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Effects of adding $LiBF_4$ on the glass-transition kinetics of 1,2-propanediol

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By applying an isoconversional method to differential-scanning calorimetry (DSC) data, we have discovered that the addition of $LiBF_4$ significantly affects the activation energy E_α of the glass transition of 1,2-propanediol. Depending upon its concentration, the dynamics of the glass transition are affected more by adding $LiBF_4$ at an early stage of the glass-to-liquid transition rather than at later stages. As the mole fraction x of $LiBF_4$ increases, the value of E_α initially increases, but it decreases dramatically during the glass transition. The abrupt decline in E_α suggests that the addition of $LiBF_4$ breaks cooperative rearranging motions into smaller parts. The expansion of cooperativity, and its fragmentation with increasing temperature, can be explained in terms of competition between the hydrogen-bond networks of the alcohol solvent and the ionic interactions due to the added salt. The variability of E_α with temperature is found to correlate exponentially with the dynamic fragility.

1. Introduction

The concepts of fragility and of the activation energy associated with structural relaxation are widely used for understanding the kinetics of the glass transition. Some glass-forming liquids, for which the activation energies seem to be constant above the glass-transition temperature T_g, are classified as “strong liquids” [1]. Conversely, liquids that deviate from Arrhenius behavior are termed “fragile” and are often described by the VFT equations [2–4]. The deviation is characterized by a “dynamic fragility index,” m [5], which is defined as the slope in the plot of the logarithmic mean relaxation time versus the change in reciprocal temperature at T_g.

Fragility is known to vary widely among materials, as it depends strongly on the nature of the intermolecular interactions [5,6]. Strong liquids, which are likely to form a three-dimensional network of covalent bonds, have small values of m, whereas fragile liquids, which are mainly controlled by nondirectional interactions such as ionic bonds or van der Waals forces, have large values of m. Hydrogen-bonded liquids often have fragilities intermediate between those typical of strong liquids such as SiO_2 ($m = 20$) and fragile ones such as *o*-terphenyl ($m = 81$) [5]. Using differential-scanning calorimetry (DSC), we have previously determined the fragility of 1,2-propanediol (12PDO) to be $m = 53$ [7]. This is quite different from that of 1,2-propanediamine (12PDA) ($m = 123$) [8], even though these liquids differ only in the types of functional groups involved in the hydrogen bonds.

A simple, universal representation of the structural relaxation kinetics of glass-forming liquids is provided by the Williams–Landel–Ferry (WLF) model [9]. The WLF equation has been used to predict the activation energy above T_g for a variety of polymeric glass-forming liquids.

The activation energy of the glass transition has also been determined by DSC measurements for various materials based on the heating-rate dependence of T_g [10–15]. Vyazovkin et al. [12,13,16] proposed an isoconversional method to account for variations in the activation energy E_α with the extent of conversion (α). They investigated variations in E_α during the glass transition by applying this method to DSC data. Typical fragile polymers were found to exhibit large activation energies E_α, which decreased markedly during the glass-to-liquid transition [16]. Recently, we have found that both the trend in E_α during the glass transition and the fragility of 12PDO are quite different from those of 12PDA [17], even though the two simple liquids are similar in molecular structure and size. This significant disparity in kinetics may be caused by differences between the polyalcohol and the polyamine in the extent or strength of the hydrogen-bond structure. We have also found an empirical correlation of the variation in E_α with m, which is valid not only for some typical polymers [16] but also for the two hydrogen-bonded liquids [17].

We have investigated the effect of adding inorganic salts on the kinetic fragility and thermodynamic parameters of the glass transition for simple hydrogen-bonded liquids [7,8]. As inorganic salts are added to such organic solvents, we found the intrinsic

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directional hydrogen-bond network to be disturbed by the dissolved ions, as the ionic interactions compete significantly with the hydrogen bonds. Such competition between quite different intermolecular interactions can affect the glass-transition kinetics. For the binary mixture consisting of 12PDO and $\mathrm{LiBF_4}$, we found that both the fragility and T_g are significantly influenced by the added ions [7]. We also expect the glass-transition activation energy E_α to be influenced significantly by the addition of $\mathrm{LiBF_4}$. While some usual salts like NaCl cannot dissolve in alcohols to a high extent, $\mathrm{LiBF_4}$ exhibits a significantly high solubility in 1,2-propanediol, and this polyalcohol solution easily transforms to a glassy state by cooling without any crystallization or phase separation [7]. Thus, we can systematically investigate the kinetics of the glass transition for a wide range of concentrations. In the present study, we investigate—for mixtures of 12PDO and $\mathrm{LiBF_4}$—how E_α varies during the glass transition with the addition of salts and how E_α correlates with m.

2. Experimental and analytical methods

Commercial 12PDO with >99% purity, purchased from Wako Pure Chemical Industries, Ltd., was purified by vacuum distillation following dehydration by the addition of metallic sodium. Lithium tetrafluoroborate ($\mathrm{LiBF_4}$; Wako, >97%) was used as received. The pure components were mixed under a dry nitrogen atmosphere to minimize contamination with water and $\mathrm{CO_2}$ vapor, and the mixture was homogenized by stirring in a sealed flask at room temperature for 6 h or more. Homogeneous mixtures of $(\mathrm{LiBF_4})_x(\mathrm{12PDO})_{1-x}$ could not be obtained for $\mathrm{LiBF_4}$ mole fractions $x > 0.50$, as this exceeded the solubility of $\mathrm{LiBF_4}$ in 12PDO at room temperature. A 3–6 mg drop of each solution was sealed in an aluminum sample pan (0219-0062ALUM., PerkinElmer, Inc., ca. 24 mg) at room temperature under a dry nitrogen atmosphere.

