Metastable Solid Phase at the Crystalline-Amorphous Border: The Glacial Phase of Triphenyl Phosphite

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The fragile glass-forming liquid triphenyl phosphite (TPP) melts at 298 K, has a glass transition at about 186 K, and can undergo a first order transition to a metastable, solid, apparently amorphous phase (denoted the glacial phase) at about 230 K. Though apparently amorphous (on the basis of preliminary X-ray data), we have shown that the glacial phase is well described as a plastic crystal composed of nanocrystallites; it is thus not a second liquid or glass nor a poor ordinary molecular crystal. This picture of the glacial phase with its close connection to the supercooled liquid from which it forms is placed in the context of the frustration-limited-domain theory of supercooled liquids, and the glacial phase is associated with the defect-ordered phase predicted by that theory. In examining the applicability of this picture, we carried out extensive experimental studies, many of them by means of NMR at both ambient and high pressures, on the glacial phase and on the dynamics of the transformations to and from this phase.

Motivation. Liquids, when supercooled below the melting points (T_m) of their corresponding crystalline phases, exhibit great increases in viscosity as the temperature (T) is decreased; the increase is most dramatic for so-called "fragile" liquids for which the effective relaxation activation free energy at temperatures below a crossover T^* increases markedly with decreasing temperature (denoted "superArrhenius" behavior).[1,2] If the liquid can be cooled sufficiently without undergoing a phase transition, below a glass temperature (T_g) its viscosity becomes too great to measure, and the system is no longer a liquid but a glass. The glass is the same phase as the liquid, but below a transition temperature which lies below T^* the supercooled liquid can form metastable phases, a well-studied example being ethanol.[3,4] These metastable phases may be crystals, liquid crystals, plastic crystals, rotational glasses, or even amorphous materials.[5,6] In the system we study, triphenyl phosphite or TPP, the transition to the metastable solid phase (for TPP denoted alternatively as the glacial or L_C phase) occurs above T_g and below T^*; one can keep the system as liquid down to $T = T_g$, or one can cause it to undergo a transition to the glacial or crystal phases.[7] The system is unusual because the glacial phase appears to be crystalline (powder) phase but with such small crystallites or grains that its X-ray diffraction pattern is reasonably similar to that of the glass and liquid, phases from which it is distinct.[7] It is this "apparently amorphous" property that we study, but furthermore, we have reason to believe that the glacial phase may be an example of a defect-ordered phase predicted by a current theory of fragile supercooled liquids, the theory of frustration-limited domains.[8]

Glacial Phase of Triphenyl Phosphite. TPP is usually liquid at room temperature, but it can be crystallized as a normal or molecular crystal which melts at $T_m \approx 298$ K. With care, and not too much delay (at a cooling rate of about 5 K per min), the liquid can be supercooled and studied as such down to $T_g \approx 190$ K. Below about 230 K, it is possible to transform the supercooled liquid to the solid glacial phase.[7,9,10] It is on this somewhat unusual phase of TPP that we focus, and in our effort to characterize it, we report a number of new experimental results including density determinations, NMR phase studies, NMR high-pressure measurements, kinetic studies by nmr, and X-ray diffraction studies. To interpret the data to the fullest, we also include a summary and utilize the results of other studies.

The solid, "apparently" amorphous glacial phase (which can exist at temperatures up to about 230 K) is distinct from the liquid, and also distinct from the glass (which turns liquid at about 190 K). The glacial-liquid transformation is a first-order transition, the glacial phase being the stabler one below about $T_{int} \approx 230$ K. Although not all agree,[11,12] we explain below that the glacial phase is also distinct from the stable normal molecular crystal.

Our focus is primarily on the structure and thermodynamics of the glacial phase, but studies of metastable phases are unavoidably perturbed by dynamical considerations. This has not, we believe, been properly considered in previous studies. The presence of competitive kinetic effects can lead to distressing, sporadic outbreaks of irreproducibility. One source of difficulty is the often unexpected and unwanted transformation

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to the molecular crystal, unwanted since its presence destroys all hope of studying the metastable supercooled liquid, glass and glacial phase. Other sources of irreproducibility are the apparent history dependence of the properties of the metastable glacial phase, and the role of impurities; by affecting the relative rates of competing processes, these effects can affect the observed metastable equilibrium properties. We have, as discussed below, made an effort to understand and overcome these difficulties, and believe that our results, combined with those of others, enable one to produce a coherent and consistent picture of the glacial phase.

Background. Extensive dynamic light scattering studies have been carried out on the viscoelastic properties of liquid and supercooled liquid TPP.[13-17] The initial observations and characterizations of the glacial phase of TPP were carried out in our laboratory.[7,9,10] These studies included opacity (turbidity), viscosity, calorimetric, ^{31}P nmr, and X-ray diffraction studies. There followed careful adiabatic calorimetry measurements;[18] calorimetric and dielectric studies;[19] a wide range of ^{31}P nmr, dynamic light scattering, dielectric relaxation, and calorimetric studies;[20,21] Raman and X-ray studies;[11,12] dielectric, X-ray diffraction and adiabatic calorimetric measurements;[22] and neutron scattering studies.[23] Earlier, before identification of and focus on the glacial phase, ^{31}P NMR studies were carried out on low-T TPP.[24] To all these we add our present studies.

Identification of Phases. In previous studies the inherent distinctions between the glacial phase of TPP and the liquid/glass and normal molecular crystalline phase were established in several ways. The X-ray diffraction pattern of the molecular crystalline phase is distinct from that of the glacial phase, but the scattering patterns of the glacial and liquid/glass phases are quite similar.[7] The viscosity of the liquid is finite, but that of both the glass and the glacial phase are immeasurably large.[7,9] The ^{31}P NMR relaxation time (T_1) is different for the glass, the glacial phase, and the molecular crystal (all measured at the same temperature below T_g).[7,20] Furthermore, the molecular crystal is almost always distinctly "white," presumably due to cracks, whereas the glacial phase looks much more glasslike, i.e., homogeneous and translucent, although it, too, can be slightly cracked. Others have differentiated between the phases by means of calorimetric measurements,[18-20,22] by Brillouin scattering,[22] by dielectric relaxation,[21,22] and by other NMR studies.[20,21] However, some have proposed that the glacial phase is the normal molecular crystal,[12] and others that it is a second liquid;[21] below we present reasons why we do not believe these last two models to be correct.

