

Chapter 5. DISCUSSION

Understanding of the dynamics for the α relaxation in a simple liquid is very important to clarify the dynamical properties of more complicated system.

The slow dynamics of fragile or intermediate liquids with -OH group has been one of the main topics of the theoretical and experimental studies on the glass-forming materials. The inter- and intra-molecular interactions exist through the hydrogen bonding and let the liquid relax non-Debye type. Moreover, these materials show the existence of several relaxation modes in spite of their simple molecular structure [50-52].

In the present work, the relaxational and calorimetric behaviors of several alcohols have been studied to clarify the role of hydrogen bonding in the glass transition and slow dynamics. The dielectric measurement covers the frequency region from 10 mHz to 10 GHz. This frequency range covers the relaxation of both the liquid and supercooled region. The complex heat capacity with the modulation period of 100 sec have been measured.

The roles of hydrogen bonding and molecular structure in the relaxation feature will be discussed in respect to the number of -OH group, the attached position of the -OH group, its substitution by heavy deuterium and -OCH₃ group, and the molecular weights. The results are explained mainly on the basis of the two order parameter model, free volume theory and cooperativity model.

5.1 Relaxations in n-Propanol, Propylene Glycol and Glycerol

There are three monomers, n-Propanol (nPrOH), Propylene Glycol (PG) and Glycerol (Gly). Their chemical skeletons are the same -C-C-C- group but with different number of -OH groups. The number of -OH groups increases from one to three for nPrOH, PG and Gly, respectively. These materials have been much investigated in the past both in the liquid and in supercooled states. However, the role of -OH group in the relaxation behavior has not yet been fully explained.

Although nPrOH has been studied by many researchers from long before [53, 54], the researches in the broadband region has been carried out quite recently by virtue of the development in electronics [50, 52, 55-57].

The dielectric and thermal results on the PG are available. The universal scaling behavior [58, 59], linear decrease of loss peak till T_a [59], two dynamical regions [60] and the broadening of loss curve [58] were reported for PG from the α relaxation results obtained with the use of the dielectric spectroscopy.

Glycerol has been widely also investigated by the dielectric spectroscopy [61-63].

5.1.1 Fragility of nPrOH, PG and Gly

Figs. 5. 1 a) and b) show the frequency dependence of the dielectric loss $\epsilon''/\epsilon''_{\max}$ of PG and Gly at several fixed temperatures, respectively. ϵ''_{\max} is the maximum value of the dielectric loss at the loss peak or relaxation frequency f_{\max} . As the temperature decreases, the loss peak broadens and f_{\max} shifts to lower frequency. The observed dielectric results have been well reproduced by the HN empirical relaxation function. The best fit to the spectra by HN function gives us the information on the f_{\max} . This loss peak has an inverse relationship with the relaxation time, i.e. $\tau = 1/(2\pi f_{\max})$.

The shift rates of the f_{\max} for the α relaxational mode in nPrOH, PG and Gly are shown in Fig. 5. 2. This feature is drawn as relaxation time τ vs. T_g/T , where T_g is the glass transition temperature at which the relaxation time is 100 sec. This Angell's representation is a very basic method to classify the liquids and to obtain information about the relaxation behavior.

According to the result of Böhmer et al. [14], the fragility indices m of these three material are 40, 52 and 53 for the main relaxation in nPrOH, PG and Gly, respectively. Since the value of m corresponds to the slope of the relaxation time at T_g , it cannot

enough describe the deviation of the relaxation behavior from the Arrhenius law. Therefore, m is not enough to represent the relaxational behavior in supercooled liquid region

It has been reported recently that the main relaxation mode in nPrOH is not concerned with glass transition whereas the secondary relaxation mode is [50, 52]. This conclusion is supported by the fact that the other relaxational results obtained from viscosity measurement and light scattering can be well explained by taking into consideration with the secondary relaxation mode. Fig. 5. 1. 2 was drawn on the basis of Hansen's analysis of nPrOH. The multi relaxation modes of several kinds of propanol will be discussed in detail in the later Chapter 5.2 and 5.3.

The fragility defined as $F_{1/2}$ for nPrOH, PG and Gly is drawn in Fig. 5 .3. The values of fragility are 0.50, 0.52 and 0.53 for nPrOH, PG and Gly, respectively. It seems that there is not relationship between the density of -OH groups a monomer and the fragility. On the contrary, another factor also affects the fragility. It can be considered that the methyl group also influences the relaxation behavior since not only hydroxyl but also methyl groups simultaneously determine the motion of the molecules. This concept was proposed by Tanaka [11] in terms of two order parameter model. The hydrogen bond renders the molecules to accumulate anisotropically and the methyl group plays a role to minimize the distance between molecules. The competition between the anisotropic interaction due to the hydrogen bond and isotropic interaction due to the presence of the methyl group determines the relaxation feature of the alcohol. In this case, the coupling between two kinds of interaction in nPrOH, PG and Gly exhibits the relaxational path from liquid to glass.

5.1.2 Summary

The relaxational features of nPrOH, PG and Gly have been compared in terms of fragility. Three materials have the same backbone, but differ only in the number of -OH groups in a monomer. It seems that the number of -OH groups is not the only factor which determines the relaxational behavior. The methyl group also plays an important role making the liquid fragile or strong. The competition between -OH and -CH₃ is the key factor for supercooled liquid to relax completely.

5.2 Differences in relaxational behaviors of propanol isomers

The dynamical properties of n-propanol (nPrOH) and i-propanol (iPrOH) have been investigated in the liquid and supercooled states using the broadband dielectric spectroscopy. These relaxation modes are compared with the earlier dielectric results and with the polarized Brillouin scattering. nPrOH and iPrOH have the same molecular weight but different chemical structure where the hydroxyl group is attached.

The presence of several relaxation processes in n-propanol (nPrOH) and i-propanol (iPrOH) using dielectric spectroscopy have already been published. However, the origins of these processes are still open problems [50, 52-54, 57].

Garg and Smyth measured the dielectric permittivity for nPrOH at 20, 40 and 60°C and proposed the origins of each relaxation modes as follows [54]:

1) the relaxation at the highest frequency region is due to the rotation of -OH group, 2) the intermediate relaxation comes from the rotation of the free or monomer molecules and 3) the lowest relaxation is connected to the breaking and forming of the hydrogen bonds.

Recently, another analysis of the lineshapes of nPrOH and iPrOH were reported by Murthy and his coworkers [23, 50]. Four different relaxation processes in both nPrOH and iPrOH exist:

1) the Debye-type α_1 process due to the flipping of the -OH group in the linear chain, 2) the non-Debye-like α_2 process, 3) the β process due to the rotation of the free molecules as a whole or segment (this process is bifurcated from α_2 process for iPrOH, but not for nPrOH) and 4) the γ process by the -OH rotation.

