tau_3$ in figure 3 (b), as a function of the sample temperature. τ_{av} is calculated as the mass centre of the lifetime distribution, and is related to the parameters of the individual lifetime components via $\tau_{av} = \Sigma I_i\tau_i$ $(i = 1\text{–}3)$. It is an integral, model-independent parameter which reflects general changes in the material under investigation. Due to the large magnitude of τ_3, the value of τ_{av} is dominated by the term $I_3\tau_3$ figure 3 (b).

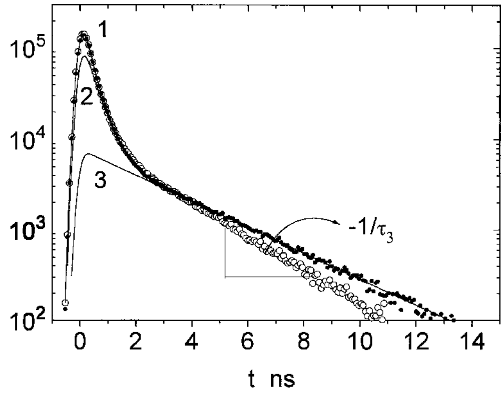

Figure 2. Positron lifetime spectra in crystalline (25°C, open symbols) and liquid crystalline (64°C, H_{II} phase, filled symbols) of **1**. Shown is the number of annihilation events N_i in the channel i as a function of the time delay t between birth and annihilation of positrons. The experimental data are displayed after subtraction of the background and source components. The spectra consist of a superposition of three exponential components with the slopes $-1/\tau_i$. The analysed lifetimes amount to $\tau_1 = 195$ ps, $\tau_2 = 402$ ps, $\tau_3 = 2.35$ ns (crystalline phase) and $\tau_1 = 204$ ps, $\tau_2 = 412$ ps, $\tau_3 = 3.05$ ns (H_{II} phase). Only the third (o-Ps) component clearly responds to material properties.

Heating the powdered material **1** in the first run from 25 to 55°C (12 h tempering) and the following cooling to 25°C increases the average positron lifetime τ_{av} from 725 to 770 (±5) ps. This is due to an increase in I_3 from 20.2 to 22.4 (±0.2)%. τ_3 stays constant at 2.35 (±0.03) ns. During the second heating run, τ_{av} remains almost constant up to a temperature of ~55°C. After that, a rapid increase from 770 ps to a plateau of 910 ps occurs in the region centred at 58°C. The increase is due to the increase of τ_3 from 2.35 to 3.05 ns, but is partially compensated for by the decrease in I_3 from 22.4 to 21.1%. During further heating of the sample, a step-like increase in τ_{av} occurs at 71.5°C, followed by a plateau at $\tau_{av} = 940$ ps, which extends up to a temperature of 82°C. τ_3 stays constant in this temperature range, but I_3 shows an increase to 22.3%. In a region centred at 82°C, τ_{av} decreases from 940 to 840 ps. This is caused by the decrease in I_3 to 18.5%, but unlike

