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ABSTRACT

In situ AC nanocalorimetry and dielectric spectroscopy were used to analyze films of vapor-deposited triphenyl phosphite. The goal of this work was to investigate the properties of vapor-deposited glasses of this known polyamorphic system and to determine which liquid is formed when the glass is heated. We find that triphenyl phosphite forms a kinetically stable glass when prepared at substrate temperatures of 0.75–0.95Tg, where Tg is the glass transition temperature. Regardless of the substrate temperature utilized during deposition of triphenyl phosphite, heating a vapor-deposited glass always forms the ordinary supercooled liquid (liquid 1). The identity of liquid 1 was confirmed by both the calorimetric signal and the shape and position of the dielectric spectra. For the purposes of comparison, the glacial phase of triphenyl phosphite (liquid 2) was prepared by the conventional method of annealing liquid 1. We speculate that these new results and previous work on vapor deposition of other polyamorphic systems can be explained by the free surface structure being similar to one polyamorph even in a temperature regime where the other polyamorph is more thermodynamically stable in the bulk.

INTRODUCTION

A single component system can have a first order phase transition between two distinct liquid phases, a phenomenon known as a liquid–liquid transition. The term “polyamorphism” encompasses this behavior and evokes an analogy with polymorphism (multiple crystal structures with the same composition). Phase transitions between two liquids with the same composition have been reported in the literature for a range of systems, including molecular systems such as water, n-butanol, and d-mannitol; atomic systems such as sulfur, phosphorus, silicon, and germanium; and more complex systems such as Y2O3–Al2O3. Despite the many examples listed above, controversy remains about the existence of the liquid–liquid transition in many systems. Alternative explanations include frustrated crystallization and the intervention of liquid-crystal phases. Often, the second liquid state is difficult to access as there can be interference from crystallization or experiments at high temperatures and pressures may be required.

One of the best-studied examples of polymorphism is the molecular system triphenyl phosphite (Tg = 205 K). Polyamorphism in this system was first discovered by Ha and co-workers in 1996; they observed a transition from the ordinary supercooled liquid (below referred to as “liquid 1”) to a second amorphous “glacial phase.” These authors found that the glacial phase could be accessed by annealing liquid 1 for several hours at 10 K–20 K above Tg. The time required for complete transformation to the glacial phase was found to increase with decreasing temperature; below 213 K, the transformation was too long to be observed in their experiments. They reported that the glacial phase was rigid and denser than liquid 1 and seemed to be stable indefinitely below 237 K. The initial understanding of the glacial phase was limited, with proposed explanations ranging from a liquid crystal or plastic crystal, to a highly correlated second liquid or a mix of nanocrystallites and untransformed supercooled liquid.

Subsequently, Tanaka and co-workers have performed several additional studies on triphenyl phosphite. They have investigated the nature of the glacial phase, the reversibility of the liquid–liquid
transition, and the relationship between the molecular relaxation and the order parameter during the liquid–liquid transition. Using fast-scanning calorimetry, these authors successfully demonstrated the reversibility of the liquid–liquid transition. They showed that, upon heating, the glacial phase first goes through the glass transition to transform into a liquid (hereafter referred to as “liquid 2") and then liquid 2 converts into liquid 1 by the reverse liquid–liquid transition. This and other observations argue that the glacial phase is the glass of liquid 2 and not a mixture of liquid 1 and nanocrystallites. In contrast with other molecular systems thought to exhibit a liquid–liquid transition, triphenyl phosphate is not a strongly hydrogen-bonded system.