There is another analysis for nPrOH performed by Hansen et al. [52] and Kudlik et al. [57]. They classified three different relaxation modes in nPrOH and other glass-forming liquids:

1) the slow Debye-type relaxation process, 2) the structural or α relaxation process whose relaxation frequency well matches those from the viscosity, photon correlation spectroscopy and Brillouin scattering results and 3) the Johari-Goldstein type β relaxation process which is bifurcated from α relaxation process. For simplicity, the Arrhenius plots on the basis of the above mentioned reports are shown in Fig. 1. 4 in Chapter 1, supposing the slow β relaxation is bifurcated from the α relaxation.

The nPrOH ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, $T_m = 147.1$ K) and iPrOH ($\text{CH}_3\text{CHOHCH}_3$, $T_m = 183.7$ K) with 60.1 g/mol were purchased from Tokyo Chemical Industry Co., Ltd. The

purity of all chemical reagents is above 99.0%.

5.2.1 Relaxational behaviors

The dielectric losses, $\epsilon''(f)$, for nPrOH at various temperatures versus frequency f are shown in Fig. 5. 4. Except of $\sigma\omega$ component, there are three different types of relaxation mode for a spectrum: a main and dominant peak in the lowest frequency region at all temperature, a small peak in the highest region, for example at 117 - 125 K and a shoulder between two peaks. It is easily found that the main peak largely shifts to lower frequency side with decreasing temperature. Involving the cooperative behavior between molecules of glass-forming liquid, the change rate of the f_{\max} against temperature is one of the most important topics in the study of liquid-glass transition.

Illustrated in Fig. 5. 5 for nPrOH at 120 and 233 K, three relaxation processes were named, so called, Debye relaxation, α relaxation and slow β relaxation by ascending turns of frequency after the Hansen's notation [52]. As shown in Fig. 5. 5, as examples of the results at 120 and 233K, the dominant Debye process was drawn by solid line adding to the raw data directly. The Debye relaxation process observed in the lowest frequency region shows the Debye-type frequency dependence, that is $\alpha_1 = \gamma_1 = 1$. The α relaxation was reproduced from the difference between the raw data and Debye process, by the HN function. For example, the values of α_2 and γ_2 at 120 K are 0.98 and 0.28.

The HN parameters α and γ have a relationship with the shape parameter β_{KWW} in KWW function ($\Phi(t) = \exp[-(t/\tau)^{\beta_{\text{KWW}}}]$), that is, $\beta_{\text{KWW}} = (\alpha\gamma)^{(1/1.23)}$ [45]. Fig. 5. 6 shows the temperature dependence of β_{KWW} for the α relaxation of nPrOH. According to the two order parameter model [11], the relaxation behavior has a crossover at the melting point T_m . The relaxation behavior of liquid above T_m obeys the Arrhenius law, $\tau = \tau_0 \exp(E/kBT)$, where E is the activation energy, and the relaxation function is exponential, $\Phi(t) = \exp(-t/\tau)$, i.e., β_{KWW} is unity. Between T_m and T_0 , the relaxation behavior can be characterized by the KWW function instead of the exponential relaxation. Therefore, the parameter of β_{KWW} is a monotonically increasing function with temperature and reach $\beta_{\text{KWW}} = 1$ at T_m and remains unity above T_m . In Fig. 5. 6, β_{KWW} in nPrOH increases with increasing temperature, however, it does not reach unity at and above $T_m = 147.1$ K.

Table 5. 1 Values of A and B in Eq. (5.1) of n-Propanol and i-Propanol

	n-Propanol	i-Propanol
A	10.4	10.9
B × 10 ³	16.4	18.1

The broadening of the peak shape which comes from the cooperative molecular behavior appears as the smaller β_{KWW} . On lowering, the molecular cooperativity of the α relaxation process increases.

At last, the slow β relaxation was again described by the HN with $\alpha_3 = 0.97$ and $\gamma_3 = 0.45$ at 120 K for the rest of the spectrum. The values of α for slow β relaxation in the studied region are above 0.9.

The difference in $\Delta\epsilon_D(T)$ in the studied temperature range between nPrOH and iPrOH is less than 3 % except above 247K. It is found that $\Delta\epsilon_D(T)$ for propanols in this study can be well described by the simple equation,

$$\Delta\epsilon_D(T) = -A + B/T \quad (5.1)$$

The values of A and B for $\Delta\epsilon_D(T)$ of nPrOH and iPrOH are listed in Table 5. 1.

Fig. 5. 7 displays the temperature dependence of the dielectric relaxation frequency as the Arrhenius plot, f_{max} vs. $1000/T$, for a) nPrOH and b) iPrOH. Both samples have three different relaxation processes in the studied frequency ranges named Debye relaxation, α relaxation and slow β relaxation. The dielectric relaxation frequency reported already for nPrOH [53, 54] and iPrOH [64, 65] are plotted together for comparison. The relaxation frequency determined by Brillouin scattering [66] through viscoelastic coupling to longitudinal acoustic phonon for nPrOH and iPrOH are drawn together in Fig. 5. 7. The highest dielectric relaxation processes for nPrOH reported by Garg and Smyth [54] and for iPrOH by Barthel et al. [5.2 Barthel] are in the extrapolated line of the relaxation determined by BS. It is believed that this dielectric relaxation process is due to the rotation of -OH [54] and is named as γ relaxation [23]. The BS result is not same with the extension of α relaxation. It shows an independent relaxation mode.

Two types of the α relaxation behavior are seen in Fig. 5. 7. One is the case for nPrOH in which there is no coinciding temperature between the α and β relaxation. For nPrOH, it is not the same as the results obtained by Hansen et al. [52], but agrees with the results by Cole et al. [53] and the prediction by Murthy [50] with some error induced from the setting of the fitting parameters. The other is for iPrOH that α relaxation is bifurcated at T_β into two relaxations upon lowering the temperature, itself and the slow β relaxation. The split temperature of iPrOH is $T_\beta = 144$ K. This point is much lower than the melting temperature. There is a nearly parallel shift for the Debye relaxation and the α relaxation in all samples studied. This decouple is nearly two decades in the studied temperature windows. It means that the origin of the both relaxations is different. The both relaxations show the non-Arrhenius temperature dependence.

