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Positron annihilation in liquid crystals

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Abstract. Positron annihilation studies of liquid crystals are reviewed with particular reference to thermotropic liquid crystals with rod-like molecules. The studies of compounds exhibiting smectic A or smectic E phases indicate that local arrangement of dipole molecules play an important role because high electron density at the end group of molecules can influence substantially formation and annihilation of positronium. The obtained *ortho*-positronium lifetimes in these phases can be explained by antiparallel pairing of molecules in case of the smectic A phase or a structure with a nanosegregation of alkyl chains and others parts of molecules into sublayers and liquid-like state of alkyl chains in case of the smectic E phase.

Key words: liquid crystals • positron annihilation • phase transitions

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Introduction

Organic materials having mesomorphic phases, known as soft mater, found more and more applications in everyday life. Advances of modern optics have been made possible because of the development of new liquid crystalline materials. The study of liquid crystals (LCs) started in 1888 when Austrian botanist Friedrich Reinitzer observed that cholesteryl benzoate had two distinct melting points. Nowadays, new LC compounds are synthesized and a variety of experimental methods are used to explore the relationship between the microscopic structure, molecular ordering, and molecular dynamics of a material and its macroscopic properties.

Positron annihilation lifetime spectroscopy (PALS) has been also used for this purpose as a suitable experimental tool to characterize the local structure in molecular substances. When positrons are injected into an insulator solid, some of them form a bound state with an electron called positronium (Ps). Ps locates in low electron density regions such as local free volume holes [1–4]. Ps is formed in two spin states: *para*-Ps (*p*-Ps) and *ortho*-Ps (*o*-Ps), reflecting the different positron and electron spin alignment, i.e., antiparallel and parallel, respectively. In vacuum, *o*-Ps decays into three quanta with the lifetime of 142 ns and *p*-Ps decays into two quanta with much shorter lifetime of 125 ps. The relative abundance of these two states is 1:3. In matter, *o*-Ps interacts with the electrons of molecules surrounding the local free volume in which it is trapped. Its lifetime is determined mainly by the annihilation of the positron with one of these external electrons. This process is called 'pick-off' annihilation.

Pick-off causes a reduction of *o*-Ps lifetime to several nanoseconds.

Usually, the positron lifetime spectra measured for molecular substances can be decomposed into three components. Each component describes the annihilation state and is characterized by the value of the lifetime τ_i and its contribution in the spectrum, i.e., the component intensity I_i ($i = 1, 2, 3$). The first lifetime τ_1 is the shortest one with the values close to 125 ps and comes from *p*-Ps annihilation. The origin of the second lifetime τ_2 with the value of a few hundreds of picoseconds (usually lower than 0.5 ns) is free positron annihilation. The third one, τ_3, is the *o*-Ps pick-off annihilation lifetime. It is of order of a few nanoseconds. It has been established that the lifetime of *o*-Ps is very sensitive to the local free volume size. Therefore, *o*-Ps is a probe of size and concentration of these free volumes in molecular substances such as polymers, molecular crystals, low-molecular-weight glass-formers, and LCs. In such substances, the Ps formation and decay is expected to be influenced by the nature of intermolecular interactions and the internal structure. It is particularly pronounced in the case of LCs that have been investigated since the early years of positron annihilation spectroscopy. Positron annihilation has been used in studies of both thermotropic (formed through temperature change) and lyotropic (formed through the action of a solvent) LCs. In some cases, PALS measurements revealed new LC phases [5, 6]. Nonetheless, the Ps formation and interactions with its surrounding in LCs is still not completely understood.

Liquid crystal phases

The LC phases, called mesophases, are intermediate states between the isotropic liquid phase and the crystal phase of long-range order. LC mesophases can be divided into four classes for the sake of the cause of their origin: thermotropic, lyotropic, barotropic (formed through pressure change), and phototropic (formed trough introducing or removing light). The main attention is focused on the thermotropic LCs, which exhibit rich polymorphism upon variation of temperature. The sequence of occurrence of thermotropic LC mesophases with a rod-like shape of molecules is as follows [7, 8]: Cr → SmH → SmK → SmE → SmG → SmJ → SmF → SmL → SmI → SmB → SmM → SmC → SmA → N(Ch) → I, where Cr, Sm, N, Ch, and I mean – the crystal, smectic, nematic, cholesteric, and isotropic liquid phase, respectively. Figure 1 shows an example
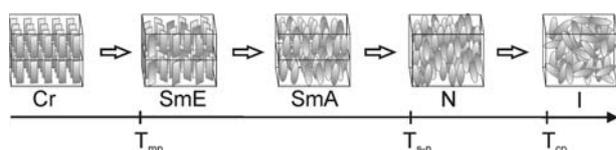
of phase transitions as a function of temperature for rod-like molecules. The LC phases are different, and they differ in the arrangement of short- and long-range order, and the degree of inclination of molecules in relation to the plane of the layer. Various relaxation processes can be observed in different frequency ranges: very slow relaxation processes, e.g. conformational motions in hertz to kilohertz range, flip-flop motions, relaxation around short axes of molecules in kilohertz to megahertz range and very fast relaxation processes, e.g. tumbling/reorientation around long axes of molecules [9].