DSC measurements were performed using a power-compensated DSC (DSC8500, PerkinElmer, Inc.) under a flow of helium gas. First, the samples were heated from room temperature to 323 K, and they were maintained at that temperature for 3 min to ensure that each sample had the same thermal history. Next, the liquid samples were cooled to 120 K below T_g at the rates of $\beta = 5$, 10, 20, 50, and 100 K min^{-1} to obtain glassy samples. After holding each sample at 120 K for 1 min, it was reheated to 300 K at the same rate β. The glass transition was measured during each heating scan. Before the measurements, the DSC equipment was calibrated for each heating rate using cyclohexane and indium. The repeatability of the DSC curves for each concentration was checked because the same baseline shift caused by the glass transition was observed repeatedly after several heating/cooling cycles.

To evaluate variations in E_α during the glass transition, we applied the advanced isoconversional method proposed by Vyazovkin [18] to the DSC data measured at different heating rates as well as those obtained in our previous study [17]. The activation energy was determined for each specified extent of conversion (α) as the E_α value that minimizes the following function $\Phi\,(E_\alpha)$:

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

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

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

The quantity α is defined to be the normalized heat-capacity change [13]:

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

where C_p is the observed heat capacity at temperature T during the glass transition and $C_p{}^{\mathrm{g}}$ and $C_p{}^{\mathrm{liq}}$ are the glassy and equilibrium liquid heat capacities, respectively, the superscript "N" indicates a normalized value. The values of ΔC_p^{N} were determined for DSC signals just before an overshoot observed during the heating scan.

3. Results and discussion

3.1. Glass transition and heat-capacity jump

We observed a single endothermic baseline shift due to the glass transition for each sample. Other thermal anomalies were not observed during the cooling and heating scans in the temperature range of 120–300 K. Therefore, any phase separations were not detected at the scan rates of $\beta = 5$–100 K min^{-1}. Fig. 1 shows the DSC data for the glass transition of representative concentrations at a standard scan rate of 10 K min^{-1}. The curves are shown as heat capacity normalized by sample mass. We determined the onset glass-transition temperatures T_g following enthalpy recovery at $\beta = 10$ K min^{-1} using the standard method of baseline extrapolation, as shown in Fig. 1. The heat-capacity jump at T_g, which is defined as $\Delta C_p = C_p{}^{\mathrm{liq}} - C_p{}^{\mathrm{g}}$, was determined from the difference between the extrapolated baselines below and above T_g.

Fig. 2 shows T_g and ΔC_p for $(\mathrm{LiBF_4})_x(\mathrm{12PDO})_{1-x}$ as functions of x. For pure 12PDO, T_g and ΔC_p were found to be 164.7 K and 71.0 J K (mol 12PDO)$^{-1}$, respectively. These thermodynamic parameters agree reasonably well with previous results [7,17]. With increasing x, both T_g and ΔC_p increase, up to 197.7 K and 131.6 J K (mol 12PDO)$^{-1}$, respectively, for $x = 0.50$. The concentration dependences of T_g and ΔC_p are different, the first showing a plateau and the second a sigmoid curve, respectively. We consider the anomalous concentration dependence of T_g to reflect the crossover in the dominant type of intermolecular interaction from hydrogen bonds between solvent molecules to ion-solvent or ion-ion interactions resulting from the addition of structure-breaking anions [7,17].

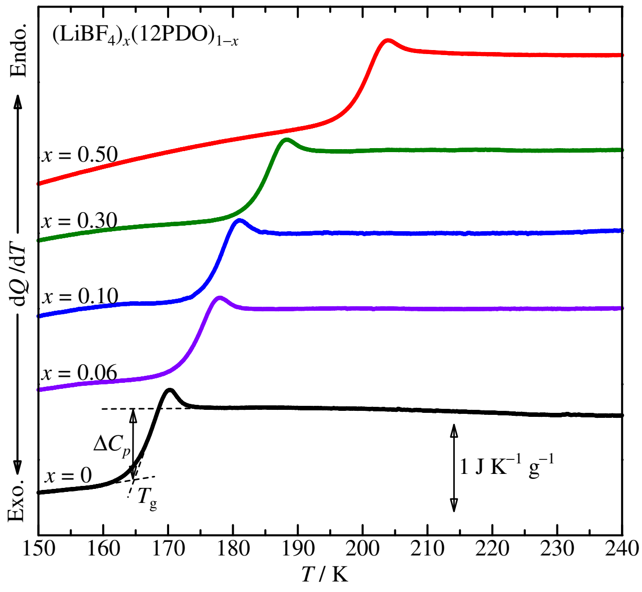

Fig. 1. DSC heating curves for glass transitions of $(\mathrm{LiBF_4})_x(\mathrm{12PDO})_{1-x}$ at typical concentrations obtained at a heating rate of 10 K min^{-1}. Each curve is normalized by the sample mass and is vertically offset for clarity. The quantity T_g is the onset glass-transition temperature, and ΔC_p represents the heat-capacity increase at T_g.