Journal of Thermal Analysis and Calorimetry, Vol. 57 (1999) 687-693

CALORIMETRIC AND DIELECTRIC INVESTIGATIONS OF GLASS TRANSITION IN INTERMEDIATE GLASS-FORMING LIQUID

I.-S. Park, K. Saruta and S. Kojima

Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Abstract

The calorimetric glass transition and dielectric dynamics of α-relaxation in propylene glycol (PG) and its five oligomers (polypropylene glycol, PPG) have been investigated by the modulated differential scanning calorimetry (MDSC) and the broadband dielectric spectroscopy. From the temperature dependence of heat capacity of PPGs, it is clarified that the glass transition temperature (T_g) and the glass transition region are affected by the heating rate. The kinetic changes of PG and PPGs near T_g strongly depend on the underlying heating rate. With increasing the molecular mass of PPGs, the fragility derived from the relaxation time against temperature also increases. The PG monomer is stronger than its oligomers, PPGs, because of the larger number density of the –OH end group which tends to construct the intermolecular network structure. Adam-Gibbs (AG) theory could still hold for MDSC results due to the fact that the dielectric relaxation time can be related to the configurational entropy.

Keywords: Adam-Gibbs theory, dielectric relaxation, glass transition, MDSC

Introduction

The dynamics of the glass-forming materials have been extensively studied theoretically and experimentally during recent years [1]. The studies on fragile or intermediate liquids are the main topics on the liquid-glass transitions because of their non-simple dynamical behaviors originated from the molecular cooperativity and the complex relaxation modes [2–4].

Experiments on the low molecular mass molecules are very important to examine the validity of the theories and simulations because of their simple structure. The calorimetric measurement and broadband complex dielectric measurement are powerful and straightforward techniques to gain insight into the molecular dynamics of many kinds of glass-forming materials.

In this work, we studied the liquid-glass transition and α-relaxation in terms of the thermal and dielectric properties of several kinds of alcohols with two –OH groups per molecule, i.e., propylene glycol (PG) and its five kinds of oligomers (polypropylene glycol, PPG) with a short [–$OCHCH_3CH_2$–] repeat chain unit. These samples have the similar chemical structure with intermolecular hydrogen bonding but different molecular mass from 76 to 4000 g mol^{-1}.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The correlation between calorimetric and dielectric relaxation properties has been studied. Both properties reflect the different glass transition phenomena. The former is a relaxation process in the freeze-in, but the latter is a non-equilibrium process during the vitrification process. However, they are closely related with each other. For this reason, the glass transition temperatures determined by both methods were compared. Both relaxation behaviors were analyzed on the basis of the Adam-Gibbs (AG) theory of which main idea is the cooperatively rearranging region (CRR).

Experimental

A method called the temperature modulated differential scanning calorimetry (MDSC) has been recently introduced and developed [5, 6]. In MDSC, a sinusoidal oscillation of temperature is used as the external perturbation superimposed upon an underlying linear temperature change, so that the sample temperature, T, at time t is given by

$$T = T_o + qt + A\sin(2\pi t/P) \tag{1}$$

where T_o is the initial temperature for the MDSC scanning, q [K min^{-1}] is the underlying heating rate, A is the amplitude of temperature modulation and P [s] is the modulation period. The most suitable amplitude A is represented as the function of the underlying heating rate and period, i.e.,

$$A = qP/2\pi \tag{2}$$

The period P was fixed at 100 s to compare the calorimetric glass transition temperature with the dielectric glass transition temperature where the relaxation time is 100 s, so that the amplitude A was changed only by the heating rate.