With the aid of the representation $[-d\log(f_{\max})/d(1/T)]^{1/2}$ vs. $1/T$, the relaxation modes are well reproduced. The Debye and α relaxation in the higher temperature ranges and β relaxation well obey the Arrhenius law. However, for the Debye relaxation of nPrOH in the lower temperature range, it seems that two different VTF functions can be well fitted to the relaxation data by the derivative method. This character was suggested for some materials including the strong B₂O₃, fragile propylene carbonate and intermediate nPrOH [39]. However, it is enough for iPrOH to use only one VTF function to describe its lower temperature behavior. Owing to the lack of the data for intermediate temperature region of α relaxation, the analysis of this relaxation for four kinds of propanols was carried out by the VTF fitting. The crossover for nPrOH (from VTF to VTF) and iPrOH (from ARR to VTF) looks like to be related to the melting phenomena because of the similarities between the crossover and melting temperatures. For example, as shown in Figs. 5. 7 a) and b), their values are $T_m = 147.1$ K and $T_{cl} = 146$ K for nPrOH and $T_m = 183.7$ K and $T_c = 177$ K for iPrOH. For nPrOH, there is a higher crossover temperature at $T_{ch} = 198$ K from VTF to Arrhenius law with increasing temperature. This crossover indicates another liquid-liquid transition. However, liquid-liquid transition in iPrOH does not exist in the studied temperature region.

5.2.2 Analysis using two order parameters model

Fig. 5. 8 shows the relaxation time of the Debye and α relaxation processes for nPrOH and iPrOH vs. T_g/T , usually called Angell plot. It is clearly seen that nPrOH is stronger than iPrOH. The fragility $F_{1/2}$ is related to the cooperativity between the molecules and

reveals the deviation from the activation behavior, Arrhenius law. The values of fragility are $F_{1/2} = 0.26$ for nPrOH and $F_{1/2} = 0.36$ for iPrOH, respectively. The hydrogen bonding can form such intramolecular and intermolecular structures as intermolecular rings, branched structures, or chain forms. nPrOH is stronger liquid than iPrOH. That's why the former may be able to make strongly longer chain network structure. However, the latter may easily form the ring dimer or shorter chain and therefore it moves independently or freely. The network structure makes liquid stronger like the covalent bonded glasses.

According to the recent two order parameter model [11], the dynamic behavior from liquid to glass state of the random frustrated systems such as spin glass and structure glass can be generalized by two order parameters, i.e. bond order parameter S and density ρ . The interaction potential between molecules can be divided into isotropic and anisotropic parts. Although the isotropic interaction is the function of only distance between molecules, the anisotropic interaction depends both on the distance and on the orientation of the molecule and its neighbors.

The densities of nPrOH and iPrOH at room temperature are 0.804 and 0.785 g/ml, respectively. The other bond order parameter S can appear as the strength of the orientational correlation. One example of this correlation is the variation of the dielectric strength $\Delta\epsilon_D$. Dielectric strengths of both nPrOH and iPrOH are drawn versus the normalized temperature to T_g , T_g/T in Fig. 5. 9. It is clear that the dielectric strength of nPrOH is larger than that of iPrOH.

For a more strong liquid which has a larger disorder strength, the pass way to vitrification through the Griffith-like phase region is to be longer than that of fragile liquid. For the alcohols, the localized structure is mainly made by the hydrogen bonding. This strong disorder effect appears really as a larger temperature interval between T_m and T_0 and also a larger value of $T_g - T_0$. For the stronger nPrOH, the values are $T_m - T_0 = 93.1$ K and $T_g - T_0 = 51$ K, and for iPrOH, 94.7 K and 31 K, respectively. However, the activation energy at higher temperature is not proportional to the value of $T_m - T_0$. From these results, it is postulated that the interval of disorder strength during the vitrification path from T_m and T_0 is wider for iPrOH than for nPrOH. Viewing the localization of the iPrOH molecules from T_m , it rapidly enhances with the decrease of temperature. The speed of the localization may determine the vitrification path and its interval $T_m - T_0$.

Murthy discussed the relationship between the molecular shape and glass formation for many glass-forming liquids [67]. The molecular asymmetry or non-spherical shape of the

liquid enhances the glass formation and is related to the approximately decreasing trend of the value T_m/T_g , where T_m indicates the melting point. The values of T_m/T_g are 1.46 for nPrOH with $T_g = 101$ K and 1.56 for iPrOH with $T_g = 118$ K. The both ratios differ only slightly. The degree of molecular asymmetry or non-spherical shape seems not to govern the fragility.

5.2.3. Summary

The dynamical properties of nPrOH and iPrOH have been investigated by the analysis of the dielectric properties. The results are summarized in Table 5. 2. In both samples, the relaxation phenomena can be well separated into three different relaxation processes above temperature near to T_g . The crossover from one VTF to another VTF or Arrhenius law is found near the melting point. The strong and fragile features are characterized on the basis of two order parameter model. The disorder effect, related to the anisotropic orientational interactions between molecules, makes the temperature interval from T_m to T_0 and from T_g to T_0 . There is a bifurcation of the α and β relaxation for iPrOH below T_β , which means that the origins of both relaxations for iPrOH have some correlation. For nPrOH, however, the correlation between α and β relaxation seems not to be present.

It is known that nPrOH is stronger than iPrOH. The fragility of Debye and α relaxation modes in nPrOH and iPrOH are shown in Table 5. 2. The difference in fragility originates only from the structural difference between nPrOH and iPrOH. The role of -OH group in both propanols is not the same. The -OH group in iPrOH plays a role in increasing the cooperativity.

Table 5. 2 Different properties between nPrOH and iPrOH

	nPrOH	iPrOH
Position of -OH	End	Middle
relaxation mode	Debye, α and β	Debye, α and β
Fitting region in Debye	3 (VTF, VTF, ARR)	2(VTF, ARR)
T_g		higher (15K)
Fragility ($F_{1/2}$)	stronge Debye relaxation : 0.26 α relaxation : 0.50	fragile Debye relaxation : 0.36 α relaxation : 0.57
merging between α and β	No T_β	T_β

5.3 Deuteration effect

In Chapter 5.2, we have studied the dielectric relaxation processes for the nPrOH and iPrOH. In the present chapter, their properties are compared with those of the deuterated analogues, nPrOD and iPrOD, to clarify the role of hydrogen bonding in slow dynamics.

The nPrOH-d1 (nPrOD, CH₃CH₂CH₂OD) and iPrOH-d1 (iPrOD, CH₃CHODCH₃) with 61.10 g/mol were purchased from Tokyo Chemical Industry Co. Ltd.

The method for the data analysis is the same as that explained in Chapter 5.2.

5.3.1 Relaxation behaviors of deuterated propanols

The temperature dependence of the dielectric strengths, $\Delta\epsilon(T) = \epsilon'_{\omega=0}(T) - \epsilon'_{\omega=\infty}(T)$, for Debye ($\Delta\epsilon_D(T)$), α ($\Delta\epsilon_\alpha(T)$) and β relaxation ($\Delta\epsilon_\beta(T)$) for iPrOH and iPrOD are shown in Fig. 5. 10. The dielectric strengths obtained from the Impedance/Gain-phase analyzer were calculated using the reported results [53, 64]. The magnitude of the dielectric strength originates mainly from the Debye relaxation. For instance, at 120K the contribution of Debye relaxation to total dielectric strength is 94.7 % and the rest 4.8 and 0.5 % are for α and β relaxation, respectively. $\Delta\epsilon_D(T)$ increases linearly with decreasing temperature, but $\Delta\epsilon_\alpha(T)$ varies non-linearly. These trends and values of the three relaxations for nPrOH and nPrOD are similar to those of iPrOH and iPrOD, respectively. The differences in $\Delta\epsilon_D(T)$ in the studied temperature window between nPrOH and iPrOH are less than 3 %, and between nPrOD and iPrOD are less than 5 % except when the temperature is above 247K.

