

# Thermal study on the impurity effect on thermodynamic stability of the glacial phase in triphenyl phosphite–triphenyl phosphate system

Ikue Tanabe, Kiyoshi Takeda\*, Katsuo Murata

*Department of Chemistry, Naruto University of Education, Naruto,  
Tokushima 772-8502, Japan*

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## Abstract

To investigate the impurity effect on thermodynamic stability of the glacial phase, an apparently amorphous metastable phase observed in triphenyl phosphite (TPP), the differential scanning calorimetry (DSC) was carried out in the temperature range 120–350 K for binary mixtures between TPP and triphenyl phosphate (TPPO). Heating up from the glassy liquid, supercooled liquid phase transformed into glacial phase below the crystallization temperature for all the samples with  $x < 0.2$ , where  $x$  denotes the mole fraction of TPPO. Both transformation temperatures from liquid to glacial and from glacial to crystal increased and temperature range that glacial phase appears narrowed with the content of TPPO. The peak intensity of exothermic effect due to the transformation from liquid to glacial becomes larger whereas that from glacial to crystal reduced. The kinetic and thermodynamic stabilities were discussed for liquid and glacial phases based on the DSC results. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Glacial phase; Triphenyl phosphite; Triphenyl phosphate; DSC

## 1. Introduction

Polyamorphism is the phenomenon that multiple non-crystalline states appear in a substance especially in classical liquids [1]. Amorphous ice [2–6] and some inorganic materials [7–13] are examples of polyamorphic substances that have been reported to transform from low to high density amorphous state under high pressure. It is still under discussion whether the transition between two amorphous modifications is really a thermodynamic phase transition or just kinetically distinct states within a phase. The glacial phase of triphenyl phosphite (TPP) has also been considered as a possible example of polyamorphic modification [14–17]. The glacial phase has been interested because of the uniqueness in its apparently amorphous nature indicated by the X-ray diffraction experiments [14,18,19] although the intermediate state in enthalpy between supercooled liquid and crystal. The polyamorphic behavior of triphenyl phosphite has been stud-

ied in many experimental techniques, such as calorimetric [20–22], NMR [18,23,24], dielectric [22,24], and Raman [25] experiments. According to their experimental results, the nature of glacial phase has been suggested as a second liquid, an aggregate of nanocrystals or a liquid crystal, but is still under discussion.

Observation of the response against the modulation of intermolecular interaction often gives insight about the essential nature of the aggregate. The thermodynamic properties of glacial phase reflect the energetic aspect of molecular aggregation in glacial phase. In the present study, we have examined the impurity effect on thermodynamic stability in glacial phase using thermoanalytical technique. Triphenyl phosphate (TPPO) was used for the impurity component in the present study. The molecular structure of TPPO is similar to that of TPP with difference that TPPO has extra oxygen atom bound to the phosphorus atom. The similarity in molecular structures of TPP and TPPO is expected not to cause drastic change in intermolecular interaction that changes the nature of glacial phase but to modulate in a moderate manner.

\* Corresponding author. Tel.: +81 88 687 6429; fax: +81 88 687 6022.  
E-mail address: [takeda@naruto-u.ac.jp](mailto:takeda@naruto-u.ac.jp) (K. Takeda).

## 2. Experimental

Commercially available triphenyl phosphite (TPP; Katayama Kagaku Kogyo Inc., Chemical grade) and triphenyl phosphate (TPPO; Katayama Kagaku Kogyo Ind., Chemical grade) were used as purchased. Materials are mixed in the Erlenmeyer flask weighing with the precise balance to determine the mole fractions of the mixtures.

