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Glass transition and structural relaxation of intermediate liquids by MDSC and dielectric spectroscopy

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Abstract

The behavior of liquid–glass transition and structural relaxation of several intermediate glass forming liquids was investigated by means of MDSC and dielectric measurements. The MDSC scan for the monomer and its oligomers of propylene glycol and propylene glycol monomethyl ether shows a step-like increase in a real part of heat capacity and a peak in an imaginary part of heat capacity. The glass transition temperature is defined as a peak point of an imaginary part of heat capacity. The calorimetric relaxation behavior was in agreement with the dielectric relaxation behavior. This fact indicates that the rotational behavior of molecules at a liquid state also plays a dominant role in a glass transition phenomenon. The glass transition temperature is controlled by both the molecular weight and the number of hydroxyl end groups. The change of glass transition temperature of several alcohols was discussed in terms of two order parameter model, using density and bond order parameters. The packing effect by alkyl group in alcohol influences the density which is controlled by the isotropic interaction among molecules. The presence of hydroxyl group controls mainly the anisotropic bond order parameter. The frustration between these two order parameters datermines the physical properties of glass-forming liquid through a glass transition.

Keywords: MDSC; Complex heat capacity; Glass transition; Slow dynamics; Two order parameter model

1. Introduction

Recently, extensive theoretical and experimental efforts have been made to study the slow structural dynamics in glass-forming materials [1–3]. They are, however, still far from satisfaction because there is still neither a generalized model nor theory to explain a glass transition completely. Differential scanning calorimetry (DSC) is a well-known conventional tool to define a glass transition at a calorimetric glass transition temperature, T_g. This phenomenon is the vitrification process from an equilibrium liquid to a non-equilibrium glass state. The α relaxation is characterized by the slow dynamics near a glass transition temperature. The relaxation time reaches 100 s at a glass transition temperature. This temperature is called as a dynamic glass transition temperature. This glass transition is related to the structural relaxation process of liquid and supercooled liquid. This relaxation process can be observed by the frequency dependent measurement, especially broadband dielectric permittivity measurement.

The measurement of a frequency dependent specific heat is one of the most useful tools in the study of both a glass transition and relaxation process [4]. In modu-

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lated temperature differential scanning calorimetry (MDSC), a small sinusoidal temperature perturbation is superimposed to the conventional DSC run [5,6]. The further developments of MDSC have been reported by various groups [7–13].

According to the Angell's classification, liquids can be classified as two limiting categories; strong and fragile liquids [14,15]. This classification is based on the temperature dependent mechanical or relaxational behavior of a supercooled liquid state. The relaxation aspects of strong and fragile liquids can be described by the Arrhenius and Vogel–Tammann–Fulcher (VTF) laws [16–18], respectively. The studies on intermediate liquids between strong and fragile liquids have been focused on attention as the main topic on the study of a liquid–glass transition. Since it is related to the inter-molecular cooperativity. Understanding of the glass transition and relaxation dynamics in a simple molecular liquid is very important to clarify the dynamic properties of more complicated system. One of the simple molecular liquids is alcohol, which consists of alkyl and hydroxyl groups.

In the present study, we focused on attention about the role of end group in alcohol related to the relaxation behaviors of a glass transition. To perform this objective, the substitution of –OH for $-OCH_3$ groups was investigated. It was carried out by the measurements of the complex heat capacity $C_p^*(\omega, T) = C_p'(\omega, T) - iC_p''(\omega, T)$ and dielectric permittivity $\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T)$. The samples studied are propylene glycol (PG) monomer and its oligomers, propylene glycol monomethyl ether (PGME) monomer and its oligomers. The liquid–glass transitions and relaxation behaviors of these glass-forming materials were discussed on the basis of the two order parameter model proposed by Tanaka [19,20].

2. Experimental

In MDSC, a sinusoidal temperature is superimposed as an external perturbation upon an underlying linear temperature change, so that a sample temperature, $T(t)$, at time t is given by,

$$T(t) = T(0) + qt + A\sin\left(\frac{2\pi t}{P}\right) \tag{1}$$

where $T(0)$ is an initial temperature for an MDSC scan, q (K min^{-1}) the underlying heating rate, A the amplitude of temperature modulation and P (s) the modulation period. Total heat flow from MDSC can be decomposed into two parts as given by the following equation:

