Orientational Correlations in the Glacial State of Triphenyl Phosphite

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Spallation neutron and high-energy X-ray diffraction experiments have been performed to investigate the local structure of the glacial and supercooled liquid states in triphenyl phosphite. The observed diffraction patterns have been interpreted using a Reverse Monte Carlo modeling technique. The results show that the glacial state 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. The structure is very different from the hexagonal crystal which is characterized by two weaker hydrogen bonds between linear arrays of molecules which are offset from each other and packed in a hexamer arrangement.

The behavior of supercooled triphenyl phosphite (TPP) has been studied extensively during the past decade[1–17] due to the possible existence of polyamorphism. Kivelson and co-workers first discovered a low-temperature rigid state in the fragile glass former by annealing the low-temperature glass at 220 K and named it the "glacial state".[1] It was argued that the glacial state was an exotic defect ordered phase and structurally distinct from the normal glass, liquid, and crystalline states, and represented the first experimental evidence of topological frustration in a supercooled liquid. This thesis has been contested by Hedoux et al.[8–14] on the basis of Raman and scattering experiments, who suggest that the glacial state is due to nanocrystallized domains of the stable crystalline phase mixed with a fraction of supercooled liquid. Other explanations have suggested it may be a liquid crystal,[18] plastic crystal,[18] new amorphous form,[19] or highly correlated second liquid.[20] Viscosity measurements indicate that the glacial state is much more viscous than the supercooled liquid.[5] Recently, calorimetric and optical studies by Kurita and Tanaka[15] have indicated that the glacial state is the glassy state of a second liquid, and the authors have argued for the existence of a liquid–liquid phase transition, although they admit a molecular-level description of the transition is still missing.[2,15]

It has been pointed out that developing a realistic structural model for the glacial state of TPP is challenging task, since there are a large number of degrees of freedom for this molecule.[16] In this letter, we have analyzed new neutron and X-ray diffraction data on TPP using a Reverse Monte Carlo simulation technique[21] to produce such a model. The results suggest that stacked ||-, L-, and T-type configurations occur between the phenyl rings of different molecules in the supercooled liquid and glacial state. In the glacial state, phenyl rings aligned in an antiparallel geometry can form weak intermolecular hydrogen-bonded clusters (or chains) with an O–H distance of ~2.75 Å. Crystallization is hampered by the strict

molecular packing requirements needed to form two weaker hydrogen bonds at longer distances.

In this study, fully deuterated and hydrogenated TPP samples were synthesized using the methods described in our previous publication.[22] The purity of the sample determined by ^1H, ^{13}C, and ^{31}P NMR was 99.8+%. High-energy X-ray experiments were performed on $P(OC_6H_5)_3$ sample using an incident beam energy of 115 keV on the 11-ID-C BESSRC beamline at the Advanced Photon Source. TPP samples for high-energy X-ray experiments were measured in the supercooled liquid ($T = 220$ K), glacial (220 K), and crystalline (250 K) states. Complementary neutron diffraction experiments were performed on $P(OC_6D_5)_3$ samples (with 99+% D) using the glass, liquid, and amorphous diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. Details of data analysis procedures for the neutron and X-ray data have been given earlier.[22]