Recently, it has been shown that physical vapor deposition (PVD) can be an effective route for accessing liquids that are structurally different from the ordinary liquid, suggesting possible polyamorphism. This has been shown for glycerol, 4-methyl-3-heptanol, and 2-methyltetrahydrofuran. In experiments on these systems, glasses were prepared by PVD and measurements were performed using dielectric spectroscopy. For glycerol, the liquid formed by heating the vapor-deposited glass had a fourfold increased dielectric relaxation strength and slower structural dynamics compared to the ordinary liquid. Comparably, in the case of 4-methyl-3-heptanol, the liquid formed upon heating the vapor-deposited glass also showed a high dielectric loss. Both the increased relaxation strength observed in glycerol and the high dielectric loss reported in 4-methyl-3-heptanol are reasonably interpreted as a change in the hydrogen bonding structural characteristics of the liquid. In contrast, for 2-methyltetrahydrofuran, heating the vapor-deposited glass produced a liquid with a decreased dielectric loss relative to the ordinary supercooled liquid. Vapor deposition has also been utilized to access both the high-density and low-density amorphous phases of water. One study showed that, similar to 2-methyltetrahydrofuran, vapor-deposited water also has a lower dielectric amplitude than what is expected from bulk water. Although PVD is typically utilized to prepare glasses with high kinetic stability, tunable molecular orientation, and enhanced translational order, this previous work on glycerol, 4-methyl-3-heptanol, 2-methyltetrahydrofuran, and water suggests that PVD could also be an important tool for studying polyamorphism. A connection between the high kinetic stability of vapor-deposited glasses and polyamorphism has been previously suggested.

Given that PVD has produced interesting new liquids in systems where polyamorphism is not well-characterized, we wanted to explore the relationship between PVD and polyamorphism using one of the best-understood polyamorphic systems. Here, we use AC nanocalorimetry and dielectric spectroscopy to investigate vapor deposition of triphenyl phosphate glasses over a wide range of substrate temperatures (0.5–1.12T_g). For substrate temperatures between 0.75 and 0.95T_g, kinetically stable glasses with reduced heat capacity are formed, consistent with previous work on many organic systems. For PVD glasses formed over the entire range of substrate temperatures, heating the glass results in the formation of liquid 1 of triphenyl phosphate, as evidenced by the narrow calorimetric transition and shape of the dielectric spectra. Thus, PVD of triphenyl phosphate does not produce the glacial phase (or liquid 2) even though liquid 2 is thermodynamically more stable than liquid 1 over almost our entire range of substrate temperatures. We propose that during PVD, molecular conformations preferred at the free surface of the triphenyl phosphate glass templates the formation of glasses associated with liquid 1 even in the temperature range where liquid 2 is more stable in the bulk.

EXPERIMENTAL METHODS

Materials

Triphenyl phosphate was purchased from Sigma-Aldrich (97% purity) and Acros Organics (99% purity). Nuclear magnetic resonance (NMR) experiments indicated that both source materials contained phenol as an impurity. Triphenyl phosphate was heated during deposition in order to reach the desired deposition rate. Based upon additional NMR experiments, we conclude that this heating process gradually produces additional phenol. For this reason, we did not attempt to remove the phenol from the starting material. In this manuscript, T_g of triphenyl phosphate will refer to the T_g of liquid 1 = 205 K, as reported previously and in agreement with the temperature at which t_d = 100 s.

Apparatus

Glasses of triphenyl phosphate were prepared by PVD in a vacuum chamber, as described previously. The molecules were deposited directly onto either the AC nanocalorimeters or the interdigitated electrode device used for dielectric spectroscopy. All measurements were then performed in situ. For both types of measurements, the molecules were introduced into the chamber via a fine leak valve. Both the base pressure and the pressure during deposition are monitored using an ion gauge. Both devices sit inside copper fingers, which are mounted to a cold cup with a liquid nitrogen reservoir. The temperature is controlled by heaters and resistive temperature detectors (RTDs) that are attached to the copper fingers. During measurements, the chamber is backfilled with nitrogen gas to about 220 Torr in order to prevent desorption of the film.