$$\frac{dQ}{dt} = \left|C_P^*(t)\right| \frac{dT}{dt} + f(T, t) \tag{2}$$

where $C_p^*(t) = C_p'(t) - iC_p''(t)$ is a complex heat capacity and $f(T, t)$ the kinetic component. The first term is reversing heat flow and the second term is non-reversing heat flow. The heat capacity obtained from the conventional DSC scan is $|C_p^*(\omega)|$. The complex heat capacity can be explained as follows: The C_p' component originates from the component of heat flow which is in-phase with the temperature modulation. The C_p'' component of a heat capacity arises from an out-of-phase response of a sample or from an enthalpy dissipation processes. The MDSC measurements (DSC-2920, TA Instruments) was used to investigate thermal and dynamic properties of liquids. The sample was encapsulated in an aluminum pan and loaded into an MDSC dynamic sample chamber at room temperature. The weight of samples were between 10 and 20 mg. It was an first cooled through T_g down to 118 K at a constant cooling rate of 5 K min^{-1} with the modulation amplitude of 1.326 K every 100 s. The sample was kept at the isothermal 118 K for 10 mm and then heated to 273 K through a glass transition region with the same ramp and modulation with the cooling case. The purge gas, which flows through a sample chamber during the experiment, was dry helium with the flow rate of 25 cc min^{-1}. Using of helium as a purge gas makes the heat flow phase baseline become flat.

Another measurement system for the study of slow dynamics is the dielectric permittivity spectroscopy. To cover the broad frequency range from 10 mHz to 10 GHz, two kinds of systems were used in this work; the Impedance/Gain-phase analyzer (Solartron SI 1260) in low-frequency range from 10 mHz to 10 MHz and the time domain reflectometry (TDR) system (HP54750A digital oscilloscope and HP54754A differential TDR plug-in) in high frequency range from 1 MHz to 10 GHz. The detailed system was already reported elsewhere [21].

The samples studied are PG and its oligomers with two –OH groups, PGME and its oligomers with a –OH and a $-OCH_3$ groups. That is, both PG and PGME family have the same chemical backbone of $[OCHCH_3CH_2]_n$, however, the different end groups such as $H[OCHCH_3CH_2]_nOH$ or $H[OCHCH_3CH_2]_nOCH_3$. Both PG (76.10 g mol^{-1}) and PGME (90.12 g mol^{-1}) were purchased from Wako Pure Chemical Industries, tri-PG (tPG, n=3, 192.26 g mol^{-1}), di-PGME (dPGME, n=2, 148.20 g mol^{-1}) and tri-PGME (tPGME, n=3, 206.28 g mol^{-1}) were purchased from Tokyo Chemical Industry.

3. Results

Fig. 1 represents the reversing heat capacity (C'_p) and kinetic heat capacity (C''_p) for PGME. Since magnitude of the heat capacity is mostly stemmed from the C'_p except in a glass transition region, $|C^*_p|$ is nearly the same with that of C'_p. Complex heat capacity shows characteristic features that a step-like increase in C'_p and a peak in C''_p around a liquid–glass transition. The mid-point of C'_p is T_g and a peak of temperature in C''_p is T_{gc}. The kinetic heat capacity can be well fitted by the Gaussion function,

$$C''_p(T) = \frac{A}{\sqrt{2\pi}\Delta T}\exp\left[-\left(\frac{T-T_{gc}}{\Delta T}\right)^2\right] \tag{3}$$

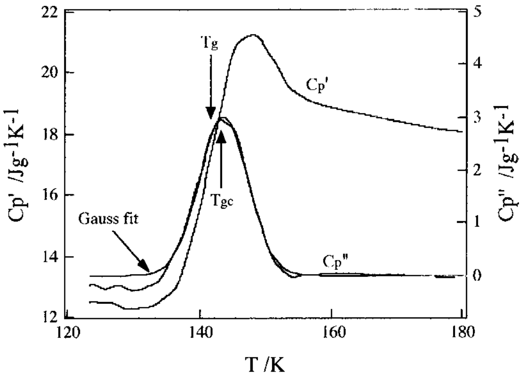

Fig. 1. The reversing heat capacity, C'_p, and kinetic heat capacity, C''_p, for PGME in the heating process obtained by MDSC with q=5 K min^{-1}, A=1.326 K and P=100 s. Two glass transition temperatures, T_g and T_{gc}, are the mid-point of total C_p (which is nearly the same as C'_p) and the peak temperature of C''_p, respectively. The kinetic heat capacity is fitted by a Gauss function.

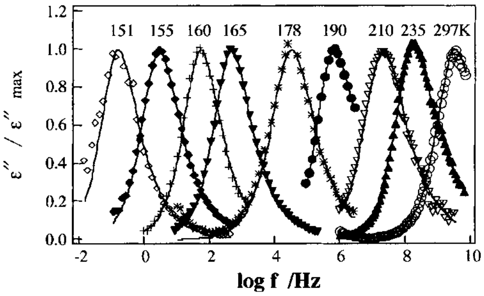

Fig. 2. The dielectric spectrum for PGME. The above number means the measured temperature (K). The solid lines are the best fits by the Havriliak–Negami function.

