

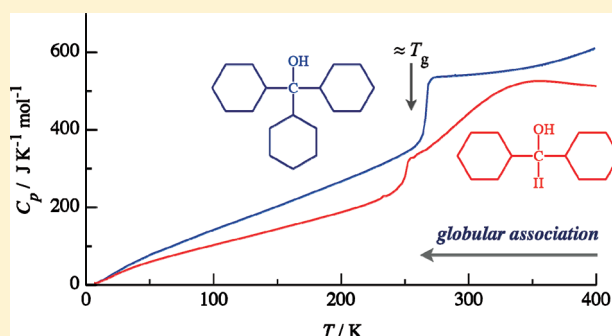
Calorimetric Study of Glass Transition in Molecular Liquids Consisting of Globular Associates: Dicyclohexylmethanol and Tricyclohexylmethanol

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S Supporting Information

ABSTRACT: Heat capacities of liquids and liquid-quenched glasses (LQGs) of dicyclohexylmethanol (DCHM) and tricyclohexylmethanol (TCHM) were measured by adiabatic calorimetry. Upon cooling the liquid compounds, they undergo glass transitions around 250 and 265 K, respectively. Temperature dependence of the FT-IR spectrum of TCHM liquid showed the gradual formation of dimers in the supercooled state with decreasing temperature. The magnitude of heat capacity jump at glass transition is discussed through a comparison with other low-molecular mass LQG. Combining the present results with previous heat capacity results on crystalline TCHM, residual entropies of LQG and standard thermodynamic quantities are established for both compounds.



INTRODUCTION

Glass transition is one of the most challenging issues in condensed matter science with a long history.^{1–3} One of main difficulties is the complexity of systems undergoing glass transition. Colloidal suspensions seem the simplest but far from dense liquid of real glass formers. Although some low-molecular mass liquids show a glass transition, most of them associate via hydrogen bonds (H-bonds), resulting in the formation of H-bonded network and/or chains. To advance the science of glass transition, it is essential to identify ideal (or model) compounds with reduced complexity. Knowing the association modes in the liquid and finding glass formers consisting of globular “particles” are strongly desired.

Dicyclohexylmethanol (DCHM) is an alcohol substituted with bulky cyclohexyl groups. The molecular structure is shown as an inset in the lower right corner of Figure 1. The crystal structure report says that H-bonds are only within a closed (cyclic) tetramer.⁴ In a previous study,⁵ the present authors found a pronounced hump in heat capacity and dielectric permittivity of the liquid DCHM. The detailed analyses of these and the temperature dependence of the Fourier transform infrared (FT-IR) spectrum indicated that the humps are due to the reconstruction of the closed tetramers on cooling. The intensity of the H-bonded OH band implied that most DCHM molecules (more than 95%) participate in the tetramer formation at a glass transition temperature ($T_g = 265$ K). The structure of the tetramer is, roughly speaking, globular, and there remains no H-bonding ability outside the tetramer. These imply that DCHM is a good candidate for a model glass former.

Tricyclohexylmethanol (TCHM, the inset in the upper left corner of Figure 1) is also an alcohol substituted with bulky

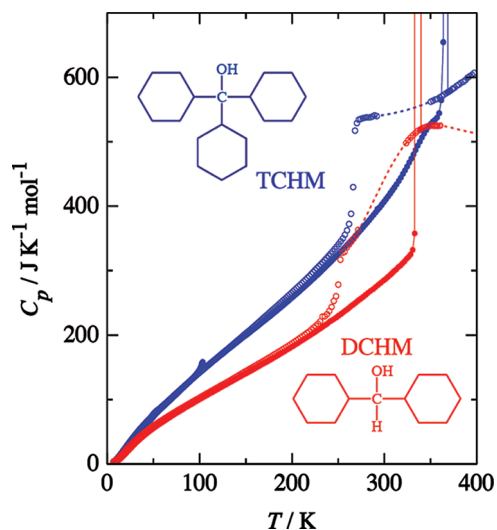


Figure 1. Measured molar heat capacities of DCHM (filled circle, crystalline L phase; open circle, liquid and LQG) and TCHM (filled circle, crystal; open circle, liquid and LQG). Molecular structures are also shown.