For AC nanocalorimetry measurements, the heaters on the nanocalorimeter membranes (Xensor XEN-39391) are driven by an externally supplied 19 Hz AC voltage. The heat produced by this voltage results in a temperature modulation at 38 Hz on the sample, and the reversing heat capacity is measured at this frequency. There are thermocouples patterned onto the nanocalorimeters, which then detect the temperature oscillation (~0.3 K). The amplitude and phase of the thermocouple voltage oscillation are measured with a lock-in amplifier; all measurements are differential between thermocouples on the device with the sample and on an empty device. A background subtraction is performed to account for slight differences between these two devices. Following the background subtraction, the signal from the differential measurement is proportional to the reversing heat capacity at 38 Hz. These films are thin enough that the results do not need to be corrected for changes in the membrane thermal expansion induced by the vapor-deposited film. The temperature on the nanocalorimeter membrane is indirectly determined using a resistor on the nanocalorimeter active area. This resistance, along with a calibration curve constructed using a relaxation times of various supercooled liquids, is used to calculate the temperature.
For dielectric measurements, we utilize an interdigitated electrode Abtech IME 1025.3-FD-Pt-U, a dual sensing borosilicate glass chip with two pairs of platinum electrodes microlithographically patterned on the surface. Each pair of interdigitated electrodes has 50 fingers, 10 μm wide each, with a 10 μm serpentine gap between the fingers. During a deposition, one pair of electrodes is open to deposition, while the other is covered to serve as a reference cell. A polyether ether ketone (PEEK) box is used to cover the reference cell and to support the 4-pin connector used to make electrical contact with the bonding pads on the device. An oscillating voltage is applied to both electrodes via a Solartron SI 1260 impedance analyzer. During an experiment, ε′ and ε″ are measured simultaneously for both the sample and reference electrodes. As described previously, the differential impedance signal is then converted to dielectric permittivity.

AC nanocalorimetry experiments

We performed both temperature-scanning and quasi-isothermal annealing experiments. The vapor-deposited glasses used for all nanocalorimetry experiments (temperature-scanning and quasi-isothermal annealing) were deposited at ~0.05 nm/s. All vapor-deposited glasses used for temperature-scanning experiments were about 200 nm thick, and a heating and cooling rate of 5 K/min was utilized. Films for the quasi-isothermal annealing experiment shown below in Fig. 5 were prepared using a bilayer geometry described previously. In this experiment, we deposited an ~300 nm thick film on top of an ~150 nm liquid-cooled glass. To initiate this isothermal experiment, the sample was heated at 8 K/min to the annealing temperature.

Dielectric spectroscopy experiments

We performed two types of dielectric spectroscopy experiments. For the first type, isothermal measurements, spectra were collected at a series of measurement temperatures sequentially from low to high temperatures. Data were collected between 10⁻¹ and 10⁷ Hz with eight points per decade. The film was heated above Tg until the α peak stopped evolving; this indicates that the glass has transformed into the supercooled liquid. Isothermal dielectric spectra of the resulting liquid were fit with a Havriliak–Negami function [see the following equation],

\[ \varepsilon'(f) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{HN}}{1 + (2\pi f \tau_{HN})^{\alpha}} \] (1)

For isothermal spectra, all parameters were freely varied during fitting.

The second type of dielectric experiments performed were temperature-scanning measurements. Here, the temperature is ramped at a constant rate of 5 K/min while measuring the dielectric loss at a fixed frequency of 19 Hz, similar to the AC nanocalorimetry measurements described above and allowing for further evaluation of kinetic stability and dynamics of the prepared glasses and liquids. This frequency was chosen to avoid observed interference from line frequency. After the sample had transformed from glass to liquid, the temperature was cooled at 5 K/min. Additional heating and cooling runs were performed to measure the response of the liquid-cooled glass. All films for both types of dielectric spectroscopy experiments were about 370 nm thick.

RESULTS

Prior to describing our results, we present an overview of the important temperatures for these experiments on triphenyl phosphite [molecular structure shown in Fig. 1(a)]. Figure 1(b) shows the range of substrate temperatures used for vapor deposition (103 K–235 K). The upper part of this panel shows an expanded view of a smaller temperature window. Liquid 2 is thermodynamically stable relative to liquid 1 below 230 K. Previous work has identified 213 K–220 K as the temperature range where isothermal annealing of liquid 1 results in a transformation to the glacial phase. Also shown in Fig. 1(b) are “dynamic Tg” values for the two liquids, evaluated for a frequency of 38 Hz; these are important for interpreting nanocalorimetry and dielectric relaxation experiments.

