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Supercooling studies in n-p-cyano-p-heptyl biphenyl using positron, lifetime spectroscopy

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Abstract
Supercooling studies have been performed in n-p-cyano-p-heptyl biphenyl using positron lifetime spectroscopy. Positron lifetime measurements have been performed during the heating cycle of samples prepared by either quenching or slow cooling from the nematic phase. The behaviour of these two samples is found to be different. In case of the quenched sample, the material seems to have transformed into a glassy solid. The o-Ps pick-off lifetime in the quenched sample exhibits a strong temperature dependence. Its value exhibits six broad peaks at 176, 195, 214, 233, 248 and 257K. These temperatures have been ascribed to various molecular motions. The sample exhibits a glass transition at about 268K.

Introduction

A large class of liquids can be supercooled far below the crystallization temperature. They transform into a disordered glassy state although it is thermodynamically unstable. The relaxation times of such systems are large compared to macroscopic observation times, therefore, they provide an ideal situation for studying the complex molecular dynamics. Simple monatomic liquids require extremely high cooling rates $10^{11}Ks^{-1}$ and, therefore, they can not be investigated. The formation of a glass-forming supercooled state is believed to be a direct consequence of the low degree of symmetry of the unstrained molecule [1]. Alkyl cyanobiphenyls fall in this category of highly anisotropic molecules which exhibit supercooling. Dielectric loss studies in a supercooled 10% v/v solution of n-p-cyano-p-heptyl biphenyl(7CB) in decalin [2] and far infrared(FIR) absorption studies of 7CB in various environments [3-5] have provided useful information about various intra- and inter-molecular modes executed by this compound.

Positron annihilation has been extensively used in the investigation of physical and chemical properties of condensed media [6]. The sensitivity of positron annihilation parameters to various conformational and structural transformations occurring in these media has been amply demonstrated [6]. Positron annihilation studies in 7CB as a function of temperature of the sample have been reported [7,8]. The system exhibits several phase transformations ranging from crystal to nematic and then to isotropic liquid. On slow cooling from the isotropic liquid, the nematic phase exhibits supercooling but no evidence of any intra- or inter-molecular modes executed by this compound has been found. These studies were confined to temperatures higher than 5°C, and no study extending to very low temperatures has been reported. One could expect that the molecular motions of these long molecules can be arrested completely in a supercooled state. However, it is likely that a free volume is available in the supercooled state in which molecular motions are possible even below the glass transition temperature (Tg). The Ps formed in this state can perhaps pick up such molecular motions. We demonstrate this possibility in this present work. The system was, therefore, quenched from

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the nematic phase using liquid nitrogen transforming it to a glassy solid. Positron lifetime measurements have then been carried out in the quenched sample during its heating cycle. The results of this investigation are presented.

Experimental

The n-p-cyano-p-heptyl biphenyl(7CB) was procured from BDH Chemicals and used without any further purification. Positron lifetime measurements were carried out using a standard lifetime spectrometer. Positron source used was ^{22}Na, it was prepared by evaporating an aqueous solution of ^{22}NaCl on a thin Mylar film and then covering it by another similar film. The source sandwich was sealed by putting it between two concentric tightly fitting copper rings. It was then placed in a specially designed sample holder. All the measurements were performed as a function of temperature. The temperature of the sample was maintained thermostatically to a constancy of ±0.1°C. In each set of measurement, a total of at least 2×10^5 counts were collected.

Results and discussion

The lifetime spectra recorded were analysed using a software, PC-PATFIT, developed by Riso National Laboratory, Denmark [9]. Details of the procedure adopted are described elsewhere [7]. All the lifetime spectra could be resolved into three components. The shortest component, τ_1, was constrained to 0.125ns, the p-Ps lifetime. The intermediate component, τ_2, has been attributed to the annihilation of positrons with electrons of the medium without forming any bound state with them. This component did not exhibit any temperature dependence and was found to be insensitive to any structural changes occurring in the medium. The longest component, τ_3, is ascribed to the pick-off annihilation of o-Ps with electrons bound to the molecules of the surrounding medium. The relative intensity, I_3, of this component is, therefore, proportional to Ps formation in the medium. Both these parameters exhibit considerable temperature dependence and sensitivity to the structural changes taking place in the medium.