cyclohexyl groups. Due to their enhanced bulkiness, TCHM molecules can form only H-bonded dimers in crystal.^{6,7} At low temperatures below 103 K, the orientations of electric dipole

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moment align with antiferroelectric order having small spontaneous polarization (weak ferroelectricity).^{7,8} Although the H-bond survives in the paraelectric state even at room temperature,^{9,10} it starts to break below the melting temperature while keeping the crystalline form.⁷ In the liquid above the normal melting temperature, the H-bond was reported to be broken almost completely.¹¹ Considering the tetramer formation in liquid DCHM, it seems reasonable to imagine the formation of H-bonded dimers in the (supercooled) liquid of TCHM upon cooling. Preliminary experiments by using differential scanning calorimetry (DSC) showed that TCHM is a good glass former. Since the H-bond is possible only in a dimer due to the bulkiness, TCHM can also be a candidate of the ideal glass former, accordingly.

Although the importance of the dynamical nature of glass transition has long been discussed and clarified,^{1–3,12–14} the glass transition is surely a phenomenon related to thermodynamics and best manifested by a sudden jump of heat capacity (drop on cooling).¹² The analysis of the magnitude of the jump (ΔC) is, however, generally difficult in usual molecular liquid-quenched glasses (LQGs) because the basic unit “particle” is hard to identify owing to the complex association inside. On the other hand, at least in the case of DCHM, the unit should be a tetramer. In this paper, in addition to characterization of the association state in the supercooled liquid TCHM, heat capacities of DCHM and TCHM are reported. The results will be compared with other low-molecular mass LQGs.

EXPERIMENT AND CALCULATION

Commercial DCHM (Aldrich) and TCHM (TCI) were purified by fractional sublimation in vacuum. The final purities were determined cryoscopically by utilizing the melting point depression of crystalline phases as 99.88 and 99.55 mol % for DCHM and TCHM, respectively.

The calorimetric samples were sealed in a gold-plated copper calorimeter vessel under atmospheric helium gas. The mass of samples was ca. 2 g for each. The sample contributed to the total heat capacity, including that of the vessel by more than 20% throughout the temperature range covered in the present study.

Heat capacity was measured by the so-called intermittent-heating adiabatic calorimetry in the heating direction. The details of the calorimeter used can be found in the literature.¹⁵ The working thermometer mounted on the calorimeter vessel was a platinum resistance thermometer (Minco, S1059), the temperature scale of which is based upon the ITS-90.

IR spectra of TCHM were recorded while sandwiching the sample between two KBr disks using a JASCO FT/IR-550 between 80 and 360 K. The temperature was measured in the vicinity of the sample using a platinum resistance thermometer.

Vibrational analyses were performed quantum chemically (at the B3LYP/6-31Gd level) on energetically optimized structures in an isolated state.¹⁶ Target molecules were DCHM, TCHM, *o*-terphenyl (*o*TP), ethanol (EtOH), and toluene. For calculation of heat capacity of each intramolecular vibration mode, a factor 0.96 was commonly applied to the vibrational frequency obtained quantum chemically.

RESULTS AND DISCUSSION

1. Heat Capacities and Standard Thermodynamic Quantities. The calorimetric results in this study are shown in Figure 1 together with those of the crystalline TCHM

previously reported.⁷ The thermodynamic quantities of fusions are summarized in Table 1. By integrating the results for

Table 1. Thermodynamic Quantities Relevant to Fusion of Crystalline DCHM and TCHM

		$T_{\text{fus}}/\text{K}^a$	$\Delta_{\text{fus}}H_{\text{m}}/\text{kJ mol}^{-1}$	$\Delta_{\text{fus}}S_{\text{m}}/\text{J K}^{-1} \text{mol}^{-1}$	sample purity
DCHM	H phase	337.51(1)	20.69(1)	61.31(1)	99.88 mol %
	L phase	335.2(1)	[22.7] ^b	[67.6] ^b	
TCHM		367.40(1)	23.15(1)	63.00(1)	99.55 mol %