Temperature-scanning experiments

Temperature-scanning experiments using AC nanocalorimetry and dielectric relaxation were used to assess the kinetic stability of the vapor-deposited glasses and the dynamic glass transition
temperatures of the resulting liquids. Figure 2 shows the heating curves for an AC nanocalorimetry and a dielectric relaxation temperature-scanning experiment on vapor-deposited triphenyl phosphite glasses. The glass measured by AC nanocalorimetry [panel (a)] was deposited at 0.85T_g. The large step in the heat capacity for the PVD glass indicates the transformation of the glass into a liquid. The temperature where the step begins (≈214 K) is the onset temperature for devitrification, as illustrated by the tangent lines shown in Fig. 2. The vapor-deposited glass has an increased onset temperature relative to the liquid-cooled glass, indicating increased kinetic stability. Following the transformation of the PVD glass, it was cooled back to 165 K and thermally cycled at 5 K/min two subsequent times to obtain the LC glass curve (only one of these two curves is shown). The 38 Hz dynamic T_g is calculated from the midpoint of the heating curve for the LC glass; this temperature also corresponds to the minimum in the complex phase data. The interpretation of the dielectric relaxation data in panel (b) is very similar. In this case, we show the storage component of the dielectric signal (ε′) obtained during heating for a glass deposited at a substrate temperature of 0.96T_g. Increased kinetic stability relative to the LC glass is also apparent for glasses deposited at this substrate temperature.

In addition to the features shown in Fig. 2(b), an additional feature was observed in the dielectric relaxation ramping experiments for substrate temperatures below approximately 190 K. For these low temperature depositions, a small peak near 190 K appeared during the first heating of the prepared film (see supplementary material, Fig. S1); this extra peak did not appear in the subsequent heatings of the same film. The NMR spectroscopy of the as-supplied material and not yet deposited material removed from the chamber after performing depositions revealed the presence of phenol as an impurity. We expect that this small peak is caused by the incorporation of a small amount (∼1%) of phenol into triphenyl phosphite glasses deposited at low substrate temperatures based upon the following observations: (1) Phenol is more volatile than triphenyl phosphate, so it is reasonable that it would only be incorporated into films at low substrate temperatures and not be observed in the second heating of a given film. (2) Annealing triphenyl phosphate glasses deposited at low substrate temperatures for a few hours at 195 K (before transforming into the supercooled liquid state) showed that this minor peak disappeared in a few hours, consistent with a volatile impurity. (3) This minor feature was not seen in AC nanocalorimetry data. Assuming identical contributions to the heat capacity for triphenyl phosphite and phenol, this indicates an impurity concentration of less than 3%. (4) Given the dielectric constant of phenol, we estimate that the process loss amplitude of phenol would be ∼10 times greater than that of triphenyl phosphate. The loss amplitude of triphenyl phosphate is ten times greater than the anomalous feature, which leads to the approximate concentration of phenol in the PVD glasses deposited at low temperatures to be 1%. Considering these observations, we do not expect that a low-level impurity in samples deposited at low temperatures has any impact on our conclusions.

Only liquid 1 is produced when PVD glasses are heated above T_g

Figure 3 summarizes the behavior of triphenyl phosphite glasses vapor-deposited over a range of substrate temperatures. Figure 3(a) shows the 19 Hz dynamic T_g value for the liquid-cooled glasses prepared by transforming the as-deposited samples [as shown in Fig. 2(b)], as measured by dielectric relaxation. These uncorrected dynamic T_g values are identical within experimental error for all samples, indicating that the same liquid has been prepared in each of these experiments. A temperature calibration based upon the dielectric response of other liquids shows that a 6 K temperature gradient is not unreasonable for our apparatus. Adding this 6 K to the uncorrected data produces values near 212 K, the dynamic T_g value expected for liquid 1 of triphenyl phosphite at 19 Hz. Thus, the reproducibility of these onset temperatures provides an initial line of evidence that only liquid 1 is produced by
heating vapor-deposited glasses for the entire range of substrate temperatures.