T_{gc} can be compared with the other dynamic glass transition temperature determined by the dielectric spectroscopy. The temperature where α relaxation time becomes 100 s is defined as the dielectric glass transition temperature, T_{gd}. The dielectric relaxation time was obtained from the dielectric loss spectra. For example, the dielectric loss spectra for PGME are illustrated in Fig. 2. ε''_{max} is the maximum value of the dielectric loss at a relaxation frequency f_{max}. This loss peak is in inverse proportion to the relaxation time, $\tau=(2\pi f_{max})^{-1}$, which was determined by the best fit to the spectra by the Havriliak–Negami (HN) empirical function [22],

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1+(i\omega\tau)^\alpha]^\gamma} \tag{4}$$

where ε_∞ and ε_s are the highest and lowest limit of angular frequency ω, respectively. In the lower frequency range, the temperature dependence of relaxation time could be well described by the VTF function given by

$$\tau_{max} = \tau_0 \exp\left[\frac{B}{(T-T_0)}\right] \tag{5}$$

where T_0 is the Vogel–Fulcher temperature. T_{gd} was determined by using this function. The temperature dependencies of relaxation time obtained by dielectric and calorimetric measurements are shown in Fig. 3. It is found like that the calorimetric results are on the extension of dielectric results within experimental uncertainty. The observed values are listed in Table 1. Both dynamic glass transition temperatures, T_{gc} and T_{gd}, are same within experimental uncertainty. The calorimetric T_{gc} includes total degree

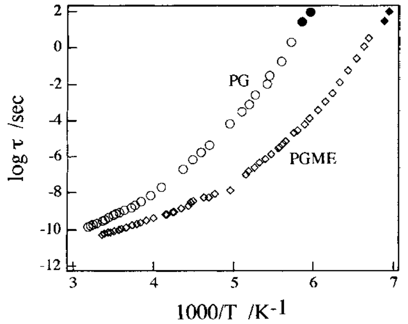

Fig. 3. Arrhenius plots for PG and PGME, log τ vs. 1000/T. The dielectric (open) and calorimetric (filled) results are coincided on the same line.

Table 1
Glass transition temperatures obtained by calorimetric and dielectric methods

Materials	Calorimetric T_{gc}	Dielectric T_{gd}
PG	168.1	169
tPG	193.6	192
PGME	144.1	146
dPGME	163.3	164
tPGME	174.1	172

of freedom such as rotation, diffusion and vibration, while the dielectric T_{gd} originates only from the reorientation of molecules. This fact strongly indicates that the main molecular motion of α relaxation near the glass transition region may be the reorientation of molecules.

4. Discussion

The molecules of alcohol are connected with adjacent molecules via the hydrogen bonding. This bonding can make molecules form inter- and intramolecular structures such as inter-molecular rings, branched structures and longer chain. The attractive interaction between molecules controls the dynamic behavior of glass transition and slow dynamics. Recently, based on the Ginzburg–Landau model, two order parameter model was introduced by Tanaka and applied to the dynamics of a liquid–glass transition of water and glass forming liquids [19]. This model took consideration on the effective attractive interaction potential among molecules. The potential is generally given by the superposition form of isotropic part of the interaction $\langle V\rangle$ and its anisotropic part ΔV: $V(r, \Omega)=\langle V\rangle(r)+\Delta V(r, \Omega)$, where r is the distance from the center of mass of the molecule and Ω represents the orientation. The latter anisotropic part causes a locally favored structure which consists of a molecule and its neighboring n molecules. Two different types of structure are generally favored in a liquid. One is favored by $\langle V\rangle$ and the other is favored by ΔV. According to this model, the dynamics of a liquid–glass transition is ruled by the two order parameters, i.e. density and bond order parameters. The former is associated with the isotropic interaction and has a role in minimizing the inter-molecule distance, packing the molecules closely and representing the long-range density ordering. On the other hand, the latter maximizes the local bonds and leads to locally favored structure which is sometimes contrary to that of the crystallization. The vitrification or crystallization is sometimes the results of the frustration between these two order parameters.