^aTemperature of fusion of the pure compound, estimated cryoscopically. Those of the calorimetric samples can be calculated in the framework of the melting point depression. ^bCalculated assuming that $S(\text{L phase}, 0 \text{ K}) = S(\text{H phase}, 0 \text{ K}) = 0 \text{ J K}^{-1} \text{mol}^{-1}$ (the third law of thermodynamics) and $T_{\text{fus}}(\text{L phase}) = 335.2 \text{ K}$.

crystalline state, standard thermodynamic quantities are calculated and given in the Supporting Information for both of DCHM and TCHM.

Prior to the measurements on liquid and LQG, the heat capacity of the crystalline states was measured for DCHM. Near the temperature of fusion of the as-prepared sample (335.2 K) of DCHM, the evolution of heat was encountered during the measurement. The sample after completion of the heat evolution exhibited a higher temperature of fusion than the as-prepared sample. This indicates the presence of crystal polymorphs. The phase with a lower temperature of fusion, i.e., the as-prepared one, is designated as the L phase, and the one with a higher temperature of fusion is designated as the H phase hereafter. According to thermodynamics, the H phase is more stable in the vicinity of the temperature of fusion. The measurement on the H phase could be conducted from the lowest temperature without any anomalous behavior such as heat evolution. The heat capacities of L and H phases are compared in Figure 2 together with that of LQG. The

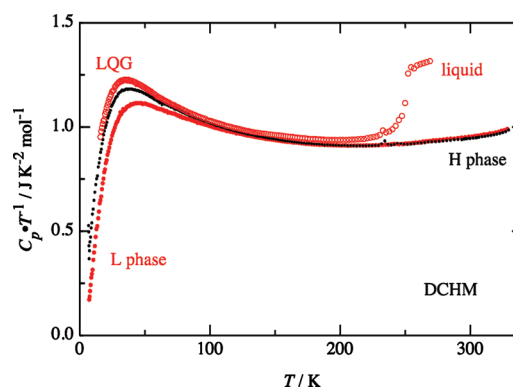


Figure 2. Heat capacities divided by temperature of crystalline L and H phases and LQGs of DCHM.

difference is notable only at low temperatures. This implies that the vibration of crystalline lattice (at low frequencies) differs notably in L and H phases, whereas intramolecular ones (at higher frequencies than the lattice vibration) do not. Roughly speaking, larger heat capacity reflects reduced stiffness due to less efficient packing of molecules. The largest heat capacity of LQG is also understood in this context, although a few exceptions have been reported.^{17,18}

The comparison of thermodynamic quantities (obtained by appropriate integrations of the calorimetric data) shows that the thermodynamic stabilities of the H and L phases is reversed around 320 K.¹⁹ Namely, the L phase is more stable over a wider temperature region below this expected temperature of transition including at the absolute zero. The prolonged time for adiabatic calorimetry was, however, insufficient to realize the phase transition between the L and H phases.

The absence of the heat evolution during measurements guarantees that the result is more reliable for the H phase. This is why the fusion of H phase was used for purity assessment (cryoscopy). It is noted that the entropies of two phases coincide with each other within an experimental error at the absolute zero. This implies that both phases obey the third law of thermodynamics [$S(0\text{ K}) = 0\text{ J K}^{-1}\text{ mol}^{-1}$]. There is no information concerning the reported crystal structure⁴ that corresponds to the two crystalline phases because this is the first report on the polymorphism of DCHM.