Fig. 5. 11 displays the temperature dependence of the dielectric relaxation frequency for a) nPrOD and b) iPrOD. Both samples have also three different relaxation processes in the studied frequency ranges named Debye relaxation, α relaxation and slow β relaxation.

Whereas nPrOD have two different VTF functions in the lower temperature range, iPrOD has only one VTF. Therefore, nPrOD has two crossover temperatures, $T_{cl} = 151$ K from one VTF to another VTF and $T_{ch} = 186$ K from VTF to ARR with increasing temperature. In the case of iPrOD, only one transition exists at $T_{cl} = 185$ K which is considered to be the melting temperature. These fitted values and their temperature regions for nPrOD and iPrOD are listed at Table 5. 3. The corresponding values for nPrOH and iPrOH are together listed.

Table 5. 3 Parameters in VTF, and Arrhenius laws and the fitting regions for nPrOH, iPrOH, nPrOD and iPrOD. E_D , E_α and E_β means the activation energies for Debye, α and β relaxation processes. T_g is the temperature where the relaxation time is 100 sec.

	Debye relaxation									
	low Temp. VTF				intermediate Temp. VTF			high Temp. ARR		
	logf ₀ (Hz)	T ₀ (K)	T _g (K)	range (K)	logf ₀ (Hz)	T ₀ (K)	range (K)	logf ₀ (Hz)	E _D (kJ/mol)	range (K)
nPrOH	11.8	54	105	113-146	10.6	72	146-198	12.7	22.7	> 198
nPrOD	11.1	64	109	119-151	12.7	88	151-186	12.7	23.1	> 186
iPrOH	9.4	89	120	122-177				13.9	29.5	> 177
iPrOD	9.2	90	120	125-185				14.1	30.4	> 185

	α relaxation								β ARR	
	low Temp. VTF				high Temp. ARR					
	logf ₀ (Hz)	T ₀ (K)	T _g (K)	range (K)	logf ₀ (Hz)	E _{α} (kJ/mol)	range (K)	logf ₀ (Hz)	E _{β} (kJ/mol)	
nPrOH	13.8	63	101	113-142	12.9	16.9	> 207	15.0	23.6	
nPrOD	13.1	65	105	119-151	12.3	13.9	> 233	14.7	22.5	
iPrOH	13.0	87	118	122-155	13.1	18.9	> 214	23.0	51.3	
iPrOD	13.0	87	118	125-156	13.1	18.4	> 216			

Table 5. 4. Values of A and B in Eq. (5.1) of n-Propanol-d1 and i-Propanol-d1

	n-Propanol-d1	i-Propanol-d1
A	8.8	9.0
B × 10 ³	12.8	14.5

For both iPrOH and iPrOD, the temperature dependent dielectric strength, $\Delta\epsilon(T)$, of three relaxation modes is shown in Fig. 5. 10. Dielectric strength has been reproduced by the Eq. (5. 1) and the values of A and B for $\Delta\epsilon_D(T)$ of nPrOD and iPrOD are listed in Table 5. 4. According to Eq. (5. 1), it is known that the extrapolation of $\Delta\epsilon_D(T)$ indicates no divergence at 0 K or at T_0 . The Eq. (5. 1) is a signal of the cooperative motions between molecules.

Both iPrOH and iPrOD have the same glass transition temperatures for Debye and α relaxation, which will be discussed in detail later. For the Debye relaxation, $\Delta\epsilon(T)$ of nPrOH is clearly larger than that of iPrOD for all temperature range studied, although the both liquids have identical T_g .

The number density of the dipoles involved in the relaxation and their dipole moment determine the magnitude of the $\Delta\epsilon(T)$. However, the strong orientational correlation between a molecule and its neighboring molecules has also an influence on it. This relation established by Kirkwood and Fröhlich [68, 69] is given by,

$$\Delta\epsilon = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{4\pi N\mu^2}{3k_B T V} g \quad (5. 2)$$

where N is Avogadro's number, μ is the dipole moment of the free molecule, V is molar volume, $k_B T$ is thermal energy and $\epsilon_0 = \epsilon'_{\omega=0}$ and $\epsilon_\infty = \epsilon'_{\omega=\infty}$ are the dielectric constants at high and low frequency limits. The measure of the orientational correlation between dipoles can be expressed as the correlation factor g in Eq. (5. 2). The approximate expression of the molecular correlation for $\Delta\epsilon(T)$ in the case of water, alcohols and other polar liquids is given by Oster and Kirkwood [68].

Both materials have g greater than unity in both supercooled and liquid states, which indicates that the molecules themselves tend to align parallelly so that to form a linear chain. This intermolecular correlation originates from the presence of the hydrogen bonding. However, as the dielectric strength is not decided only by the orientation of the dipoles, g can not fully describe the orientational correlation [70]. From the definition of g which is expressed in the form,

$$\mu \cdot \mu = g \mu^2 \quad (5. 3)$$

g is related to the orientational interaction between dipoles. The orientational interaction of a molecule and its neighbors leads the potential asymmetry according to two order parameter model. On the other hand, the bond formation such as chain or ring structure due to hydrogen bonding affects the value of the dielectric strength. This formation plays a role to make the locally favored structure and is an important element to illustrate the features of the glass transition phenomena.

The deuteration of -OH group in propanol may affect the dielectric strength as a result of changes in the dipole moment, density and orientational correlation between molecules. For iPrOH and iPrOD, as the density at room temperature is 0.785 and 0.798, respectively, the molar volume due to the deuteration does not change and is the same as the value of 76.56 ml/mol. The dielectric strength may be dominantly governed by the correlation between dipoles. It can be postulated that the deuterated materials reduce the interaction between molecules and have less orientational correlation, so that the deuterated propanols, i.e. nPrOD and iPrOD, have smaller dielectric strength than undeuterated nPrOH and iPrOH.

For the α relaxation, however, $\Delta\epsilon_{\alpha}(T)$ for iPrOH and iPrOD is similar. $\Delta\epsilon_{\alpha}(T)$ does not increase monotonically, but has an abrupt jump near to T_g . Such a behavior indicates that the contributions from the Debye and α relaxation are not coupled in the supercooled state.