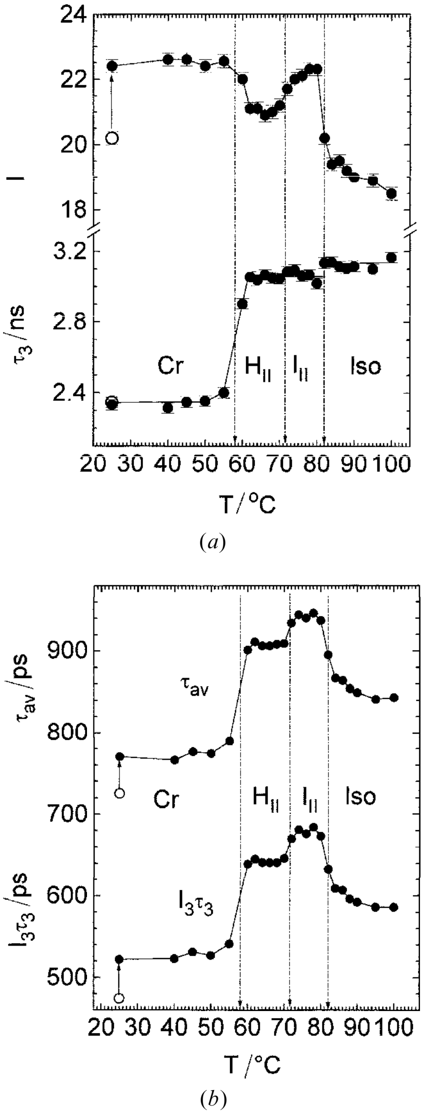

Figure 3. (*a*) Intensity I_3 and lifetime τ_3 of the *o*-Ps component in **1** as a function of the sample temperature T. In order to reduce the statistical scatter in the lifetime parameters, τ_1 was fixed to its average of 200 ps in the final spectrum analysis. Open circle denotes first run, filled circles denote second run following annealing of the powder at 55°C for 12 h. (*b*) As in (*a*), but the average positron lifetime $\tau_{av} = \Sigma I_i \tau_i$ and the parameter $I_3\tau_3$.

I_3, the *o*-Ps lifetime τ_3 shows a slight increase from 3.06 to 3.12 ns. As can be observed in figures 3 (*a*) and 3 (*b*), the *o*-Ps lifetime parameters show abrupt changes at temperatures of 58, 71.5, and 82°C and these lie very close to the phase transition temperatures Cr• 59• Col(H_{II})• 74• Cub(I_{II})• 85• Iso identified from DSC and polarizing microscopy investigations [15]. This shows that the *o*-Ps annihilation process is affected by variations in the structural arrangement of molecular dipoles. The small deviations between the positron and DSC results may be due to small amounts of water vapour absorbed from the air which cannot be totally excluded under the experimental conditions, and which can change the phase transition temperatures [15], as well as to the different heating rates applied in the DSC and positron studies.

4. Discussion

In this section we discuss in more detail the *o*-Ps annihilation mechanism which affects the values of τ_3 and I_3. It is well known that when *o*-Ps is formed in matter, it may decay via self-annihilation or, with a much higher probability, due a variety of quenching processes [1]. The most important quenching channel is pick-off annihilation; this is the annihilation of the positron in the Ps with an electron other than its bound partner and with opposite spin during collisions of Ps with molecules. Other quenching processes may, however, also be of importance, such as *ortho–para*-spin-conversion due to internal or external magnetic fields or chemical quenching. Unlike the pick-off process, the latter quenching process changes the number of annihilations of *p*-Ps and *o*-Ps and in this way the intensities I_1 and I_3 (see the discussion in later sections). The reduction of the *o*-Ps lifetime $\tau_{o\text{-Ps}}$ due to the various quenching processes may be described by [1]

$$\tau_{o\text{-Ps}} = 1/(\eta\lambda^0_{o\text{-Ps}} + \lambda_{\mathrm{po}} + \lambda_{\mathrm{qu}}) \tag{2}$$

where $\lambda^0_{o\text{-Ps}} = (\tau^0_{o\text{-Ps}})^{-1}$ is the *o*-Ps self-annihilation rate ($\tau^0_{o\text{-Ps}} = 142$ ns), $\lambda_{\mathrm{po}} = (\tau_{\mathrm{po}})^{-1}$ is the pick-off annihilation rate and λ_{qu} denotes the rates of all other possible quenching mechanisms. η is the so-called contact density or relaxation parameter which describes the relaxation of Ps in matter compared with in a vacuum. The diameter of the Ps probe behaves as $0.106\eta^{-1/3}$ nm and the *p*-Ps and *o*-Ps lifetimes due to self-annihilation relate to η as 125 ps/η and 142 ns/η, respectively. Estimates from magnetic quenching experiments [1] suggest that η is around 0.8 for hydrocarbons.