Formation of Glacial and Crystal Phases. Although the results outlined here are not directly relevant to our discussion, as explained above understanding of the history of sample preparation is important and has been overlooked in the study of metastable phases. The supercooled liquid and the glass can be formed by quick cooling (at a rate of about 5 K per min), thereby by-passing the first-order transitions to both molecular crystal and glacial phase. The glacial phase of TPP is distinguishable from the glass because it is a solid that can be formed at temperatures many degrees above T_g (faster at higher temperature); during the transformation the opacity first increases and then decreases, a phenomenon consistent with nucleation associated with a first-order transition.[7,9] See Figure 1. In contrast, the conversion of liquid to glass upon cooling through T_g is a characteristic continuous change accompanied by almost no change in opacity. Upon slow heating (less than 5 K per min) from below T_g, the glass first turns to liquid, then to glacial phase, then to molecular crystal (with possibly some
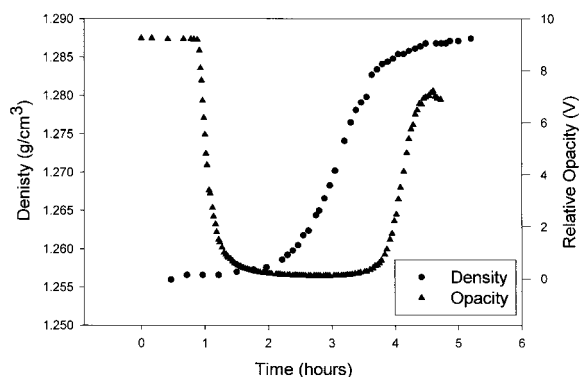

Figure 1. Density and opacity of TPP as a function of time during formation of the glacial phase from liquid at 218 K.
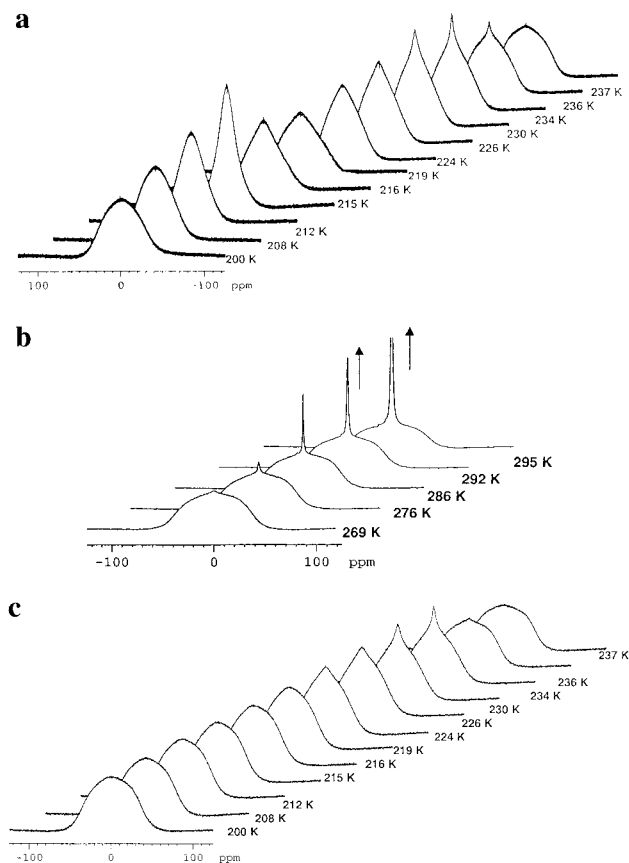

Figure 2. ^{1}H NMR spectra with changing temperature at a heating rate of 0.3 K per min. The very small side-peak observed above 276 K is, according to the manufacturer (Bruker) due to material in the probe and not due to impurity in the sample. (a) glass → liquid → glacial → crystal, (b) crystal, and (c) glacial → crystal.

degree of melting first);[7,18] upon rapid heating from below T_g the glass can be converted to liquid and maintained as liquid to temperatures all the way above melting, T_m.

An alternative way of forming glacial phase or crystal is by cooling the liquid rather rapidly to a given temperature below about 220 K and keeping the system at that T for a prolonged period of time. If that T is below 216 K, a glacial phase forms slowly, the rate of formation being longer the lower the temperature; the transformation appears to be first order and to occur via a nucleation process. See Figure 2.[7,9,10] If the system is held at a T above 230 K, a molecular crystal rather than a glacial phase forms through what is clearly a slow nucleation process; one can see small "balls of crystal" develop and grow, the number of balls being greater and their ultimate sizes being

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smaller the lower the *T*. Although the crystalline sample, structured into balls at first looks quite translucent, upon heating (regardless of the temperature at which it was formed) it turns powdery white, presumably because of thermal expansion leading to cracking on the surfaces of the balls. If the temperature at which the system is held is in the range 230 to 216 K, the system appears to form a mixture of crystal and glacial phase; this is relevant to the question of whether the glacial phase is distinct from the molecular crystal.[11,12]

We interpret the first-order liquid-to-glacial transformation as a nucleation process in which the rate of formation of critical clusters of glacial phase is appreciable below 225 K and increases with decreasing *T*; on the other hand, the rate of glacial growth decreases as *T* is lowered. The liquid-to-molecular crystal transition is a similar nucleation process, which is more efficient than the liquid-to-glacial transition at temperatures above 230 K, less efficient below 216 K, and comparably efficient in the intermediate range. Furthermore, the presence of glacial nuclei catalyzes the liquid-to-molecular-crystal transition, which explains why quick-quenched glass (in which few glacial or molecular crystal nuclei have had a chance to form) can be rapidly heated above $T_m \approx 298$ K without formation of either glacial or molecular crystalline phase. On the other hand, slowly heated glass always converts to glacial phase (which undergoes a solid-to-solid transition to the crystal only very slowly); above 220 K the glacial phase premelts, and in the presence of the glacial phase the liquid can convert readily to crystal.

Impurities. All studies to date, including ours, of the TPP glacial phase have assumed that the TPP is a 1-component system. The kinetics are certainly dependent upon walls and impurities, and this could lead to corresponding dependences for the metastable products; in fact, we believe that some of the differences reported by different groups may be attributable to such effects. We have purified the TPP by distillation to the extent that we could not detect impurities either by mass spectrometry or by nmr. Alternatively, since one never knows how pure the system must be to be describable as a 1-component system, we have studied TPP doped with small amounts of phosphoric acid; doping studies were also carried out by Dvinskikh et al.[21] Although our studies were neither systematic nor exhaustive, they are the most complete experiments of their kind on TPP, and they suggest that the results we report are robust to small impurity levels.

Density. The determination of the densities of crystals by means of X-ray diffraction studies and of liquids by the use of a pycnometer is straightforward, but the determination of densities of glassy or poor crystalline materials is a challenge. The difficulty arises, on one hand, from the fact that the X-ray diffraction pattern is rather unrevealing and, on the other hand, from the fact that the volume occupied by the sample is a consequence not only of its crystalline structure but of the mesoscopic and macroscopic cracks as well. All we wish to do here is to distinguish the density of the glacial phase from that of the liquid/glass and the crystal. We have developed a method that is not ideal, but appears to be sufficiently reliable to accomplish our objectives. TPP was placed in a 25 mL specific gravity bottle which was weighed and to which was attached a tube with 0.01 mL graduations. The system was cooled to the desired temperature after which sufficient precooled ethanol was added to bring the liquid up into the graduated tube.

As the glacial phase formed, the density changed, as indicated in Figure 1. The TPP was then crystallized (molecular crystal) by being heated to 283 K, after which the temperature was lowered to 218 K and the volume of the ethanol-TPP system

measured; the resulting density of the crystal at 218 K could thus be measured. Regardless of the uncertainty in the absolute densities, the fact that the densities of all three phases were measured with the same sample and in the same way gives confidence in the relative values obtained and in the qualitative features of the curve in Figure 1.

Quantitative results were obtained by utilizing the density, $\rho(\text{liq},T)$, of liquid TPP, both as reported[25] and as measured by us: $\rho(\text{liq, 218 K}) = 1.256$ g.cm^{-3} and $\rho(\text{liq, 295 K}) = 1.152$ g.cm^{-3}. This leads to $\rho(\text{glac, 218 K}) = 1.288$ g cm^{-3} for the glacial phase and $\rho(\text{xtal, 218 K}) = 1.293$ g cm^{-3} for the molecular crystal. The density measurements were repeated several times with a standard deviation of 0.0007 g cm^{-3}. The Archimedes method was used to determine $\rho(\text{xtal, 298 K}) = 1.26$ g cm^{-3} just below the melting point.