Heat flow (HF) from MDSC can be separated into two parts: one is reversing heat flow (RHF) and the other is non-reversing heat flow (NHF) in the following equation:

$$\mathrm{d}Q/\mathrm{d}t = C_p\mathrm{d}T/\mathrm{d}t+f(T, t) \tag{3}$$

where C_p is the heat capacity and $f(T, t)$ is the kinetic component. Heat capacity, which indicates the thermodynamic property of materials, can be derived from the RHF only. The non-reversing heat flow is associated with kinetic processes, such as relaxation, crystallization or melting. The MDSC (TA Instruments, DSC-2920) system was used to investigate the thermal property of materials. At first the samples were cooled down from 313 to 120 K with 2, 5 and 10 K min^{-1} heating rates, then remained at 120 K for 10 min, and finally reheated to 313 K with the same heating rates in cooling. The values of modulated temperature amplitude in this study were determined by Eq. (2). Their values were 0.53, 1.33 and 2.65 K with 100 s period for the 2, 5 and 10 K min^{-1} heating rates, respectively. The instrumental resolution of

MDSC depends on the product of the heating rate and the modulation period, i.e., *qP*. These values, for example, were 3.3, 8.3 and 16.7 K at 2, 5 and 10 K min^{-1} heating rates, respectively.

To measure the dielectric relaxation time, two kinds of dielectric measurement systems were used in this work to cover the broad frequency range: the Impedance/Gain-phase analyzer (Solartron SI 1260) in low frequency range from 10 mHz to 10 MHz and the time domain reflectometry (TDR) system (HP54750A digital oscilloscope and HP54754A differential TDR plug-in) in high frequency range from 1 MHz to 10 GHz [7].

The samples used were PG monomer and its five kinds of PPG oligomers which have the molecular mass 192 (triPG), 425 (PPG-425), 725 (PPG-725), 2000 (PPG-2000) and 4000 g mol^{-1} (PPG-4000). All of them have the same –C–C–O– backbone. The repeat numbers of [$–OCHCH_3CH_2–$] are 3 for triPG and nearly 7, 12, 34 and 69 for PPG-425, -725, -2000 and -4000, respectively. These samples are classified into intermediate glass-forming liquids [8].

Results and discussion

The typical schemes of HF, NHF and C_p for PPG-4000 are shown in Figs la, lb and lc, respectively, for the different heating rate, 2, 5 and l0 K min^{-1} with their corresponding modulation amplitude. The MDSC results of other samples have the similar features as PPG-4000.

The kinetic transitions of PG and PPGs are clarified from the fact that the NHF changes stepwise around calorimetric glass transition temperature, T_g. The NHF data for PPG-4000 in Fig. lb shows that the feature of the NHF strongly depends on the underlying heating rate. For 2 K min^{-1} case, the values of the NHF change and a sharp valley appears at 201.6 K, which is related to the enthalpy relaxation. For 5 and 10 K min^{-1} ones, the NHF values only reveal step-like change across the transition regions, which depend on the heating rate, are approximately 10 and 20 K, respectively.

The midpoint of the NHF was determined by the average of the onset and offset points of the NHF, indicated as the T1 and T2 at the case of 5 K min^{-1} in Fig. 1b. The values of midpoint of NHF are 198. 5 and 211.3 K for 5 and 10 K min^{-1}, respectively. The changed values of NHF at the bottom temperature in case of 2 K min^{-1} and at the midpoint temperature in 5 and 10 K min^{-1} are 0.0071, 0.0131 and 0.0245 W/g, respectively. From these results, it could be concluded that the transition region and the amount of NHF change across this region. These are very sensitive to the heating rate.

