

Chapter 1. INTRODUCTION

1.1 Glass transition and slow dynamics

What may happen when a liquid is cooled below the melting temperature (T_m) ? Two possibilities are shown in Fig. 1.1. The liquid may either crystallize (route **a**) or vitrify (route **b**) [1]. If the thermodynamic barrier to nucleation can be overcome, a crystal of the equilibrium phase is formed and the volume of the system decreases discontinuously. If nucleation does not occur, on the other hand, the liquid remains in metastable supercooled liquid even below T_m and the volume decreases continuously. At lower temperatures the molecular mobility of the liquid decreases, and eventually the molecules become trapped in fixed positions. This occurs over a range of temperature called the glass transition region. Glass can be formed through many routes [2]. Generally, glass is obtained by freezing-in supercooled liquid as a sufficiently rapid rate to avoid crystallization as shown in Fig. 1.1. This vitrification process which leads to glass retains the structural disorder of liquid in the solid state. Glass, however, has lost its ability to flow. The properties of glass are distinguishable from both liquid and crystalline systems.

Besides of the use of glass which is indispensable in architecture, transport, lighting and conditioning, glass can be applied in the field of optics, electronics, optoelectronics and biotechnologies in modern technology [1]. Concerning to application, the fundamental study of glass has become very important and has been focused on with special attention.

The glass transition is a very general phenomenon taking place in a vast number of different materials such as simple molecular liquids, organic and inorganic glass-forming materials, ionic and metallic liquids, polymers, liquid crystalline systems, and even biological macromolecules [3]. The glass transition temperature (T_g) is generally defined as the point of intersection of lines extrapolated from the glass and supercooled liquid ranges as shown in Fig. 1.1.

Kauzmann discussed the origin of the glass transition [4]. As shown in Fig. 1.1, the slopes of entropy for both supercooled liquid and crystal are different below T_m . The former is steeper than that of the latter derived from the vibration motion. This difference makes the extrapolated entropy of supercooled liquid smaller than that of crystal below T_m . To prevent this thermodynamic crisis, the glass transition occurs at T_g from supercooled liquid.

Recently, it has been extensively studied with much interest on the glass-forming materials theoretically and experimentally to clarify the mechanism of the slow dynamics [5]. It is, however, far from satisfaction. The understanding of the glass transition phenomenon in relatively simple systems can bring new ideas in other fields of science and technology [6].

On cooling a glass-forming liquid, the main relaxation time increases to time of about 100 sec at T_g . In this glass transition region, the relaxation of glass-forming liquids is slow enough to be detected by human observers.

To explain this phenomenon, many theories and models has been proposed.

Cohen and Turnbull et al. achieved the successful and simple explanation on the basis of the free volume concept long before [7]. This free volume model assumed that the relaxation of a liquid molecule or a polymer segment occurs whenever a molecule has a free volume greater than a critical volume. It was found that this model provide a convincing rational of such equations as the Williams-Landel-Ferry (WLF) equation [8], which describes the temperature dependence of relaxation time for an enormous number of glass-forming liquid.

The configurational entropy model proposed by Adam and Gibbs was based on a modification of transition state theory in the liquid [9]. The main idea of this Adam-Gibbs model is the concept of cooperatively rearranging region (CRR). The viscous liquids must overcome cooperatively the energy barriers to rearrange. The size of this CRR would increase as temperature decreases. This model leads to an expression in terms of the relaxation time, which contains configurational entropy.

The concept of cooperativity is popular. Matsuoka et al. achieved another modification called the domain model, which is based on configurational entropy [10]. From the decreasing feature of enthalpy, this model calculated the domain size, which is the number of conformer in a domain. The conformer is the minimum unit of relaxation.

Recently, two order parameter model was proposed by Tanaka [11,12]. According to this simple model, the feature of vitrification or crystallization is the result of the frustration between the density order parameter and the bond order parameter. The former governs the isotropic interaction among molecules and the latter rules the anisotropic one. There are two types of origins about the glass-liquid transition: one is the anisotropic interactions that are not consistent with the crystallographic symmetry, the other is the quenched disorder in structures of particles or molecules.

1.2 Present trend

1.2.1 Classification of liquid and fragility

In the 1980's, Angell introduced the concept of fragility to classify the liquids into two categories: strong and fragile liquid. These two schemes depend on the changing rate of viscosity or relaxation time with the normalized inverse temperature T_g/T . The Angell representation is described in Fig. 1.2 on the basis of viscosity data, $\log_{10}\eta$. Usually relaxation time is proportional to viscosity. The strong liquids, with the directional bonds such as covalent network structure, exhibit a slow linear reduction of the relaxation time with increasing temperature. The temperature dependence of relaxation time well obeys Arrhenius law, $\tau = \tau_{0A} \exp(\frac{E}{T})$ stems from the activation behavior. This class has small changes in the heat capacity at T_g , denoted to $\Delta C_p(T_g)$ hereafter.