The method above is based upon the assumption that the ethanol evens out the spatial irregularities (and possibly fills the cracks) in the glacial and crystal phases, and that the ethanol remains separate from all three phases of TPP. This separation could be maintained at 218 K both because of low solubility and high viscosity. Slices of TPP glacial phase formed in the presence of ethanol were taken, heated above the TPP melting temperature, and checked for ethanol by means of ^{1}H NMR; no ethanol was detected.

Our present results indicate that the crystal is denser than the glacial phase; this contradicts our previous report which was not based upon a direct measurement.[7] The NMR line widths are also consistent with these results, the line width of the crystal being greater than that of the glacial phase. The data in Figure 1 are consistent with first-order crystallization via a nucleation processes. It has been noted that the change of viscosity does not parallel the change of opacity,[7] nor, as we have shown, can the change of viscosity parallel the change of density.

NMR as a Tool. Our current NMR investigations follow along the lines developed by Dosseh et al.,[26,27] in their studies of defects in organic crystals. It was found that a small fraction of the molecules, presumably those at grain boundaries, are much more mobile than those within crystallites, and that these mobile molecules give rise to sharp, liquidlike, Lorentzian ^{1}H NMR lines, whereas the majority of molecules which are presumably located within the crystallites give rise to broad, solidlike, Gaussian ^{1}H NMR lines. The fraction of molecules at the grain boundaries could then be estimated from the ratio of the integrated intensity of the sharp Lorentzian line to that of the broad Gaussian line.

Simple considerations, supported by AM1 structural calculations, suggest that the TPP molecule is a near-symmetric-top with the P atom on the symmetry axis. Our only current interest in ^{31}P NMR arises from the fact that Huang et al. reported a narrow Lorentzian component (characteristic of a liquid well above the glass transition) at *T*'s as low as 156 K, i.e., well below the glass transition.[24] We checked, and no such liquidlike component exists below 210 K in the glass, molecular crystal, or glacial phase.

Because in TPP there are many inequivalent protons that lie off the symmetry axis, the proton NMR spectra should be sensitive to both spinning and tumbling motion. In addition, the ^{1}H NMR spectrum, especially that for solids, is sensitive to intermolecular magnetic interactions. One expects and finds the ^{1}H NMR spectrum for amorphous or powdered (crystalline) solid TPP or for very viscous liquid (slowly tumbling molecules) to be a broad Gaussian (inhomogeneous broadening) with little *T* dependence; such spectra yield structural, not motional information. When the spinning (but not the tumbling) motions

become sufficiently rapid, the NMR spectrum should be motionally narrowed, but only partially so; the broad Gaussian line characteristic of the solid should then be slightly narrowed but remains Gaussian (still inhomogeneously broadened and characteristic of structure). When the tumbling motion becomes sufficiently fast, motional narrowing leads to a sharp Lorentzian line (homogeneous broadening) located at the center of the broad Gaussian line observed in the solid; this sharp Lorentzian line, which becomes markedly narrower as T is increased, signals the presence of liquid and yields information about motion, not structure, see Figure 2. By means of 2D ^{31}P NMR Dvinskikh et al.,[21] determined that in both the liquid and glacial phases of TPP the rotational motion was isotropic, i.e., the spinning and tumbling rates are comparable.

NMR Studies of Phase Transitions. Our NMR spectra are depicted in Figure 2, parts a, b, and c. The spectra were taken on a Bruker ARX- 500 with a VT-2000 temperature controller. The TPP was quick-quenched (at 10 K per min) down to 200 K, and then heated at 0.3 K per min. Below 210 K, the spectrum (of the glass in Figure 2a) is quite Gaussian and broad, which we take to mean that the molecules are held quite rigidly. Above 210 K, the Gaussian line begins to narrow and turn Lorentzian, i.e., the glass turns into liquid with an NMR $T_g \approx 210$ K. (The time scale for T_g determined via viscosity and dielectric measurements is 10^3 s, whereas that determined by our proton NMR studies is about 5×10^{-6} s. (Operationally, T_g is taken more or less equivalently (and arbitrarily) as the temperature at which the viscosity reaches 10^{13} Poise, the rotational relaxation time reaches 10^3 s, and the heat capacity versus T curve exhibits a sharp drop at a cooling rate of 10K per min.) The NMR-T_g is set by the fact that in our NMR experiments relaxation times are determined by motional narrowing which cannot be detected for relaxation times longer than the reciprocal of the Gaussian line width associated with the rigid structure.) As T is increased further the spectral line becomes fully Lorentzian and narrows; this behavior is characteristic of a liquid. The temperatures at the sample location were calibrated against the known chemical shifts in a methanol sample.

At about 216 K, the NMR line once again becomes broad and Gaussian, this time the shape being indicative of the glacial phase (a fact established by consideration of the history and future of the sample). As T is increased still further, the NMR spectra give evidence of coexistence of two phases, i.e., the spectra can be well-represented by a sharp Lorentzian superimposed upon the broad solidlike spectral line. The spectra were fit to a summation of a Lorentzian and a Gaussian. Such analyses require 4 adjustable parameters, which can be taken as the half-widths and the integrated intensities of the Lorentzian and Gaussian lines. The ratio of the integrated intensity of the sharp Lorentzian line to that of the broad solidlike line is taken as the ratio of the number of molecules tumbling to the number rigidly held.

Upon further heating, the small Lorentzian line develops and narrows; the Lorentzian peak-height increases in part because the line narrows and in part because of an increase in its integrated intensity. At a heating rate of 0.3 K per min, the integrated intensity of the Lorentzian peak reaches a maximum at about 230 K and disappears at about 237 K, and the spectrum again consists of a broad Gaussian which is here indicative of crystal formation. As the crystal is heated, a sharp small central Lorentzian peak develops, and it narrows while its integrated intensity increases. See Figure 2b. At 298 K, the crystal melts and the spectrum then consists of a very sharp Lorentzian line; just below 298 K the NMR spectrum is dominated by the liquid

Lorentzian line which at first sight suggests that most of the crystal has already melted, but this is an illusion due to the fact that the Lorentzian line, though weak in the sense that its integrated intensity is much less than that of the broad Gaussian associated with the crystal, is very narrow. Figure 2c represents a different thermal treatment: the glacial phase is formed by heating liquid to 218K, cooled to 200K, and then heated slowly with the results shown.

We interpret the NMR spectra in Figure 2 as follows: The liquid converts to glacial phase at about 216 K; this is not a thermodynamic transition, and it must lie below the liquid-glacial thermodynamic transition temperature. The sharp Lorentzian component that develops as the glacial phase is heated is associated with mobile (tumbling) molecules; as T is increased, these molecules become more liquidlike (tumbling more rapidly), and the number of such free-tumbling molecules increases. *This indicates that there are two classes of molecules in the glacial phase, those that are rigidly held and those that are freely tumbling; this phenomenon is strongly indicative of an ordered structure with some molecules within a grain or crystallite and a small number at the boundaries.* This behavior is not expected for amorphous materials and is not found at the glass transition where all molecules change in the same way as T is increased. This makes characterization of the glacial phase as a second liquid/glass phase problematic. The fact that the number of liquidlike molecules increases with increasing T can be interpreted as a form of "premelting," the premelting occurring at the grain or crystallite boundaries and/or taking place because of the decomposition of the smallest (presumably least stable) crystallites.