To model the nearest-neighbor phenyl ring interactions in the liquid and glacial forms, Reverse Monte Carlo (RMC)[21] simulations were performed simultaneously on the measured neutron and X-ray data.[23] The RMC technique fits a three-dimensional model to the average bulk structure, with the neutron/X-ray combination providing very different constraints on the model. The neutron spectra are most sensitive to hydrogen (deuterium)–carbon interactions and the X-ray spectra dominated by the carbon–carbon orientational correlations. For TPP in the hexagonal crystalline state, the unit cell has an unusually large platelet-like shape in which groups of six nearest-neighbor molecules align to form hexagonally packed antiparallel rods of ~17 Å in diameter.[7] The (hexagonal) TPP molecule itself does not exhibit the ideal C_3 propeller-shaped symmetry, but has one inverted phenyl ring[7] (e.g., see Figure 4). In addition, a new metastable monoclinic polymorph of triphenyl phosphite has recently been discovered by mixing TPP with an ionic liquid.[24] The monoclinic crystal shows a different molecular conformation to the hexagonal structure and forms rods in a double layer arrangement.
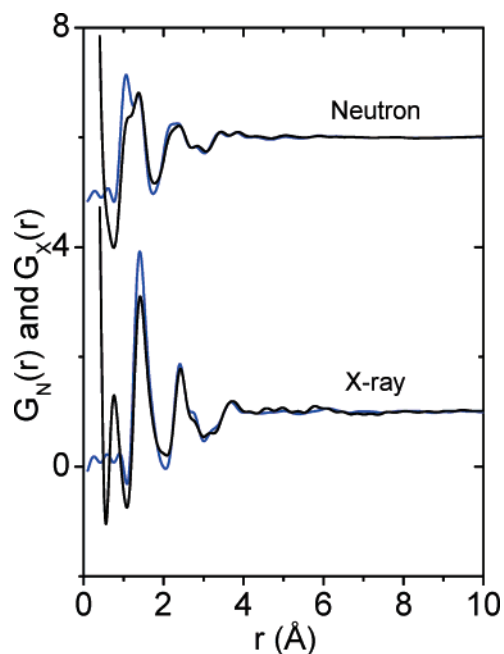
Figure 1. Top: Neutron radial distribution function for the deuterated TPP in the glacial state at 220 K (black line) together with the RMC fits to the data (blue line), displaced by +4. Bottom: X-ray radial distribution function for the fully hydrogenated TPP sample in the glacial state at 220 K (black line) together with the RMC fit to the data (blue line). Both data were Fourier transformed using a $Q_{max} = 20$ Å^{-1} and have a Lorch function applied.

Figure 2. The hydrogen−hydrogen partial pair distribution function $g_{HH}(r)$ for the monoclinic and hexagonal crystals[7,24] and glacial and supercooled liquid forms of TPP obtained from the RMC configurations.

To model changes in molecular conformation and short-range interactions in the RMC simulations, strict coordination constraints were used to keep the molecule in tact; however, it was necessary to allow each atom in the molecule to move independently during the simulation so increased positional disorder was allowed[25] leading to a slight distortion of the phenyl rings in the final fit.[26] The starting configuration for the simulations contained 27 randomly oriented molecules with hexagonal conformation in an oversized cubic box which was gradually reduced in size during the simulation (with the molecules moving) until a number density of $\rho = 0.094$ atoms/Å^{-3} was reached, which is identical to that of the hexagonal crystal.[7]

In practice, the reciprocal space data sets are limited by the measurement window function of the diffractometer, and a Lorch modification function $M(Q)$ is used to minimize Fourier transform artifacts in obtaining the radial distribution function $G(r)$,[27] where

