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Metastable polymorph formation in a supercooled liquid 2-biphenylmethanol: Luminescence study

J. Baran [a], N.A. Davydova [b,*], V.I. Melnik [b], V.P. Vorob'ev [b]

[a] *Institute of Low Temperature and Structure Research, PAS, 50-950, Wroclaw, Poland*
[b] *Institute of Physics, NANU 46 pr. Nauki, 03028 Kiev, Ukraine*

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ABSTRACT

We report for the first time on the transformation of the luminescence spectrum of the molecular compound 2-biphenylmethanol (2BPM) on heating from the glassy to liquid phases. The formation of a metastable polymorph after melting of the glassy state has been observed at room temperature. In the luminescence spectra a metastable polymorph manifests itself in the appearance of a new band at 277 nm, which is absent in the spectrum of the stable polymorph. The comparison of the luminescence spectra of the metastable polymorph with that of the glassy phase recorded at 4.2 K shows that the clusters of metastable polymorph are incorporated into the glass structure. In addition temperature-dependent luminescence spectra of both polymorphic forms are presented.

1. Introduction

Experiments on glass-forming molecular liquids reveal the slowing down by many orders of magnitude of the structural relaxation as a liquid is supercooled towards its glass transition temperature. Moreover, the liquid dynamics becomes progressively more heterogeneous when the temperature decreases. Many theories envisage a supercooled liquid as a heterogeneous mixture of clusters, domains, locally favoured or frustration-limited structures [1–4]. For a review of the current knowledge regarding the heterogeneous nature of structural relaxation, see Refs. [5–10], and references therein. Experimental evidence for microscopic regions of different relaxation time has been obtained by multidimensional nuclear magnetic resonance [11], dielectric hole-burning spectroscopy [12], the salvation dynamics [13–17] and excess light scattering near Tg [18].

However, up till now, many aspects of the kinetic slowing down and growing dynamic heterogeneity continue to be one of the major unsolved and debated issues of condensed matter physics.

Recently we have found for benzophenone [19] and 2-biphenylmethanol [20] using differential scanning calorimetry method, that in their supercooled liquids the metastable nuclei start to appear for temperatures $T<1.2Tg$. Their size is smaller than the critical nucleus size. Thus we can conclude that the nuclei are responsible for the slow relaxation of the supercooled liquid below $1.2Tg$, and the finite lifetime of nuclei gives rise to dynamic heterogeneity of the supercooled liquid. On cooling these nuclei are incorporated into the glass structure, while with increasing temperature through the glass transition temperature they get the possibility to grow rather easily to a metastable polymorph. An optical Kerr effect spectroscopy study was recently published where a complicated relaxation process in benzophenone and 2-biphenylmethanol below $1.2Tg$ has also been observed [21,22].

As for benzophenone its stable and metastable polymorphs have been the subject of many crystallographic [23], vibrational [24–27], and luminescence studies [28–33]. In [32] phosphorescence spectra of the stable and metastable polymorphic forms and glassy phase of benzophenone and their temperature dependence have been investigated. It was shown, that the phosphorescence spectra of benzophenone exhibit a simple progression of the broad bands, whose intervals correspond to the frequency of the carbonyl stretching vibration. The influence of the film thickness on the lifetime and the decay behaviour of the glassy benzophenone phosphorescence were studied in [33], and time-resolved phosphorescence spectra of crystalline benzophenone in the range from 1 to 30 ms were studied in [34]. For the sake of completeness, two other studies on benzophenone using time-resolved phosphorescence spectroscopy should be cited [35,36]. Namely, the effect of disorder on transport of an electronic excitation in organic solids, including benzophenone was studied in [35]. In the paper [36] time-resolved phosphorescence spectra of vitreous benzophenone have been recorded at low temperatures within the time domain of 2 μs to 20 ms for sampling times between 2 and 500 μs.

As for 2BPM its luminescence has never been studied. However it is interesting to perform a luminescence study not only with the aim of confirming our DSC results [20] as to the metastable polymorph

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[*] Corresponding author. Tel.: +380 44 525 35 15; fax: +380 44 525 15 89.
E-mail address: davydova@iop.kiev.ua (N.A. Davydova).

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formation in the supercooled liquid, but also to get information about luminescence spectra of different polymorphs of 2BPM. This information can be useful for the identification of the different polymorphic forms of 2BPM.

The luminescence measurements were as follows: (1) we prepared the glassy state and during heating from 4.2 to 255 K the luminescence spectra were recorded (Fig. 2); (2) at room temperature time-dependent evolution of the luminescence spectra from liquid state to crystal was studied (Fig. 3); and (3) we compared the obtained spectrum with those of the stable crystalline and glassy phases at 4.2 K. In addition we have performed a temperature-dependent luminescence study of both stable (Fig. 5) and metastable (Fig. 6) crystalline phases of 2BPM in the temperature region 4.2–255 K.

2. Experimental

Aldrich material 2-biphenylmethanol [($C_6H_5C_6H_4CH_2$–OH)] of 99% purity was used without further purification. Its molecule structure is shown in Fig. 1. The hydroxyl groups (OH) are involved in the formation of an intermolecular hydrogen bonding.

Dry powder was added to cylindrical glass tubes. Using a heat gun, one can easily melt the powder ($T_{\mathrm{melt}} = 326$ K) to form a liquid. The glass phase could be obtained by abrupt cooling of the liquid phase below the glass transition temperature ($Tg = 242$ K).