The premelting of the glacial phase cannot be completed because it inevitably turns to molecular (normal) crystal at about 230 K after only a small fraction of the material has premelted. This is to be contrasted with the behavior of liquid TPP that has been quick-quenched to 230 K and allowed to stand; the latter remains liquid for quite some time, turning only slowly to crystal.

By examining the liquid at various temperatures while cooling (rather than heating) one can study the properties of the supercooled liquid over the temperature range from normal melting temperature T_m down to T_g, the temperature range over which our studies of the glacial and molecular crystal phases were carried out. Some of the results are illustrated in Figure 3. The Lorentzians observed in the glacial and molecular crystalline phases are somewhat broader than those observed in the liquid phase. This is consistent with the view that although the free-tumbling molecules at the crystallite boundaries are liquidlike, they tumble less freely than do liquid molecules at the same temperatures. The actual temperature range over which quantitative information concerning molecular relaxation in the liquid can be obtained by this method is limited to the approximate range 218 to 245 K. See Figure 3a. At the low temperature end, it is the fact that the motions are so slow that other relaxation processes dominate, and at the high end it is the fact that the single liquid-line is actually an unresolved triplet that limits (or at least complicates) the study; because of this latter effect the three high-T points for the liquid in Figure 3a are not directly indicative of molecular relaxation rates.

The Gaussian lines characteristic of the glacial phase are somewhat narrower than those associated with the molecular crystalline phase, which is compatible with the fact that the molecular crystal is denser than the glacial phase. This difference of line width is too small to provide a useful tool for distinguishing between these two phases. But what is of
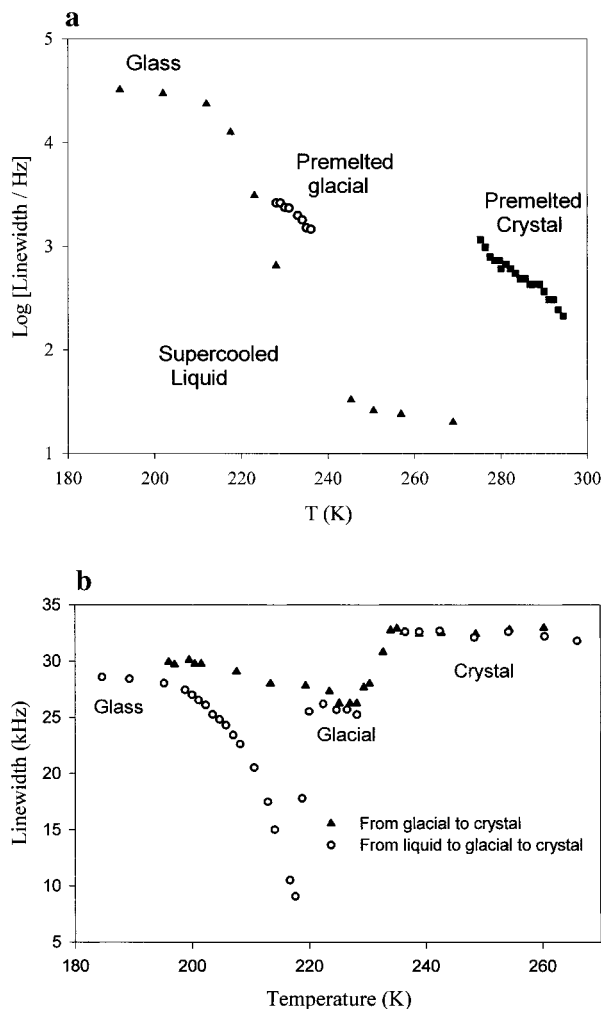
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Figure 3. ^{1}H NMR line widths as a function of *T* for different phases of TPP at a heating rate of 0.3 K per min. (a) liquidlike lines, (b) broad lines.

Figure 4. Heat capacity versus *T* for TPP. Taken from the adiabatic calorimetric data of van Miltenburg and Blok, 1996. Note the transition temperature, T_{int}. Note also the T_g determined from viscosity studies (Zhao,1995) and the T_{gcal} determined calorimetrically (von Mithenburg, 1996).

importance here is the implication on the molecular level that the glacial phase and the molecular crystal are distinct phases; this is in contradiction to the conclusions of Hedoux et.al.[12]

We have examined both the glacial phase and the molecular crystal by studying the ^{1}H spin−lattice relaxation following an induced spin flip. For the molecular crystal the sharp, liquidlike, Lorentzian component relaxes more rapidly than does the broad, solidlike, Gaussian component; for the glacial phase, the reverse seems to be true but the relaxation times for the solid and liquidlike components are very close. See Figure 5. That the sharp and broad spectral components have slightly different spin−lattice relaxation times is further evidence that they are associated with distinct groups of rather freely tumbling and rather rigidly held molecules, which in turn suggests that there exists a nano-crystalline glacial structure with rather uncon-strained molecules between crystallites.

Comparison of NMR and Adiabatic Calorimetry Data. Our picture of premelting is consistent with the adiabatic calorimetric data.[18,22] See Figure 4, which is a plot of some of the data of van Miltenburg and Blok.[18] In particular, the adiabatic calorimetry studies of the glacial phase indicate a premelting or softening transition starting at about 210 K, a transition that is aborted sharply by the intervention of crystal-lization at 230 K. The Δ*H* for the glacial to liquid transition has been obtained by van Miltenburg and Blok, and if it is indeed premelting that takes place between 210 K and 230 K,
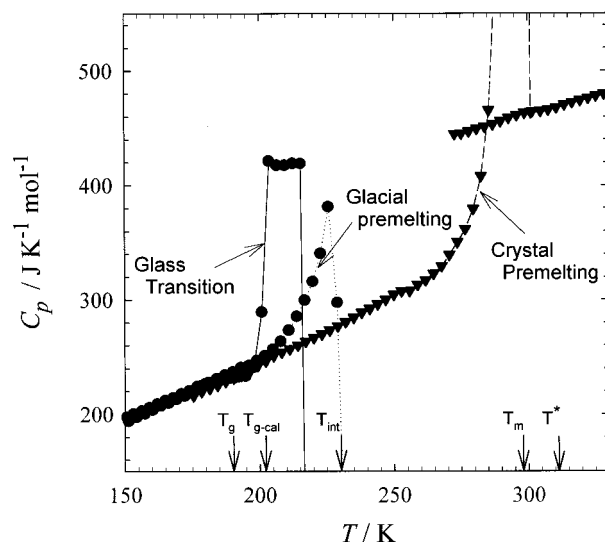
then we estimate that about 10% of the Δ*H* of transition has been absorbed before the occurrence of complete crystallization. Qualitatively, this is in accord with the observation of premelting by NMR, although there are some quantitative discrepancies. (see Figure 5)

Although the calorimetric data on the glacial phase could be interpreted as either premelting or as softening between 210 and 230 K (i.e., as a dynamic transition such as a glass transition), *the NMR data point to premelting and not to softening*. The premelting signature, i.e., an increase in the number of liquidlike molecules over a range of temperatures, can be understood by recognizing that *small crystallites are likely to be less stable than big ones, that a polydisperse collection of small crystallites will have a range of stabilities, and that, consequently, the melting of the crystallites will take place over a range of melting temperatures, the smaller crystallites melting at lower temperatures*. This is in contrast to a glass-to-liquid transition, which is not characterized by the presence of two species (tumbling and rigid), but by an increase in mobility of all molecules.