From C_p results in Fig. lc, it can be also easily known that the glass transition region depends on the heating rate. The onset and offset points were obtained by the same way in case of NHF. Their onset, offset and midpoints of triPG and PPG-4000 are listed in Table l. The midpoint of C_p data was assigned as T_g. The midpoints determined from the C_p data are not the same as those of NHF ones. For example, the difference of midpoints is 20 K at the case of 10 K min^{-1}. The onset point decreases

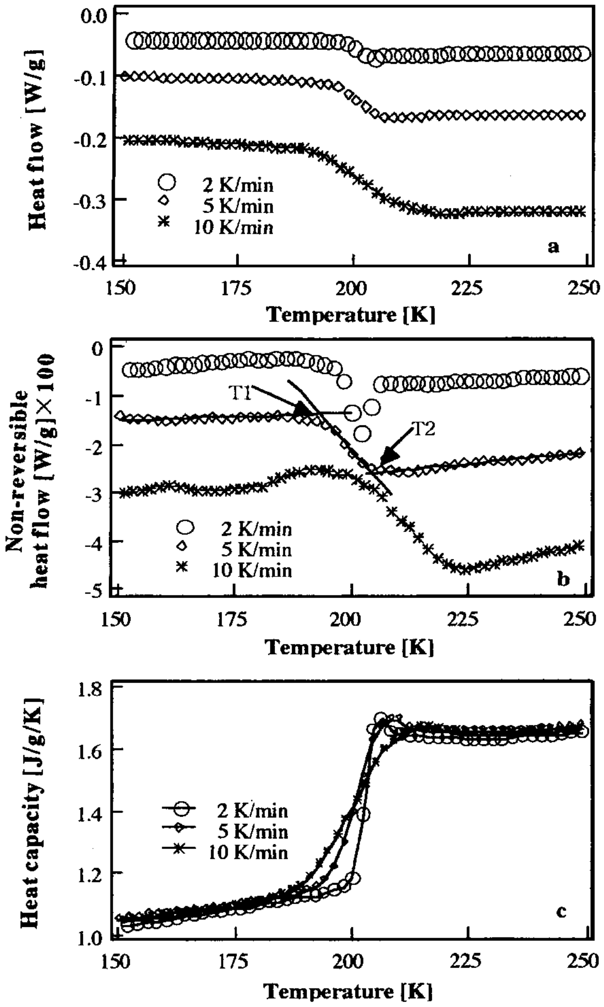

Fig. 1 The typical schemes about a) total heat flow b) non-reversible heat flow and c) heat capacity derived from the reversible heat flow for PPG-4000

Table 1 The onset, offset and midpoints of triPG and PPG-4000

Heating rate/ K min^{-1}	Onset point/K		Offset point/K		Midpoint/K	
	triPG	PPG-4000	triPG	PPG-4000	triPG	PPG-4000
10	180.6	189.4	194.8	206.7	187.7	198.1
5	185.6	194.9	193.0	204.4	189.3	199.7
2	188.3	199.4	192.9	203.0	190.6	201.2

and the offset point increases with the increase of heating rate. The values of T_g are related to the heating rate q by the equation [9, 10],

$$\log q = -\Delta h/RT_g \tag{4}$$

where Δh is the activation enthalpy and R is the gas constant. According to Eq. (4), the inverse glass transition temperature, $1/T_g$ should linearly decrease with the log scale of heating rate. The earlier results for PG and several PPGs show that Eq. (4) can be well applied to the DSC data [11]. In our case, however, the T_g from the C_p data decreases with the increase of heating rate. This difference comes from the modulation effect of the MDSC. The dielectric glass transition for triPG and PPG-4000, where the relaxation time is 100 s, are 192 and 201 K, respectively when the heating rate is nearly 1 K min^{-1}. They are comparable with the calorimetric results with the heating rate 2 K min^{-1}. As the heating rate becomes fast, the peak of the overshoot shifts to the higher temperature, while the peak height becomes lower.