The differential scanning calorimetric (DSC) measurement was carried out using DSC instrument (Seiko Instruments Inc., DSC10) equipped with liquid-nitrogen cooling unit for low temperature measurement. Since the samples of TPPO mole fraction  $x > 0.6016$  included solid at room temperature, the uniform liquid solution was obtained by heating up above its fusion point before loading into sample container. One or a few drops of sample solution were introduced using a Pasteur pipette into a semi-closed-top sample container of  $\sim 5 \times 10^{-2} \text{ cm}^3$  in capacity. The sample mass was weighed by precise chemical balance and DSC signals were reduced by masses of samples. All the samples in liquid state at room temperature were cooled down at  $5 \text{ K min}^{-1}$  at maximum rate after loading the sample container into the chamber. The others are loaded after the cryostat was cooled down below their glass transition temperature namely below 200 K to avoid the samples in crystal at room temperature crystallizing and phase separating on cooling at usual rate. After cooled down to 150 K, all the samples were heated at  $1 \text{ K min}^{-1}$ . The temperature range measured was from 150 K to the one ranging from room temperature to 350 K dependent on fusion point of each sample. The outputs of DSC signal and temperature were recorded on the electrical recorder (Seiko I&E; SR-410) and the data were simultaneously acquired by a digital multimeter (Keithley Instruments Inc.; DMM-2000) and a notebook personal computer (NEC Co.; PC-9821Ne) via PC card type GP-IB interface (CONTEC Co., Ltd.; GP-IB(PM)).

The temperatures of exothermic stabilizations were determined as the temperatures at maxima of DSC peaks. Fusion, eutectic and glass transition temperatures were determined as the temperature at the intersection between baseline below the anomaly and extrapolation at steepest increment point during endothermic peaks or baseline shift.

## 3. Results

Results of DSC for neat TPP are shown in Fig. 1. The sample cooled down to 150 K gave glassy liquid states. On heating the glassy liquid, the glass transition phenomenon was observed at 202.0 K. Two sharp and large exothermic peaks are also observed successively following to the glass transition at 227.4 and 241.1 K. At 296.5 K, a large endothermic peak due to fusion was observed. This thermal behavior of neat TPP is essentially agreed with previously reported results [20–22]. The observed glass transition can be assigned for glass transition of supercooled liquid. And the exothermic peak at lower temperature due to liquid to glacial phase

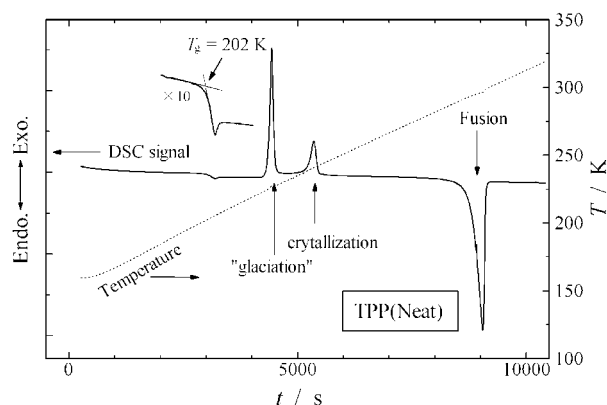


Fig. 1. DSC curve measured for neat TPP.

(called as “glaciation” temperature  $T_G$  hereafter) and glacial to crystalline phase (crystallization temperature  $T_{\text{cry}}$  hereafter).

Fig. 2 shows DSC results for  $(\text{TPPO})_x(\text{TPP})_{1-x}$ . For neat TPPO one large and several small and broad exothermic effects due to crystallization followed by a large endothermic effect due to melting were observed. The endothermic peak of melting is associated with small several prepeaks which are supposed to be due to minor unidentified impurities. For samples of  $x \leq 0.0582$ , two definitely separate exothermic peaks were observed above the glass transition  $T_g$ . On the other hand, the high temperature exothermic peak merges to

