Entropic evidence of the order-disorder nature of the phase transition in *p*-terphenyl crystal

Entropic evidence of the order–disorder nature of the phase transition in p-terphenyl crystal*

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Abstract. The heat capacities of p-terphenyl-based crystals that are mixtures with 3, 6-diphenyl-1, 2, 4, 5-tetrazine have been measured by adiabatic calorimetry below room temperature. The concentration dependence of the apparent entropy of transition for the twist transition of the host p-terphenyl crystal is examined, and clearly shows that the phase transition is of order–disorder type, where the conformation of an individual molecule plays the role of an Ising spin variable.

1. Introduction

It is known that an order–disorder phase transition is characterized by an entropy gain associated with the number of available discrete states in which a particle can reside. If the number of these states is two as in the case of Ising spin, the entropy of transition amounts to $R \ln 2$, where R is the gas constant, having a numerical value of about 8.3 J K^{-1} mol^{-1}. On the other hand, the entropy of transition is much smaller for displacive phase transitions accompanied by soft mode(s) than for order–disorder phase transitions, though a large entropy of transition is also possible for some types of displacive phase transition [1]. The experimental entropy of transition determined from calorimetric measurements is, therefore, often used for elucidation of the nature of a phase transition.

The molecule of p-terphenyl (C_6H_5–C_6H_4–C_6H_5, TP) has twisting degrees of freedom around the long molecular axis as shown in figure 1. The intramolecular potential governing the conformation results from two competing effects, i.e., π-conjugation favourable to a planar conformation and steric repulsion between *ortho*-hydrogen atoms. Crystalline p-terphenyl undergoes a structural phase transition related to a twisting degree of freedom at 193.5 K [2]. While the molecule is seemingly planar in the room temperature phase, adjacent phenyl rings in the molecule are twisted alternately below the phase transition temperature. Analysis of the room temperature crystal structure has been successfully carried out by assuming that the seemingly planar molecule at room temperature is a superposition of two opposingly twisted molecules [3]. That is, the room temperature phase is disordered. Other experimental studies [4–11] have also supported the conclusion that the transition is of order–disorder type. The entropies of transition reported so far are, however, 0.49 (for normal compounds) [12], 1.08 (for fully deuterated compounds) [12], 1.80 (for normal compounds)

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[13], and 1.63 J K^{-1} mol^{-1} (for normal and deuterated compounds) [14]. Although a large variation is apparent, all of the values are much smaller than $R \ln 2 \approx 5.8$ J K^{-1} mol^{-1}, the value attained when the conformation of an individual molecule behaves as an Ising spin.

One way to resolve the inconsistency between the order–disorder nature of the transition and the magnitude of the entropy of transition is to assume the existence of strong correlation between the conformations of neighbouring molecules in the room temperature phase. For example, the entropy of transition is reduced by a factor of four if four neighbouring molecules change their conformations synchronously. Any experiment but calorimetry (and this is indirect) would find it difficult to detect such correlation, and no study has been reported paying attention to such a point.
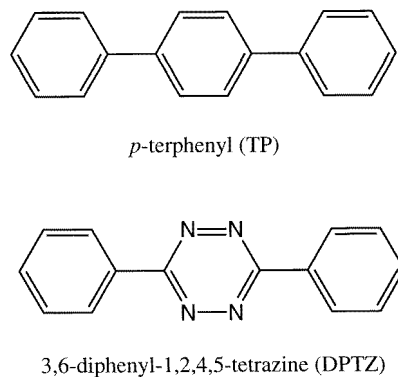

p-terphenyl (TP)

3,6-diphenyl-1,2,4,5-tetrazine (DPTZ)

Figure 1. Structures of the molecules.

Another way of interpreting the inconsistency between the order–disorder nature of the transition and the magnitude of the entropy of transition is to emphasize the ambiguity involved in the baseline for estimation of the 'excess heat capacity'. This may be applicable to the present case where the spin variable is the molecular conformation. That is, it is rather difficult to establish to what extent the conformational degree of freedom can be separated from the intramolecular and/or lattice vibrations. This point is in sharp contrast with the case for magnetic phase transitions, in which the relevant spin degree of freedom is clearly separated from the lattice degrees of freedom. The entropy of transition is, therefore, usually well accounted for in terms of the spin multiplicity. The arbitrariness involved in setting the baseline leads to diversity in the reported entropies of transition for *p*-terphenyl, because the heat capacity curves generally coincide well with each other. The two dimensionality of the twist phase transition [4, 9–11, 14, 15] increases the difficulty of setting a reasonable baseline, as the heat capacity anomaly of a two-dimensional system has a long tail on both the low- and high-temperature sides of the phase transition. Consequently, the discrepancy between the experimental and theoretical entropies of transition has been implicitly or explicitly attributed to the ambiguity involved in determining the baseline [13, 14].