In the smectic phase, the molecules are arranged in layers and their centers of gravity form a plane. The molecules in the layers are variously arranged, depending on the type of mesophase. In the nematic phase, ordering of molecules consists in the fact that their long axes are arranged averagely along the highlighted (emphasized) direction called the director (direction of uniaxial vector $\hat{n}$). The rotation of the molecules around short axis of molecules is strongly inhibited while the molecules can freely diffuse in any direction. In other words, the rotational degree of freedom is frozen in nematic phase. The molecules in the SmA phase – called orthogonal smectic – are arranged in layers, and their centers of gravity determine the so-called smectic plane. Director in the SmA phase is perpendicular to the smectic plane. No long-range ordering of molecules, as in the nematic phase, is present. The SmB phases, in which the molecules are arranged orthogonally in layers, may be of hexatic type, where the centers of gravity of molecules are arranged hexagonally (with only short-range positional order), or the crystalline type (sometimes denoted as SmL), wherein the centers of masses form a hexagonal structure in each plane with long-range positional order. SmE phase also is of crystalline type and it is distinguished by the arrangement of the centers of gravity of the molecules in a tetragonal system. The crystal-like phases of SmL and SmE have features similar to phases being of plastic-crystalline type. In these phases, there is still the possibility of rotations around the long and the short molecular axes. In addition to orthogonal phases described above, there are phases in which the arrangement of molecules occurs at a certain angle ϕ to normal to the layer, wherein the other characteristic features of the phase are unchanged.

Polarized light microscopy is a vivid method showing textures characteristic for given LCs. It enables to establish the phase symmetry or distinguish between different types of uniform molecular orientations. Figure 2 shows examples of textures for selected mesophases of 4-n-heptyl-2,3′-difluoro-4′-nonyloxybiphenyl.

Fig. 1. Example of phase transitions as a function of temperature for rod-like molecules. T_{mp}, T_{s-n}, and T_{cp} are the temperatures at the melting point, smectic-to-nematic transition, and clearing point, respectively.

Positron annihilation in liquid crystals

The early studies of positron annihilation in LCs performed in 1960s and 1970s showed that *o*-Ps annihilation changes not only during fusing but also during transitions between different mesophases [10–12]. There were also attempts to apply the an-
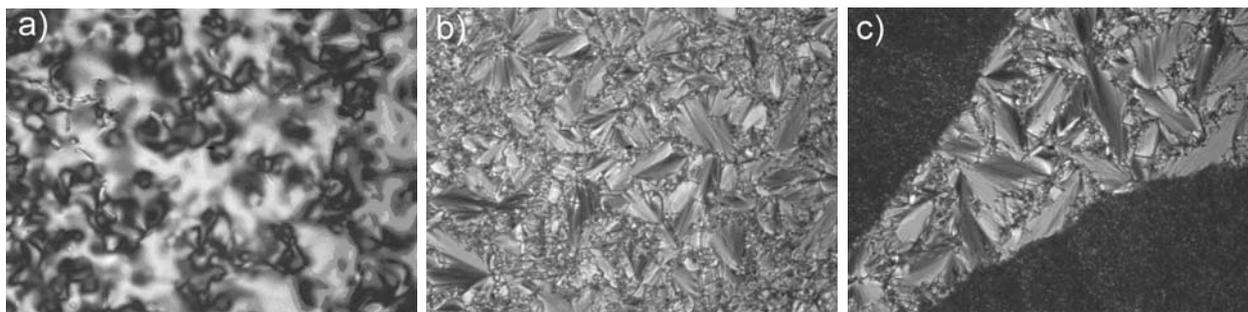
Fig. 2. Examples of texture obtained by polarizing microscopy method for 4-n-heptyl-2,3′-difluoro-4′-nonyloxybiphenyl. Nematic phase thread-like texture (a), fan-shaped texture of SmA (b), and transition between SmA and crystal phase (c).

gular correlation of annihilation radiation (ACAR) for studies of LCs [13]. The density changes during the molecular crystal to LC transition can be significant, which is reflected in changes of the free volume available for Ps formation and annihilation. However, the density changes accompanying the transitions between mesophases are usually small. Then the rearrangement of the molecules and resulting alteration of the degree of order was considered as the cause of changes of the longest positron lifetime attributed to o-Ps annihilation and its intensity in that case. Nevertheless, the interpretation of the results was not straightforward. Different processes can influence Ps formation and annihilation.