The role of -OH or -OD in interactions between the molecules can be estimated from the values of $F_{1/2}$ for nPrOH or nPrOD and iPrOH or iPrOD. The change of $F_{1/2}$ between nPrOH and nPrOD is more pronounced than that between iPrOH and iPrOD. For example, the values of $F_{1/2}$ for Debye process are 0.26 and 0.29 for nPrOH and nPrOD, respectively. The similar values are 0.35 and 0.34 for iPrOH and iPrOD, respectively. For α relaxation, the respective values are changed from 0.50 to 0.46 for nPrOH and nPrOD, and from 0.57 to 0.58 for iPrOH and iPrOD. The substitution effect between -OH and -OD groups largely influences the relaxation behavior of n-propanol. It has, however, only a minor influence on behavior of i-propanol. The properties of the linear structure and its network, like nPrOH and nPrOD, is mainly governed by the length of the chain which depends on the length of the hydrogen bonding. However, the spherical structure made from dimer or smaller liner chain of iPrOH and iPrOD should behave independently or freely with ease.

5.3.2 Discussions on the origin of each relaxation process

From the comparison of the results for the nPrOH and nPrOD, the predominant deuteration effect appears in both the Debye and α relaxation since the relaxation frequency curves are shifted to lower temperature as shown in Figs. 5. 7 and 5. 11. For the iPrOH and iPrOD, however, the deuteration effect does not appear.

The values of T_0 and T_g at low temperature range and E at high temperature range for both the Debye and α relaxations are similar as listed in Table 5. 3. For example, calculated T_g for Debye relaxation are 105 and 109 K for nPrOH and nPrOD, respectively. However, these values are the same at 120 K for both iPrOH and iPrOD. For α relaxation, these temperatures are 101 and 105 K for nPrOH and nPrOD, respectively, and 118 K for both iPrOH and iPrOD.

As for as the origins of these processes are concerned, it may be proposed that:

The forming and breaking of hydrogen bond in the linear chain and its network structure play a dominant role in the Debye relaxation in propanol. Therefore, the fragility of the main Debye relaxation in 4 kinds of propanol is smaller. The α relaxation can be characterized by the movement of a whole molecule or its segment in the surface of network cooperatively with neighbor segment. The Debye and α relaxation are separated with the difference of the approximately two order. The ratio between the dielectric relaxation time τ_D and the volume relaxation time τ_V , τ_D/τ_V , is order of two. Floriano and Angell explained the origins of the dielectric and mechanical relaxations [71]. The dielectric relaxation reflects the behavior of the hydrogen bonded clusters of molecules and the mechanical relaxation occurs through molecules on the outside of the clusters. The mechanical relaxation and α relaxations are strongly coupled and may have the same origin. The dielectric strengths of Debye and α relaxations are nearly 95 % and 5 %. These very different values originate from the different motions of the relaxation modes.

On the other hand, the slow β relaxation for undeuterated and deuterated propanols exhibits no marked difference in terms of both dielectric strength and relaxation frequency. The origin of the β relaxation has nothing to do with hydrogen bond. If it relates to the hydrogen or deuterium, the behavior of the β relaxation should show a great deal of difference and may show a non-linear temperature dependent relaxation behavior. The observed lack of difference between deuterated propanols and undeuterated ones may

confirm that the slow β relaxation originates from the freely rotational parts. It is described in other terms such as the rotation of the free molecules and the uncorrelated region outside CRR and so on.

5.3.3 Summary

The deuteration effect on nPrOH is more marked than that on iPrOH. It is proved the fact that the fitting parameters, such as T_0 , $F_{1/2}$ and T_g calculated from the extrapolation of the VTF and E in Arrhenius equation, are much different for nPrOH and nPrOD.

The Debye relaxation is related to the hydrogen bond in network structure. The β relaxation, as compared with the Debye relaxation, is in agreement with the mechanical relaxation and originates from the segmental motion of the surface of the cluster. The more significant change of the relaxation behavior of nPrOH and nPrOD is explained by the effect due to hydrogen bonding. This appears as the difference in the behavior between deuterated and undeuterated propanols, for example, Debye and α relaxation. The β relaxation indicates the existence of free rotation part because there is similarity in dynamics between deuterated and undeuterated propanols.

5.4 Role of end group in glass transition and slow dynamics

To investigate the roles of hydrogen bonding in both glass transition and slow relaxation, the substitution effect between -OH and -OCH₃ groups was studied by the measurements of the complex dielectric permittivity ϵ^* and heat capacity C_p^* .

The samples studied are propylene glycol (PG) and its oligomers with two -OH groups, propylene glycol monomethyl ether (PGME) and its oligomers with a -OH and a -OCH₃ groups. That is, both PG and PGME family have the same chemical backbone of $[\text{OCHCH}_3\text{CH}_2]_n$, however, the different end groups, $\text{H}[\text{OCHCH}_3\text{CH}_2]_n\text{OH}$ or $\text{H}[\text{OCHCH}_3\text{CH}_2]_n\text{OCH}_3$. A monomer and 5 oligomers of PG family and monomeric PGME, diPGME (dPGME) and triPGME (tPGME) have been investigated. The detail dielectric data for PGME family will be presented in this Chapter, whereas those of PG family will be discussed in Chapter 5.5.

5.4.1 Slow dynamics of PG and PGME monomers and oligomers

The dielectric loss spectra for PGME, dPGME and tPGME were shown at various temperatures from stable liquid state to near T_g in Figs. 5. 12a), b) and c). Only the main relaxation mode was extracted from the spectra by virtue of the HN function.

Figs. 5. 13a) and b), respectively, represent the real and imaginary parts of the complex heat capacity, C_p' and C_p'' , of PGME and tPGME. The results were obtained in the heating process. The almost magnitude of heat capacity is related to the real part C_p' . Therefore, the real part of heat capacity has an abrupt increase near T_g which is usually found in the conventional heat capacity results as seen in Fig. 5. 13a). The imaginary part, C_p'' , has a peak at T_g as illustrated in Fig. 5. 13b), which corresponds to the calorimetric glass transition temperature T_g . The T_g values for PG, tPG, PGME, dPGME and tPGME are listed in Table 5. 5 together with the results from the dielectric relaxation time. Both glass transition temperatures differ each from the other by 1 - 3 K. As already explained in Chapter 4, the slow dynamics of α relaxation is the result of the structural relaxation during the liquid-glass transition.

Table 5. 5 Values of T_g measured by the calorimetric (T_{gc}) and dielectric (T_{gd}) methods

	PG	tPG	PGME	dPGME	tPGME
T_{gc} (K)	170.1	192.2	144.7	164.2	174.6
T_{gd} (K)	169	192	141	165	172

From the dielectric spectra, the dielectric strength can be calculated from the fitting to the HN function. The dielectric strengths of PG, tPG, PGME and tPGME are drawn in Fig. 5. 14. Four samples obey the relationship of $\Delta\epsilon = -A + B/T$ well. It is found the decrease of the dielectric strength in PGME family is predominant compared to the PG family. These two families differ only by the end group at one side, therefore this structural change is the cause of the observed decrease of the dielectric strength. The number of the -OH end groups strongly affects the dielectric strength.