NMR Rate Studies. The properties of the glacial phase, as conveniently reflected in the NMR spectra, are dependent upon the rate of heating. For samples quenched to 200 K and then heated at a constant rate, it was found that at a given temperature the number of freely tumbling molecules in the glacial phase increased with increasing heating rate and that the temperature at which the slightly premelted glacial phase turned to molecular crystal also increased. See Figure 6.

We have interpreted the data in Figure 6 by assuming that the rate of glacial-phase melting is fast while the rate of transformation of the slightly premelted glacial phase to molecular crystal is slow, becoming faster at higher *T*. The assumption of fast melting and slow crystallization is physically reasonable. The fact that the temperature at which the glacial phase converts to molecular crystal increases with increasing sweep rate is compatible with the assumption of slow crystal-lization which speeds up at higher *T*. The crystallization temperature obtained by adiabatic calorimetry is 230 K, which is lower than that obtained by our temperature sweeps in NMR experiments and consistent with the fact that adiabatic calo-rimetry corresponds to extremely slow heating rates.
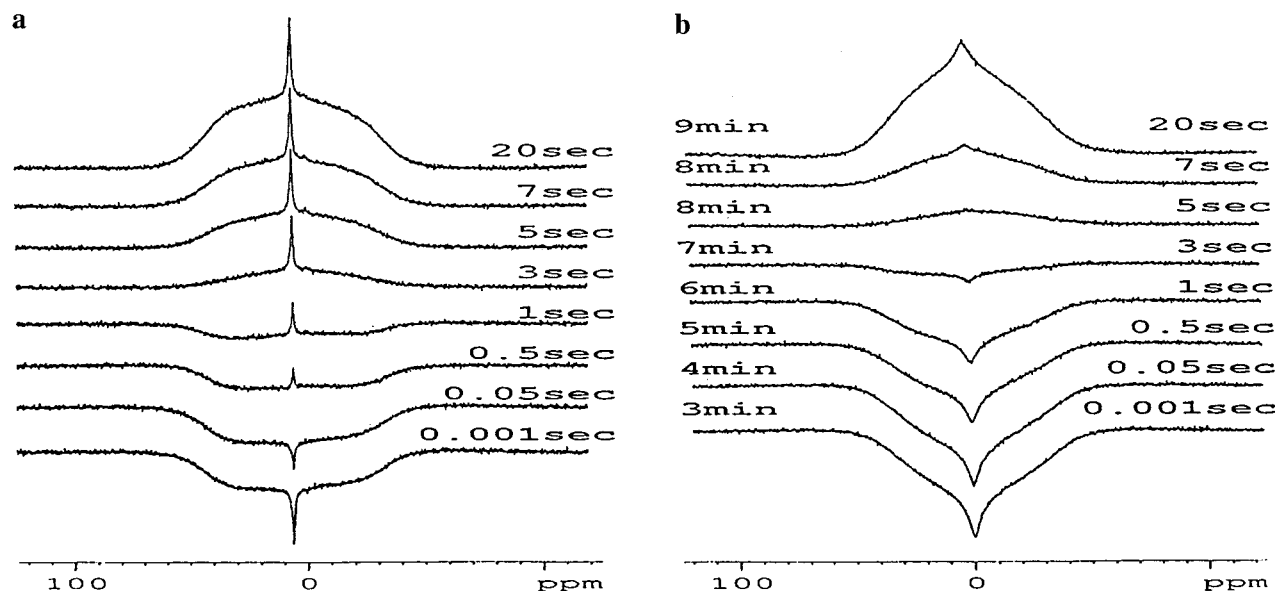
a

b

Figure 5. [1]H spin−lattice relaxations: Inverse recovery method (500 MHz). 180° pulse after time τ_{180}, followed by 90° pulse at time τ_{90} later; τ_{180} on left, τ_{90} on right. (a) molecular crystal. (b) glacial phase: τ_{180} measured after reaching 226 K after 2 min heating from 221 K.
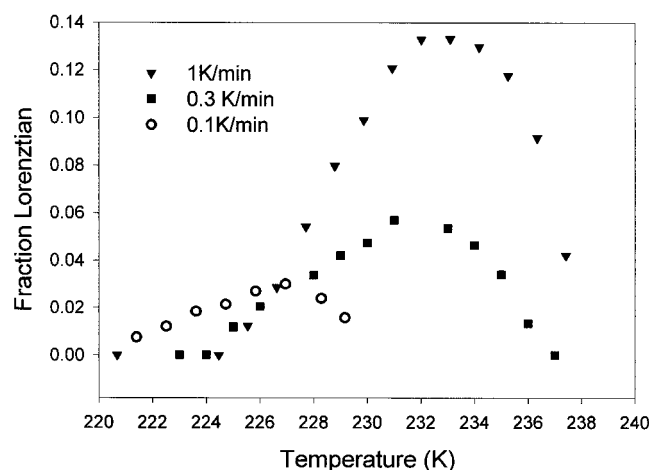

Figure 6. Fraction of freely tumbling TPP molecules as a function of *T* at different heating rates.

We have also studied the premelting of the glacial phase by a series of NMR scans where instead of heating the sample at constant temperature we raised the temperature by 1 K jumps and then allowed the system to remain for about 15 min at each temperature. The results are exhibited in Figure 7. In this figure the relative integrated intensity of the sharp liquid-line (which is presumably proportional to the number of liquid molecules) is plotted as a function of time at each temperature. Premelting of the glacial phase at each temperature seems to take about 1 min (most likely the time for thermal and melting equilibration), and thereafter, the liquid at each temperature decreases slowly, presumably due to some form of crystallization. The crystallization process is very slow at low temperature but increases as the temperature is increased. We have confirmed that if the system is kept at each temperature for times of about 40 min, the apparent amount of liquid present decays completely. We attribute the disappearance of the liquid (melted glacial phase) to "crystallization," but the crystallization could be to the molecular crystal, as reported by Hedoux et al.,[12] or back to the glacial phase, which is compatible with the observations of Alba-Simionesco and Tarjus.[23] In view of the analysis presented here, we believe that it is the smaller, less stable crystallites of

glacial phase that premelt and then recrystallize as either molecular crystal or glacial phase, and that the larger glacial crystallites remain metastable.

The adiabatic calorimetric data of van Miltenburg and Blok given in Figure 4, in contrast to the NMR data, suggest that some of the liquid formed from premelted glacial phase remains metastable. This apparent discrepancy is a consequence, we believe, of the applicable time scales: the adiabatic calorimetric data were taken with a residence time of about 20 min at each temperature which is roughly the time over which the decay of liquid as measured by means of NMR is reported in Figure 7. This suggests that the adiabatic calorimetric data should be compared with the locus of 15 min decay points in Figure 7. Presumably, adiabatic calorimetric measurements with much longer residence times at each temperature would result in a glacial heat-capacity-versus-temperature curve with less upward curvature than that in Figure 7, perhaps even one with downward curvature. However, the locus of 15 min decay points in Figure 7 suggest less than 1.5% liquid present, whereas the calorimetric data suggest a rise of nearly 10%. In addressing this apparent discrepancy, one should note that NMR measures the number of freely tumbling molecules, whereas calorimetric studies measure the amount of energy absorbed, some of which might not be simply associated with complete release of rigidly held molecules.