Ps inhibition is a process that takes place at the stage of Ps formation. A fast positron implanted into a molecular solid loses its energy by ionization and excitation of molecules. According to a spur model of Ps formation, the thermalized positron reacts with one of the free electrons at the end of the positron ionization path $e^+ + e^- \rightarrow$ Ps [2]. This process competes with other spur processes such as recombination of ionized molecules (denoted by M^+) with free electrons ($M^+ + e^- \rightarrow M$) or trapping of free electrons or positrons by scavengers. Changes in these processes or alterations of the positron or electron mobility may cause a rise (anti-inhibition) or a reduction (inhibition) of Ps formation probability and an increase or a decrease in the o-Ps intensity but the o-Ps lifetime remains unchanged.

If, after formation, the o-Ps annihilation takes place through pick-off process, the radius R of the free volume hole, where o-Ps is formed, may be calculated according to the semiempirical Tao-Eldrup model [14, 15]:

$$(1) \qquad \tau_{po} = \frac{1}{2}\left[\begin{array}{l} 1 - R_0/(R_0 + \Delta R) + (1/2\pi) \\ \cdot \sin\left(2\pi R_0/(R_0 + \Delta R)\right) \end{array} \right]^{-1}$$

where τ_{po} is the pick-off lifetime, R_0 is the radius of a spherical free volume hole, and $\Delta R = 0.166$ nm is an empirical parameter. If pick-off is the main process of o-Ps annihilation, the longest lifetime component τ_3 is approximately equal to τ_{po}. The probability of 3γ annihilation is two order of magnitude smaller and can be neglected.

Apart from pick-off annihilation, which does not change the intensity of o-Ps component, chemical quenching and spin conversion affect both the o-Ps lifetime and intensity. Chemical quenching

includes oxidation reactions in the wake of which Ps decays into a free positron, Ps + M $\rightarrow$ e^+ + M$^-$, or the complex formation: Ps + M $\rightarrow$ [M$^-$, e^+]. In both the cases, the intensity of o-Ps increases and its lifetime decreases if the reaction rate increases. If the paramagnetic molecules or atoms are present in the medium, spin conversion may occur when Ps collides with them, i.e., o-Ps + M $\rightarrow$ p-Ps + M and p-Ps + M $\rightarrow$ o-Ps + M. Because usually the conversion rate is much lower than the annihilation rate of p-Ps, i.e. 8 ns^{-1}, the second process is not visible. If the conversion rate increases, both p-Ps and o-Ps components are replaced by one component with lifetime 0.5 ns, which is the spin-averaged Ps lifetime and intensity equal to 4/3 of the initial o-Ps intensity.

In liquids, Ps is strongly repelled by the molecules and creates itself a bubble that hosts it. The so-called bubble model of Ps formation was introduced by Ferrel [16] to explain the unexpectedly long lifetime of the o-Ps in liquid helium. In a bubble state, the inwards pressure owing to the surface tension and the external pressure are counterbalanced by the outwards pressure owing to the Ps molecule repulsion and the zero-point energy of Ps. The equilibrium radius of the Ps bubble R_{eq} is determined by the minimum of the sum of the Ps energy $E_{Ps}(R)$, the energy related to the external pressure $E_{Ps}(R) = 4\pi R^3 p/3$ (which for normal pressure can be neglected) and the surface energy $E_\sigma(R) = 4\pi R^2 \sigma$:

$$(2) \qquad \frac{d}{dR}\left[E_{Ps}(R) + E_\sigma(R) + E_p(R) \right] = 0$$

where σ is the surface tension coefficient and p is the external pressure. It should be noticed that the surface tension depends on curvature and σ differs from the macroscopic surface tension σ_∞ (for a flat surface). The relation between these two quantities is $\sigma = \sigma_\infty/(1 - \delta/R)$, where δ is called Tolman's length [17]. In the simplest case, Ps is considered as a point particle that is assumed to be situated in a finite square well potential. If the finite square well potential is replaced by an infinitely deep square well potential, the radius of the well $R + d$ is broadened by a parameter d [18, 19]. Then, $E_{Ps}(R) = \pi^2 \hbar^2/4m_0(R + d)^2$, where m_0 is the mass of an electron. For the depth of a potential well 1 eV and for the radius R equal to 0.4 nm, the value of d is 0.158 nm [19].