In solids and liquids, Ps is repelled by most of the molecules, except those of high electron or positron affinity, due to the Coulomb force and the exchange effect. The latter is a consequence of the Pauli principle. In perfect crystals Ps may move freely in interstitial regions (empty space between the lattice planes). During collisions with molecules, the *o*-Ps lifetime reduces from 142 ns to the low ns range due to the pick-off annihilation process. Assuming no quenching channels other than pick-off, $\tau_3 = \tau_{o\text{-Ps}} \approx \tau_{\mathrm{po}}$ follows from $\lambda_{\mathrm{po}} \gg \lambda^0_{o\text{-Ps}}$, equation (2). Lightbody *et al.* [17] observed that the *o*-Ps lifetime in low molar mass hydrocarbon crystals decreases with increasing packing coefficient C as

$$\tau_{\mathrm{po}}(\mathrm{ns}) = 7.92 - 9.616C. \tag{3}$$

The packing coefficient is defined as $C = V_{\mathrm{vdW}}/V$, where V_{vdW} is the van der Waals volume of a chemical unit (per mol) and V is the specific (molar) volume. Following this interpretation, we may estimate from the value of $\tau_3 = 2.35$ ns a crystalline packing coefficient of $C = 0.56$. This value is relatively small and may be attributed to the open structure of the crystal formed by the bulky molecules of **1**. In *n*-alkane crystals (number of carbons 20–40) a lifetime of $\tau_3 = 1.50$ ns [17] has been observed, for example, which corresponds to a packing coefficient of $C = 0.67$. In polyethylene crystals $\tau_3 = 1.20$ ns has been estimated, from which $C = 0.69$ follows [18]. Unfortunately, the crystal structure of **1** is not known, because no appropriate crystals have yet been obtained.

Another reason for the relatively high *o*-Ps lifetime in the crystals of **1** could be found in the possible occurrence of open-volume lattice imperfections (vacancy-type lattice defects). The powdered nature of the crystalline sample has no observable effect on the lifetime spectrum since the grains (diameter 30 to 100 μm) are so big compared with the mean positron diffusion length (~0.1 μm) and the mean *o*-Ps diffusion length (~2 nm) that they are sensed as bulk material. The empty space between the grains is too macroscopic to be detected by Ps. Due to the repulsive interaction with molecules, Ps tends to be confined within open-volume defects (holes) of molecular and atomic size. The size of the hole that confines the positronium can be estimated from the *o*-Ps lifetime due to the dependence of the pick-off process and the associated *o*-Ps lifetime on the frequency of collisions of the *o*-Ps with the surrounding walls, and therefore on the dimension of the hole. This picture is valid assuming that no quenching channels other than pick-off occur.

From equation (2) it follows that the observed lifetime of *o*-Ps confined in a hole may be expressed by $\tau_{o\text{-Ps}} = 1/[(1 - W)\eta\lambda^0_{o\text{-Ps}} + W\lambda_{\mathrm{m}}] \approx W^{-1}\,\tau_{\mathrm{m}}(\lambda_{\mathrm{m}} \gg \eta\lambda^0_{o\text{-Ps}})$. W is the fraction (weight) of Ps density which overlaps with the electron layer at the inner surface of the hole and $\tau_{\mathrm{m}}(\lambda_{\mathrm{m}})$ is the *o*-Ps lifetime (annihilation rate) inside the layer. τ_{m} is well approximated by the spin-averaged Ps lifetime of 0.5 ns which is also observed in densly packed molecular crystals [17]. For calculating the value of W a simple quantum mechanical model is used which assumes that the Ps is confined in a spherical potential well of radius r and infinite depth, and that the Ps has a spatial overlap with molecules within a layer δr of the potential wall. This provides a well accepted relationship between the *o*-Ps pick-off lifetime, $\tau_{o\text{-Ps}} = \tau_{\mathrm{po}} = \tau_{\mathrm{m}} W^{-1}$, and the radius of the hole [19–21]:

$$\tau_{\mathrm{po}} = 0.5\left[1 - \frac{r}{r + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r}{r + \delta r}\right)\right]^{-1}\ \mathrm{ns}. \qquad (4)$$