Nmr Studies at High Pressures. To construct the phase diagram of TPP, we examined the ^{1}H NMR spectrum of supercooled TPP under pressures ranging up to 6 kbar. We made use of a standard Be−Cu clamp cell, with TPP taking the place of the pressure medium inside a Teflon cup. In preparation for the measurements, a coil was wound and then attached to a 50 ohm plug inserted inside the cup before assembly. The pressure decreased approximately 1 kbar upon cooling in the gas-flow cryostat from ambient temperature to 200 K. Measurements were carried out at 35 MHz and data were collected with a home-built spectrometer.

Our results are shown in Figure 8. We could not raise the temperature much above 300 K and so we could not directly determine the pressure dependence of the melting point, $T_m(p)$; however, since ΔH_m and ΔV_m at the melting point are known, $T_m(p)$ could be estimated with the aid of the Clapeyron equation.

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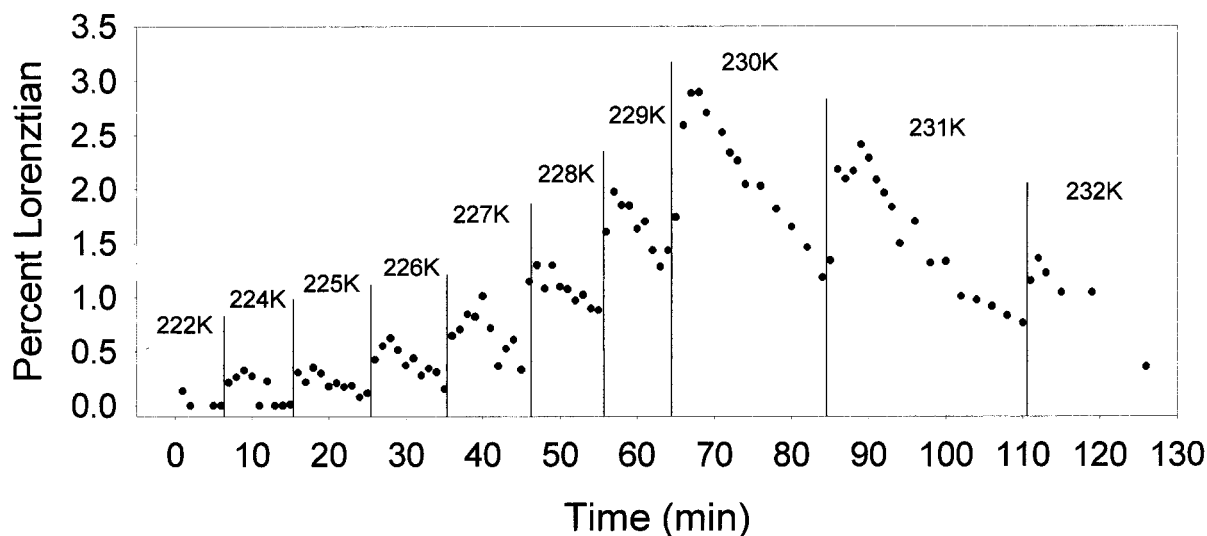*J. Phys. Chem. B, Vol. 105, No. 11, 2001* **2113**

Figure 7. Integrated intensity of liquidlike ^{1}H NMR line as a function of time at a succession of temperatures.
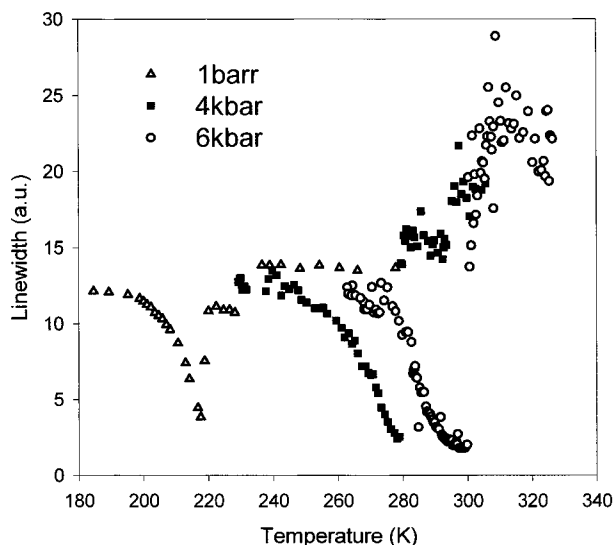

Figure 8. ^{1}H NMR line widths as a function of temperature at various high pressures. The low-T plateaus represent "glass;" the temperatures at which the plateaus start to decrease specify the NMR T_g's; the lowest temperatures at which the line widths first rise rapidly indicate the liquid-to-glacial kinetic transitions; the medium-T plateaus represent glacial phase; the second lowest set of temperatures at which the line widths increase rapidly represents the glacial-to-molecular crystal transitions (presumably via the glacial-to-liquid-to-molecular crystal route); and the high-T plateaus represent the molecular crystal.

See solid line in Figure 9. The NMR $T_g(p)$ measured as a function of pressure are given in Figure 9. One can estimate the pressure dependence of the "true" $T_g(p)$ by assuming that it lies at a more or less constant 25 K below the NMR T_g, the temperature difference at 1 atm. See Figure 9.

We were also able to measure the temperature at which the glacial phase turned to molecular crystal under high pressure, but we were not able to detect reliably the glacial-liquid melting line indicative of a thermodynamic transition from one meta-stable phase to another. Our experiments were carried out at a heating rate of 0.1 K per min. At 1 atm, the premelting of glacial phase to liquid is observed, both by NMR and by calorimetry, but full melting (which is spread over a small range of temperatures) never takes place because of the intervening crystallization. However, it seems reasonable to expect the
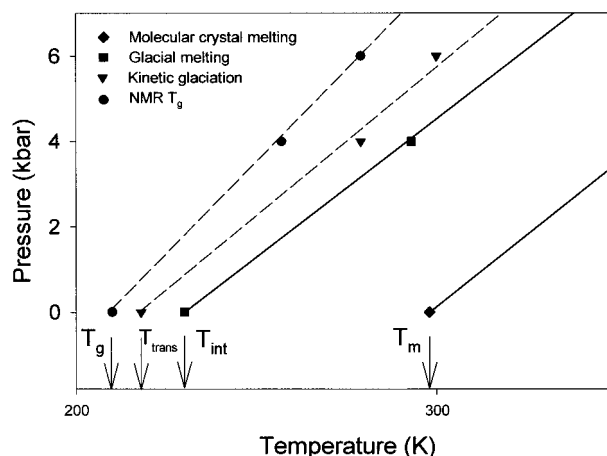

Figure 9. Phase diagram for TPP.

thermodynamic glacial melting point to be about 1 K above the crystallization temperature obtained at the slow heating rate of 0.1 K per min that was used. See Figure 9.

The glacial melting curve can also be estimated by means of the Clapeyron equation with the ΔH of glacial melting given by van Miltenburg and Blok,[18] and with the ΔV obtained by us. The glacial melting curve so determined is also given in Figure 9.

