

# On Polyamorphism of Triphenyl Phosphite

J. Wiedersich, A. Kudlik, J. Gottwald, G. Benini, I. Roggatz, and E. Rössler\*

Physikalisches Institut, Universität Bayreuth, D-95444 Bayreuth, Germany

Received: February 26, 1997; In Final Form: May 21, 1997<sup>®</sup>

We investigated the glass former triphenyl phosphite by calorimetry, Brillouin scattering, and dielectric and nuclear magnetic resonance spectroscopy. Time-resolved experiments demonstrate the conversion between three distinctly different phases, namely, the supercooled liquid, a recently discovered apparently amorphous phase (glacial phase), and the crystalline phase. The temperature dependencies of the properties provided by the different methods are compared. We find significant molecular motion in the glacial phase. From this we hypothesize that the glacial phase is a different highly viscous liquid or a solid phase with some kind of cooperative relaxation.

## Introduction

In a recent publication Ha et al.<sup>1,2</sup> reported the identification of a new, apparently amorphous phase of the glass former triphenyl phosphite (TPP), to which the supercooled liquid converts at  $T > T_g$  ( $T_g$ : glass transition temperature) by way of a first-order phase transition (cf. also ref 3). The new phase was called the glacial phase. It is well distinguished from the glass formed by supercooling TPP below  $T_g$ . The glacial phase is believed to be amorphous, because X-ray scattering does not show any Bragg peaks and resembles that of the conventionally formed glass. The existence of more than one amorphous phase for a given compound has been called polyamorphism.<sup>4,5</sup>

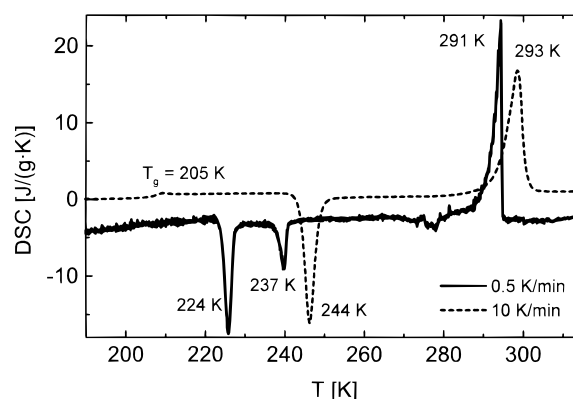
Here we report on further investigations of TPP by applying calorimetry, Brillouin scattering, nuclear magnetic resonance (NMR), and dielectric spectroscopy. In all experiments time-resolved measurements were carried out that demonstrate a conversion between distinctly different condensed phases. The three phases, namely, supercooled liquid, glacial, and crystalline phases, are characterized by comparing physical properties obtained by the four methods. In particular, we will demonstrate that the glacial phase exhibits pronounced molecular motion.

## Experimental Section

TPP was purchased by Acros; the degree of purity was 99%. The sample was used without further purification. The calorimetric experiments were performed with a Netzsch DSC 200 differential scanning calorimeter (DSC). Brillouin scattering experiments were carried out with a Sandercock tandem Fabry-Perot spectrometer in backscattering geometry, employing an argon-ion laser at 514.5 nm. Dielectric spectroscopy was done with a Schlumberger SI 1260 frequency response analyzer in connection with a current to voltage converter BDC from Novocontrol. <sup>31</sup>P-NMR studies were performed at a Larmor frequency  $\omega/2\pi = 161.9$  MHz on a Bruker DSX 400 spectrometer. The solid state spectra were recorded by taking a Hahn echo sequence, and the spin–lattice relaxation was monitored by applying a saturation sequence followed by a Hahn echo sequence.

## Results

**1. Calorimetry.** In the DSC experiments the TPP sample was cooled to the glassy state ( $T < 200$  K) at a rate of about 10–20 K/min and subsequently heated at different rates. Figure