$$G(r) = \frac{1}{2\rho\pi^2 r} \int_0^{Q_{max}} Q[S(Q) - 1]M(Q)\sin(Qr)\,dQ$$

Due to the limited size of the simulation box, the measured X-ray and neutron data for the glacial state are most appropriately compared to the RMC model in real space (see Figure 1). The fit to the supercooled water data was slightly better (not shown). We note that the largest disagreement between experiment and our model is in the first intramolecular peak in $G(r)$, but beyond 2 Å, the fit is much more reasonable. For the neutron case, the most likely explanation of the misfit of the first peak comes from the difficulty in removing the Plazeck (inelastic) contribution from the measured data.[28] For the X-ray case, the difference is likely to be due to the assumption of the independent atom approximation in the electronic form factor analysis.[29] Both these effects have a long
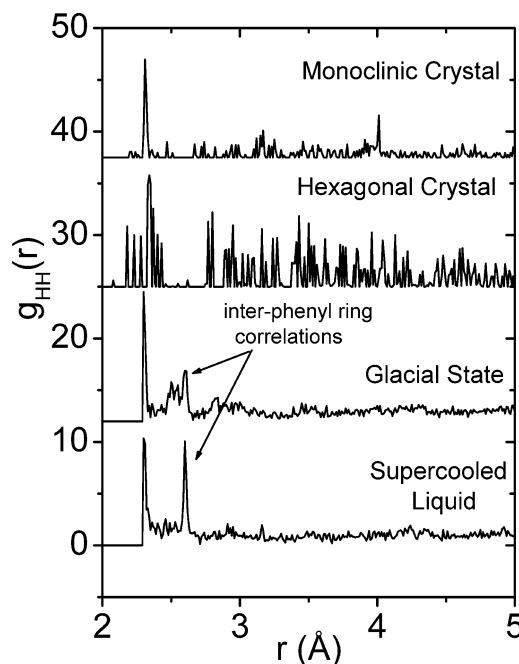
wavelength in Q-space and appear at the lowest r-values, decreasing rapidly with increasing r. In addition, it should be noted that the technique presented has some drawbacks, since the measured diffraction pattern cannot distinguish between phenyl ring interactions between the same or different molecules and RMC is known to give the most disordered structure consistent with the data. Despite these difficulties, the technique presented does provide us with an important insight into the phenyl ring interactions most consistent with the measured diffraction data.

The most dramatic changes between the different TPP forms occur in the hydrogen−hydrogen partial pair distribution function, $g_{HH}(r)$ shown in Figure 2, where a large inter-phenyl ring correlation peak appears at ∼2.6 Å in the supercooled liquid, which is not present in the hexagonal and monoclinic crystals, and arises from orientational correlations between nearest-neighbor phenyl rings. This peak decreases in intensity in the glacial state, and a broader peak appears at ∼2.5 Å as weak hydrogen bonding starts to take place,[13] slightly altering the alignment between phenyl rings. Information on the orientational correlations between phenyl rings can also be obtained from the C−C−C angle distribution shown in Figure 3. A sharp peak at 24° and the broad peak centered on 90° are due to nearest-neighbor ||, L- and T-type configurations. The RMC simulation shows adjacent phenyl rings in both intermolecular antiparallel and intramolecular parallel alignments. The rings in an antiparallel arrangement are able to form hydrogen bonds (see Figure 4), but it is not possible to comment if the parallel arrangement we observe is real or just an artifact of the simulation. We also note that the monoclinic crystal shows two intermolecular H···O contacts at a distance of 2.83 Å, between a phenyl ring orientated in a T configuration with an adjacent ring on the same molecule[24] (see Figure 4), which may also occur to a lesser extent in the glacial state.

From total neutron diffraction reactor measurements on fully deuterated TPP, it has been suggested that the glaciation process can be considered an aborted crystallization attempt,[8] but the reason for this is not clear. Raman spectra show two unusually
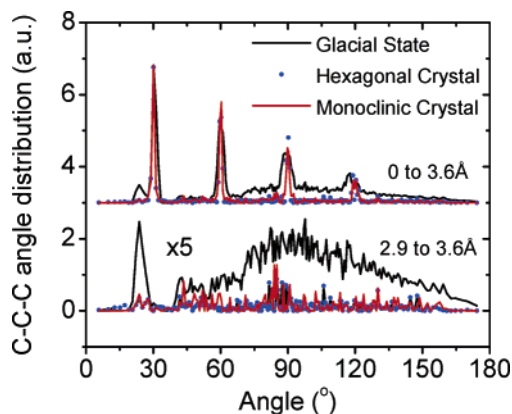
Letters

