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Structural changes during the glaciation process in the molecular liquid triphenyl phosphite

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Infrared spectroscopy was used for the first time to investigate the structural changes in triphenyl phosphite during the glaciation process at 215, 218 and 220 K and crystallization process at 240 K. It has been shown that the nanocrystals emerge in a glacial phase and grow with time during glaciation process. The supercooled liquid during glaciation process also transformed. The transformation of the supercooled liquid apparently occurs in another highly viscous phase or even an amorphous solid phase, in which the crystalline nuclei grow. Thus we believe that the glacial phase can be described as composed of the nanocrystals of the stable phase coexisting with the transformed extremely viscous liquid (or amorphous solid phase).

1. Introduction

Triphenyl phosphite (TPP) is well known to exhibit an intriguing transformation of the supercooled liquid [1]. If TPP is cooled rapidly enough, it first enters into a supercooled liquid state below the melting point as usual liquids, and then into a glass phase at the glass-transition temperature (Tg). On the other hand, if TPP is quenched to a certain aging temperature (Ta) between 212 and 225 K (above Tg) and then annealed at that temperature, a new phase emerges in a supercooled liquid and grows with time. This new phase was found to be distinct from the glass, supercooled liquid, normal liquid and crystal. So, this phase was named glacial phase and the transformation to the glacial phase was named as glaciation process. The nature of the glacial phase is a controversial topic in the literature. Kivelson et al. [1,2] have suggested that the glacial phase is a poorly crystallized defect-ordered phase with a large unit cell and small crystallites which could result from structural frustration predicted by the "frustration-limited domain theory" [3]. Tanaka et al. [4–7] have indicated that the glacial state is the glassy state of a second type of supercooled liquid (a liquid with very anomalous molecular reorientation), and the authors have argued for the existence of a liquid-liquid phase transition. Time-resolved polarized and depolarized small-angle light scattering study on the kinetics of liquid-liquid transition in TPP [6,7] allowed the authors to suggest that the primary process is liquid-liquid transition, whose order parameter is of non-conserved nature, but accompanying micro-crystal formation. Mosses et al. [8] using the technique of fluorescence lifetime imaging interpreted the liquid-liquid transition as a phase transition associated with frustrated molecular clusters. Other explanations have suggested it may be a liquid crystal or plastic (orientationally disordered) crystal [9,10], a highly correlated second liquid (a liquid phase possessing more developed structural correlation than the ordinary liquid) [11–13]. Schwickert et al. [14] using a small angle neutron scattering and high-energy X-ray diffraction experiments have shown that the

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glaciation process can be interpreted via a four-stage model, including cluster formation, rapid nucleation, agglomeration, and saturation. However, the reason for saturation still remains elusive. Hedoux et al. [15–21] have suggested that the glaciation process can be considered as an aborted crystallization and a glacial state is not amorphous but formed by nanocrystals, mixed with a fraction of a non-transformed supercooled liquid, which strongly depends on the aging temperature *Ta*. Below 224 K, where nucleation is much faster than crystal growth, the crystallization process stops when the liquid is saturated with seed crystals [17]. Conversely, Mei et al. [22,23] by means of a spallation neutron and X-ray diffraction methods have shown that the glacial phase forms unusually weak intermolecular hydrogen bonds between an oxygen atom connected to a phenyl ring and an adjacent phenyl ring aligned in an approximately antiparallel configuration. Also claimed that the glacial state is not a simple two-component mixture of the nanocrystalline and supercooled liquid phases.

It is seen that there is still no consensus even on the nature and origin of the glacial phase thus further experiments are necessary to gain a deeper insight into structural properties of the glacial phase. That was the motivation of the work presented here to study this unusual phase in TPP in order to characterize it. To do this, we first used the infrared (IR) spectroscopy method to investigate the glaciation process at three aging temperatures 215, 218 and 225 K and crystallization process in TPP. This method allows analyzing in real time the structural evolution during different transformations.

In this paper, we provide experimental evidence strongly indicating that the glacial phase is composed of the nanocrystals of the stable phase which are embedded in a matrix of an extremely viscous liquid. We would like to stress that the matrix is not just a non-transformed supercooled liquid as suggested by Hedoux et al. [15–21], but a modified liquid.

2. Material and method

TPP [$P(OC_6H_5)_3$] of 99% purity was purchased from Aldrich and used without further purification. The molecule and crystal structure of TPP has been studied in ref. [20]. The molecule is highly flexible, insofar as six torsion angles can be identified. The *P* atom is tricoordinate. TPP crystallizes in the trigonal system and is characterized by an unusual large hexagonal unit cell, space group R3. The number of TPP molecules within unit cell is equal to 18. In addition to the conventional crystalline phase, which melts at 299.1 K, TPP can crystallize in another polymorphic phase, which melts at 291.6 K [24]. The glass transition temperature $Tg = 207$ K (for a heating rate of 10 K/min).