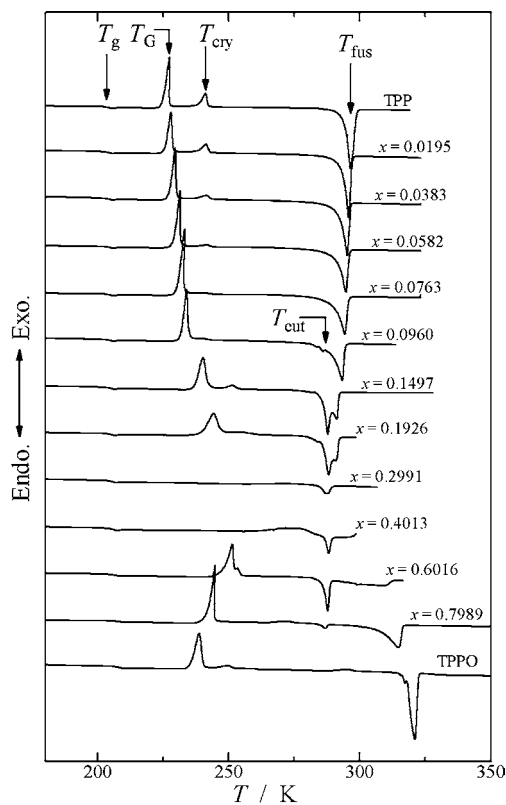


Fig. 2. DSC curves for  $(\text{TPP})_{1-x}(\text{TPPO})_x$  binary mixtures.

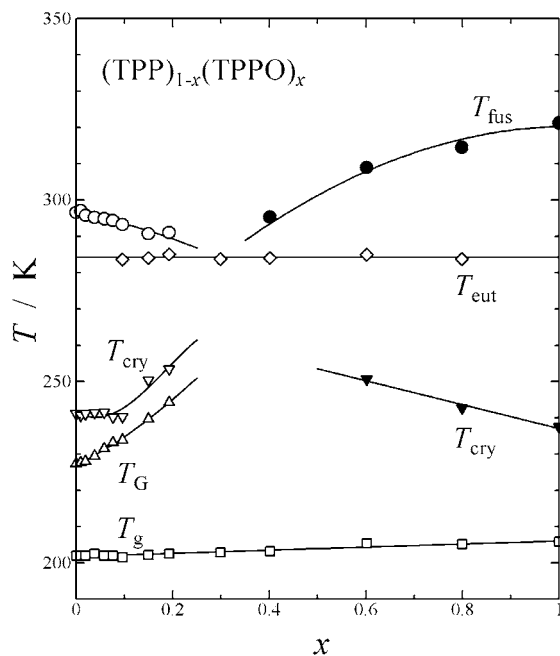


Fig. 3. Composition dependence of observed thermal anomalies: ( $\square$ ) glass transition temperature  $T_g$ ; ( $\Delta$ ) glaciation temperature  $T_G$ ; ( $\nabla$ ), ( $\blacktriangledown$ ) crystallization temperature  $T_{cry}$ ; ( $\circ$ ), ( $\bullet$ ) fusion temperature  $T_{fus}$ ; ( $\diamond$ ) eutectic point  $T_{eut}$ . The open and closed marks indicate those of TPP and TPPO, respectively.

the lower peak as shoulder for sample of  $x \geq 0.0763$ . However, transformation from liquid to crystal still proceeds in two steps implying the existence of glacial phase in between.

In Fig. 3 observed peak temperatures were plotted as functions of mole fraction of TPPO. Fusion points of both pure components decreases with blending the other component. Also, the peaks of fusion are associated with peaks independent on concentration in temperature and their intensity maximized around  $x \sim 0.3$ . It is clearly illustrated that present binary mixtures forms eutectic melting system with eutectic point at  $T_{eut} = 284$  K and  $x \sim 0.3$  although the precise concentration is not precisely determined in this stage.