**Figure 1.** DSC traces of triphenyl phosphite for heating rates of 10 K and 0.5 K/min, signal shifted for visibility.

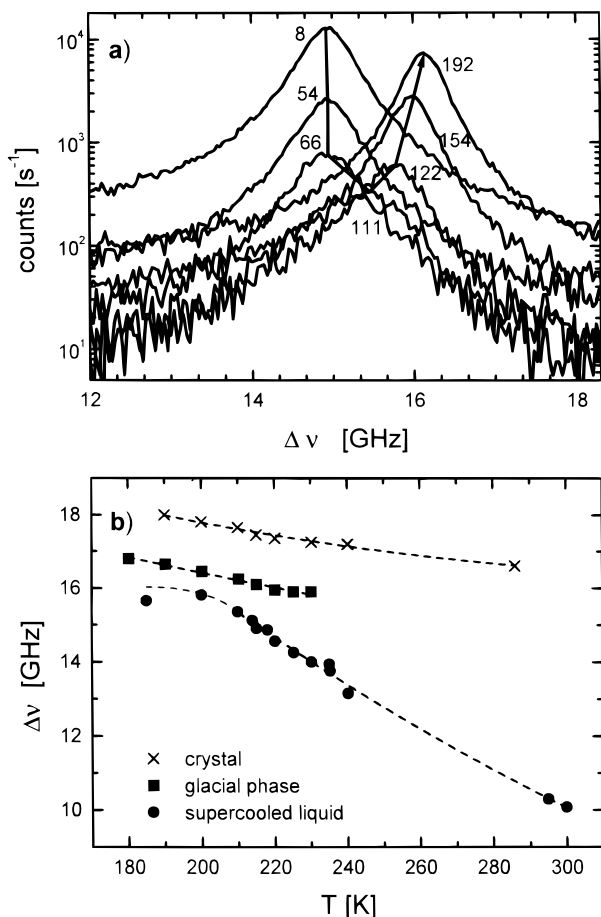
1 shows the traces of two experiments with heating rates of 10 and 0.5 K/min, respectively. At 10 K/min the onset of the glass transition was determined to be at 205 K. Crystallization of the sample occurred at 244 K (onset), releasing an enthalpy of 51 J/g. The onset of melting occurred at 293 K, and the melting enthalpy was determined to be 80 J/g. These findings are in agreement with the results reported in ref 3. Ha et al.<sup>7</sup> estimated  $T_g = 176$  K from viscosity studies. The significantly higher  $T_g$  classifies TPP as a fragile glass former (cf. also ref 6).

In the case of slow warming, two exothermic peaks are observed at 224 and 237 K. Here the heating rate is sufficiently slow to allow for the formation of the glacial phase around 224 K, which upon further heating converts to the crystal at 237 K. An integration over both peaks yields an enthalpy of 44 J/g, which is somewhat lower than that of the crystallization of the supercooled liquid. Our interpretation of this discrepancy is that the phase transformations may not be complete.

On scanning the crystalline phase between 180 K and room temperature no transition is observed. In the case of slow heating of the crystalline phase some small changes in the DSC trace are observed around 280 K, indicating some kind of structural change even in the crystalline state formed from the glacial phase (cf. Figure 1).

**2. Brillouin Spectroscopy.** To our knowledge Brillouin experiments have only been carried out on the ordinary liquid TPP so far.<sup>7</sup> We recorded Brillouin spectra as a function of both time and temperature for all phases. The Brillouin lines reflect the longitudinal phonon modes in the system. Since the refractive index is not known for all the phases, we only consider

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, July 1, 1997.

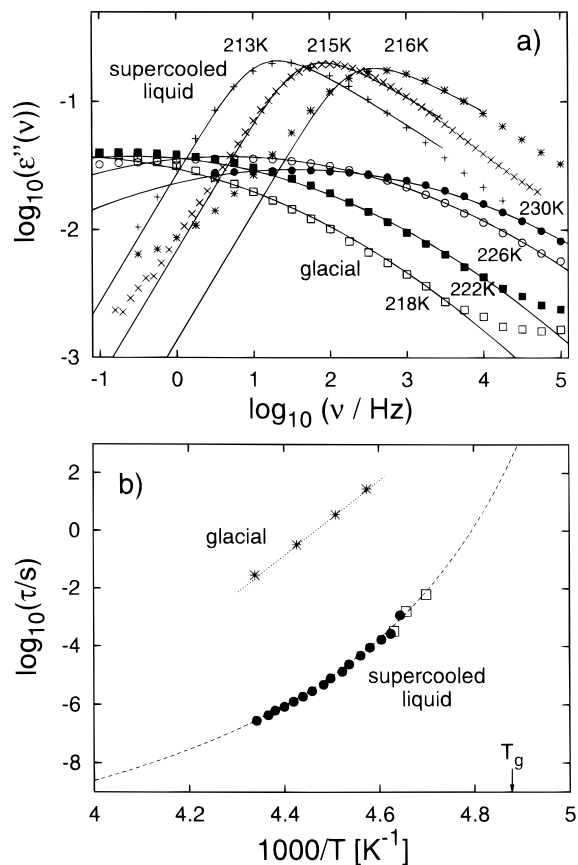


**Figure 2.** (a) Brillouin spectra of triphenyl phosphite. Numbers indicate the time (in minutes) after equilibrating the liquid at 215 K; arrow line indicates the evolution of the maximum. (b) Brillouin shift in various phases as a function of temperature. Dashed lines: guide for the eye.