The crystallization and glaciation processes were easily monitored by following the changes in the IR transmittance spectra. Infrared measurements were done on a Fourier-transform infrared spectrometer (Bruker model IFS-88) at a resolution of 2 cm^{-1} and 32 scans were typically co-added for an individual spectrum. Data processing was performed with OPUS software. For the IR measurements, a liquid sample was sandwiched between two *CsI* windows at room temperature. The thickness of such a cell was approximately a few micrometers. Such a sample was then fixed in a closed cycle Oxford cryostat providing for a temperature variation in the range 330–12 K.

3. Results

We have studied the IR transmittance spectra in the 400–4000 cm^{-1} spectral range focusing especially on the 840–910 cm^{-1} spectral region; where the stretching vibrations of P-O and C-O bonds occur (see Fig. 4 of ref. [20]). It should be noted that the changes in the IR spectra during phase transitions were observed in the whole spectral range. They are associated with the huge conformational flexibility of TPP molecule which leads to the occurrence of different stable conformations very close in energy but with different bond lengths P-O and C-O, and values of the angles O-P-O, P-O-C, P-O-C-C. In Fig. 1 we show the continuous transformation of the IR transmittance spectra of the liquid TPP during cooling from 310 K (dashed curve in Fig. 1) through the glass transition temperature ($Tg = 207$ K) down to 70 K (solid curve). It can be seen that in this spectral range the spectrum consists of two overlapping bands at 862.3 and 875.5 cm^{-1}. Their position and shape in the IR spectrum during transformation from the liquid to glass state are virtually unchanged except for the changes associated with the evaporation of the liquid sample until the liquid phase transforms into the glass phase at *Tg*. Below 200 K (short dashed curve) all the curves coincide.

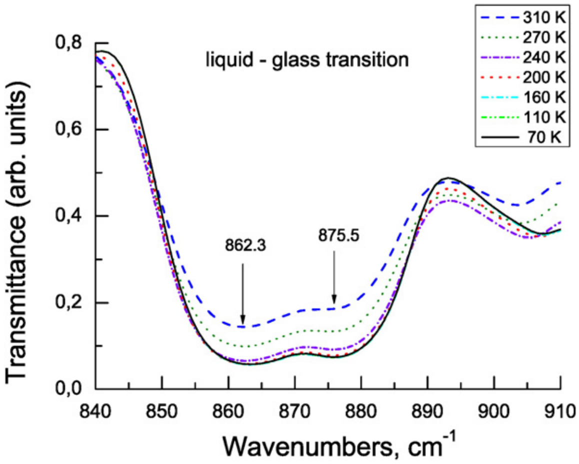

Fig. 1. Evolution of the IR transmittance spectra on cooling starting from the liquid state in the 840–910 cm^{-1} region. Temperatures are (top to bottom): 310 (dashed), 270, 240, 200, 160, 110, and 70 K (solid).

As it is known from the literature for the preparation of the glacial phase liquid sample must be heated starting from below *Tg* to an aging temperature *Ta* in the range 210–230 K. At *Ta* the glacial phase will be isothermally formed on the time scale of several minutes to hours depending on *Ta* [18]. Based on this information to obtain a glacial phase in our experiment, we used three aging temperatures *Ta*: 215, 218, and 225 K at which the glaciation process we investigated by measuring the IR spectra during isothermal aging (Fig. 2a,b,c, correspondingly).

In Fig. 2(a) the process of glaciation at $Ta = 215$ K is shown. Dashed curve 1 shows the spectrum of the supercooled liquid phase recorded immediately after reaching 215 K. Next curves (2–5) were recorded in 90, 100, 140, and 180 min, respectively, after recording the spectrum (1). It is seen that the IR spectra changes with time. The band centered at 862.3 cm^{-1} shifts to the high-frequency side and reaches the position at 864.5 cm^{-1}. At the same time the band centered at 875.5 cm^{-1} does not change its position. A small shoulder at 890.0 cm^{-1} appears on the high-frequency side of the band at 875.5 cm^{-1} at the end of transformation (solid curve 5). The changes in the spectra stopped after 180 min (solid curve 5). Thus we can conclude that the transformation associated with the glaciation process at 215 K is completed within 3 h.

In Fig. 2(b) the process of glaciation at $Ta = 218$ K is shown. Dashed curve 1 shows the spectrum of the supercooled liquid phase recorded immediately after reaching 218 K. The next curves (2–5) were recorded in 20, 60, 80, and 120 min, respectively, after recording the spectrum (1). In that case it can be seen that the band centered at 262.3 cm^{-1} is more strongly shifted to the high-frequency side compared with the process of glaciation at $Ta = 215$ K and reaches the position at 265.1 cm^{-1} (solid curve 5). Also the shoulder at 889.5 cm^{-1} increases in intensity (solid curve 5) and becomes stronger as compared with the glaciation process at $Ta = 215$ K. It can be seen that the changes in the spectra stopped after 120 min. Thus we can conclude that the transformation associated with the glaciation process at 218 K is completed within 2 h.