In this point of view, the alkyl group and the hydroxyl group in alcohol may play essential roles as density and bond order parameters, respectively. The characteristic index of relaxation behavior such as fragility and a glass transition temperature can be ruled by these two order parameters. From the calculation of the fragility [23], $F_{1/2}=2T_g/T_{1/2}-1$, where $T_{1/2}$ is the temperature $\tau=10^{-6}$ s, it was found that the fragility increases with the increase of the molecular weight and decreases with the density of the hydroxyl group in a molecule. That is the outline why the relaxation dynamics is ruled out by both the bond and density order parameters. The details will be discussed elsewhere [24]. The similar trend appears as far as the relationship holds between a glass transition temperature and molecular weight as shown in Fig. 4. The samples are the monomer and oligomers of PG and PGME family. For the PG family, the results of polypropylene glycol (PPG) with molecular weight of 425, 725, 2000 and 4000 g mol^{-1} are added. The molecular weight dependencies of T_g for PG and PPGs were attributed [21,25]. It is based on the free volume theory [26] which predicts the relation, $T_g \propto -1/\mathrm{Mw}$. It shows only the role of density in a liquid–glass transition. To know the dependence of T_g with two order parameters, T_{gc} for PG and PGME family was

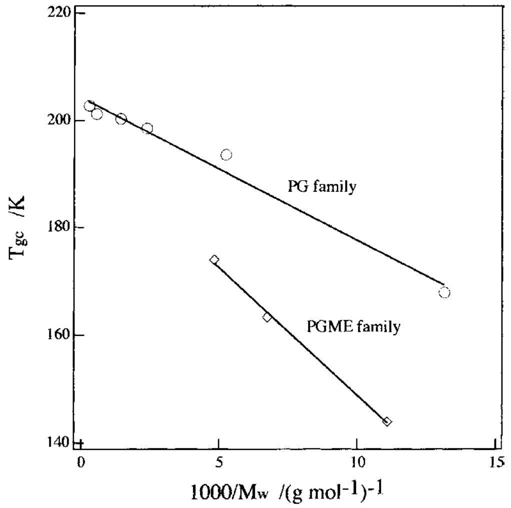

Fig. 4. The values of T_{gc} for PG (○) and PGME (◇) families are drawn in terms of molecular weight (Mw). The solid lines are the fits of T_g=$A-B$/Mw.

expressed in terms of inverse Mw in Fig. 4. These temperatures were obtained from the kinetic heat capacity in MDSC scan.

The larger difference of T_{gc} between PG and PGME monomers indicates the important roles of the hydroxyl group as the bond order parameter. The difference of T_{gc} between PG and PGME oligomers decreases with increasing molecular weight. It can be originated from the fact that the hydroxyl group play a minor part to determine T_{gc} because hydroxyl groups cannot control any larger structure. It is reasonable that the methyl or alkyl groups act as the density order parameter. So that, it can be concluded that the frustration between bond and density order parameters controls T_{gc}.

The forming of hydrogen bonding makes the anisotropic interaction and leads the liquid to be stronger. The strong anisotropic interaction among molecules can affect a glass transition temperature and dielectric strength. The dielectric strength is the difference of two limit dielectric constants ε_s and ε_∞ in Eq. (4). The orientational correlation between a molecule and its neighboring molecules has been established by Kirkwood and Frohlich. It is given by [27,28]

$$\boldsymbol{\mu} \cdot \boldsymbol{\mu} = g\boldsymbol{\mu}^2 \qquad (6)$$

where $\boldsymbol{\mu}$ is a dipole moment vector. The index of g is related to an orientational dipole–dipole interaction. The anisotropic interaction can be represented as g-factor. However, g cannot fully describe orientation of the dipoles [29]. The increase of the number of hydroxyl groups gives rise to the increase of a glass transition temperature. In Fig. 4, it is shown that the difference of the glass transition temperature between PG and PGME family is near 20–30 K in the molecular weight range studied, provided the same molecular weight. It indicates that a hydroxyl group per molecule affects a glass transition temperature to shift 20–30 K and its influence becomes weak with increasing molecular weight.

On the other hand, the packing effect of the alkyl groups in the PG or PGME monomer or oligomers has the influence to minimize the distance between molecules. The isotropic packing effect increases with increasing the repeat unit. Even though the repeat unit increases further, however, the evaluating rate of T_{gc} becomes small. This effect makes the feature of T_{gc} have a saturation at some higher molecular weight. The isotropic interaction in the higher molecular weight region suggests that the glass transition is likely to be saturated above that of PPG72S [21].

5. Conclusion

The features of glass transition and structural relaxation of PG and PGME monomer and their several oligomers were discussed on the basis of two order parameter model. The glass transition and slow dynamics are characterized by a glass transition temperature with molecular weight and number of hydroxyl groups. These relaxation behaviors are explained by the frustration between the density and bond order parameters. The presence of hydroxyl groups in alcohol controls mainly the anisotropic bond order parameter and the packing effect for alkyl groups by the isotropic interaction among molecules influences the density.

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