In contrast, the fragile ones are well seen in the materials with no directional bonds, for example, van der Waals or ionic system. The behavior of relaxation time of fragile liquid can be characterized to a faster reduction near T_g and a slower in the higher temperature limit with a curvature. This feature stems from the cooperative motion among the molecules and can be well reproduced as the Vogel-Tammann-Fulcher (VTF) law, $\tau = \tau_{0V} \exp(\frac{B}{T - T_0})$. Fragile liquids have larger $\Delta C_p(T_g)$.

According to Angell, both relaxation time and entropy depend on the depth and density of the potential energy hypersurface.

The most popular classification of liquid makes use of the concept of fragility. It has been found that many properties of liquid are related to the fragility of liquid. The measure of fragility addresses the deviations of liquid relaxation from the Arrhenius behavior, $\tau = \tau_{0A} \exp(\frac{E}{T})$. Fragility is a qualitative concept and can be quantified in various ways.

For example,

- 1) The strength parameter D [13] in the VTF law given by,

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (1.1)$$

As the liquid is more fragile, its value of D decreases.

- 2) The index m [14] is defined by,

$$m = \left[\frac{1}{T_g} \frac{d \log \tau}{dT} \right]_{T=T_g} \quad (1.2)$$

This index is related to the slope of the relaxation time at T_g . For VTF law, m has

$$\text{inverse relationship with } D, \text{ i.e. } m = \frac{D(T_0/T_g)}{(\ln 10)(1 - T_0/T_g)^2} \approx 16 + \frac{5}{D}. \text{ Even}$$

though this definition is commonly used, it is unreliable because the experimental uncertainty of freezing-in region of slow dynamics and its ambiguity of extrapolation for taking the slope.

3) The ratio of Vogel-Fulcher temperature to glass transition temperature, T_0/T_g ,

4) Fragility $F_{1/2}$ [15] is defined by,

$$F_{1/2} = 2 \frac{T_g}{T_{1/2}} - 1 \quad (1.3)$$

Here, $T_{1/2}$, is the temperature where the relaxation time τ is 10^6 sec, which is half time between glass transition ($\tau = 10^2$ sec) and vibration phonon lifetime ($t = 10^{-14}$ sec). Fig. 1.3 shows some examples for $F_{1/2} = 0$ (Arrhenius law), 0.16 and 0.8, respectively.

In this work, $F_{1/2}$ is used as the measure of the fragility by the advantage that its value is independent of data fitting function.

1.2.2 Relaxation modes

For the liquid-glass transition, various relaxation modes are found as shown in Fig. 1.4 as an example of the relaxation map. The explanation about the origin of these modes, however, is not satisfactory enough to be clarified.

It is well established that the α relaxation shows universal features regardless of the type of glass-forming liquids [5]. The main characteristic features of the α relaxation, which are related to the liquid-glass transition, are known as follows: (1) non-exponential relaxation function in the time window or non-Debye behavior in the frequency window, (2) non-Arrhenius temperature dependence of the characteristic relaxation time or viscosity without any discontinuity at a glass transition temperature and (3) the split of the α relaxation into itself and β relaxation at T_β and so on. Several concepts and models have been proposed to clarify the universal properties of the glass transition or α -relaxation; 1) free volume [7], 2) molecular cooperativity, for example, in terms of CRR

[9], domain and conformer [10] and dynamically correlated domain [16] etc., 3) mode coupling theory (MCT) [17], 4) dynamical heterogeneity [9, 16, 18], 5) coupling model [19], 6) strong/fragile liquid [13] and 7) two order parameter model of liquids [11] etc.

On lowering the temperature for the liquid in the Arrhenius plot, the slow secondary or β relaxation is decoupled from the α relaxation at $T_\beta (>T_g)$ where the relaxation time of β relaxation is identical to that of α relaxation. Several scenarios for the decoupling between α and β relaxations were suggested [20]. The slow β relaxation is also generally observed at the frequency higher than α relaxation both below and even above T_g . The temperature dependence of relaxation time for β relaxation is expected to obey the Arrhenius function given by

$$\tau_\beta = \tau_{0\beta} \exp(E_\beta/RT) \quad (1.4)$$

The origin of slow β relaxation for glass-forming liquid has been interpreted in terms of 1) the partial relaxation by local motions in a variety of local environments [21], 2) the potential barrier hindering the molecular rearrangements [22], 3) the rotation of the free molecules as a whole or segment [23], and so on.