J. Phys. Chem. B, Vol. 110, No. 20, 2006 **9749**

Figure 3. Top: The carbon−carbon−carbon bond angle distributions for the monoclinic and hexagonal crystalline and glacial forms of TPP out to 3.6 Å calculated from the RMC configurations. The sharp peaks at 30°, 60°, 90°, and 120° originate from internal C−C−C angles within the phenyl ring. Bottom: carbon−carbon bond angle distributions in the glacial state between 2.9 and 3.6 Å arising from orientational correlations between different phenyl rings which do not occur in the hexagonal and monoclinic crystal. The noise in the crystal data sets arises from box edge effects in the RMC configuration.
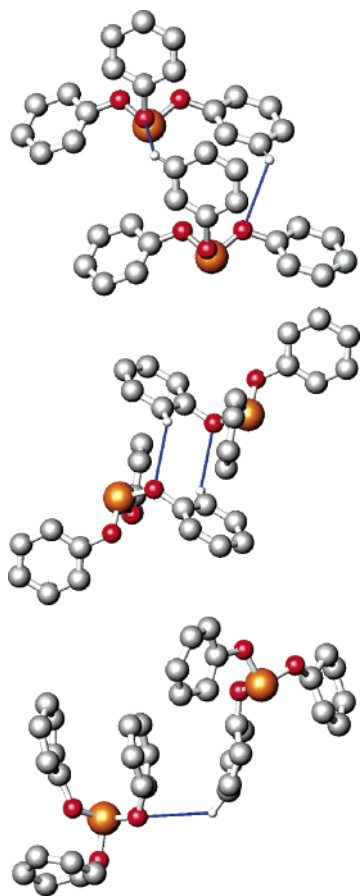

Figure 4. Intermolecular hydrogen contacts between TPP molecules in the hexagonal crystal (top), monoclinic crystal (middle), and glacial state (bottom). Only hydrogens possibly involved in intermolecular bonding are shown for clarity as small white spheres. The oxygen atoms are shown as red spheres. The thin blue line represents weak intermolecular hydrogen bonds.

weak hydrogen bonds existing in the hexagonal crystalline state (characterized by two different distances at 2.91 and 2.97 Å in the crystal structure), but no detectable vibrational bands exist for the C−H⋯O stretch in the spectra for the normal glassy or liquid states. Only one of these hydrogen bonds is present in

the glacial state,[13] which has been used to support the nano-crystalline/supercooled liquid mixture interpretation, since the data can be decomposed into supercooled liquid and crystal contributions. However, results of calometric and optical birefringence experiments[2,15] suggest that this may occur because the pure glacial form only exists when the supercooled liquid is annealed between $205 < T < 215.5$ K, and above this temperature range, microcrystallites become embedded in the amorphous glacial state. Total neutron diffraction studies also suggest that the glacial state is not a simple two-component mixture of the nanocrystalline and supercooled liquid phases, since significant structural rearrangements in the glacial state have to occur in the region around 3.0 Å (attributed to hydrogen correlations) before ordering at 4.5 Å can take place.[22] The RMC model is consistent with these observations where an OH peak at a distance of ∼2.75 Å distinguishes the glacial state from the broader distribution of OH correlations in the supercooled liquid. The result is in excellent agreement with powder synchrotron X-ray diffraction results, which give an intermolecular O⋯H distance of 2.74 Å even when the diffuse scattering part of the diffraction signal is neglected.[13]

Figure 4 shows typical intermolecular hydrogen interactions in the glacial state compared to the hexagonal and monoclinic crystals. In the hexagonal crystal, the neighboring molecules are offset in the same molecular conformation allowing the formation of two weak hydrogen bonds, the shorter one forming between the inverted phenyl rings. In the monoclinic crystal, the conformation alters slightly, and intermolecular T configurations are associated with the shortest hydrogen−oxygen contacts. In the glacial state, two neighboring molecules are able to form slightly stronger hydrogen bonds when their phenyl rings are in an approximately antiparallel alignment, which is the most likely cause of frustration in the crystallization process and the structural origin of the glacial state. In addition, although calorimetric and diffraction measurements indicate that both hydrogenated and deuterated TPP structures appear to have an identical behavior with temperature and aging conditions,[22] it was also found that the delicate formation of hydrogen bonds can be altered in hydrogen/deuterium mixtures where the glacial state occurs much more slowly and at significantly higher temperatures. This finding prevents the use of isotopic substitution in neutron diffraction as a possible tool for obtaining $g_{HH}(r)$. The further investigation of this isotope mixing effect in TPP is in progress in our laboratories.

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