The relaxation time can be obtained from the HN function by fitting it to the spectra shown in Fig. 5. 12. Fig. 5. 15 shows the dielectric and calorimetric relaxation times vs. $1000/T$. From the calculation of the fragility, $F_{1/2} = 2T_g/T_{1/2} - 1$, where $T_{1/2}$ is the temperature at $\tau = 10^{-6}$ sec, the deviation from the ARR law is quantified. The values of fragility for PG family are 0.52 and 0.63 for PG and tPG, respectively. These values for PGME family are 0.58, 0.62 and 0.63 in PGME, dPGME and tPGME, respectively. The fragility increases with increasing number of repeat units and with decreasing number of -OH end groups. It means that the relaxation dynamics is governed by the number of the -OH groups and the molecular weight.

5.4.2 Fragility and glass transition temperature

The relationship among the fragility and molecular weight and number of -OH end groups was described in Fig. 5. 16. The samples with the same backbone are listed at Table 5. 6. The number of the () means the molecular weight in g/mol. As can be seen in Fig. 5. 16, especially well seen in PG family, with increasing molecular weight the fragility increases with a steeper slope in the low molecular weight region and then the increasing is slower. It is also worth to notice that the material with more -OH end groups is stronger, providing the samples compared have the same molecular weight.

Table 5. 6 Sample list used at the calculation of the $F_{1/2}$ and T_g . The number means the molecular weight

1 -OH end group	2 -OH end group	3 -OH end group
PGME (90)	PG (76)	Gly (92))
dPGME (148)	tPG (192)	
tPGME (206)	PPG-425 (425)	
	PPG-725 (725)	
	PPG-2000 (2000)	
	PPG-4000 (4000)	

The similar trend appears as far as the relationship between the glass transition temperature and molecular weight and number of -OH end groups is concerned. This feature is shown in Fig. 5. 17. The samples are the same as those of Fig. 5. 16, which are listed at Table 5. 6. The value of T_g was evaluated with both molecular weight and number of -OH groups.

The fragility and glass transition temperature are very important two quantities which describe the glass transition and slow dynamics. These values seems to be controlled by the molecular weight and the chemical structure. To explain this phenomenal feature, two order parameter model is applied. This model was advocated by Tanaka in 1998 [2.4, Tanaka]. It originates from the consideration of the interactions which depend not only on the distance but also on the orientation between molecules. It is necessary to know two kinds of order parameter to describe these interaction more precisely. That is density and bond order parameter. The density order parameter has a role in minimizing the distance between nearest-neighbor molecule, packing the molecules and representing the long-range density ordering. The bond order parameter, on the other hand, maximizes the number of surrounding molecules and leads to locally favored structure which is not identical to that of the crystallization. The locally favored structure breaks the symmetry and makes the interaction anisotropic. The frustration between density and bond order parameter rules the path of crystallization or vitrification.

The -OH group and the -CH₃ group in alcohol may play dominant roles as two order parameters each other. In the present situation, the molecular weight of -CH₃ group can be assigned to the density order parameter and the presence of -OH group is related to the bond order parameter. The forming of hydrogen bonding makes the interaction anisotropic and leads the liquid to be stronger. So that the curve of the fragility of the materials with higher -OH density, i.e., number of -OH groups, is situated in the lower

side of the graph as shown in Fig. 5. 16. The increase of the number of -OH groups gives rise to the shift of the fragility to the upper side at the molecular weight and fragility plane. On the other hand, the methyl group in the PG or PGME monomer or oligomers plays a role to minimize the distance between the molecules. The isotropic packing effect increases with increasing the repeat unit. Even though the repeat unit increases more, however, the evaluating rate does not increase so much. This effect makes the feature of the fragility have a curvature. The strong anisotropic interaction corresponds to the evaluation of the glass transition temperature and dielectric strength, which is illustrated in Fig. 5. 17 and Fig. 5. 14, respectively. The isotropic interaction in the higher molecular weight region suggests that the glass transition is likely to be saturated above PPG725.

5.4.3 Summary

The roles of end groups, -OH and -OCH₃, have been investigated in both glass transition and slow relaxation. The substitution between -OH and -OCH₃ groups gives the different relaxation behavior from the point of view of the dielectric permittivity and calorimetric measurement.

The glass transition and slow dynamics are characterized by the glass transition temperature and fragility with molecular weight and number of -OH groups. These relaxation behavior is explained by the frustration between the density and bond order parameters on the basis of the two order parameter model. The presence of -OH group controls mainly the anisotropic bond order parameter and the packing effect by -CH₃ influences the density which makes the interaction between molecules isotropic.

5.5 Role of molecular weight

The molecular weight dependence of both slow dynamics of α relaxation and glass transition of intermediate glass-forming materials has been studied. Propylene glycol (PG) and its five oligomers (poly propylene glycol, PPG) were chosen as materials studied in this work. They have the same chemical structure of $\text{H}[\text{OCHCH}_2\text{CH}_2]_n\text{OH}$, however, different molecular weights, from 76 to 4000 g/mol, indicated by the number n of the repeated unit. Since PG and PPGs have the similar chemical structure, the intermolecular cooperativity is mainly related to the change of the relaxation behavior.

The quantities such as fragility, $F_{1/2}$, glass transition temperature T_g and excess heat capacity at T_g , $\Delta C_p(T_g)$ were obtained from both dielectric and thermal measurements. The molecular weight dependence of $F_{1/2}$, T_g and $\Delta C_p(T_g)$ will be discussed. The fragility and cooperativity are related to the characteristic properties of these liquids in both liquid and supercooled liquid states. The comparison between domain model and the Adam-Gibbs theory give us the possibility to use the efficient VTF equation and to obtain information about minimum configurational entropy and the variation of domain size with temperature. The relationship between the shape parameter of Kohlrausch-Williams-Watts (KWW) functions and intermolecular cooperativity, i.e., the domain size, was clarified.

The dielectric and thermal results for the monomer PG and PPGs oligomers are available. Several behaviors of the α relaxation in PG were reported [58-60]. The presence of two or three relaxation processes for PPG with the molecular weight above 1300 g/mol was also studied by the viscoelastic [72-74], dielectric [72, 75-78] and NMR [79] methods. However, there are only few results analyzing both dielectric and thermal properties of PG and PPGs in terms of the fragility and cooperativity and calculating the physical properties such as domain size or minimum configurational entropy.