In looking at the phase diagram in Figure 9, one might ask whether the glass-to-glacial transition could be observed even in the solid state at temperatures below $T_g(p)$, especially if one were to take the system to low T and large pressures far from the coexistence line, $T_{int}(p)$? We have taken the glass at 1 atm down to 130 K, kept it there for an hour, and then brought it up above 210 K to check by NMR whether the glass had converted to glacial phase; in the course of an hour it had not.

X-ray Scattering from a Distinct Glacial Phase. The X-ray pattern of the TPP molecular crystal (powder) is very distinctive with many sharp lines,[7,9,10,12] whereas those of the liquid and glass have relatively few peaks and at low Q are dominated by a broad peak at $Q \approx 1.5$ Å^{-1} and a weaker broad pre-peak at slightly lower Q.[28] The pattern for the glacial phase is very similar to that of the glass,[7,9,10,22] but a few additional weak low-Q peaks have been observed, one of which is relatively narrow with a half-width of $\Delta Q_{1/2} \approx 0.5$ Å. (These X-ray studies were carried out with a Rigaku RAXIS II Imageplate detector,
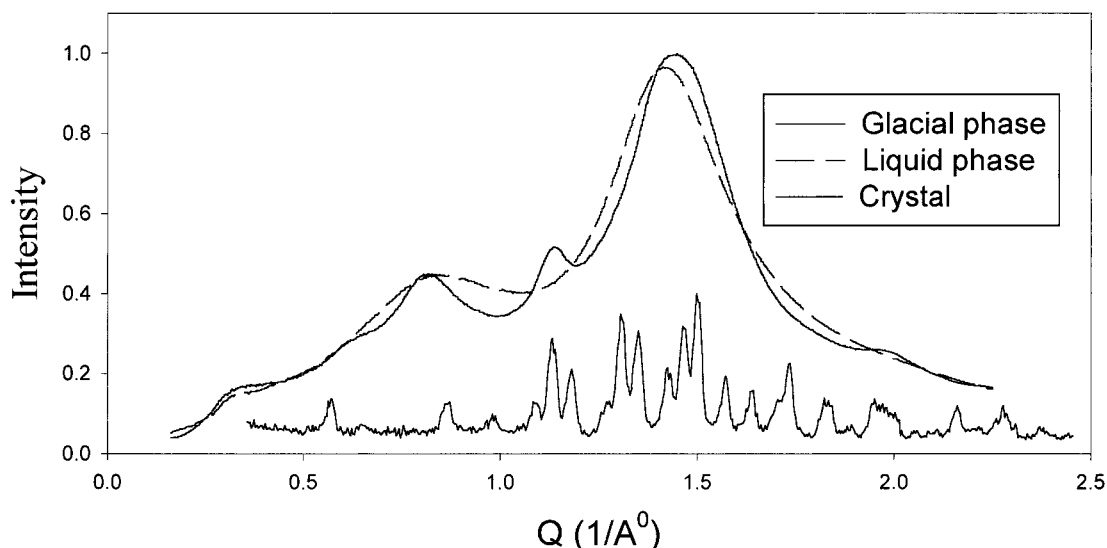
Figure 10. X-ray scattering patterns for liquid and glacial phase at 218 K. The glass (i.e., the liquid below 200 K) looks much like the liquid at 218 K. Note that the "lines" of the glacial phase are sharper, and more numerous, than those of the liquid. A four-Lorentzian fit indicates that the first line to the left of the main peak for the glacial phase has a half-width-at-half-height of 0.05 A^{-1}. The slight difference in Q values of the peak of the main peaks is attributable to density differences.

a Rigaku RU-200 generator running at 50 kV and 100 mA, a Molecular Structure Corporation Cryostat.) See Figure 10 and Hedoux et al.[12] (The glacial phase X-ray pattern in Figure 10 was fitted by the sum of 4 Lorentzians). Whenever there is a mixture of molecular crystal and glass or glacial phase, the scattering due to even a small amount of crystal is readily observed.

Distinctiveness of Glacial Phase. Although our diffractograms for "pure" glacial TPP are similar to those of Hedoux et al.,[12] our studies lead to different conclusions. Hedoux et al., find that with sufficiently long equilibration times many sharp peaks characteristic of the crystal develop, the higher the *T* the more crystal-like the end-product. They envisage the glacial phase not as a distinct phase but as poorly formed crystal that anneals to better crystal with time; in accord with this interpretation they envisage the "pure" glacial phase diffractogram as the envelop of the perfectly crystalline one, but this is an almost necessary consequence of similar packing at reasonable densities. In support of the view that the glacial phase is distinct, we refer to all the evidence discussed above that suggests first order transitions between phases. Furthermore, the dielectric relaxation data imply rotational motion in the glacial but not in the molecular crystal phase.[21,22] We believe that what Hedoux et al., see may indeed be annealing, but annealing of glacial phase to the molecular crystal phase via premelting of the glacial phase. This is what is indicated by both the calorimetric and NMR data. Because the crystal is the underlying stable phase, there is always danger of both liquid and glacial phase being converted to crystal via heterogeneous nucleation, the outcome being dependent, as discussed in the "background" section, on the handling of samples. By placing our sample in a cryo-loop we reduced both the X-ray scattering and the nucleation effects associated with walls; we did not see evidence of a glacial-to-crystal transition at 218 K. Recent neutron scattering data also show no build up of crystal peaks at temperatures below 230 K.[23]

Length Scales. Of primary interest to us is the possibility of supermolecular structures and correlation lengths in the glacial phase. Although no such lengths associated with structure have been detected in the glass or liquid,[23,29] there is considerable evidence of supermolecular correlations of relaxation properties

in deeply supercooled liquids, i.e., correlations extending over 4 or 5 molecular diameters.[30] There is reason to believe that such dynamical correlations must have structural counterparts that might be difficult to detect both because of unfavorable form factors for scattering off domains and because the density contrast between correlated regions may be small.[31] We have already mentioned that X-ray data indicate the existence of a characteristic length of from 20 to 120 Å.

Recent low-angle neutron scattering measurements[23] indicate a very low-Q peak at about 0.07 Å for the glacial phase, one that is not found in either the crystal or glass (liquid). In addition, Alba-Simionesco and Tarjus[23] find a Porod-law contribution which is suggestive of grain size (or defect separations) of about 200 Å.

Crystallites and Length Scales. We take the NMR demonstration of the coexistence of liquid and glacial phase and of glacial premelting as indicative of a glacial structure that is crystalline but divided into very small polydisperse crystallites. Alba-Simionesco and Tarjus interpret the neutron scattering data on the basis of 90 Å unit cells and 200+ Å crystallites, i.e., crystallites that are truly small since they consist of only about 20 unit cells. It is not clear just how the X-ray minimum length of 20 to 120 Å enters this or alternative models, but for the present discussion the important fact is that the X-ray and neutron data indicate supermolecular length scales in the glacial phase.

Conclusions. The liquid (glass), glacial, and molecular crystalline phases of TPP are distinct and the transitions among them are all first order. The similarity of the X-ray scattering patterns of the liquid, glass, and glacial phases of TPP lead us to denote the glacial phase as *apparently amorphous*. However, by taking the ^{1}H NMR spectrum as resulting from two distinct sets of molecules − a small number tumbling nearly as freely as in the liquid and a large number held constant, we conclude that the *glacial phase is crystalline*. This interpretation is compatible with the supermolecular length scales obtained from both neutron and X-ray scattering. Although we take the glacial phase to be crystalline, the premelting determined by both NMR and calorimetric studies, together with the nanometer length scale obtained from X-ray and neutron scattering, indicate that is it is a powder composed of polydisperse nanocrystallites.