By fitting equation (4) to the observed *o*-Ps lifetime of known mean hole radii in porous materials, $\delta r = 0.166$ nm was obtained [20, 21]. Thus, equation (4) represents a calibration curve for the dependence of the *o*-Ps lifetime on the hole radius r. It is widely used to estimate the mean size of free-volume holes appearing as a consequence of the structural disorder in amorphous polymers [3, 4, 18–22], and is also used to identify lattice vacancies in molecular crystals [1, 17]. Assuming that *o*-Ps annihilates from inside holes of the crystal, a hole radius and volume of $r = 0.316$ nm and $v = 4\pi r^3/3 = 0.132\ \mathrm{nm}^3$ follow from $\tau_3 = 2.35$ ns using equation (4). In view of the structure of the material, the estimated hole size is in a plausible range. The separation of neighbouring carbon atoms in hydrocarbons is 0.15 nm; the tetravalent C_6H_2 group occupies a van der Waals volume of $0.064\ \mathrm{nm}^3$ [23, 24]. The molecular length amounts to 2.2 nm in the most extended conformation assuming an all-*trans*-conformation of the alkyl chains.

Due to the repulsion by molecules, Ps is also confined in ‘holes’ in liquids. These holes are created by the Ps probe itself and are called Ps bubbles. Their size can be estimated from the *o*-Ps lifetime via equation (4). In a bubble state, the inward pressure due to the surface tension is counterbalanced by the outward pressure due to the Ps-molecule repulsion and the zero point energy of the Ps (Heisenberg uncertainty principle). Assuming that the Ps is situated in a square well potential of depth U and radius r in the liquid, the total energy in the bubble state is (see, for example, [1, 6, 25, 26])

$$E = E_0(U, r) + 4\pi r^2\gamma + 4\pi r^3 p/3. \qquad (5)$$

$E_0(U, r)$ is the Ps zero point energy in the potential, and the second and third terms are the surface (γ = surface tension) and pressure-times-volume energies, respectively. If it is assumed that the square well has infinitely high potential walls and that the pv term is insignificant, as is normally found, we get from the equilibrium condition $\mathrm{d}E/\mathrm{d}r = 0$ the relation

$$r = (\pi\hbar^2/16m_{\mathrm{e}})^{1/4}\gamma^{-1/4} = 1.241\gamma^{-1/4} \qquad (6)$$

for the equilibrium radius of the bubble [25]. Here $\hbar$ is Planck’s constant and m_{e} the mass of an electron (positron). For $\gamma = 20\ \mathrm{dyn\,cm^{-1}}$, for example, one obtains $r = 0.59$ nm. An empirical relation between the macroscopic surface tension γ and the *o*-Ps pick-off lifetime τ_{po} has been found by Tao [19] as

$$\tau_{\mathrm{po}} = (k\gamma^n)^{-1}\ \mathrm{ns} \qquad (7)$$

where for *n*-alkanes, values of $k = 0.061$ and $n = 0.50$ and for oxygenated short chain hydrocarbons, $k = 0.046$ and $n = 0.55$ have been determined (γ is given in $\mathrm{dyn\,cm^{-1}}$).

Considering that the bubble radius is normally between 0.3 and 0.6 nm, it is of great interest to know whether a bubble of this size can be treated with macroscopic surface tension, since only a small number of molecules is involved and the effect of the radius of curvature on surface tension may be significant [27–29]. Nakanishi *et al.* [28] found that for methane and other molecular liquids, the microscopic surface tension for molecules with low dipole moments with a bubble radius larger than 0.3 nm is given by their macroscopic values, while the microscopic values are found to be much smaller than the macroscopic value for molecules with high dipole moments or with strong intermolecular interactions. We may expect that in liquid crystals the microscopic surface tension depends on the type of molecular orientation, and affects in this way the size of the Ps bubble and the *o*-Ps lifetime. As has been discussed by Gregory *et al.* [26], the energy function $E(r)$, equation (5), is very shallow with respect to thermal energies kT, so a distribution of Ps bubble states is expected. From this it follows that the size of the Ps bubbles estimated via equation (4) from the *o*-Ps lifetime has to be considered as a mean value of a bubble size distribution. The influence of solvents on the Ps bubbles cannot be excluded. However, due to the low mobility of Ps in polar liquids, this effect is expected to be small as long as the solvent concentration is small.