According to x-ray experiments [20] the structure of the metastable polymorph is monoclinic and consists of the hydrogen-bonded chains of molecules, while the structure of the stable polymorph is triclinic and consists of cyclic tetramers of molecules [36].

Luminescence spectra were recorded within a wide temperature range from 4.2 to 293 K using a MPF-4 Hitachi spectrofluorimeter in the spectral range 260–550 nm. Excitation from xenon source was used. The spectra were recorded using the 250 nm line as an excitation filtered by a monochromator. The width of the spectral slit is 2 cm^{-1}. The emission from the crystal was recorded with a FEU-79 photomultiplier in the photon-counting regime.

3. Results and discussion

3.1. Temperature-dependent luminescence spectra of the glassy phase

To analyze the structure transformation of the supercooled liquid we first prepared the glassy state of 2BPM. The liquid sample was cooled to 77 K, mounted on the cryostat, and then cooled to 4.2 K. The temperature is then increased and the transformation of the glassy state into the supercooled liquid state was investigated from the analysis of the luminescence spectra.

The temperature-dependent luminescence spectra in the process of heating of the glassy phase are shown in Fig. 2. At 4.2 K (curve 1) we observe two types of emission: fluorescence and phosphorescence with different spectral distributions. The first broad fluorescence band in the region 275–375 nm characterized by a short lifetime (~tens of nanoseconds) corresponds to singlet–singlet transition. The other broad phosphorescence band in the region 425–550 nm has a lifetime of ~milliseconds and corresponds to triplet–singlet transition. The evolution of the luminescence spectra with increasing temperature shows the next characteristics. The positions of the fluorescence and phosphorescence bands in the spectra of the glassy phase practically do not change upon heating. At the same time, the phosphorescence drastically decreased and the fluorescence was getting dominant with increasing temperature. It should be noted that the glass transition temperature Tg is 242 K and higher than this temperature the glassy state converts into a supercooled liquid, thus the fluorescence spectrum at 255 K (Fig. 2, curve 6) shows the spectrum of the supercooled liquid. It is seen that in the liquid state the intensity of the phosphorescence band is negligible.

3.2. Time dependence of the luminescence spectrum during the transformation

As was mentioned above the metastable phase could be obtained only from the glassy state by converting it to supercooled liquid and further heating up to room temperature.

The time dependence of the luminescence spectrum during the transformation of the supercooled liquid recorded at room temperature in the spectral region of fluorescence band is shown in Fig. 3. The spectra in the phosphorescence band region we do not show due to its very low intensity. We are continuing to study the previous sample at room temperature after melting its glassy phase (curve 1 in Fig. 3). The next two spectra (curves 2 and 3) were recorded since 15 and 30 min after recording the spectrum 1 (Fig. 3). For comparison, curve 4 in Fig. 3 shows the room temperature luminescence spectrum of the liquid sample, before it is quenched. When the curve 4 is compared with curve 1 (Fig. 3) it is seen that they differ in that a new band centered at 277.2 nm appears in spectrum 1. This means that the liquid before quenching corresponds to another physical state than the liquid after procedure of quenching followed by heating. According to our prediction, the growth of the nuclei into the clusters is responsible for the changes in the liquid structure. The position of the band at 277.2 nm does not change with time, but grows reflecting the increase of the average fraction of the solid clusters in the supercooled liquid (curve 2). After 30 min, the spectrum (curve 3) is not transformed with time, indicating the formation of a crystal. It is seen that fluorescent spectrum of the newly formed crystal (hereafter referred to as metastable polymorph) consists of three bands. During

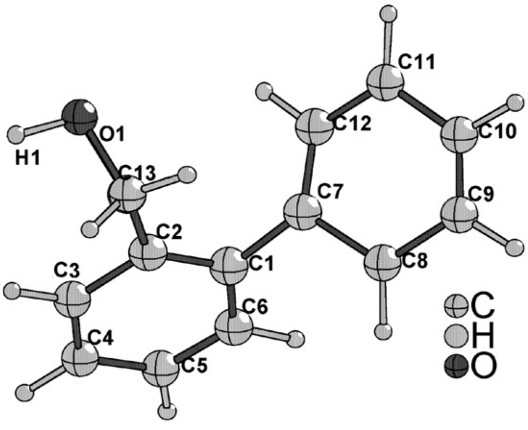

Fig. 1. The structure of 2BPM molecule (x-ray data) and the atom numbering.

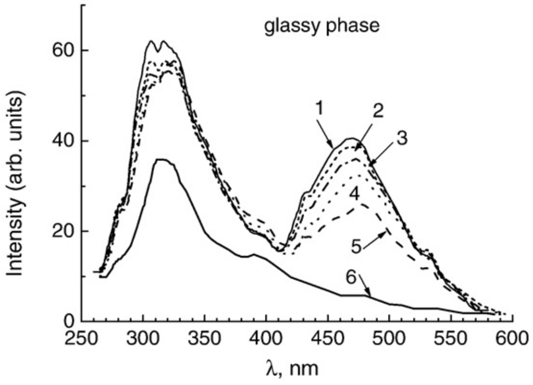

Fig. 2. Temperature-dependent luminescence spectra variations of the glassy 2BPM. Spectra were measured in the temperature region from 4.2 K to 255 K. 1—4.2 K; 2—30 K; 3—50 K; 4—90 K; 5—130 K; 6—255 K.