The Glacial State of Triphenyl Phosphite

Q. Mei[1,2], P. Ghalsasi[1], C.J. Benmore[2], and J.L. Yarger[1]

[1]University of Wyoming, Laramie, WY 82071.
[2]Argonne National Laboratory, Argonne, IL 60439.

Introduction

Kivelson and co-workers have discovered a low-temperature rigid state in the fragile glass former triphenyl phophite (TPP) [1]. It was discovered by annealing the low temperature glassy phase at 220K. The annealed (high density) form was initially reported to be amorphous and named as the "glacial state". They argue that the locally preferred structure (glacial) and ideal crystal structures are expected to be slightly different. The glacial phase could provide the first experimental evidence of topological frustration in super-cooled liquid, and the investigation of polyamorphism of TPP would contribute to the understanding of the supercooled liquid state and the subsequent glass formation. However, the nature of the glacial state is a matter of debate and several different interpretations have now been proposed. Hedoux et al. [2] have performed Raman, X-ray diffraction and inelastic neutron scattering experiments, and argue that the glacial state is not amorphous but formed by nanocrystallized domains of the stable crystalline phase, mixed with a fraction of under-cooled liquid. The relative fractions of these components depend on the aging temperature. Raman spectra have shown that there exists a weak C-H...O hydrogen bond in glacial state at 222K~226K, which has been used to support the nanocrystalline-supercooled liquid mixture interpretation.

Methods and Materials

High-energy x-ray experiments were made on hydrogenated TPP sample (the H-TPP purity was greater than 99+%) that was sealed in a 4mm inner diameter silica tube and loaded into a helium cryostat. The experiments were performed using an incident beam energy of 115 keV and an angular range of $2\theta=0.3\text{-}20^{o}$, on the 11-ID-C BESSRC beamline at the Advanced Photon Source, Argonne National Laboratory, USA. Hydrogenated TPP samples for high-energy x-ray experiments were measured in the supercooled liquid, glassy, glacial and crystalline states. Typical uncertainties in the temperatures for this experimental set up were ~0.1K. The glass was measured at 190K and the crystal at 250K. The supercooled liquid was measured at 220K for 2 hours. The glacial state was formed by annealing the supercooled liquid, as the transformation is known to occur more slowly than by annealing the glass.

Results

Changes in the x-ray structure factor showed the glacial state was fully formed by annealing the supercooled liquid at 220K after 4 hours, since subsequent data collected for 6 hours observed no significant changes in the diffraction pattern.

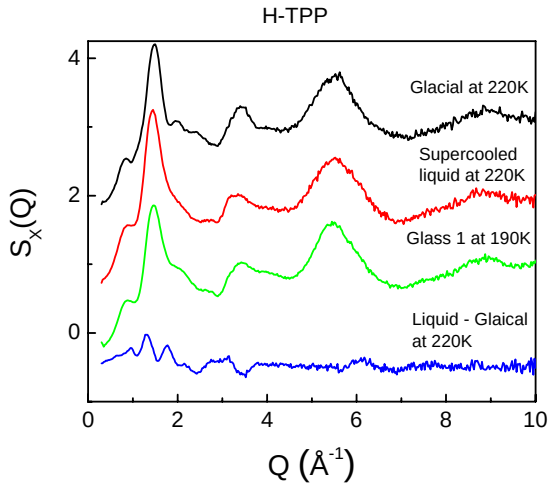

Fig.1. Measured structure factors of TPP in the supercooled liquid, glassy and glacial states.

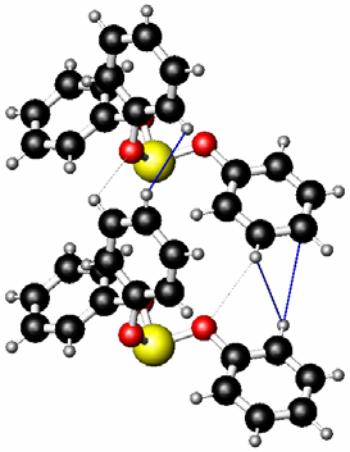

Fig.1. Two very weak hydrogen bonds form between molecules in the crystal at distances of ~3Å.

Discussion

The high energy x-ray diffraction data show a *decrease* in correlations at 3.12 Å which is attributed to changes in C-O/P intramolecular interactions between the glacial and

crystalline forms. Significant changes are also observed in the 4-5Å region which are attributed to C-C interactions between phenyl rings. These results suggest that changes in molecular conformation and nearest neighbour interactions are responsible for the existence of the glacial state.

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