the frequency shift. At the transition from supercooled liquid to glacial phase it was possible to obtain a spectrum every 10 min. Figure 2a shows the Stokes side of some spectra, recorded while the sample was held at 215 K. The Brillouin line of the supercooled liquid has its maximum at 14.9 GHz. On waiting for about 50 min the intensity of the Brillouin line decreases as the sample gets more and more turbid due to the glaciation process. After about 2 h the intensity of the Brillouin doublet reaches a minimum and a rather sudden shift to higher frequencies is observed between the recordings of two consecutive spectra. After a total of about 3 h, the sample gets clear again, the peak of the Brillouin lines having shifted to 16.1 GHz.

Figure 2b shows the positions of the Brillouin doublets as a function of temperature for the different phases of TPP. A Lorentzian line could be fitted to all spectra of the supercooled liquid, the glass, and the glacial phase. The spectra of the polycrystalline sample were distinctly different from the others, because of the distribution of lattice directions with respect to the scattering vector. Here we simply give the value of maximum intensity.

Figure 2b shows that both the supercooled liquid and the crystal behave as expected. While the crystal shows only a slight temperature dependence, the supercooled liquid shows a significant change due to an increase of the compressibility of the liquid when heated. The glacial phase exhibits a Brillouin shift in between that of the glass and the crystal with a temperature dependence comparable to that of the crystal. For an isotropic medium the shift of the Brillouin line is given by  $\Delta\nu = \pm C_{ad}q$ , where  $q$  is the wave vector and  $C_{ad}$  the adiabatic sound velocity.



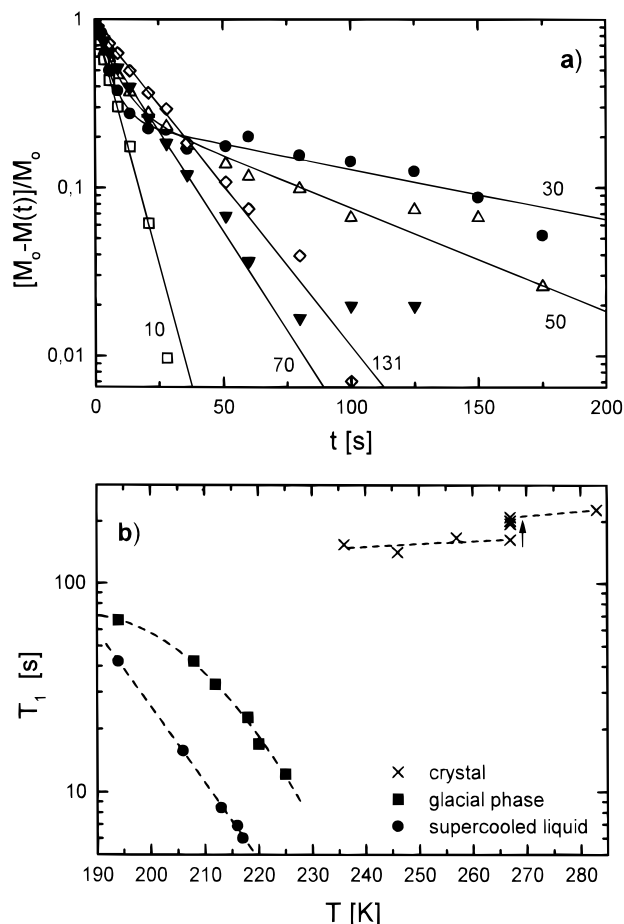
**Figure 3.** (a) Dielectric susceptibility  $\epsilon''(\nu)$  of triphenyl phosphite as a function of frequency  $\nu$ . Solid lines: fit by a Cole–Davidson spectral shape (supercooled liquid) and by a Gaussian spectral shape (glacial phase). (b) Correlation times estimated from analyzing  $\epsilon''(\nu)$  (in the case of the glacial phase  $-\log \nu_{\text{peak}}$  is plotted). Solid circles: data taken from ref 6. Dashed line: fit by a Vogel–Fulcher–Tammann law (cf. ref 6). Dotted line: attempted Arrhenius fit.