The distinct increase of the *o*-Ps lifetime τ_3 from 2.35 to 3.05 ns during melting of compound **1** at about 60°C, figure 3(*a*), corresponds to an increase in the mean size of the holes probed by *o*-Ps from $r = 0.316$ nm ($v = 0.132$ nm^3) to $r = 0.367$ nm ($v = 0.207$ nm^3), equation (4). From the previous discussion, it follows that this increase can be attributed to the formation of Ps-bubbles during the transition of **1** from the crystalline solid to the liquid crystalline H$_{\text{II}}$ phase, which is an inverse hexagonal columnar mesophase consisting of cylindrical aggregates. It may be expected that Ps forms bubbles in the regions of the hydrophobic alkyl chains, but also in regions of the hydrogen bonding networks. *Ortho*-Ps lifetimes τ_3 of 1.8 ns and ~3 ns have been observed for water and for liquid alkanes, respectively [1]. From the comparison of these values with our estimate of $\tau_3 = 3.05$ ns, we may conclude that in compound **1**, *o*-Ps preferentially forms and annihilates in the regions of the hydrophobic alkyl chains which are in a mobile, liquid-like state. This picture is in agreement with the observation that τ_3 does not change when going from the columnar H$_{\text{II}}$ phase to the cubic I$_{\text{II}}$ phase (69°C). The slight increase of τ_3 to the value of 3.12 ns ($r = 0.372$ nm, $v = 0.216$ nm^3) during the transition from the I$_{\text{II}}$ phase to the isotropic liquid at 82°C can be attributed to a decrease in the surface tension γ. This transition is associated with a significant decrease in the viscosity [15]. During cooling from 100 to 25°C, the value of τ_3 decreased only slightly, in accordance with DSC investigations which have shown that the columnar mesophase of **1** can be supercooled to room temperature without crystallization [15].

The *o*-Ps intensity I_3 varies throughout all of the phase transitions occurring in compound **1**, figure 3(*a*). I_3 can be affected by several different and complex processes so that its interpretation is often not simple. I_3 can vary due to two different processes: inhibition and quenching [1].

Ps inhibition is a complicated and quantitatively difficult process to describe. When a fast positron penetrates a polymer it loses energy by ionization and excitation of molecules. The thermalized positron may react with a free electron formed in the last part of the ionization path (spur model, [1]) to form Ps, $e^+ + e^- \rightarrow$ Ps. This process competes with the recombination of ionized molecules with free electrons, $M^+ + e^- \rightarrow M$, and with trapping of free electrons and/or positrons by scavengers. These processes are also affected by the mobility of both positrons and free electrons. Any change in the intensity of these processes may lead to a decrease (inhibition) or increase (anti-inhibition) of the Ps formation probability P. In the annihilation spectra, the intensities of the *o*-Ps component I_3 decrease or increase as the Ps yield P, $I_3 = 3P/4$, but, as mentioned previously, the lifetime τ_3 will not change.

Once formed, Ps reactions (quenching) may change lifetimes and/or intensities. The most important quenching process here is pick-off annihilation, which reduces the *o*-Ps lifetime, but leaves the intensities of the lifetime components unchanged. In contrast, however, the processes where Ps converts from one Ps state to the other, or to the positron state and *vice versa*, lead to a change in all or some of the intensities and lifetimes. A complete treatment of the kinetic equations of Ps reactions is published by Mogensen ([1], p. 155), for example. Other important Ps quenching processes are chemical quenching and spin conversion. During chemical quenching, a Ps may decay into a free positron e^+ and an ionized molecule M^-, via the oxidation reaction *o*-Ps (*p*-Ps) + $M \rightarrow e^+ + M^-$, with a rate κ_{ox}. If the oxidation rate κ_{ox} increases, the intensities I_3 would increase, while the lifetimes τ_3 would decrease. The complex formation reaction *o*-Ps (*p*-Ps) + $M \rightarrow [M^-, e^+]$ has an analogous effect to oxidation. Spin conversion may occur during a collision of a Ps atom with paramagnetic molecules or atoms, i.e. *o*-Ps + M → *p*-Ps + M. With increasing conversion rate κ_{con}, τ_1 and I_1 disappear, while τ_3 decreases towards a value of 0.5 ns (the spin-averaged Ps lifetime), and the intensity I_3 increases to 4/3 of the initial intensity.