The shape and peak frequency of dielectric spectra provide an additional method for identifying which liquid is formed upon heating vapor-deposited glasses of triphenyl phosphite. Figure 4 shows isothermal dielectric loss spectra for the liquid of triphenyl phosphite that is produced by transforming PVD glasses. Regardless of the deposition temperature, the same liquid is formed, based upon the shape of the observed dielectric response. The loss spectrum reported for liquid 1 has a FWHM of 2.0 decades,\textsuperscript{24} which compares well with the value of 1.95 decades we observe in the spectra of our vapor-deposited films. In contrast, the dielectric response of liquid 2 is much broader,\textsuperscript{24} as we discuss below.

One aspect of Fig. 4 seems difficult to understand, given previous literature reports. Films deposited at the highest substrate temperatures are deposited above \(T_g\) and include the temperature range typically used to transform liquid 1 into liquid 2. For example, the deposition performed with a substrate temperature of 217 K took place over 3 h, which is comparable to the half-life of the transformation to the glacial phase reported previously for this temperature.\textsuperscript{24,43} Thus, we expected that the glacial phase would begin to form in our vapor-deposited film during deposition. However, if this had occurred, we would not observe the excellent overlap of spectra seen in Fig. 4. This issue may be connected with the intermittent failure of triphenyl phosphite to transform in the isothermal annealing experiments discussed below.

### Kinetic stability of PVD glasses

The onset temperature from a temperature-scanning experiment provides a convenient means to compare the kinetic stability of PVD glasses prepared at different substrate temperatures. Figure 3(b) shows the corrected onset temperatures normalized by \(T_g\) for triphenyl phosphite glasses prepared at a wide range of substrate temperatures; here, the temperature has been corrected based upon the difference between the dynamic \(T_g\) observed in the second scan and that expected for liquid 1. Onset temperatures from both AC nanocalorimetry (red) and dielectric relaxation (blue) are shown. Figure 3(b) illustrates that for substrate temperatures between 150 K and 200 K (\(\sim 0.75 \text{ to } 0.95T_g\)), triphenyl phosphite forms a kinetically stable glass. The most kinetically stable glass, as
FIG. 5. Quasi-isothermal annealing of a triphenyl phosphite glass vapor-deposited at 0.85T\(_g\) (∼174 K). The film transforms into liquid 1 of triphenyl phosphite in about 10\(^{3.3}\)\(\tau\) when annealed at 208 K. Previous systems with high kinetic stability take at least 10\(^3\)\(\tau\) to transform. The lower x axis is transformation time normalized by \(\tau\) of triphenyl phosphite at the annealing temperature.

indicated by the highest onset temperature, is achieved with a substrate temperature of ∼175 K. This substrate temperature is equal to ∼0.85T\(_g\), which is consistent with results for other systems known to form kinetically stable glasses via PVD.\(^{35,37,44,45}\)

Quasi-isothermal nanocalorimetry experiments can further quantify the kinetic stability of a vapor-deposited glass. Figure 5 shows the result of isothermal annealing on the vapor-deposited glass of triphenyl phosphite with the highest onset temperature. The glass was deposited at 0.85T\(_g\) and annealed at ∼208 K (T\(_g\) + 3 K). We normalize the transformation time by the structural relaxation time at the annealing temperature; this allows for comparison with other molecules that form stable glasses via PVD. The transformation time was determined using a previously established procedure involving linear time axis plots of the data in Fig. 5.\(^{36,44,45}\) The glass of triphenyl phosphite shown in Fig. 5 took about 10\(^{3.3}\)\(\tau\) to fully transform into the supercooled liquid. While some other PVD glasses can have transformation times approaching 10\(^5\)\(\tau\), a transformation time of 10\(^{3.3}\)\(\tau\) is quite large compared to what can be achieved by aging a liquid-cooled glass for a reasonable period of time.\(^{44}\)

Transformation of liquid 1 into the glacial phase

Since vapor deposition of triphenyl phosphite did not directly produce liquid 2 or the glacial phase, as a control experiment, we followed literature procedures\(^ {20,47}\) to obtain the glacial phase by isothermal annealing of liquid 1. Figure 6(a) shows about 10\(^{3.3}\)\(\tau\), a transformation time of 10\(^{3.3}\)\(\tau\) is quite large compared to what can be achieved by aging a liquid-cooled glass for a reasonable period of time.\(^ {44}\)

is an incubation time of about 700 s, which is comparable to the 500 s incubation time reported at 220 K in Ref. 47. Additionally, the heat capacity of the glacial phase is smaller than that of liquid 1, as reported by Ref. 23 and confirmed below from our experiments. Figure 6(a) shows that at 218 K, the half-time of the transformation is about 1700 s and the transformation appears to be complete in about 1 h. References 24 and 43 report that, at this annealing temperature, the transformation is complete within 2 h–3 h. We do not understand the reason for this difference, but potentially it could be related to our thin film geometry or the presence of a free surface in our system.