The latter is determined by the density  $\rho$  and the compressibility  $\kappa_{ad}$ ; explicitly  $C_{ad}^2 = 1/(\rho\kappa_{ad})$ . Thus, assuming that the refractive index (that determines  $q$ ) is not significantly different in the three phases, we find  $\rho\kappa_{ad}(\text{liquid}) > \rho\kappa_{ad}(\text{glacial}) > \rho\kappa_{ad}(\text{crystalline})$ .

**3. Dielectric Spectroscopy.** Measuring the dielectric response of TPP was hampered by the onset of crystallization in most experimental runs (cf. also ref 6). However, we were finally able to observe the transformation from the supercooled liquid into the glacial phase.

In Figure 3a the imaginary part  $\epsilon''(\nu)$  of the dielectric permittivity is plotted as a function of the frequency  $\nu$ . The sample was quickly cooled to the glassy state and then heated. At 213 K  $< T < 216$  K spectra are observed that are typical of a supercooled liquid. In particular, a main relaxation, namely, the  $\alpha$ -process, is found. In order to obtain a time constant, the spectral form is interpolated by a Cole–Davidson (CD) function. We note that the CD function provides a poor interpolation. Nevertheless a reasonable estimate of the correlation times can be obtained and is plotted in Figure 3b. Our findings agree well with those of ref 6. As expected, a pronounced non-Arrhenius temperature dependence is observed in the supercooled liquid.

At a constant temperature of 216 K the spectrum changes with time; after 20 h no further change could be observed. A broad relaxation contribution is observed, which we consider to be the relaxation spectrum of the glacial phase. The dielectric loss had decreased at higher frequencies, whereas contributions at lower frequencies appeared. On heating the glacial phase



**Figure 4.** (a) Normalized relaxation function of triphenyl phosphite. Numbers indicate the time (in minutes) after equilibrating the liquid at 218 K. (b) Spin–lattice relaxation time  $T_1$  as a function of temperature for the supercooled liquid, glacial, and crystalline phases of triphenyl phosphite. Arrow indicates change of  $T_1$  at 267 K within 450 min.

this broad maximum shifts to higher frequencies, as is displayed in Figure 3a. We conclude that some slow molecular motion is present in the glacial phase.

In order to estimate the time constant of the relaxation process in the glacial phase, we assumed a Gaussian spectral shape. This gives a fair interpolation of the high-frequency wing of the process and provides some estimate for the temperature dependence of the relaxation process. The time constants obtained are also plotted in Figure 3b. A temperature dependence of the same order as that of the supercooled liquid is found, despite a shift to longer times. Comparing the relaxation strength  $\Delta\epsilon$  of the relaxation in the supercooled liquid and in the glacial phase, it is estimated that  $\Delta\epsilon(\text{glacial}) \approx 0.7\Delta\epsilon(\text{supercooled liquid})$ .

**4. NMR.** The  $^{31}\text{P}$ -NMR solid state spectrum is determined in all phases by a well-resolved axially symmetric chemical shift (CS) tensor even though no proton decoupling was applied. No significant differences are found for  $\Delta\sigma = \sigma_{zz} - \sigma_{yy}$  in the three phases. We find  $\Delta\sigma = 238 \pm 5$  ppm for all phases. This is expected because the CS tensor is essentially a molecular property. However, as already reported by Ha et al.,<sup>1</sup> the spin–lattice relaxation time  $T_1$  is different in the three phases.

Figure 4a presents the normalized relaxation functions  $\Phi(t) = [M_0 - M(t)]/M_0$  as determined in consecutive runs after equilibrating the sample at 218 K and during the glaciation process.  $M(t)$  is the magnetization as a function of time, and  $M_0$  is its equilibrium value. The relaxation of the supercooled liquid is clearly exponential (10 min after equilibration). This

is also observed for other temperatures (cf. Figure 4b). First indications for a nonexponential relaxation are found after waiting for 30 min: a second significantly slower relaxation appears. However, this slow relaxation becomes faster as time goes by. Seventy minutes after equilibration this slow decay disappears and the relaxation function becomes essentially exponential again. Only in the early stages of the phase transformation is the relaxation biexponential, with the short relaxation time corresponding to that of the supercooled liquid. Thus some kind of two-phase model cannot explain the data over the whole transformation process.