The situation described above shows that the nature of the phase transition of *p*-terphenyl still remains open to question, especially as regards its entropic aspect. The purpose of this paper is to elucidate the nature of the phase transition of *p*-terphenyl on the basis of an entropic assessment. To this end, an experimental method free from the arbitrariness involved in setting a baseline is employed. The entropy of transition is determined solely from the numbers of 'pseudo-spins' participating in the transition. If 'non-

magnetic' particles are substituted for a proportion of the 'spins', the entropy of transition is proportionally reduced in the low-concentration region of non-magnetic particles. The total entropy of transition of the pure system is thus estimated from the concentration dependence of the entropy of transition, using a working baseline that is arbitrarily chosen but common to the systems with different compositions. It should be noted that the estimate of the entropy change between the low- and high-temperature limits in the Ising system will be exact even if the system is affected by defects and/or inhomogeneity in the impurity distribution, while that is rather hard to achieve for the transition temperature. The assessment of the nature of the phase transition based on the entropy of transition is, therefore, direct and free from dependence on the specific model and/or approximation.

As the 'non-magnetic' impurity, 3, 6-diphenyl-1, 2, 4, 5-tetrazine (C_6H_5–C_2N_4–C_6H_5, DPTZ) is chosen for this study. The structure of the DPTZ molecule is shown in figure 1. The similarity in molecular structure to the host (*p*-terphenyl) is favourable to the formation of a solid solution, and relatively weak deformation of the crystalline lattice around DPTZ molecules may be expected. Since the central tetrazine ring has no hydrogen atoms that will, if present, stabilize the twisted conformation through steric repulsion of the *ortho*-hydrogen atoms on the outer phenyl rings, the stable conformation of the DPTZ molecule is expected to be planar in an isolated state. Indeed, the molecule is planar with no conformational disorder in crystals of pure DPTZ at room temperature [16]. Consequently, a virtual crystal of DPTZ that has the same crystal structure as that of *p*-terphenyl would undergo no twisting phase transition because of the flatness of the molecule. The DPTZ molecule, therefore, behaves as a 'non-magnetic' impurity in *p*-terphenyl crystal.

2. Experimental procedure

Commercially available *p*-terphenyl (Wako Pure Chemical Industries, Limited) and DPTZ (Aldrich Chemical Company, Incorporated) were purified by means of fractional sublimation in vacuum at about 412 and 385 K, respectively. The TP-DPTZ mixed crystals prepared were of two compositions: 'TP-DPTZ 2%' (containing 2.05% DPTZ mole fraction) and 'TP-DPTZ 5%' (4.87%). For the preparation, appropriate amounts of the purified *p*-terphenyl and DPTZ were sealed in a glass ampoule with He gas (at 40 kPa at room temperature). The mixture in the ampoule was melted at around 200 °C, and then cooled quickly to 0 °C using ice. The formation of a solid solution was confirmed by observing that there was no change in colour on cooling down to liquid nitrogen temperature, as crystalline DPTZ shows thermochromism between room and liquid nitrogen temperatures, going from deep purple to bright orange [17].

The measurements of the heat capacity were carried out using a laboratory-made adiabatic calorimeter [18]. Each of the samples was loaded into the calorimeter vessel after pulverization and sealed with He gas (at 100 kPa at room temperature) to assist quick thermal equilibration in the vessel. The mass of the TP-DPTZ 2% sample loaded into the calorimeter vessel was 3.812 49 g (0.016 5479 mol) after buoyancy correction and that of the TP-DPTZ 5% sample was 3.558 59 g (0.015 4385 mol). Each sample contributed more than 40% at all temperatures to the total heat capacity including that of the vessel. The apparatus and the operation of the adiabatic calorimeter have been described elsewhere [18]. The working thermometers were platinum (Minco Products, Incorporated, S1055) and germanium (Lake-Shore Cryotronics Incorporated, GR-200B-500) resistance thermometers and were used above and below 13.8 K, respectively. The temperature scales of both of the thermometers are based upon the ITS-90.