In accordance with the preliminary results by DSC, both compounds were easily supercooled and underwent glass transitions. After cooling to the lowest temperature, the heat capacities of LQGs were measured normally for DCHM and TCHM. Upon passing through the glass transition (softening), the supercooled liquids crystallized. On the other hand, the heat capacities of supercooled liquids could be measured from about 10 K below the temperature of fusion without crystallization. In the intermediate region, the temperature dependence of heat capacity was observed using a commercial DSC (TA, Q200) in cooling runs. After applying a small correction to the DSC results, the heat capacities of supercooled liquids were determined as shown by broken curves in Figure 1 as reported previously.⁵

As a quantity directly related to the frozen-in disorder, the residual entropies (enthalpies) of LQGs were calculated as $15.1\text{ J K}^{-1}\text{ mol}^{-1}$ (11.6 kJ mol^{-1}) and $10.5\text{ J K}^{-1}\text{ mol}^{-1}$ (7.1 kJ mol^{-1}) for DCHM and TCHM, respectively.

2. H-Bond in Liquid TCHM. To observe the effect of temperature on molecular association in TCHM, the IR spectra were recorded. Typical results are shown in Figure 3 together with the results on the crystal. Since the interest here is the H-bond, we concentrate our attention on the relevant regions (ca. 3500 cm^{-1} and 800 cm^{-1}). We can recognize gradual change in both regions upon temperature variation. It is well-known that the OH stretching frequency is around 3400 cm^{-1} in the bonded state for weak H-bonds such as OH–O, whereas it is around 3600 cm^{-1} in the free state.²⁰ The main band due to OH stretching in the crystal is definitely within the former region.

The temperature dependence of the population of the OH groups participating in H-bonds was estimated from the intensity of the OH stretching band around 3400 cm^{-1} . The ratio of the integrated intensities of the OH stretching band and the CH stretching bands (between 2900 and 3000 cm^{-1}) in the crystal was normalized to unity at the lowest temperature studied. The resultant temperature dependence is shown in Figure 4. The intensity of the crystal remains essentially constant below room temperature, and on heating, gradually decreases below the temperature of fusion, where a broad hump in heat capacity was observed. Upon the fusion, the corresponding band almost disappears in accordance with a previous report.¹¹

The OH stretching band gradually becomes stronger on cooling the liquid, as seen in Figure 3a. This clearly indicates

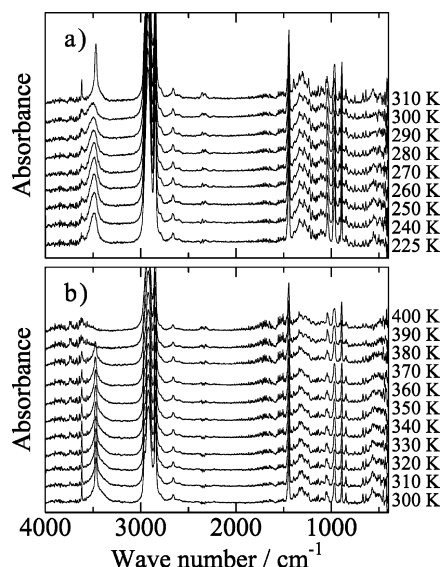


Figure 3. IR spectra at various temperatures of TCHM upon heating LQGs (a) and crystal (b). The spectrum at 310 K in panel a is of crystal formed from supercooled liquid, and those at 390 and 400 K in panel b are of liquid.

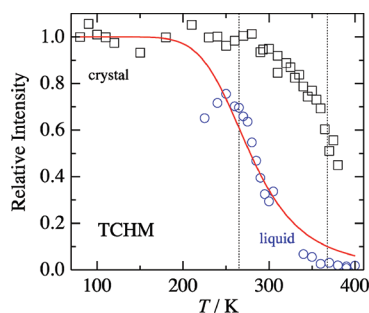


Figure 4. Normalized intensity of the OH stretching band at ca. 3400 cm^{-1} (circles) and the population of OH bonds participating in H-bonds calculated according to the model (dotted line).

the formation of H-bond dimers in the supercooled liquid. The population of the OH groups participating in the H-bonds gradually increases on cooling. It is about 0.7 at the glass transition temperature. This temperature dependence can be modeled by a simple two-state model (two-level system) with a degeneracy ratio of 8000 and an energy difference of 30 kJ mol^{-1} , which is acceptable as the energy of the H-bond in a dimer.²⁰ This model gives a large Schottky hump in heat capacity with a maximum of ca. $90\text{ J K}^{-1}\text{ mol}^{-1}$ around 265 K. Although one may be doubtful of its presence, the analysis in the next section clearly indicates its presence.