In Figure 4b we summarize the relaxation data obtained. The temperature dependence of  $T_1$  in the supercooled liquid is strong, which is the usual behavior for highly supercooled liquids. In the case of the glacial phase a similar behavior is found, but the corresponding  $T_1(T)$  curve is shifted to higher temperatures. This demonstrates the presence of significant molecular motion which, for a given temperature, is slower than in the supercooled liquid. The relaxation time in the crystalline phase is much longer and exhibits no significant temperature dependence. However, at 267 K we observed a change of the relaxation time after waiting for several hours. Thus, some conversion takes place also in the crystalline phase (cf. also Figure 7).

## Conclusions

We have studied supercooled, glacial, and crystalline phases of TPP by several techniques. Each method clearly provides evidence that the supercooled liquid transforms into a new “glacial” phase which is quite different from the standard crystalline phase. The transformation can easily be reproduced in all cases, except for dielectric spectroscopy, where it was difficult to avoid crystallization. The transformation process itself appears to be different from that of crystallization. Neither the data sets of the NMR experiments nor those obtained by light scattering can be explained by a two-phase model. In particular, we have never observed a superposition of two Brillouin lines corresponding to the liquid and glacial phases during glaciation, in contrast to the case of crystallization from the liquid. In the Brillouin experiments, the glacial phase appears to be isotropic on the length scale of phonons. No indications of different wave vectors for different orientations are found as characteristic for (poly)crystalline materials; this is in accordance with the findings of Ha et al.<sup>1</sup> that the glacial phase is “apparently amorphous”.

A remarkable result of our investigation is the presence of a strong relaxation process in the glacial phase as discovered by means of both dielectric spectroscopy and NMR. Attempting to fit the dielectric relaxation times to an Arrhenius behavior leads to an apparent activation energy of 250 kJ/mol and a prefactor of  $10^{-58}$  s. Such a low prefactor cannot correspond to any single particle motion. Thus considerable collective motion takes place in the glacial phase. One possible explanation for the experimental findings reported here and elsewhere<sup>1–3</sup> is that the glacial phase is a different type of supercooled liquid, having longer relaxation times and being more rigid than the ordinary supercooled liquid. Transformations from a fragile to a strong liquid have been recently discussed.<sup>5</sup> Interpreting the relaxation of the glacial phase as the main relaxation of a supercooled liquid, we estimate  $T_g(\text{glacial})$  to be around 220 K (assuming  $\langle\tau(T_g)\rangle \approx 100$  s). However, we note that we could not detect a step in the heat capacity of the glacial phase indicating a glass transition, although we observed some peculiarities in the DSC trace of the glacial phase around 208 K  $< T < 225$  K (cf. also ref 3). The dielectric relaxation times suggest that the glacial phase is stronger than the ordinary liquid,

which is very fragile. Also, the broad shape of the dielectric spectra indicates deviations from the behavior expected for a simple glass former.

It may also be possible that the glacial phase is a rigid solid with some cooperative motion similar to that found in orientational glasses or in glassy crystals. Proposing the existence of order, however, clashes with the results of X-ray diffraction<sup>2</sup> and the absence of a distribution of phonon wave vectors. The structural configuration of the glacial phase and the nature of the relaxation process remain open questions.

**Acknowledgment.** Financial support through Sonderforschungsbereich 279 is appreciated. The authors thank S. Benkhof and J. Wolber for assisting in parts of the experiments.

## References and Notes

- (1) Ha, A.; Cohen, I.; Zhao, X.; Lee, M.; Kivelson, D. *J. Phys. Chem.* **1996**, *100*, 1.
- (2) Cohen, I.; Ha, A.; Zhao, X.; Lee, M.; Fischer, T.; Strouse, M. J.; Kivelson, D. *J. Phys. Chem.* **1996**, *100*, 8518.
- (3) Miltenberg, K. van; Blok, K. *J. Phys. Chem.* **1996**, *100*, 16457.
- (4) Angell, C. A. *Science* **1995**, 257, 1924.
- (5) Angell, C. A.; Shao, J.; Grabow, M. In *Non-equilibrium phenomena in supercooled fluids, glasses and amorphous materials*; Giordano, M., Leporini, D., Tosi, M. P., Eds.; World Scientific: Singapore, 1996; p 50.
- (6) Schiener, B.; Loidl, A.; Chamberlin, R. V.; Böhmer, R. *J. Mol. Liq.* **1996**, *69*, 243.
- (7) Gomperts, S. N.; Variyar, J. E.; Greenfield, M.; Shen, Y.-C.; Kivelson, D. *Chem. Phys.* **1993**, *172*, 117, and references therein.