3. Results and discussion

The heat capacities of the mixed crystals TP-DPTZ 2% and TP-DPTZ 5% were measured between 10 and 303 K. After each energy input was over, thermal equilibrium within the calorimeter vessel was attained in about 3 min below 50 K, 5 min at about 80 K and 8 min above 100 K. The time taken for the thermal equilibration was not elongated even in the transition region. No anomalous behaviour due to a possible impurity-induced phase transition or phase separation was encountered over the whole temperature region studied.
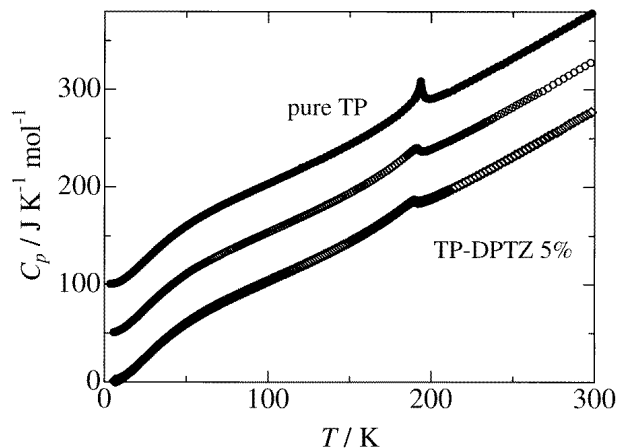

Figure 2. The measured molar heat capacities of the TP-DPTZ 2% and 5% mixed crystals, and pure *p*-terphenyl [14]. The left-hand ordinate is for TP-DPTZ 5%. The other curves are shifted by steps of 50 J K^{-1} mol^{-1} upwards.

Figure 2 shows the heat capacities of the mixed crystals and that of pure *p*-terphenyl [14]. The magnitude of the heat capacity of the mixed crystal is almost the same as that of pure *p*-terphenyl. This may be understood as a result of a competition of two opposing effects, i.e., the decrease in the intramolecular motional degrees of freedom due to the decrease in the number of the atoms and the increase in the molecular mass.

There is an anomaly in each of the heat capacity curves of the mixed crystals at around 190 K, as well as in that of pure *p*-terphenyl. This anomaly is attributed to the twist phase transition of crystalline *p*-terphenyl. With increase in the concentration of DPTZ, the anomaly becomes smaller and the top of the peak is rounded. There are two possible causes of the rounding of the anomaly. The local strain induced by the presence of the impurity (DPTZ) molecules may broaden the phase transition even if a homogeneous distribution of the impurity within the mixed crystals had been attained. Also, the spatial inhomogeneity of the impurity distribution would lead to a distribution of values of the transition temperature. Although the molecular structure of the impurity, DPTZ, is very similar to that of *p*-terphenyl as seen in figure 1, there is no reason to rule out one or both of the possibilities.

The expected decrease in the entropy of transition is, at most, $0.05R \ln 2 \approx$ 0.3 J K^{-1} mol^{-1} for the TP-DPTZ 5% mixed crystal made from pure *p*-terphenyl, while the third-law entropy of pure *p*-terphenyl, which includes all of the contributions from the vibrational and configurational degrees of freedom, is 221 J K^{-1} mol^{-1} at 230 K [14]. That is, the expected decrease in the entropy of transition is comparable to the accuracy of modern adiabatic calorimetry (0.1%). On the other hand, the precision and repeatability of the adiabatic calorimeter is better than that accuracy by about one order of magnitude as

deduced from repeated experiments on many samples. It is therefore preferable to use data obtained by just one calorimeter. The data for the mixed crystals fulfil this requirement, but the data for pure *p*-terphenyl [14] do not.
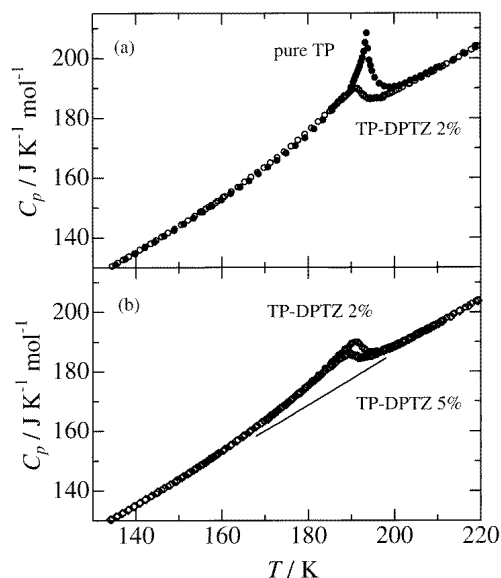

Figure 3. The measured molar heat capacities around the twist phase transition of the TP-DPTZ 2% and pure *p*-terphenyl [14] (a) and the TP-DPTZ 2% and 5% (b). The solid line in (b) is a working baseline used to estimate the 'excess heat capacities'.