The o-Ps lifetime is expected to increase at the transitions from one LC mesophase to another with lower degree of order or to isotropic liquid. This is

due to the higher temperature in which the less--ordered phase exists, and this is connected to lower surface tension. Nevertheless, it is not the case for different cyanocompounds, i.e., homologs of alkyl cyanobiphenyls (nCB) and alkyloxy cyanobiphenyls (nOCB) where n is the number of carbon atoms in the alkyl chain. Quite opposite tendency is shown for the transition from the LC phase (N or SmA) to isotropic liquid. The small but visible decrease of order of 0.1 ns was attributed to a diminishing extent of the antiparallel pairing of molecules in the isotropic liquid [20]. Then this is an example of influence of molecular arrangement on the o-Ps lifetime.

Different cyanocompounds, which are the members of nCB and nOCB homologous series, have been investigated by Sharma *et al.* [20–22]. Molecules of both types of compounds have strong polar group CN at the terminal position, see Fig. 3. The molecules of the first compounds, i.e., nCB have alkyl chain and the second, i.e., nOCB have alkyloxy (OC_nH_{2n+1}) group there. For these compounds, the abrupt increase in o-Ps lifetime, τ_3, during solid to LC phase transition was observed [20–22]. The relative changes in τ_3 are much higher than the relative decrease in density. This was explained by the phenomenon of antiparallel pairing of molecules in LC phases that causes lower availability of free dipolar endings, so their influence on the o-Ps pick-off annihilation diminishes and pick-off annihilation rate decreases, hence a higher τ_3 value in the mesophase. Molecular dimers that are formed by CN-CN end group contacts are already present in molecular crystals [23, 24].

One of the differences between molecular crystal and LC phases concerns packing coefficient. Lightbody *et al.* [25] proposed the following empirical relation between the longest lifetime ascribed to o-Ps pick-off annihilation in bulk material and packing coefficient k for hydrocarbon molecular crystals:

$$(3) \qquad \tau_{po} \ [\text{ns}] = 7.92 - 9.616 \cdot k.$$

The packing coefficient is defined as the ratio of volume occupied by the molecules in the cell (the van der Waals volume) to the volume of the cell. Table 1 presents values of the τ_{po} calculated from Eq. (3) for solid and LC phases of nOCB using packing coefficients from Ref. [26] or calculated using crystallographic data [23, 24] and for n-alkyl--isothiocyanato-biphenyls (nTCB) using packing coefficients from Ref. [27]. It can be seen that for all nOCB in crystal phase, the values predicted from Eq. (3) are much lower than that of experimental ones. Moreover, the observed o-Ps lifetime is proportional to the molecular volume (Table 1). It seems that for these compounds, the crystal structure is relatively close packed and observed lifetime τ_3 is too high to originate from the o-Ps pick-off annihilation in bulk. It may come from annihilation of o-Ps trapped in lattice imperfections, e.g., molecular vacancy type of defects. The intensity of this component is lower than 10% and increases to about 20% during the transition. A similar conclusion was drawn in the case of 4TCB crystal phase for which I_3 is even lower, i.e., it increases from 0% to 5% with temperature before the transition and then to 21% during the transition [28]. The value of τ_3 between 1.8 ns and 1.9 ns is in accordance with the size of the molecular vacancy for 4TCB crystal lattice. 6OCB is exceptional among the compounds listed in Table 1, because it exhibits a high value of I_3 for the crystal phase, i.e., about 30% and it decreases during the molecular crystal to LC transition. This behavior was ascribed to less-packed structure of ordered molecular crystal. However, the calculated packing coefficient does not differ significantly from those for other nOCB compounds with higher number of carbon atoms in the alkyl chain. Nonetheless, 6OCB has a different crystal packing in crystal phase in spite of similar molecular conformations and formation of dimers [23, 24]. 6OCB exhibits transition to nematic phase and its crystal structure is closely related to a nematic, while for 8OCB to a smectic. The smectic structure for a mesophase is stable for $n \geq 8$ in that case.