The temperature dependence of the positron annihilation parameters τ_3 and I_3 in the quenched and slow cooled samples, as obtained in the present work, are shown in Figures 1 and 2. Figure 1 shows the temperature dependence of τ_3 in the tempera-

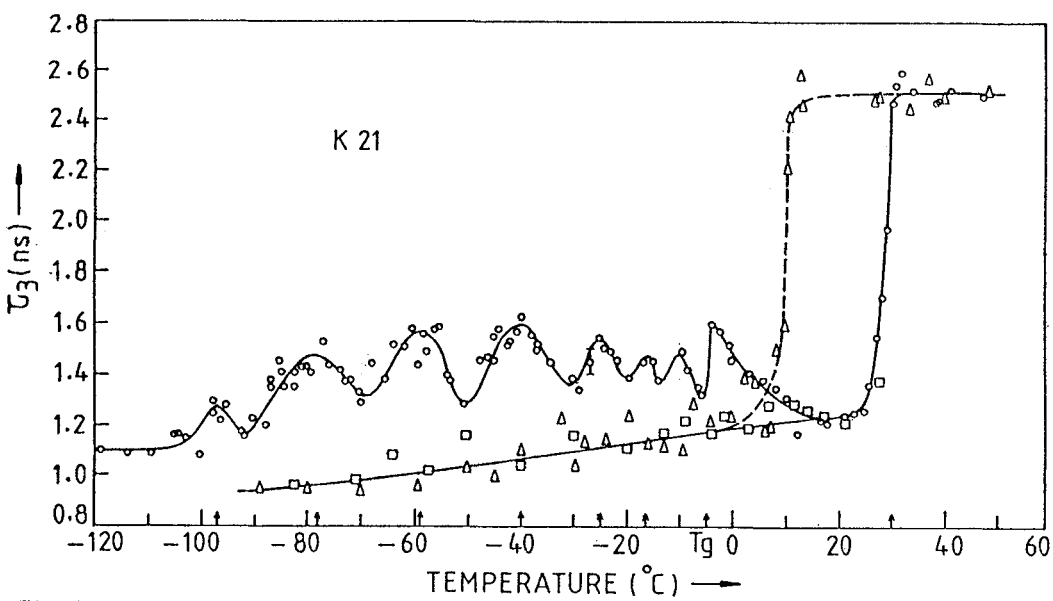

Fig. 1 :Temperature dependence of τ_3 in 7CB ;--o--, quenched sample; □ , heating cycle of slow cooled sample; Δ ,cooling cycle.

ture range 150-325K for three different samples of 7CB: (i) heating cycle of the sample prepared by quenching from the nematic phase to the liquid nitrogen temperature, (ii) heating cycle of the sample prepared by slow cooling from the nematic phase to a temperature of ~ 150K and (iii) cooling cycle of the sample from isotropic liquid to ~ 150K. The corresponding temperature dependence of I_3 for these three samples is shown in Figure 2.