The increase of I_3 from 20.2% to 22.4%, without any change in τ_3, figure 3(*a*), due to the annealing of the powder of compound **1** at 55°C, may be attributed to an anti-inhibition of Ps formation. Possibly, small amounts of water vapour absorbed by the powder are desorbed during tempering. It is known that the Ps yield may decrease due to solvation of electrons and positrons by the polar water molecules. In pure liquid water, values of $\tau_3 \approx 1.8$ ns and $I_3 \approx 18\%$ have been observed [1]. The decrease of I_3, which is accompanied by an increase of τ_3 during melting at 59°C, could be due to the decreasing rate of an oxidation reaction. However, no mechanism for such an oxidation reaction is known for our material. Since the increase in τ_3 can be well understood by the Ps bubble formation discussed previously, the decrease of I_3 may indicate a decreasing Ps yield. This could be due to a decreasing mobility of electrons and positrons as a consequence of the transition from a periodically ordered crystalline structure to a less ordered columnar H_{II} phase. The nature of the increase of I_3 during the H_{II}–I_{II} phase transition at 69°C is not known, but may possibly also be due to mobility effects. Since τ_3 is almost constant after melting, the variations in I_3 can be attributed to inhibition and not to chemical quenching reactions. The distinct decrease of I_3 during the transition from the I_{II} to the isotropic phase can be explained by solvation of positrons and electrons via the free dipoles, and to decreased positron/electron mobility in the disordered phase. Generally, a change in the strength of the solvation of electrons and positrons due to the different structural arrangements of the polar molecules in the different phases could cause changes in the Ps yield. Since solvated electrons and positrons cannot participate in Ps formation, the recombination reaction $e^+ + e^- \rightarrow Ps$ competes with the solvatation of the particles. When the mean time for solvation decreases (increases), the Ps yield may increase (decrease).

5. Conclusions

The lifetime of the *o*-Ps probe, τ_3, and its intensity, I_3, as well as the average positron lifetime, $\tau_{av} \propto I_3 \tau_3$, respond to variations in the structural regularities of the environment. Although not all microscopic mechanisms affecting τ_3 and I_3 are well known, positron annihilation lifetime measurements can be considered a useful tool for studying phase transformations in liquid crystals. In the compound **1**, the lifetime parameters τ_3, I_3 and τ_{av} show abrupt changes during the phase transitions Cr• 59• Col(H_{II})• 74• Cub(I_{II})• 85• Iso, known from optical microscopy, calorimetry and X-ray diffraction experiments [14, 15]. For the first time, to the best of our knowledge, we have observed the transition from a thermotropic columnar to a thermotropic micellar cubic phase using PAL experiments.

Indications of Ps quenching processes other than pick-off annihilation were not observed. Assuming this, τ_3 reflects the size of the free volume in which *o*-Ps annihilates, and I_3 indicates the Ps yield. The value of $\tau_3 = 2.35$ ns determined for the crystalline phase may be interpreted as a crystalline packing coefficient of 0.56 or, alternatively, as *o*-Ps confined in vacancy-type crystal imperfections of a volume of 0.132 nm^3. During melting, τ_3 increases to 3.05 ns which is attributed to the occurrence of Ps bubbles with a size of 0.207 nm^3, formed preferentially in the liquid-like regions of the hydrophobic alkyl chains. The bubble size stays at this value during the H_{II}–I_{II} transition and increases slightly to 0.216 nm^3 during transformation to the isotropic phase.

While τ_3 only shows small variations following melting, the phase transitions can be well identified in the behaviour of I_3 (and τ_{av}). This response is discussed in terms of variations in the Ps yield due to changes in the solvation processes of electrons and/or positrons by the polar molecules, or in the mobility of these particles as a consequence of the change in the structural order during the phase transitions.

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