The above mentioned 4TCB as a representative of nTCB homologous series has a polar group NCS

Table 1. Molecular volume and packing coefficient from Refs. [26] and [27] or calculated using crystallographic data [23, 24]. Values of the o-Ps lifetime were calculated using Eq. (3) for solid and LC phases nOCB and nTCB compounds. The experimental o-Ps lifetime are from Refs. [20] and [28]

Compound	Molecular volume [Å³]	Packing coefficient k	o-Ps lifetime calculated using Eq. (3) [ns]	o-Ps lifetime observed [ns]
6OCB (Cr)	290.79	0.713	1.06	1.40[3]
8OCB (CrI)		0.738	0.82	
(CrII)	326.70	0.725	0.94	1.8–1.9[3]
(CrIII)		0.71	1.09	
9OCB (Cr)	344.81	0.754[1]	0.67	1.95–2.05[3]
(SmA)		0.678[1]	1.40	2.55[3]
10OCB (Cr)	362.74	0.709[1]	1.10	2.15–2.25[3]
(SmA)		0.650[1]	1.67	2.90[3]
4TCB (Cr)	249.30	0.75[2]	0.71	1.80–1.90[4]
(SmE)		0.623[2]	1.93	2.21[4]
6TCB (SmE)	277.64	0.600[2]	2.15	2.40

[1] Ref. [26].   [2] Ref. [27].   [3] Ref. [20].   [4] Ref. [28].
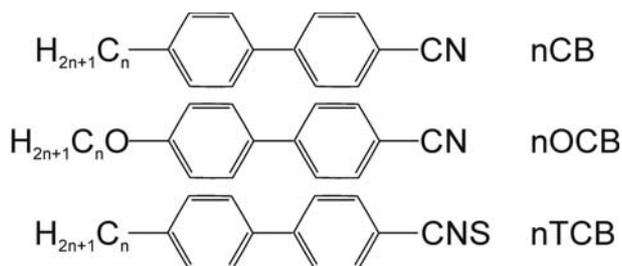
Fig. 3. The chemical structure of rod-like molecules of cyanocompounds studied using PALS.

at the terminal position, see Fig. 3. It exhibits the SmE mesophase which is the LC phase closest to an ordered crystalline phase. There is a growing interest in mesogens showing the SmE phase as organic semiconducting materials [29]. Therefore, finding out more about the structure of the SmE is important. As it was mentioned, this phase has a layer structure. The molecules exhibit spatial periodicity in three dimensions with orthorhombic symmetry and exhibit no fluidity within the layer [27]. They form herringbone array in layers with highly disordered vertical orientation of molecules (head-to-tail disorder). The SmE phase of *n*TBC have been extensively investigated and new models of the SmE lamellar structure with two types of sublayers consisting of aromatic cores and alkyl chains of molecules has been proposed [30, 31]. This is connected to the previous reports concerning molten state of the alkyl chains in the SmE phase which has been confirmed by thermodynamic, structural, and spectroscopic studies including PALS results [28, 32, 33]. Formation of Ps bubbles in mobile liquid-like regions of hydrophobic alkyl chains was also found for the racemic triple chain amphiphilic diol **1** that exhibits hexagonal columnar and cubic mesophases [34]. It seems that liquid-like state of alkyl chains play an important role in Ps formation and annihilation in LCs.

Chandramani Singh *et al*. also investigated supercooled LCs [21, 35]. They reported the correlation between the series of maxima and minima in the τ_3 dependence on temperature and activation of different intra- and intermolecular motions for quenched 6OCB and other nematic LCs. The supercooled SmE phase of 4TCB does not exhibit such maxima and minima in the τ_3 dependence although activation of different modes of molecular motions also takes place with rising temperature [36]. The character of the I_3 dependence on temperature indicates thermal activation of the sites where *o*-Ps is formed and it can be explained within two-state model of glass transition assuming that Ps can be formed in liquid-like domains in the sample [37, 38]. Increase in I_3 with temperature can be related to the increase in the liquid-like fraction of the sample. It is very difficult to crystallize 4TCB. Then the crystallization does not interfere with the possible molecular glass softening during PALS measurement. These two processes occurring in the supercooled sample on heating may cause an increase and subsequent decrease in the *o*-Ps lifetime and intensity I_3.

Conclusions

Studies of LCs using PALS can deliver new information on these complex systems despite the fact that not all details of Ps formation, localization, and annihilation are fully understood. The observed changes of the local free volume during phase transitions reflect the changes in the molecular arrangement to a higher degree than the changes in the density or surface tension. This can be connected to dipole character of molecules. High electron density at the end group of molecules of LCs can influence the pick-off annihilation rate. However, the arrangement of molecules where the strong dipoles owing to the end groups tend to be opposed diminishes that influence. PALS can also shed light on the problem of glass formation in these highly anisotropic systems.

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