The complex dielectric spectra, $\varepsilon^*(\omega)$, were well reproduced by the Havriliak-Negami (HN) function,

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\,/\,[1 + (i\omega\tau)^\alpha]^\gamma, \quad 0 < \alpha,\gamma \leq 1 \tag{5}$$

where ω is the angular frequency, τ is the characteristic relaxation time and ε_∞ and ε_0 are the dielectric constant in the high and low frequency limits, respectively. The dielectric relaxation times of the samples were determined by Eq. (5). The temperature dependence of the relaxation times from the dielectric measurements on PG and PPGs is shown in Fig. 2 *vs*. normalized T_{gd}/T. The T_{gd} is the temperature where the dielectric relaxation time is 100 s. This temperature was determined by the extrapolation of the data through Vogel-Tammann-Fulcher (VTF) law, $\tau=\tau_0\exp[DT_0/(T-T_0)]$. It is hard to distinguish the data of PPG-425 with PPG-725, -2000 and -4000, so that only the results of PPG-425 are drawn.

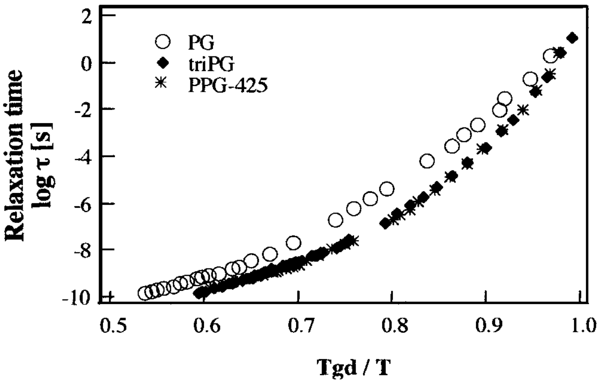

Fig. 2 The temperature dependence of the relaxation time from the dielectric spectroscopy for PG, triPG and PPG-425 is shown *vs*. normalized T_{gd}/T

Angell classified the liquids into strong and fragile ones from the dependence of the viscosity or the relaxation time *vs.* T_{gd}/T [8]. The temperature variations of the relaxation time for strong and fragile liquids well obey the simple Arrhenius law, $\tau = \tau_0 \exp(E/T)$ and the VTF law, respectively. The strength parameter, D, in VTF law indicates the measure of the fragility of the materials. It can be known from the Fig. 2 that the fragility increases with increasing the molecular mass. The values of D from the VTF fitting are 16.9, 8.3, 7.7, 6.2, 5.8 and 5.6 in the order of increasing molecular mass. As the number density of the –OH end group in PG monomer is larger than that of PPGs with long chain, the intermolecular network structure can be easily constructed by the hydrogen bonding even though it is classified as the weak interaction.

The temperature dependence of relaxation time τ (T) in glass-forming liquids can be described by the Adam-Gibbs equation [12], that is

$$\ln\tau = \ln\tau_0 + \Delta\mu s_c^*/k_B T S_c(T) \tag{6}$$

where $\Delta\mu$ is the activation energy per mole, s_c^* is the minimum configurational entropy, k_B is the Boltzmann constant and $S_c(T)$ is the configurational entropy. As the value of $\Delta\mu s_c^*$ is invariant during the relaxation process, the linear relationship between $\ln\tau$ and $(TS_c(T))^{-1}$ can indicate the validity of the AG theory. The relaxation time, τ, is evaluated from the dielectric measurements and the $S_c(T)$ is from the calorimetric measurements.

The configurational entropy $S_c(T)$ was evaluated by the heat cpacity, $C_p(T)$, including the glass transition regions by following equation,

$$S_c(T) = S_c(T_0) + \int_{T_0}^{T} dT\,[C_{pl} - C_{pg}]/T \tag{7}$$

where C_{pl} and C_{pg} are heat capacities of supercooled liquid and glass, respectively, and T_0 is the Vogel-Fulcher temperature in VTF law. The relationship between $\log\tau$