## 4. Discussion

### 4.1. Glaciation and crystallization temperatures

In the heating process from glassy liquid of TPP, it has been observed that the supercooled liquid stabilizes into glacial phase above  $T_g$  for samples of  $x < 0.2$ . The glacial phase transforms into crystal at  $T_{cry}$  (crystallization). Thus the glacial phase of TPP can be considered as metastable phase whole temperature region it appears. For pure TPP, it was reported that the supercooled liquid above  $T_g$  ( $\approx 200$ – $204$  K) stabilize into glacial phase at  $T_G = 224$ – $230$  K and the glacial phase crystallizes at  $T_{cry} = 235$ – $240$  K [18–22]. The differences in the transformation temperatures are probably due to the difference in experimental conditions such as heating rate.

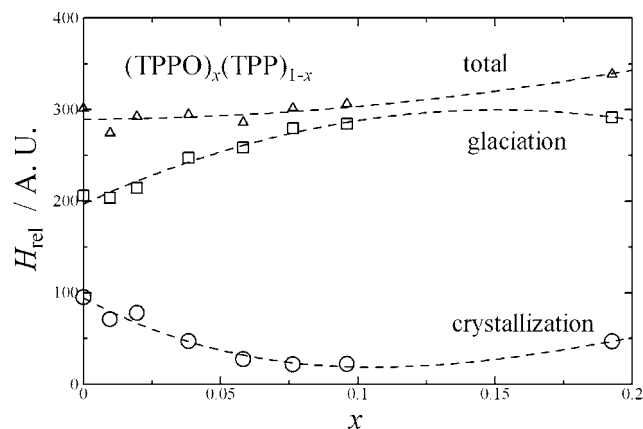


Fig. 4. Relative peak areas of glacial and crystallization peaks plotted as functions of mole fraction of TPPO.

Since both the glaciation and crystallization processes proceed by the nucleation-and-growth mechanism [14,18,19], the growth process controls the total transformation rate at relatively high temperature. The growth process is controlled by molecular diffusion process, and the transformation rate should be totally described as a thermal activation processes. Under constant heating rate, the transformation temperatures reflect, therefore, the enthalpy barriers in transformation to be passed over.

Fig. 3 shows that the change of glaciation temperature  $T_G$  with TPPO concentration is steeper than that of crystallization  $T_{cry}$  at dilute concentration range. This trend indicates the enthalpy barrier of glaciation increases more than that of crystallization with blending TPPO. Increment in enthalpy barrier from liquid to glacial phase indicates that the molecular diffusion process slows down by adding TPPO as impurity. The glaciation proceeds in nucleation and growth mechanism [14,18,19] and nucleation process is expected to be equilibrated enough because the present samples had already been experienced low temperature before starting the glaciation. Thus the present change in glaciation rate results from slow down of growth process. It is strongly desired to carry out further investigation for understanding of detailed mechanisms of glaciation process.

### 4.2. Enthalpies of glaciation and crystallization

Relative enthalpies of transformations per unit mass are obtained by integrating the DSC curves with the baseline subtracted. In Fig. 4 peak areas were plotted as functions of mole fraction  $x$  of TPPO. It is observed that the enthalpy of glaciation increases and that of crystallization decreases in the concentration of  $x < 0.1$ . The enthalpies of glaciation  $\Delta_{liq}^G H$  and crystallization  $\Delta_G^{cr} H$  can be expressed as follows:

$$\Delta_{liq}^G H(T_G) = H_G(T_G) - H_{liq}(T_G)$$

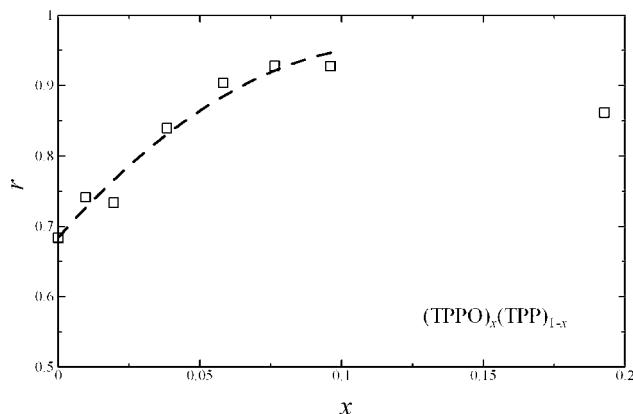


Fig. 5. Concentration dependence of the ratio  $r = \frac{\Delta_{\text{liq}}^{\text{G}}H}{\Delta_{\text{liq}}^{\text{G}}H + \Delta_{\text{G}}^{\text{cr}}H}$ .