1.2.3 Dielectric and calorimetric measurements

The dynamical properties of the α relaxation have been studied to clarify the dynamics of the liquid and supercooled liquid by the measurements of viscosity, dielectric susceptibility, NMR, light scattering, neutron scattering, ultrasonic attenuation and so on [3, 5].

The complex dielectric measurement is a powerful and straightforward technique to gain insight into the molecular dynamics of many materials. When an electric field is applied to a dielectric material, the permanent dipoles inherent in most molecular matters tend to orient to the same direction of the electric field. The rotational response of the polarization to the external electric field is complex dielectric susceptibility. Both the rotational and translational dynamics of molecules can be observed from the broadband dielectric loss, which includes both the dielectric orientational relaxation and dc conductivity, respectively.

There is an isothermal system under a small amplitude temperature modulation. Far above T_g , the system can be soon relax in equilibrium state. Considerably below T_g , on the other hand, the system will not respond structurally to the changing temperature. In both cases, the heat flow will be in phase with the temperature modulation. This is true that phase lag between temperature modulation and heat modulation is present for the glass transition region. The measurement of complex heat capacity was proposed in 1968 [24] and the real measurement of the frequency dependent heat capacity from the response of a sample was in the middle of 1980's [25]. The developed commercial equipment named modulated differential scanning calorimetry (MDSC) was introduced more recently [26].

The glass transition temperature (T_g) is generally defined as the temperature where the heat capacity ΔC_p changes in the conventional DSC system. From the ΔC_p data in heating process, the midpoint between the onset and end points of abrupt change in ΔC_p is defined as T_g . This temperature is called the calorimetric glass transition temperature. There are other convenient definitions of T_g from the data of viscosity η and relaxation time τ . From the temperature dependent viscosity or relaxation time data, the temperatures where $\eta = 10^{13}$ poise or $\tau = 100$ sec are also defined as glass transition temperatures.

For MDSC, T_g at which the imaginary part of heat capacity shows a peak can be calculated easily without ambiguity.

1.3 Aim of this thesis

1.3.1 Alcohols and hydrogen bonding

The dynamics of fragile or intermediate liquids is one of the main topics of the study of the glass-forming materials theoretically and experimentally. The alcohols having -OH group has a simple structure. In spite of this simple structure, there are the inter- and intra-molecular interactions through hydrogen bonding. These interactions cause the non-simple dynamical behaviors and the complex relaxation modes, which are originated from the molecular cooperativity. Such materials as n-propanol (nPrOH), propylene glycol (PG) or glycerol (Gly) are the representatives of alcohols.

Alcohols are classified into fragile or intermediate liquid. However, their $\Delta C_p(T_g)$ is

even larger than that of more fragile liquids due to the contribution of hydrogen bonding. This abnormal relationship between relaxation behavior and $\Delta C_p(T_g)$ makes the research on alcohol one of the most popular topics in condensed matter.

According to the two order parameter model, the anisotropic interaction between molecules can be caused by the covalent or hydrogen bonding. The formation of hydrogen bonding reduces the degree of freedom in the configuration between the molecules.

In this thesis, it is studied which factor determines the relaxation behavior such as fragility in detail: the density of -OH group a monomer, comparison between -OH and -OD groups, the adhered position of -OH group, molecular weight, comparison between -OH and -OCH₃ groups.

1.3.2 Organization of this thesis

In this study, the relaxational dynamics of several monomeric and oligomeric glass-forming alcohols have been systematically investigated by using broadband dielectric spectroscopy and MDSC.

This thesis is written as follows:

In Chapter 2, several theories or models on the glass transition and slow dynamics are briefly discussed, especially free volume theory, configurational entropy model by Adam and Gibbs, domain model by Matsuoka et al., two order parameter model by Tanaka and mode coupling theory.

In Chapter 3, the basic experimental principle and setup of time domain reflectometry (TDR) and MDSC are described. All the samples used in this study are also given.

In Chapter 4, the experimental results investigated by dielectric loss and MDSC are shown and the methods of the analysis are described in detail.

In Chapter 5, concerning to the glass transition and slow dynamics, we discuss the role of the number of -OH group, the effect of isomers and deuteration, the role of end groups such as -OH and -OCH₃ groups and the effect of molecular weight. The results are compared with and accounted for several models discussed in Chapter 2

In Chapter 6, the important conclusions are summarized.