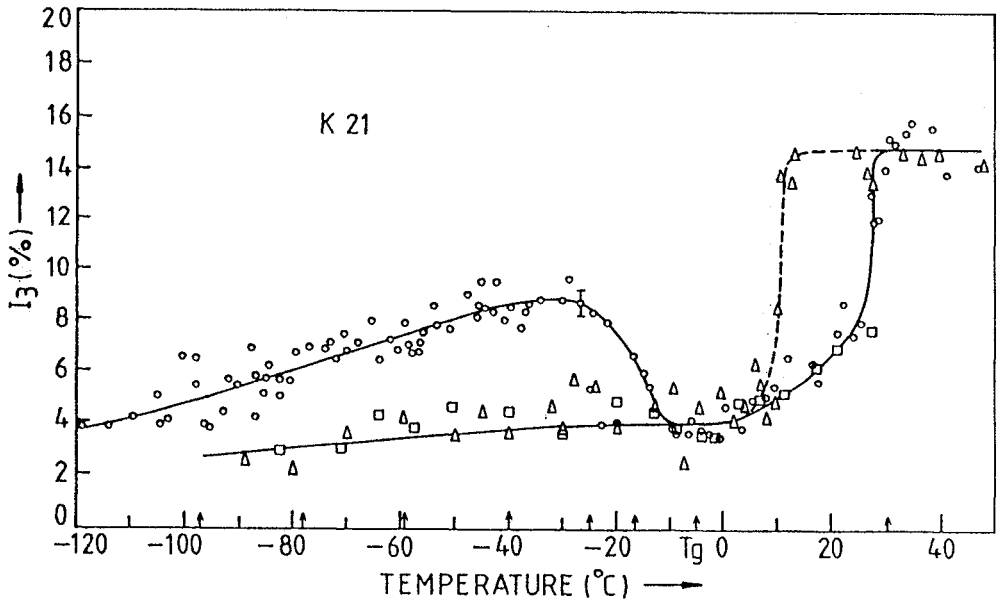

Fig. 2 : Temperature dependence of I_3 ; o, quenched sample; □ , heating cycle of slow cooled sample; Δ , cooling cycle.

It is seen from Figure 1 that the heating cycle of the slowly cooled sample exhibits no sign of the formation of a glassy state. In this state the τ_3 value increases linearly with increasing temperature indicating the thermal expansion of the crystal lattice. An abrupt change in its value is observed at ~ 301K indicating crystalline solid to nematic transformation. In the cooling cycle also the behaviour of the sample is similar except that the nematic phase exhibits a supercooling by ~ 20K. The transition temperatures obtained for various transitions are in agreement with the literature reported values [7,10,11]. The behaviour of these two samples vis-a-vis Ps formation is also similar. It is seen from Figure 2 that in case of slowly cooled sample, the I_3 value increases more or less linearly with temperature and begins to increase first gradually at ~ 273K and then abruptly at ~ 301K. There is very little Ps formation in the crystalline solid phase, it is found to increase in the nematic phase. The behaviour of the sample quenched from the nematic phase is observed to be quite different from that of the slowly cooled sample. The temperature dependence of τ_3 during the heating cycle of the quenched sample (Fig.1) exhibits some interesting features. Its plot in Figure 1 can be divided into four distinct regions : (i) region I, extending from 150 to 240 K, (ii) region II, from 240 to 263K, (iii) region III, from 263 to 288K, and (iv) region IV, from 288K onwards. The region I is characterised by four well defined broad peaks observed at 173, 195, 214 and 233K. It may be remarked that the τ_3 plot in this region when extrapolated to higher temperatures, nearly approaches the τ_3 value in the nematic phase from where the sample was quenched. In region II, the τ_3 value exhibits two more peaks located at 248 and 257K. In region III, the system exhibits some kind of relaxational behaviour, indicating a glass transition at ~ 268K. Beyond this temperature, it decreases gradually finally flattening out at 288K, where the sample has completely transformed to a crystalline solid. At temperatures beyond 288K i.e. region IV, the transition from crystal to nematic phase is indicated at 301K.

The response of quenched sample towards Ps formation is seen in the temperature dependence of I_3, shown in Figure 2. It is different from the behaviour of the slow cooled sample. The I_3 value increases more or less linearly upto a temperature of 243K and then begins to decrease gradually till it finally merges with the I_3 value characteristic of the crystalline phase. It may further be noted that temperature dependence of I_3 at low temperatures, when extrapolated to higher temperatures, tends to merge with that in the nematic phase; a behaviour also exhibited by τ_3 . Both these observations indicate that, on quenching, the molecular order of the nematic phase gets frozen and maintained in the glassy solid formed in this process.

7CB is a large asymmetric polar molecule. It has a dipole moment at a small angle to the long molecular axis. Hence, a larger component of the dipole moment lies along the long molecular axis [12]. Further, the spatial structure of the molecule is such that the two phenyl rings are not in the same plane. In the liquid crystalline or nematic phase, the system exhibits a partial order, namely the long range orientational order. Because of these special features, this class of materials exhibits various kinds of molecular motions both intra-molecular as well as collective modes. Extensive work to study such motions in 7CB has been done using FIR [3-5]. A typical FIR spectrum of 7CB exhibits a broad absorption at 100 cm^{-1}, a sharp absorption at 150 cm^{-1} and a series of absorptions around 180 cm^{-1}. The broad absorption at 100 cm^{-1} is attributed to whole molecule torsional oscillation. The two absorptions at 160 and 180 cm^{-1} are intra-molecular in origin, they represent two C-N modes of different frequencies which give fluctuating dipole components normal to the long axis. The absorptions observed at 150 and 175 cm^{-1} have been attributed to collective modes arising out of the partial ordering in liquid crystal [13]. The extended moleculer order in these systems provides the possibility of long range coupling and existence of these collective modes. These modes do not coincide with the phonon modes present in solids.