It is interesting to note that the glass transition to LQG in TCHM occurs at a temperature where the contribution of the H-bond to the heat capacity is significant in contrast to the case of DCHM.⁵ Since the time scales of H-bond formation/breakage and (simple) structural relaxation can, in principle, differ from each other, there is a possibility that the supercooled liquid of TCHM exhibits two separate glass transitions²¹ if the dynamical coupling between the two degrees of freedom is weak enough.^{21,22} Such a symptom is not discernible in the present experimental result. The degree of coupling will be clarified in the future through an experimental study of dynamical properties.

3. Heat Capacity of LQG. Properties of a glass transition are often compared in terms of T_g/T_{fus} and $\Delta C_p/C_{p,Cr}(T_g)$. These forms have been acceptable as a result of past struggles because some normalization is necessary for comparison. However, they are not rational enough to accept from a logical point of view. First, they are normalized by the quantities of a phase (crystal) other than the glass. Second, in $\Delta C_p/C_{p,Cr}(T_g)$, no distinction is made between relevant and irrelevant degrees of freedom to the glass transition. For example, we can easily imagine the following: Is the vibration of an atom encapsulated in a fullerene relevant to the (hypothetical) glass transition concerning the positional degrees of freedom (the formation of LQGs)? In this case, the atomic vibration certainly contributes to (total) heat capacity, but not to ΔC_p . No universality in the relative contribution of many degrees of freedom can be expected. Third, the preceding consideration leads to another issue: the heat capacity of a harmonic oscillator depends on temperature due to a quantum effect. Since some colloidal suspension, which is free from quantum effects, undergoes a glass transition, the effects should be accounted for before comparison.

Due to the difference in energy scale by an order of magnitude, intramolecular vibrational frequencies scarcely change depending on aggregation states, as exemplified in Figure 2 for two crystalline phases in DCHM and Figure 3 for liquid, LQGs, and crystals of TCHM. This implies that they are slightly involved in a glass transition. To incorporate this, the contributions of intramolecular vibrations were subtracted from the total heat capacities. The results are shown in Figure 5 for

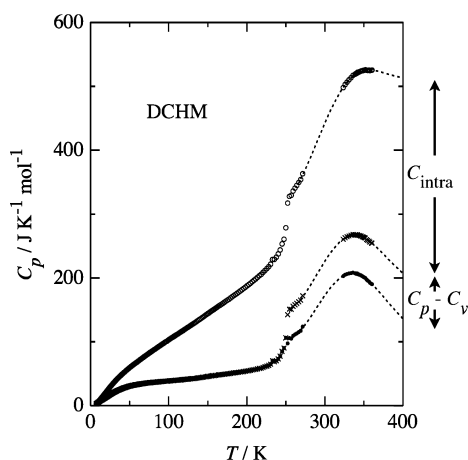


Figure 5. Correction on the C_p of liquid and LQGs of DCHM. Bars with arrowheads indicate the intramolecular contribution and $(C_p - C_v)$ correction, respectively.

DCHM as an example. For comparison, the same was applied to σ TP,²³ EtOH,²⁴ and toluene,²⁵ all for which heat capacity data as reliable as the present data were reported for the LQG state. The residual heat capacity of LQGs (shown in Figure 6) saturates to ca. $50 \text{ J K}^{-1} \text{ mol}^{-1}$ except for toluene, where the internal rotation of methyl groups can contribute to heat capacity by more than R (gas constant). The magnitude of saturated heat capacity is just the classical value $6R$ for three translational and three librational (rotational) vibrations per molecule.

