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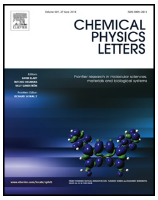

Difference in variation of glass transition activation energy between 1,2-propanediamine and 1,2-propanediol

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ABSTRACT

Variations of the effective activation energy (E_α) throughout the glass transition were determined for 1,2-propanediamine (12PDA) and 1,2-propanediol (12PDO) by applying an isoconversional method to differential scanning calorimetry (DSC) data. E_α was found to markedly decrease throughout the glass transition of 12PDA, whereas such drastic change in E_α was not observed for 12PDO. Although the two simple liquids are similar in molecular structure and size, their trends in E_α and fragility m throughout the glass transition can be quite different. The significant disparity in the kinetic parameters can be caused by differences in hydrogen-bonding structure between 12PDA and 12PDO.

1. Introduction

Kinetics of glass transition are often understood based on fragility and structural relaxation activation energy near the glass transition temperature (T_g). Some glass-forming liquids with constant activation energies above T_g are classified as strong liquids [1]. On the other hand, some liquids that deviate from Arrhenius behavior are fragile and are often described by VFT equations [2–4]. The deviation from Arrhenius behavior is characterized by dynamic fragility, m [5]. In general, the value of m is small for strong liquids such as inorganic oxide glasses but large for fragile ones such as polymers.

The glass transition activation energy (E_α) has been determined for various materials based on the heating-rate dependence of T_g using differential scanning calorimetry (DSC) [6–9]. E_α variations have been discussed in relation to fragility. Some fragile liquids have been found to exhibit a large E_α, which markedly decreases with an increase in temperature throughout the glass transition [10].

The structural relaxation kinetics near T_g have been explained using the Williams–Landel–Ferry (WLF) equation [11]. The WLF equation has been used for predicting the activation energy of a variety of polymeric glass-forming liquids with a simple universal representation [11].

Hydrogen-bonding liquids often have an intermediate value of m, which widely varies depending on the type of materials [5,12]. For example, we previously determined the fragilities of 1,2-propanediol (12PDO) and 1,2-propanediamine (12PDA) from DSC measurements [13,14]. Although these two hydrogen-bonding liquids are similar in molecular structure, except in terms of the types of functional groups involved in the hydrogen bonds, a large difference in fragility was identified between them. Thus, a significant difference in their respective changes in E_α during the glass transition can be expected.

To investigate variations in E_α throughout the glass transition, Vyazovkin et al. [7,10] proposed an isoconversional method for the DSC data. The method was deemed applicable for some typical polymers. However, for small non-polymeric simple liquids, the variation in E_α during the glass transition is not completely understood. In this study, we investigate the difference in the activation energies of 12PDA and 12PDO during the glass transition. Based on the results, we attempt to explain the difference in terms of hydrogen-bonding networks and fragility. Moreover, we verify the applicability of the WLF model to the two glass-forming liquids and then examine an empirical correlation of the variation in E_α with fragility.

2. Materials and methods

12PDA (purity > 95%) and 12PDO (purity > 99%), purchased from Wako Pure Chemical Industries, Ltd., were individually purified by vacuum distillation. A drop of each liquid pipetted by a Pasteur pipette was sealed in an aluminum pan (0219-0062ALUM., Perkin Elmer, Inc., ca. 24 mg) at room temperature under a dry nitrogen atmosphere to minimize contamination by water and CO_2 vapor. The weight of the sealed samples of 12PDA and 12PDO were 3.35 and 1.03 mg, respectively.

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DSC measurements were performed using a power-compensated DSC (DSC8500, Perkin Elmer, Inc.) under a flow of helium gas. First, the samples were heated from room temperature to 323 K and held at this temperature for 3 min to ensure the same thermal history. Next, the liquid samples were cooled to 50 K below T_g at the rate of $\beta = 5$, 10, 20, 50, and 100 K min^{-1} to obtain glassy samples. After holding 50 K below T_g for 1 min, the glassy samples were reheated to 50 K above T_g at the same rate of β. The glass transition was measured at each heating scan. The DSC equipment was calibrated for each heating rate with cyclohexane and indium prior to the measurements.

To evaluate variations in E_α during the glass transition, we applied the advanced isoconversional method proposed by Vyazovkin [15] to the DSC data measured at different heating rates. The activation energy was determined for each specified extent of conversion (α) as the E_α value minimizes the following function $\Phi(E_\alpha)$

$$\Phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (1)$$

where n is the number of heating programs used, and J is defined as follows:

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] \mathrm{d}t \quad (2)$$

The α is determined as the normalized heat capacity change defined as [6]

$$\Delta C_p^N = \frac{\left(C_p - C_p^{\mathrm{g}}\right)|_T}{\left(C_p^{\mathrm{liq}} - C_p^{\mathrm{g}}\right)|_T} \equiv \alpha \quad (3)$$

where C_p is the observed heat capacity at T during the glass transition, and $C_p{}^{\mathrm{g}}$ and $C_p{}^{\mathrm{liq}}$ are the glassy and equilibrium liquid heat capacities, respectively.