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Although the interpretation of the dielectric data for glacial TPP is still somewhat uncertain, on the basis of studies by Dvinskikh et al.[21] and by Mizukami et al.[22] it appears that the rotational relaxation, though anomalous,[32] is nearly complete. This suggests that the glacial phase, though marginally crystalline, is actually a plastic crystal, one that differs from most plastic phases studied in having positional order only over nanometers and possibly having large unit cells.

Specifically we have determined that the glacial phase is not truly amorphous (i.e., a second liquid or glass phase) and that it is not merely a form of the molecular crystal composed of nanocrystallites. The crystallites of glacial phase are very small, but the molecules within rotate, which is not the case for the molecular crystal. The glacial phase thus seems to be a rather unusual metastable plastic crystalline phase whose physical and theoretical origins are worthy of study. We have been able to construct a *phase diagram* for the stable and metastable phases of TPP.

We have given consideration to the effects of thermal history on the state of the glacial phase, noting, in particular that glacial phase formed by slow cooling of liquid (as done by Hedoux et al.)[12] is more likely to contain inclusions of crystal than glacial phase formed by heating from the glass. Other than the pre-melting phenomenon, we have not addressed the problem of long-time relaxations or aging in the glacial phase, a phenomenon that has been brought up in a number of studies.[7,21,22]

It would seem unlikely that a small, nearly disklike molecule such as TPP would form a liquid crystal, and furthermore, in contrast to TPP, liquid crystals do not typically have immeasurably high viscosities (in any direction). If TPP did form a liquid crystal one would expect large depolarization ratios; although such ratios have not been measured for the glacial phase they appear modest in the liquid.[33] Furthermore, the dielectric relaxation of the glacial phase, though still not understood, does not suggest the presence of liquid crystal.[21,22]

Theoretical Framework: FLD. There is no well-developed theory for intermediate metastable phases to which the supercooled liquid can transform, but we attempt, via the theory of frustration-limited domains (FLD), to relate the properties of these phases (e.g., the glacial phase) to those of the supercooled liquids from which they form.[8] The property of supercooled liquids on which we focus is their domain structure, the domains being polydisperse supermolecular dynamically correlated aggregates;[30] the great slowing of relaxation processes is associated with these aggregates or domains. Although structural (in contrast to dynamical) evidence of such domains has not yet been produced, the FLD theory provides a physical mechanism (and an associated quantitative theory) for the formation of polydisperse structural domains in supercooled liquids which increase in size and become more monodisperse as T is lowered;[34] furthermore, the theory provides a description of the associated dynamical implications. In brief, according to the theory, the supermolecular domains form because of the growth of an incipient phase with a nearest-neighbor structure similar to that found in the high-T liquid but with the sizes of the structured regions being limited by the increasing strain associated with such growth, the strain being due to the inability of the system to tile space with this structure, i.e., due to structural frustration.

In addition to the above, the FLD theory predicts that fragile supercooled liquids undergo a first-order transition from the supercooled liquid to a defect-ordered phase. (The transition temperature may lie either above or below T_g; if it lies below, it may be difficult to effect the phase change.) This defect-ordered phase, which is not the normal molecular crystal, could, among other forms, be a modulated or striped phase with supermolecular unit cells.[35] We tentatively associate this predicted defect-ordered crystalline phase with the observed glacial phase of TPP.[10] Furthermore, we envisage this defect-ordered crystalline or glacial phase as composed of large unit cells (or widely spaced defects encompassing many molecules) which might be associated with, but need not necessarily be equivalent to, the supermolecular domains constituting the supercooled liquid from which the glacial phase is formed. The molecular relaxation within the supercooled-liquid domain could be very different from its counterpart unit cell within a crystallite. Although a connection between the crystal and the liquid from which it is formed is not central to phase transitions between equilibrium phases, it may well be so for metastable phases for which *kinetic accessibility* plays a major role. One reason a fragile liquid such as TPP can be deeply supercooled might be that the domain structure it acquires as it is supercooled makes accessibility to the normal stable molecular crystal more difficult than for the high-T unstructured liquid, while, at the same time, because of its domain structure, its access to the defect ordered or glacial phase is, most likely, eased. This picture of the supercooled liquid and the glacial phase is compatible with all observations, but specifics such as the size and character of the structural elements have yet to be firmly established. The properties of the defect-ordered phase predicted by the FLD theory have yet to be well-investigated.

The model outlined above envisages *kinetic controlled growth of the glacial crystallites from the domain-structured supercooled liquid*, the polydispersity of the domains in the liquid being transferred to the unit cells of the developing glacial crystallites, thereby leading to the formation of small crystallites. Such a picture can represent only the initial stages of crystal formation[36] because equilibration would almost certainly destroy the size-polydispersity of the unit cells and lead to large glacial crystallites (good crystal). However, although equilibration in the liquid, where polydispersity is the "equilibrated" form of supercooled liquid, is rapid, in the solid it is ordinarily immeasurably slow, and so in practice one should encounter only very small crystallites in the glacial phase. Although it may be almost a truism to state that intermediate metastable solid phases form from the liquid because they are kinetically most accessible, the model proposed for the glacial phase of TPP suggests that this kinetic accessibility might be related to the structure of the supercooled liquid specifically at the glacial transition temperature (and not that at the normal melting point); this viewpoint might be considered a modification of Ostwald's step rule.[37] We note that not all intermediate metastable phases are composed of small crystallites and large unit cells;[3,4] consequently, such phases are not likely to be the defect-ordered ones predicted by the FLD theory.

For completeness in the appendix we mention (and interpret) other studies on the TPP glacial phase that while yielding results compatible with our picture of the underlying phenomenology have not been directly incorporated into our analysis.

Appendix. Other Studies of the TPP Glacial Phase. Wiedersich, et al.[20] studied the Brillouin scattering observed during the transition from liquid to glacial phase at a constant *T*. As the glacial phase starts to form, the Brillouin lines observed in the liquid broaden but do not shift; ultimately, the lines become too broad to detect, after which they begin to appear as broad lines shifted to higher frequencies, and with time these new (solid phase) Brillouin lines become sharper. This phenomenon is analogous to that observed in opacity experiments where the liquid at first becomes increasingly turbid, and then clears up;[7] in both experiments the wavelengths are of the order of hundreds of nanometers, and the waves (acoustic or electromagnetic) at first scatter off the forming particles of glacial material and then off the remaining puddles of liquid.

Wiedersich et al.,[20] also noted that the ^{31}P NMR T_1 spin relaxation time decreases as the glacial phase starts to develop and then increases; we believe that what is happening is that at first, the T_1 decreases because the rotational relaxation slows down due to clustering of molecules, and that as the clusters grow, the rotational relaxation becomes so slow that the T_1 passes through a minimum and increases (reaching values that are possibly even above those in the crystal). In the liquid, the lattice motions that lead to spin relaxation are associated with molecular rotations and translations, but these motions are effectively damped within glacial clusters; within small clusters, there are no substitute low-frequency motions that can effectively relax the spins, but for large clusters or macroscopic aggregates there is likely to be a sufficient density of low-frequency phonons which could couple to the spins and lead to spin relaxation.

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