The samples used were PG monomer and its five kinds of PPG oligomers which have the molecular weights 192 ($n=3$, tPG), 425 ($n=7$, PPG-425), 725 ($n=12$, PPG-725), 2000 ($n=34$, PPG-2000) and 4000 g/mol ($n=69$, PPG-4000). All the samples are classified as intermediate glass-forming liquids.

5.5.1 Results obtained from dielectric method

The normalized dielectric loss curves for tPG and PPG-4000, $\epsilon''/\epsilon''_{\max}$, are shown as a function of frequency at several temperatures in Figs. 5. 18a) and b), respectively, where ϵ'' is the dielectric loss and ϵ''_{\max} is its maximum value at the peak position. Only the peaks of α relaxation are revealed. All the curves in Fig. 5. 18 may be well described by the Havriliak-Negami (HN) empirical relaxation function. The relaxation frequency, dielectric strength and shape parameters α and γ were obtained from this fitting. On cooling PG and PPGs from liquid to glass state, the maximum characteristic relaxation frequency, $f_{\max} = 1/(2\pi\tau)$, decreases dramatically and loss peak broadens. The f_{\max} change rate upon temperature is the main factor which allows to classify the liquids as strong or fragile one. The broadening of the loss peak is related to the intermolecular cooperativity strength which is represented by the number of the rotation unit in a domain.

The temperature variation of f_{\max} for PG and PPGs is shown in Fig. 5. 19 as the Arrhenius plot, f_{\max} vs. $1000/T$. The dielectric glass transition temperature, T_{gD} at which the relaxation time becomes 100 sec.

The agreement of f_{\max} with VTF law, $f_{\max} = f_0 \exp(-\frac{B}{T-T_0})$, provides good description of the loss peak positions in all the experimental temperature windows for PG and PPGs. The method of temperature derivative analysis [39] was employed to determine its dependence precisely for the following VTF dependence,
$$\left[\frac{-d \log f_{\max}}{d(1/T)}\right]^{-1/2} = \frac{1}{B^{1/2}} \left(1 - \frac{T_0}{T}\right).$$

From this dielectric analysis, we determined the VTF and parameters of VTF law, which represent the characteristic properties of slow dynamics, such as $F_{1/2}$, T_0 and T_{gD} .

Matsuoka et al. developed the VTF equation in terms of intermolecular cooperativity [10]. According to this model, the molecular segments in a domain can only relax cooperatively. The domain size is defined as the number of conformers in a domain. Domain size is unity at the high-temperature limit, T^* , and infinity at a low-temperature limit, usually called as the Vogel-Fulcher temperature T_0 . At T_0 , therefore, every conformer becomes meshed with all others and the entire body becomes one huge meshed domain when an electric field is impulsed and the conformational entropy is zero.

According to this domain model, the VTF equation is given by,

$$f_{\max} = f_0 \exp\left(-\frac{\Delta\mu^*}{R} \frac{1}{T - T_0}\right) \quad (5.4)$$

where $\Delta\mu^*$ is the activation energy for independently relaxing conformers or Vogel-Fulcher energy of kcal/mol, which is expressed in terms of the repeat chain unit in case of oligomers or polymers and R is the gas constant. Vogel-Fulcher energy $\Delta\mu^*$ evaluated from Eq. (4. 16) are 3.9, 2.6, 2.5, 2.1, 2.0 and 1.9 kcal/mol for PG, tPG, PPG-425, -725, -2000 and -4000, respectively. For poly(propylene oxide) which have the -C-C-O- backbone as same as PG and PPGs, the Vogel-Fulcher energy is 1.8 kcal/mol [10]. This value is compatible to that of the higher weight PPG oligomers.

It is clear that the fragility, $F_{1/2}$, increases with the increase of molecular weight as illustrated in Fig 5. 18 already. The similar results could be also seen at the other alcohols by the viscoelastic [72-74], or dielectric results [72, 75-78]. The increase of $F_{1/2}$ with molecular weight indicates that PG monomer is located at the far side from the fragile limit than its oligomers.

PG has the four hydrogen bonding sites in a molecule [80], which are able to create a transient crosslinking structure with neighboring molecules via hydrogen bond. The end -OH groups of the PPGs are able to form two types of hydrogen bonds: end-to-end and end-to-ether group. Both can form inter- and intra-molecular structures such as intramolecular rings, branched structures and longer chain. There are many such structures for low molecular weights because of the high number density of hydroxyl end group. For increasing molecular weights, the possibility of intramolecular hydrogen bonds decrease because the hydroxyl end groups are less likely to attach to the other atoms or the second terminal group of their own chain. The bond strength of molecule is the one of the elements to determine the fragility of liquids. The liquids with covalent network structure are good examples of strong ones whose fragility is smaller. On the other hand, those with van der Waals structure are fragile with higher fragility. From this point of view, on increasing the molecular weight, the number density of end -OH group decreases. It leads to the degradation of the molecular bond strength to form H-bonding structure, and makes the liquid more fragile with increasing the molecular weight.

5.5.2 Cooperativity and domain size

The PG and PPGs have similar chemical structures but different molecular weights or the monomer repeat unit numbers. The dielectric properties caused by the intermolecular cooperativity can depend on molecular weight. One of the measure of cooperativity is the number of conformers in a domain introduced by Matsuoka et al. [10].

There are two limit temperatures, T^* and T_0 , where the number of conformer is 1 or infinity. The values of T_0 listed in 116, 155, 162, 169, 171 and 172 for PG, tPG, -425, -725, -2000 and -4000, respectively. It increases with the increase of molecular weight, but the changing rate against molecular weight was slow except of the rapid increase for the higher weights. There is a high-temperature limit T^* where the relaxation vs. temperature plots for most polymers approximately converges and it is pointed out 773 K with the relaxation time of 30 ps [10]. It is, however, very hard to find the dielectric results for alcohols which coincide this universality. The T^* was determined as the temperature where the relaxation time is 30 ps. According to the VTF fittings, the temperatures are 411, 474, 474, 507, 541 and 546 K for PG, tPG, PPG-425, -725, -2000 and -4000, respectively. The values of T^* for PG and PPGs were lower than those for polymers, universal temperature 773 K, below 200 - 350 K.

Between these two extreme temperature limits, the domain size, Z , is the function of temperature according to the following equation,

$$Z = \frac{T^* - T_0}{T^*} \frac{T}{T - T_0} \quad (5.5)$$

The temperature dependence of Z for the samples studied is shown in Fig. 5. 20

The domain size increases with decreasing temperature, starts to increase around T_g and diverges at T_0 at which the configurational entropy is zero. These features are different from the results calculated directly from the heat capacity data for several glass-forming molecular liquids such as toluene, ethylbenzene, 3-bromopentane, 1-butene and *O*-terphenyl for whose size increases markedly around T_g but becomes constant below T_g [81, 82]. This difference between the fact that the domain size diverges at T_0 and the fact that it becomes constant below T_g comes from the difference between the assumption that the configurational entropy is zero below T_0 and the real measurement that it is constant below T_g . The domain size at T_g , $Z(T_g)$ increases with molecular weight in the manner of 2.3, 3.5, 3.7, 4.3, 4.8 and 4.8 for PG and PPG oligomers. The domain size for the oligomers with the higher molecular weight is compatible to the case of several glass-forming molecular liquids mentioned above, four to eight at T_g . In case of PG, however,

it is somewhat smaller to rotate with cooperation. It may be related to the fragility of the PG and PPGs. The decrease of the density of -OH groups results in the oligomer to be fragiler and more cooperative.