Figure 7 shows the heating curve of a temperature-scanning AC nanocalorimetry experiment on a liquid-cooled glass of triphenyl phosphite.
phosphite (gray) compared to the glacial phase of triphenyl phosphite obtained by annealing the ordinary liquid at 218 K (purple). Three features in the glacial phase curve illustrate the differences between the glacial phase and a liquid-cooled glass. First, the transition is much broader. In the glacial phase (purple), the transformation occurs over about 20 K, whereas the transformation in the liquid-cooled glass (gray) is completed within 5 K. Second, the transformation of the glacial phase occurs about 10 K higher; this is most easily illustrated by looking at the midpoint of the heat capacity step, indicated by the 38 Hz $T_g$. Finally, the step size is smaller in the glacial phase. All of these characteristics have been previously observed upon heating the glacial phase.\(^{23,47}\)

The transformation of liquid 1 of triphenyl phosphite into the glacial phase was also observed in dielectric relaxation measurements during isothermal annealing. Figure 6(b) illustrates the evolution of the dielectric loss of triphenyl phosphite during annealing at 216 K–218 K. The initial annealing temperature was 218 K as determined from $\tau_g$ of liquid 1 in the first spectrum. The half-time of the transformation of this experiment is \(\sim 300 \) s longer than the corresponding nanocalorimetry experiment performed at 218 K. Fitting the dielectric loss spectrum after the transformation to the response of the glacial phase, prepared by isothermal transformation of liquid 1, as shown in Fig. 6(a). The step height of the liquid-cooled glass has been scaled to account for differences in film thickness, as described previously.\(^{24}\) Note that the dynamic glass transition is much broader for the glacial phase and also occurs in a higher temperature regime.

DISCUSSION

In this work, we vapor-deposited a known polymorphic system (triphenyl phosphite) in order to learn more about polymorph selection via physical vapor deposition. As described above, we found that triphenyl phosphite forms a kinetically stable glass when prepared at substrate temperatures from \(0.75 T_g\) to \(0.95 T_g\). Additionally, for the wide range of substrate temperatures employed here, only liquid 1 is accessible by vapor deposition. As a control, we produced the glacial phase and liquid 2 by the conventional approach of isothermal annealing liquid 1. Below, we compare triphenyl phosphite to other systems that, when vapor-deposited, apparently exhibit polymorphism. Additionally, we propose two possible explanations for why liquid 1 is always observed when PVD glasses of triphenyl phosphite are heated.

Comparison to previous work on polymorph selection with PVD

As described in the Introduction, there are several examples in the literature of PVD producing unusual liquids. For example, when glasses deposited onto substrates from 0.7–1.0$T_g$ were heated, liquids of similar dielectric response were formed, and in all cases, the enhancement of the dielectric strength was about 3.5 (relative to the ordinary supercooled liquid of glycerol). For 2-methyltetrahydrofuran, similar to glycerol, deposition across a wide range of substrate temperatures produces glasses that yield a liquid other than the ordinary supercooled liquid (in this case, the new liquid has a smaller dielectric response by about a factor of two). Glycerol and 2-methyltetrahydrofuran are similar to triphenyl phosphite in producing only a single liquid via PVD, but in contrast to triphenyl phosphite, PVD of these two systems leads to a liquid other than the ordinary supercooled liquid.
For 4-methyl-3-heptanol and water, in contrast, vapor deposition can result in a wide range of different liquid states, depending on the deposition temperature. For 4-methyl-3-heptanol, deposition at substrate temperatures below $T_g$ results in an unusual liquid (up to 11 times larger dielectric response), but deposition at $T_g$ gives rise to the ordinary supercooled liquid.\textsuperscript{26} For water, deposition at 80 K results in low-density amorphous ice, while deposition at 11 K reportedly produces high-density amorphous ice,\textsuperscript{2} but this study did not demonstrate the preparation of multiple liquid states.