3. Results and discussion

3.1. Glass transition

Figure 1 shows DSC data for the glass transition of 12PDA and 12PDO obtained at a standard scan of 10 K min^{-1}. For comparison, the curves are shown in terms of heat capacity normalized by sample mass. While heating 12PDA, an exothermic anomaly due to crystallization was observed above 170 K after the glass transition. The heat capacity of 12PDA was found to change to a greater extent than that of 12PDO during the glass transition. T_g was determined to be 144.1 K and 167.3 K for 12PDA and 12PDO, respectively; the values were in good agreement with previous results [13,14].

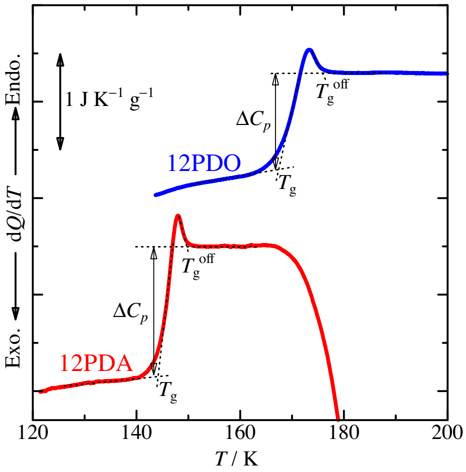

Figure 1. DSC heating curves for glass transitions of 1,2-propanediamine (12PDA) and 1,2-propanediol (12PDO) obtained at a heating rate of 10 K min^{-1}. Each curve is normalized by the sample mass and is vertically offset for clarity. T_g and T_g^{off} are onset and offset glass transition temperatures, respectively, and ΔC_p represents the heat capacity increase at T_g.

The temperature width of the glass transition measured by DSC was used as a rough measure of fragility [16,17]. The relaxation time of a fragile glass former is known to rapidly change with temperature and thus will have a narrow T_g window. The extrapolated glass transition offset temperatures (T_g^{off}), defined as the temperature at which the overshot due to enthalpy recovery finishes above T_g, were determined to be 149.8 K and 175.9 K for 12PDA and 12PDO, respectively. The glass transition width, defined as $T_g^{\mathrm{off}} - T_g$, was 5.7 K for 12PDA and 8.6 K for 12PDO at the heating rate of 10 K min^{-1}. The results corroborate earlier assertions that the fragility of 12PDA is larger than that of 12PDO [13,14].

The change in heat capacity during the glass transition has been studied in terms of molecular motion and association. Although a coherent comparison between different compounds in the jump in heat capacity at T_g seems difficult because the thermodynamic properties of liquids strongly depend on chemical substances [18], a large heat capacity increase during the glass transition can be interpreted as an abrupt change in molecular motional or configurational degrees of freedom [14,18]. The heat capacity increase at T_g is 101.9 J K mol^{-1} for 12PDA, which is larger than the increase of 73.7 J K mol^{-1} for 12PDO. From the results, we suggest that the changes in molecular kinetics and association during the glass transition of 12PDA are more drastic than those of 12PDO.

3.2. Variation of activation energy

Using Eq. (3), the normalized heat capacity changes of 12PDA and 12PDO were obtained for each heating scan as shown in Figures 2 and 3, respectively. The increase in the heat capacity due to the glass transition gradually shifts to higher temperature with increasing β. The shift in temperature over which the heat capacity increased during the glass transition was found to be narrower for 12PDA compared to that of 12PDO. For example, at $\alpha = 0.5$, the width of the shift was 2.2 K for 12PDA and 4.9 K for 12PDO for this heating-rate range. Figure 4 shows the estimated variations of E_α with α after applying the isoconversional method to the ΔC_p^{N} vs. T curves.

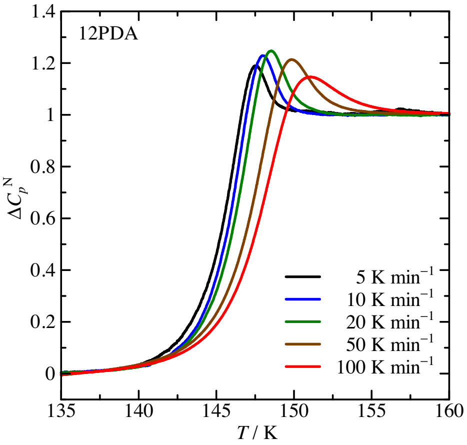

Figure 2. Normalized heat capacity change for the glass transition of 12PDA at different heating rates.