5.5.3 Domain size and non-exponentiality

The larger domain size should be reoriented in a more cooperative manner. This results in the broadening of the dielectric loss peak, then the broad distribution of relaxation time and the non-exponential decay relaxation function. This broadening is equivalent to the smaller values of the parameters α and γ in the HN function, or the β_{KWW} in the KWW function. The parameter β_{KWW} is numerically connected to the parameters α and γ in HN, $\beta_{\text{KWW}} = \alpha\gamma^{1/1.23}$ [45].

The values of β for PG and PPGs drop with an approximately linear relationship with decreasing temperature. Therefore, the value β_{KWW} at T_g , $\beta_{\text{KWW}}(T_g)$ can be extrapolated by the linear approximation. The values are 0.67, 0.54, 0.44 and 0.44 for PG, tPG, PPG-425 and PPG-4000, respectively, and were drawn against $Z(T_g)$ in Fig .5. 21. The increase of the domain size at $Z(T_g)$ corresponds to the smaller β_{KWW} , that is, larger non-exponentiality. It implies that the non-exponentiality is directly affected by the intermolecular cooperativity. The increase of non-exponentiality coincides with the increase of the domain size.

5.5.4 Results obtained from calorimetric method

A typical set of the temperature dependence of heat capacity, $C'_p(T)$, was calculated from the reversing heat flow during heating process as shown in Fig. 5. 19. The temperature variations of heat capacities are very similar to those obtained by the conventional DSC with constant 10 K/min heating rate [80].

The peak of the $C''_p(T)$ was assigned as the glass transition temperature in heating. The $\Delta C_p(T_g)$ was determined in this manner. The heat capacity data were well approximated as linear functions of temperature which were determined by the least-squares fitting of the data well below and well above the T_g as $C_{pg} = A_g + B_g T$ (for $T < T_g$) and $C_{pl} = A_l + B_l T$ (for $T > T_g$), respectively.

The value of $\Delta C_p(T)$ was obtained from the difference of these two extrapolated lines, i.e., $\Delta C_p(T) = C_{pl}(T) - C_{pg}(T)$ as illustrated in Fig. 5. 19.

Detail discussion on the molecular weight dependence of T_g and $\Delta C_p(T_g)$ for PG and PPGs was reported in ref. 80. The fact that T_g increases remarkably and reaches a limiting value for a chain containing 20 monomer units was reported and discussed in terms of the Fox-Flory and the entropy theory. The initial increase of $\Delta C_p(T_g)$ from PG to PPG 200 is attributed to the decrease of H-bonding sites and further decrease with the increase of molecular weight to increasingly large amplitude of the β process for $T < T_g$. The values of calorimetric T_g in our case increase till 201 K at PPG-425 and remain nearly constant for PPGs with larger molecular weight. It coincides with the results of ref. 80 obtained by the DSC with 10 K/min ramp.

The $\Delta C_p(T_g)$ values increase initially from 0.59 J/K/g for PG to 0.60 J/K/g for tPG but gradually decrease to 0.49 J/K/g for PPG-4000. The values of T_g and $\Delta C_p(T_g)$ are shown in 5. 22. Its changing scheme is similar to the results of ref. 80 with 20 K/min ramp. The molecular weight dependence of T_g/T_0 was derived at Eq. (4. 17) on the basis of free volume and was shown in Fig. 5. 23 for PG and PGME family. The value of T_g/T_0 is not dependent on the materials.

The relationship between the heat capacity change at T_g , $\Delta C_p(T_g)$, and the fragility was discussed by Angell [13] and Hodge [48]. There is a direct relationship between fragility and $\Delta C_p(T_g)$. From the concept of fragility introduced by Angell, the liquid having larger $\Delta C_p(T_g)$ is more fragile. The exception from this rule are alcohols as an intermediate liquid but the $\Delta C_p(T_g)$ is larger than that of fragile one. It was described in terms of the high density of minima and depth on the potential energy hypersurface, but still relatively strong.

5.5.5 Relationship between glass transition and slow dynamics

The relationship between T_{gD} from the dielectric analysis and T_g from the calorimetric measurement for PG and PPGs are represented in Fig. 4. 5 already. Both are the same within the experimental uncertainty. It indicates that the glass transition strongly affects the α -relaxation.

For VTF equation from both the Adam-Gibbs relation and domain model, the minimum configurational entropy s^* has been derived already in Chapter 4.

$$s^* = \frac{T_g \Delta C_p(T_g) T^* - T_0}{T_0 T^*} \quad (5.6)$$

The minimum configurational entropy, s^* , for a mol conformer is

$$s^* = R \ln(W), \quad (5.7)$$

where W is the number of states that a conformer can take.

The calculated values s^* for PPGs by the Eq. (5.6) are 6.9, 6.7, 6.0, 5.6 and 5.5 cal/K/mol for the repeat unit [OCHCH₃CH₂] of tPG, PPG-425, -725, -2000 and -4000, respectively. The value for PG monomer of 76 g/mol molecular weight is 11.1 cal/K/mol. It is compatible to those of toluene 9.8, ethylbenzene 15.4 and 1-butene 15.5 cal/K/mol [82].

5.5.6 Summary

The α relaxation in glass transitions of the PG and its five PPG oligomers, which have similar chemical structure but different molecular weights 76 - 4000 g/mol, was studied by both calorimetric and dielectric measurements methods and these results were compared in detail.

Enthalpy relaxation by the glass transition is compatible to the main α relaxation by dipole relaxation, which is proved by equivalence between calorimetric and dielectric glass transition temperatures, T_g and T_{gD} .

The drop of the $F_{1/2}$ with decreasing molecular weight, which implies that the monomer is more strong liquid than PPGs, was explained in terms of the number density of end hydroxyl group. The strong/fragile scheme of PG and PPGs are governed by the number density of end hydroxyl group.

Comparing the Adam-Gibbs theory and domain model, the minimum configurational entropy s^* and domain size are qualitatively calculated for the liquid interacted via hydrogen bonding.

The domain size was derived from only two limit temperatures and expressed as function of temperature. As domain size increases, the relaxation behavior is more non-linear and the distribution of relaxation broadens what means the increase of the cooperativity between molecules.