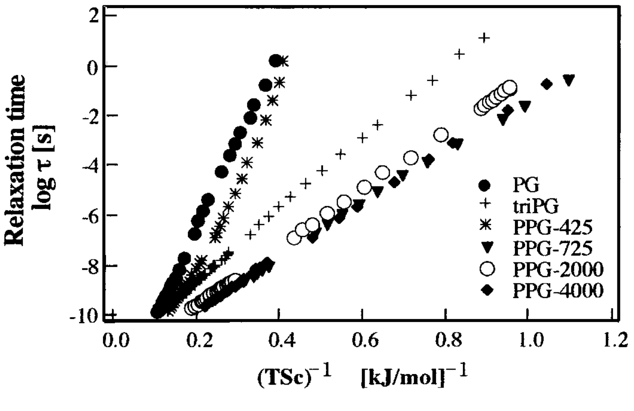

Fig. 3 $\log\tau$ *vs.* $(TS_c)^{-1}$ plots for PG, triPG, PPG-425, -725, -2000 md -4000. A good linearity holds for these plots

vs. $(TS_c(T))^{-1}$ is shown in Fig. 3 for PG and five PPGs where a good linearity holds for all of the data.

Summary and conclusions

The MDSC has some advantages against the conventional DSC for the temperature modulation effect. By the application of the modulation, total heat flow can be divided into RHF and NHF. The heat capacities derived from the RHF and that from conventional DSC have different features. The kinetic relaxation in the liquid-glass transition process can be clarified by the change of NHF.

The heat capacities of PPGs are different from the earlier DSC results in the manner of the variation of the T_g with heating rate. The NHF changes of PG and PPGs strongly depend on the underlying heating rate. The transition region and its midpoint of both RHF and NHF do not coincide, therefore it is concluded that the two transitions occur separately. The glass transition may be related to the α-relaxation from the view point that the transition temperatures by C_p and dielectric relaxation time are similar. The fragility increases with the increase of the molecular mass which has the same meaning that the number density of –OH end group becomes low. The density of the –OH group in PG and PPGs, which constructs the intermolecular network structure by the hydrogen bonding, may determine the fragility of the liquids.

The relationship between the calorimetric glass transition and the dielectric relaxation still remains valid through the AG theory. It is clearly explained by the linearity between the dielectric relaxation time, $\ln\tau$, and the configurational entropy in terms of $(TS_c(T))^{-1.}$

* * *

The authors are thankful to Dr. Y. Amo and Prof. Y. Tominaga, Ochanomizu University, for their kind advice on TDR technique and the supply of their TDR software. This work was partly supported by the Grant-in-Aids from the Ministry of Education, Science, Sports and Culture.

References

1 Special issue on Relaxation in Complex Systems, ed. K. L. Ngai, E. Riande and M. D. Ingram: J. Non-Cryst. Solids, 235-237 (1998).
2 S. S. N. Murthy, Mol. Phys., 87 (1996) 691.
3 S. Kojima, K. Saruta and A. Yoshihara, Jpn. J. Appl. Phys., 36 (1997) 2981.
4 C. Hansen, F. Stickel, T. Berger, R. Richert and E. W. Fischer, J. Chem. Phys., 107 (1997) 1086.
5 M. Reading, E. Elliott and V. L. Hill, J. Thermal Anal., 40 (1993) 949.
6 P. S. Gill, S. R. Sauerbraun and M. Reading, J. Thermal Anal., 40 (1993) 931.
7 I.-S. Park, K. Saruta and S. Kojima, Mol. Cryst. Liq. Cryst., 322 (1998) 329.
8 C. A. Angell, J. Non-Cryst. Solids, 131-133 (1991) 13.
9 H. Sasabe and C. T. Moynihan, J. Polym. Sci. Phys. Ed., 16 (1978) 1447.
10 C. T. Moynihan, A. J. Eastal, J. Wilder and T. Tucker, J. Phys. Chem., 78 (1974) 2673.
11 G. P. Johari, A. Hallbrucker and E. Mayer, J. Poly. Sci.: Part B: Poly. Phys., 26 (1988) 1923.
12 G. Adam and J. H. Gibbs, J. Chem. Phys., 43 (1965) 139.