and

$$\Delta_{\text{G}}^{\text{cr}}H(T_{\text{cry}}) = H_{\text{cr}}(T_{\text{cry}}) - H_{\text{G}}(T_{\text{cry}}).$$

Here,  $H_{\text{G}}$ ,  $H_{\text{liq}}$  and  $H_{\text{cr}}$  are enthalpy values of glacial, supercooled liquid and crystal, respectively. It is noted that both  $\Delta_{\text{liq}}^{\text{G}}H$  and  $\Delta_{\text{G}}^{\text{cr}}H$  are negative as these are exothermic processes. Neglecting the difference between  $T_{\text{G}}$  and  $T_{\text{cry}}$  (about 15 K at most) and the heat capacity difference between glacial and crystal in the temperature range where the glacial phase appears, the sum of stabilization enthalpies is nearly equal to the enthalpy difference between liquid and crystal, i.e.

$$\Delta_{\text{liq}}^{\text{G}}H + \Delta_{\text{G}}^{\text{cr}}H \approx H_{\text{cr}} - H_{\text{liq}} = \Delta_{\text{liq}}^{\text{cr}}H.$$

Using the above assumption, the relative thermodynamic stability of glacial phase to liquid and/or crystal can be roughly estimated by the ratio  $r$  defined as

$$r \equiv \frac{\Delta_{\text{liq}}^{\text{G}}H}{\Delta_{\text{liq}}^{\text{G}}H + \Delta_{\text{G}}^{\text{cr}}H} \approx \frac{\Delta_{\text{liq}}^{\text{G}}H}{\Delta_{\text{liq}}^{\text{cr}}H}.$$

With the definition the ratio  $r$  goes to unity as the enthalpy of glacial phase approaches that of crystal and to zero as approaching that of liquid.

In Fig. 5, concentration dependence of the ratio  $r$  calculated from the peak areas are shown. The  $r$  value increases with the TPPO concentration. This indicates the glacial phase is stabilized most among the three condensed phases, liquid, glacial and crystal. It has been reported that molecular motion of some kind is observed in glacial phase from calorimetric, NMR and dielectric measurement [22,24]. The molecular motion in glacial phase is associated with weak dielectric loss and broad distribution of relaxation time. The high pressure NMR experiment [19] elucidated that compression narrows the temperature range in which the glacial phase appears. Since the density of glacial phase is higher than that of liquid, the glacial phase is more stabilized than liquid under pressure. These features given by compression seem to be similar to those of impurity as shown above. This implies that the modulation of the environment for each molecule is

similar to that induced by pressure. The effect of pressure on the molecular environment should be contraction of free volume distributed to each molecule. Doping TPPO as impurity is consistently considered results in the free volume decreases in glacial phase.

## 5. Conclusion

The glacial phase as an apparently amorphous state considered as a new type of polyamorphism. The difference of molecular aggregation between glacial and supercooled liquid is important to understand the nature of glacial phase. The present study elucidated that thermodynamic stability of glacial phase become stable more than supercooled liquid state by doping TPPO. Also the increment in enthalpy barrier against transformation from liquid to glacial reflects the molecular mechanism of transformation. The study of impurity effect of glacial phase from the viewpoint of molecular dynamics is desired for TPP-TPPO system. It is also a question that the doping effect on thermodynamic stabilities presented in this paper is common in the system containing other impurities. The change in thermodynamic stability of glacial phase in relation to molecular structure of impurity is expected to give much insight about the manner of molecular aggregation in glacial phase. Thus changes both in phase behavior and in thermodynamic aspect give essential information for seeking the nature of the glacial phase.

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