**Why does PVD of triphenyl phosphite only produce liquid 1?**

One might have expected that liquid 2 would result from vapor deposition at substrate temperatures below 230 K; as shown in Fig. 1, below 230 K, liquid 2 is thermodynamically more stable than liquid 1, i.e., lower in free energy. We briefly discuss potential explanations for why PVD glasses of triphenyl phosphite form only liquid 1 over the wide range of substrate temperatures investigated here.

One possible explanation is related to the structure of triphenyl phosphite preferred at the liquid/vapor interface. Several recent papers support the view that vapor-deposited glasses inherit their structure from the structure of the liquid at the vacuum interface.\textsuperscript{31,48} For example, it was shown that vapor deposition of posaconazole, a molecule without liquid crystalline phases, can result in glasses with smectic liquid crystalline order.\textsuperscript{30} The authors show that the free surface structure of the isotropic equilibrium liquid is highly anisotropic, with the rod-like posaconazole molecules standing nearly vertically at the free surface. During the deposition at substrate temperatures just below $T_g$, mobility at the free surface allows the formation of highly aligned molecules at the free surface and further deposition traps this arrangement into smectic layers. This system shows that the free surface structure can direct the formation of a bulk glass with a structure much different than the bulk structure expected at equilibrium. Applying this idea to triphenyl phosphite, we speculate that the structure preferred at the free surface is similar to liquid 1 throughout the entire temperature range investigated such that the vapor-deposited glasses that are formed are similar to liquid 1 and heating them results in the formation of liquid 1. A related explanation was recently advanced to rationalize the unusual liquid prepared by vapor deposition of 4-methyl-3-heptanol; in this case, it is suggested that the deposition process allows hydrogen-bonded chains of molecules to be formed even though such structures do not play an important role in the bulk liquid.\textsuperscript{26} Surface sensitive x-ray techniques on the supercooled liquids of these systems would be highly beneficial in clarifying the role of vapor deposition in polymorph selection.

An alternative possibility is inspired by the recent work from Vila-Costa et al. on vapor-deposited Freon 113 (1,1,2-trichlorotrifluoroethane); this system forms a plastic crystal at a low temperature.\textsuperscript{50} The authors reported that samples deposited between 110 K and 120 K formed plastic crystals in which the ratio of trans to gauche isomers depended systematically on the substrate temperature. In contrast to the posaconazole example above, in which the packing of rod-like molecules was key, for Freon 113, the authors interpreted the production of plastic crystals with different trans/gauche conformational populations to conformational equilibration during the deposition process. For triphenyl phosphite, it is possible that molecular conformation also plays a role in distinguishing the two liquids\textsuperscript{5} and that the deposition process is critical in selecting conformational populations.

We vapor-deposited triphenyl phosphite over a range of substrate temperatures to determine the effect of vapor deposition on a known polymorphic system. We found that, similar to other organic molecules, triphenyl phosphite forms a kinetically stable glass when prepared at substrate temperatures of $\sim$0.75 to 0.95$T_g$. The transformation time of the most kinetically stable glass of triphenyl phosphite is comparable to previously studied systems with high kinetic stability. We prepared the glacial phase of triphenyl phosphite (the glass of liquid 2) by the conventional method of annealing liquid 1 and studied the glacial phase with AC nanocalorimetry and dielectric spectroscopy. With these measurements as a control, we were able to compare the characteristics of the two liquids of triphenyl phosphite to the liquid obtained by heating the vapor-deposited glasses. Both nanocalorimetry and dielectric spectroscopy indicate that vapor deposition of triphenyl phosphite, regardless of the substrate temperature, always results in liquid 1 upon heating. This may be due to trapping of the preferred free surface structure by the deposition process.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for a representative temperature-scanning experiment that displays the small additional peak discussed in the dielectric loss data.

**AUTHORS’ CONTRIBUTIONS**

M.S.B. and B.J.K. share first author status.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**