In addition, the temperature dependence in the transition region is clearly different for pure [14] and mixed crystals as shown in figure 3(a). The shape of the anomaly of the TP-DPTZ mixed crystal is much broadened in comparison with that for pure *p*-terphenyl. The low-temperature side of the anomaly of the mixed crystals is less steep and larger, except in the vicinity of the anomaly, than that of pure *p*-terphenyl, and the tail on the high-temperature side is smaller than that of pure *p*-terphenyl. The temperature dependence of the heat capacity is, thus, different over most of the range of the anomaly for pure *p*-terphenyl and the mixed crystals. A wide temperature range such as 100 to 250 K should be assumed as a working transition region so that a common baseline may be drawn for pure *p*-terphenyl and the mixed crystals. Since the expected change in the entropy of transition is small, a narrow range is preferable for the working transition region. For these reasons, only the data for two mixed crystals are used for comparison, as follows.

Figure 3(b) shows an enlarged plot of the heat capacities of the mixed crystals in the transition region. The heat capacities of the mixed crystals coincide well within the experimental precision below 140 K and above 220 K. It is, therefore, reasonable to draw a common baseline between 140 and 220 K. The baseline to be drawn is only operational and has a large arbitrariness as stated in the introduction. A smooth interpolating curve, as shown in figure 3(b), is drawn in this study.

The 'excess heat capacities' are separated by subtracting the normal heat capacity given by the baseline from the experimental heat capacities. The excess heat capacities obtained are divided by their temperature, and then integrated numerically. The resulting temperature evolutions of the excess entropy are shown in figure 4. The difference in the
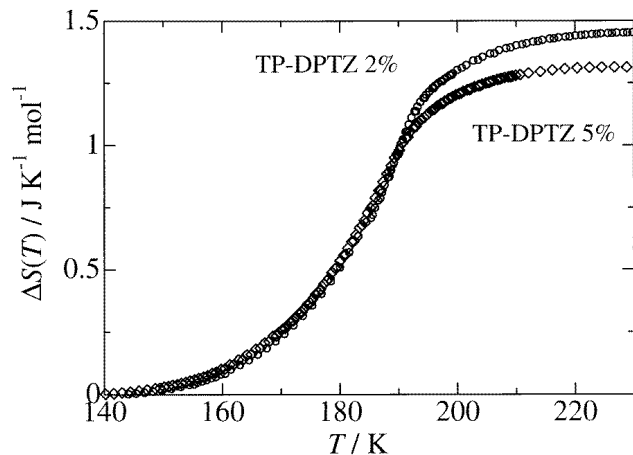
Figure 4. The temperature evolution of the excess entropies of TP-DPTZ 2% and 5%.

integrated values between the TP-DPTZ 2% and 5% well above the transition temperature, say at 230 K, indicates a change of the entropy of transition with the increase in DPTZ concentration from 2.05 to 4.87%. The difference is about 0.13 J K^{-1} mol^{-1}. This corresponds to 2.3% of $R \ln 2$, which is the entropy change in an order–disorder-type transition where the molecular conformation plays the role of an Ising spin variable. The value is slightly small, but favourably compared with the difference in the concentration of DPTZ (about 2.8%). It is noted that a similar analysis for pure *p*-terphenyl and the mixed crystals gives a larger estimate of the entropy of transition by about a factor of two. This agreement, though it seems rather poor at a glance, implies that the present data are consistent with the previous data for pure *p*-terphenyl [14] with an accuracy of the order of 0.1% of the absolute magnitude of the molar heat capacity. The agreement is, therefore, certainly tolerable if one takes into account the difference between the calorimeters used.

The above assessment clearly shows that the correct entropy of transition that is physically meaningful for the twist transition of *p*-terphenyl crystal is comparable to $R \ln 2$. The smaller values reported are due to the difficulty of deriving a physically correct baseline [14]. Since a displacive phase transition may involve a large entropy of transition for the strongly anharmonic potential that a particle 'senses' [1], it is logically incorrect to claim purely on the basis of the entropy of transition that the twist transition of *p*-terphenyl crystal is of order–disorder type. Taking into account the many experimental results that support the order–disorder nature of the phase transition [3–11], however, the result of the present entropic assessment should be regarded as indicating that the physically correct entropy of transition might be $R \ln 2$. The fact that the experimental entropy gain at the phase transition is smaller than the ideal value can be rationalized if a small contribution from outside the transition region assumed as the working area is taken into account. It is, therefore, concluded that the twist transition of *p*-terphenyl crystal is of order–disorder type, and that in it the conformation of an individual molecule behaves as an Ising spin.