What we have seen here is that the heat capacity of LQG around T_g can be understood similarly to that of crystals. Especially, the clear indication of heat capacity saturation to the

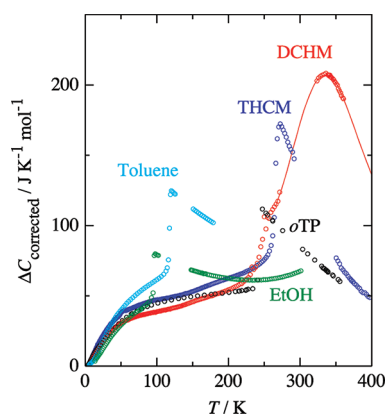


Figure 6. $(C_p - C_v)$ -corrected heat capacities of liquid and LQG of DCHM, TCHM, σ TP,²³ EtOH,²⁴ and toluene²⁵ after subtracting the heat capacities of intramolecular origins.

classical magnitude implies that the glass transition is a phenomenon to be understood not in the quantum but classical picture. Since the heat capacity is not anomalous around T_g , the magnitude of jump in heat capacity is governed by the heat capacity of supercooled liquids. It should be noted that there have been anomalous behaviors in heat capacity of amorphous solids (typically LQGs) at low temperatures in comparison with normal crystalline solids.^{26,27} The largest heat capacity of the LQG among three solid states of DCHM shown in Figure 2 is probably a symptom of this behavior.

4. Jump in Heat Capacity ΔC_p . Although the difference in molecular species is successfully corrected for LQGs by subtracting intramolecular contribution, ignoring possible effects of anharmonicity, there remains a pronounced difference in the residual heat capacity of liquid, irrespective of normal and supercooled states. Since the liquid phase is located at the higher temperature side of the LQG, the anharmonic effects of vibration are expected to be more effective. This can be corrected by applying the so-called $(C_p - C_v)$ correction. According to thermodynamics, the correction is given as $C_p - C_v = \alpha^2 VT/\kappa_T$, where α is the coefficient of volume thermal expansion, and κ_T is the isothermal compressibility. For ordinary organic liquids, α is typically ca. 10^{-3} , and κ_T is ca. 10^{-9} .²⁸ On the other hand, molar volume (V_m) differs significantly depending on compounds because $V_m = M_w/\rho$, where M_w is the molar mass, and ρ is the density (ca. 1.1 g cm^{-3}). As M_w is the only quantity that differs significantly depending on compounds, the $(C_p - C_v)$ correction becomes larger for compounds with a larger molecular size (within ordinary organic liquids). Indeed, the trend that larger heat capacity for a larger molecule can be recognized.

Since all of necessary quantities are not available for compounds, the $(C_p - C_v)$ correction was performed for only the liquids assuming the typical magnitude for each quantity mentioned above, yielding the results compared in Figure 6. Even applying the $(C_p - C_v)$ correction, the residual heat capacity of liquid is, at least around T_g , much larger than that of LQG, which is compatible with the classical magnitude expected for six harmonic oscillators. On heating, the residual heat capacity of liquids except for EtOH decreases notably, probably heading for $3R$ ($\approx 25 \text{ J K}^{-1} \text{ mol}^{-1}$), the heat capacity of the classical ideal gas consisting of molecules (having general shape). Although the decrease in heat capacity from $6R$ (assembly of classical oscillators in three translational and three librational degrees of freedom) to $3R$ (classical ideal gas

consisting of particles with rotational degrees of freedom) is rather easy to understand, the decrease starting from a much larger heat capacity than $6R$ in Figure 6 is certainly nontrivial. This issue should be resolved in the science of liquids.