Now coming to the response of the quenched sample to positron annihilation measurements, it may be noted that Ps formation in this sample is higher than that in the slow cooled sample. This indicates that the quenched sample has larger free volume or greater availability of void space where Ps formation can take place. In the glassy state, normally all molecular motions are expected to be frozen till the material is heated upto Tg. However, the availability of free volume and voids, as demonstrated by higher I_3 values in this sample can make whole molecular motions possible even below the glass transition T_g. The temperature dependence exhibited by τ_3 reveals the existence of such molecular motions. As the quenched sample is gradually heated, different possible modes get excited at temperatures corresponding to their characteristic frequencies. These motions are picked up by o-Ps annihilating in the system and are reflected in the behaviour of τ_3 . The temperatures corresponding to various broad peaks observed (Fig. 1) and the wave numbers of the corresponding molecular motions are given in Table I. In the range of temperatures considered, the molecules can execute some torsional motions only, the rotational and vibrational modes require much larger energy and hence occur at higher temperatures. It is seen from Table I that the wave numbers for modes corresponding to temperatures 214, 233, 248 and 257K agree closely with those observed in FIR spectra, namely at wave numbers 150, 160, 175 and 180cm^{-1}. Out of these, the modes corresponding to temperatures at 214 and 248K are due to the collective modes arising out of the long range orientational order of the nematic phase [5]. In a study made by Evans and Evans [4] on several related compounds, it has been shown that a torsional mode could arise at ~ 110cm^{-1} due to some relative movement of the phenyl rings with respect to each other. In the present work, the peak observed at 176K or 122cm^{-1} may be attributed to this kind of molecular motion. As regards the mode corresponding to the peak observed at 195K, it could possibly arise from the torsional motion of the whole molecule about the long molecular axis. Evidence for this kind of motion has been obtained from FIR studies in dipolar molecules [14-17]. As mentioned earlier, in the FIR spectra [5], the broad peak at 100cm^{-1} is ascribed to this kind of motion. In the present context, as the molecules are embedded in highly viscous surroundings, this kind of motion is likely to get hindered and, therefore, might require a higher energy. Due to this, the corresponding mode might be observed at a higher wave number. Based on this logic, the peak at 195K or 136cm^{-1} could be attributed to the torsional motion of the whole molecule about the long axis.

Table I : Molecular modes exhibited by 7CB molecules as observed in the present work.

S.No.	Peak Temp. (K)	Wave number (cm^{-1})	Nature of motion
1	176	122	Relative torsional motion between the two phenyl rings
2	195	136	Torsional motion of whole molecule about long axis
3	214	149	Collective mode
4	233	162	C-N torsional mode
5	248	172	Collective mode
6	257	179	C-N torsional mode

It is seen in Figure 2 that the temperature dependence of I_3 undergoes a marked change at ~ 243K, the onset of region II. It falls steeply with increasing temperature indicating a decrease in the free volume available in the system. This could arise due to (i) a decrease in the size of voids, (ii) a decrease in their number, or (iii) both. The near constancy of the average value of τ_3 in this region, however, indicates that the size of voids is not much changed, and it is rather the number of voids which decreases. This collapse of the free volume or the number of voids is, perhaps, a result of breakdown of some molecular order characteristic of the nematic phase - as is indicated by the change in the slopes of τ_3 and I_3 plots away from tending to the nematic phase. This order is ascribed to the anti-parallel bimolecular association [18,19] commonly occurred in this type of strongly dipolar molecules (dipole moment of 7CB, 4.33D). Such an association is expected to get dissociated at some stage of the heating process before the sample actually transforms into a crystalline solid. The threshold energy of this process is then provided by the thermal energy corresponding to the temperature, ~ 243K, the onset of the region II. Equating this to the interaction energy of two short dipoles each having a dipole moment **p** separated by a distance r, we get the separation between the dipoles as 8 Å. This is of the order of the size of phenyl ring and is quite expected as it is also, in turn, the order of magnitude of the nearest possible interaction of the two molecules which are supposed to be individually undergoing torsional oscillation.

The present work demonstrates the usefulness of positron lifetime spectroscopy in the study of complex molecular motions. The results obtained from this technique agree with those obtained from FIR and dielectric relaxation studies.

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