The above feature seems to exert some effect on the reported values of the entropies of transition of the crystals of related compounds. Since deuteration of the *p*-terphenyl molecule has no appreciable effect on the transition mechanism [14], the inherent entropy of transition should also be $R \ln 2$ for deuterated *p*-terphenyls. Large entropies of transition in comparison with that for *p*-terphenyl have been reported for *p*-quaterphenyl [19] (C_6H_5-

C_6H_4–C_6H_4–C_6H_5) and 4, 4‴-difluoro-p-quaterphenyl [20] (F–C_6H_4–C_6H_4–C_6H_4–C_6H_4–F), whose crystals undergo twist transitions at 233 and 200 K [21], respectively. The inherent entropies of transition would also be $R\ln 2$, because the order–disorder character is stronger for the latter than for p-terphenyl judging from a systematic study of the twist phase transitions in a series of p-polyphenyls [20]. On the other hand, no effect is expected on the magnitude of the entropy of transition of crystalline biphenyl [22] (C_6H_5–C_6H_5), as the twist transition of biphenyl crystal is of displacive type and shows completely different behaviour upon formation of mixed crystals [23]. It is very interesting to see what occurs in crystalline 4, 4″-difluoro-p-terphenyl (F–C_6H_4–C_6H_4–C_6H_4–F), where the twist transition is believed to lie in the crossover region between the order–disorder and displacive types [21, 24]. An experiment along these lines is in progress in this laboratory.
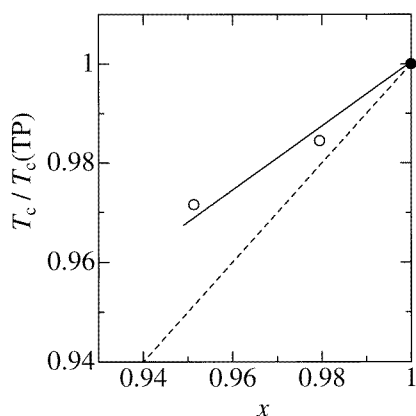

Figure 5. The concentration dependence of the twist phase transition temperature in the p-terphenyl–DPTZ system. The broken line indicates the dependence predicted by the mean-field approximation.

Before concluding this discussion, we briefly discuss the concentration dependence of the transition temperature. As is clearly seen in figure 2, the anomaly of the mixed crystals shows appreciable rounding as discussed above. The determination of the transition temperature is, therefore, not a simple task. It is, thus, assumed that the temperature at the top of the rounded peak coincides with the transition temperature. Then the transition temperatures of TP-DPTZ 2% and 5% are 190.5 K and 188.0 K, respectively. Figure 5 shows the concentration dependence of the transition temperature. The transition temperature shifts downward with increase in the concentration of DPTZ, as is often the case for order–disorder phase transitions. The broken line in figure 5 indicates the concentration dependence of the transition temperature in the case of the mean-field approximation. It is known that the mean-field approximation is exact if the spatial range of the interparticle interaction is infinite. Indeed, the concentration dependence reaches the line given by the mean-field approximation with growth of the range of the interparticle interaction [25]. There is no simple model that shows an order–disorder phase transition and gives a less steep concentration dependence than that of the mean-field approximation, as long as homogeneous distribution of impurities is assumed. The weak concentration dependence observed in the present study suggests, therefore, that the present mixed crystals are rather inhomogeneous. It is, however, emphasized again that the entropic assessment carried out in this study is still valid, as described in the introduction, even if the sample is inhomogeneous.

4. Conclusion

In order to determine the physically correct entropy of transition for crystalline *p*-terphenyl, the concentration dependence of the apparent entropy of transition was examined for TP-DPTZ mixed crystals by adiabatic calorimetry. The inherent, but virtual, entropy of transition was derived as $R \ln 2$ from this dependence, as many experiments support the order–disorder nature. The derived entropy of transition is larger by a factor of at least three than those reported previously, but clearly indicates that the conformation of the individual molecules behaves as an Ising spin. The concentration dependence of the transition temperature is weaker than that of the mean-field approximation, and suggests that the mixed crystals used in the present study are rather inhomogeneous.

Acknowledgment

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