Since the internal contribution and effects of anharmonicity were corrected, although approximately, and the resultant residual heat capacity of LQG is compatible with the classical magnitude of solids, the idealized jump in heat capacity can be determined by subtracting $6R$ from the residual heat capacities

Table 2. ΔC_p and ΔC (Corrected for Thermal Expansion for Liquid)

	T_g/K	$\Delta C_p/J\ K^{-1}\ mol^{-1}$	$\Delta C/J\ K^{-1}\ mol^{-1}$	N^a
DCHM	250	90	56	4
TCHM	265	155	122(36) ^b	<2
<i>o</i> TP ²³	235	118	62	4
EtOH ²⁴	97	39	30	4
toluene ²⁵	117	64	56	7

^aCluster size at T_g . For *o*TP, EtOH, and toluene, it is assumed to be the same as the number of molecules in the CRR.^{23,25} That of EtOH was calculated using the data in the literature.²⁴ ^bThe value in parentheses is that after the correction for the effect of H-bond breakage in terms of the two-state model explained in the text.

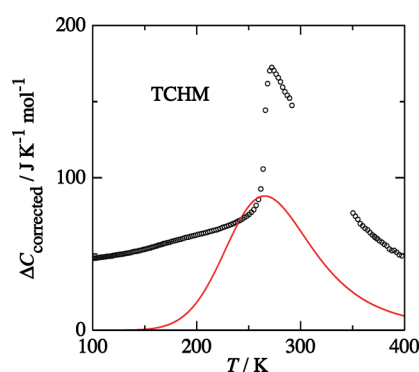


Figure 7. Schottky heat capacity according to the H-bond model (solid line) and $(C_p - C_v)$ -corrected heat capacities of liquid and LQGs of TCHM after subtracting the heat capacities of intramolecular origins.

of supercooled liquid except for toluene. From the residual heat capacities in Figure 6, ΔC is deduced as summarized in Table 2. The ΔC for TCHM ($122\ J\ K^{-1}\ mol^{-1}$) is about twice as large as those of other compounds. If the breakage of the H-bond upon the destruction of dimers is taken into account (Figure 7), the ΔC is reduced to $36\ J\ K^{-1}\ mol^{-1}$, which is comparable to those of other compounds.

It is emphasized that ΔC in Table 2 is expressed on a “per mol of molecule” basis. There are no reasons why we should compare the ΔC in this unit. Indeed, the LQG is characterized by the presence of midrange order. The correlation length and/or the size of the correlated reorienting region (CRR) are often used as parameters characterizing the midrange order. The CRR is a kind of structural cluster present in the supercooled liquid undergoing a glass transition. The CRR has been reported to consist typically of few to several molecules. In the cases of DCHM and TCHM, on the other hand, the sizes of cluster formed by H-bonds are 4 and 2 (in maximum) as evidenced by the IR spectra. If the size of cluster is a governing parameter of the behavior of liquids, at least, monotonous correspondence is expected between the size of the cluster and

the jump in heat capacity at a glass transition. However, no correlation can be found in the magnitude of ΔC in Table 2. This may be rationalized most naively as follows: The properties of liquids are so compound-specific that no common behavior is observed in thermodynamic properties because the hypothetical glass transition, which should exhibit some universality, cannot be reached by the kinetics, which strongly depends on compounds.

CONCLUDING REMARKS

The analyses of the heat capacities of liquids and LQGs of two organic compounds, DCHM and TCHM, show that the heat capacity of LQGs can be understood similarly to those of crystalline solids, whereas that of liquid cannot, even if the correction for thermal expansion is applied. On the basis of this fact, it is concluded that the glass transition is a phenomenon to be understood in the classical view of nature, and that the jump in heat capacity at T_g , which is regarded as an important parameter characterizing glass transitions, is governed by the heat capacity of supercooled liquid. Even considering the size of clusters around T_g , a coherent comparison of the jump in heat capacity seemed difficult. Since the effect of H-bond formation/destruction on physical properties is notable in DCHM and TCHM, investigations on their dynamical properties are especially interesting in relation to the dynamical nature of glass transition.^{1–3,13,14} An experimental study along this line is underway in this laboratory.

ASSOCIATED CONTENT

Supporting Information

van't Hoff plots for cryoscopic assessment of sample purities, and standard thermodynamic quantities (calorimetric entropy, enthalpy and Gibbs energy). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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