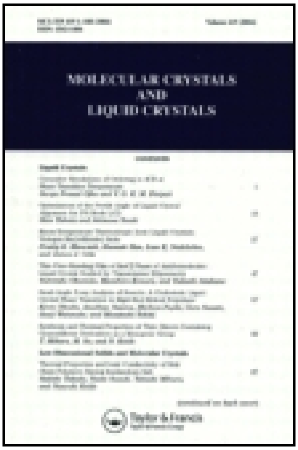

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Broadband Dielectric Relaxation of Organic Glass-Forming Liquids : Molecular Weight Dependence

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In order to study the molecular weight dependence of the dielectric properties, the dynamics of the α-relaxation in both liquid and supercooled liquid of the dyhydroxyl propylene glycol monomer (PG) and its five oligomers (poly propylene glycol, PPG) has been investigated as the organic fragile glass-forming materials in the frequency range from 10mHz to 10GHz by means of broadband dielectric spectroscopy. The frequency dependence of the complex dielectric permittivity is analyzed by the Harvrilliak-Negami(HN) expression. The temperature dependence of the characteristic loss peak frequency f_{max} for the α-process shows a Vogel-Tammann-Fulcher(VTF) behavior. The PG monomer is more fragile liquid than its oligomers because of the linear increase of the measure of non-linearity to 1/Mn.

Keywords: fragile liquid; poly propylene glycol; non-linearity.

INTRODUCTION

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 an electric field. The complex dielectric measurement is a powerful and straightforward technique to gain insight into the molecular dynamics of many materials. Currently, the relaxation dynamics of simple glass-forming liquids have been extensively studied to clarify the dynamics of the liquid, supercooled liquid, and glass by the measurements of viscosity, dielectric constant, NMR, light scattering, neutron inelastic scattering, ultrasonic attenuation etc.[1-4]. From these results it is well established that the α-relaxation shows universal features regardless of the type of the glass-forming liquids. The main characteristic features of this relaxation are the non-Debye behavior or stretched exponential time decay of the response function and the non-Arrhenius temperature dependence of a characteristic relaxation time.

In the present paper, we studied the dielectric relaxation of dyhydroxyl alcohols i.e., propylene glycol monomer and its oligomers as intermediate glass formers and discussed molecular weight dependence of the dielectric properties in the supercooled and liquid states in the frequency range 10 mHz to 10 GHz . The dielectric[5] and thermal[6] properties of these material were already reported, but the frequency of dielectric measurement was limited to 1MHz. We extended the frequency limit to 10 GHz to clarify the whole picture of the α-relaxation.

EXPERIMENTS

Two kinds of measurement systems were used in order to cover the broad frequency range from 10 mHz to 10 GHz. One is the Impedance/Gain-phase analyzer(Solartron SI 1260) in low-frequency range from 10 mHz to 10 MHz. In this case, a sample was kept between two electrodes of which distance was fixed to 0.4 mm. Frequency scans were performed at a constant temperature, which was decreased step by step. The current amplifier was also used additionally below 100 Hz. The other is 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.

The experimental TDR equipment is schematically shown in Figure 1. The TDR plug-in generates a 0.2V voltage step pulse and sends it to a sample as an

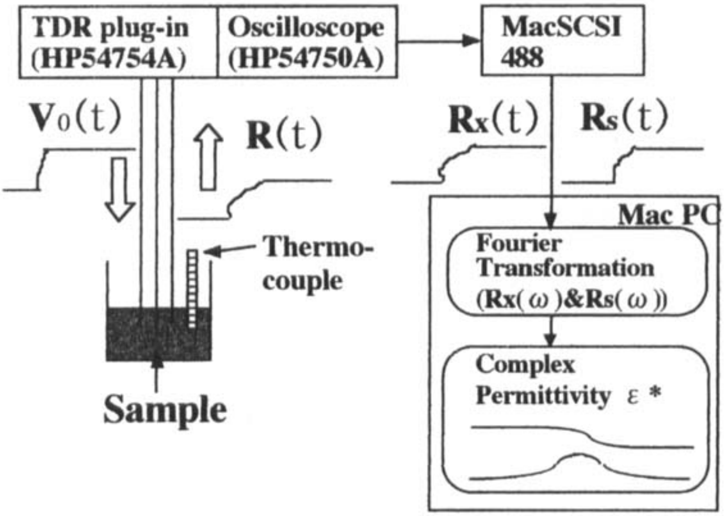

FIGURE 1 Block diagram of TDR system.

incident signal, $V_0(t)$, through a transmission line. The oscilloscope records both the incident and reflected, R(t), steps. The complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ was calculated by the following equations, where $Rs(\omega)$ and $Rx(\omega)$ are Fourier transforms of reflection signals of standard sample, Rs(t), and unknown one, Rx(t).

$$\varepsilon_X^* = \frac{\rho(\varepsilon_S^*/x_S\cot x_S)\,x_X\cot x_X}{1-g^2(\omega d/c)^2\rho(\varepsilon_S^*/x_S\cot x_S)} \qquad (1)$$

$$\rho = \frac{c}{gd}\,\frac{(Rs(\omega)-Rx(\omega))}{i\omega\,(Rs(\omega)+Rx(\omega))} \qquad (2)$$

$x_k = (\omega d/c)(\varepsilon^*_k)^{1/2}$ (k = s and x), c the speed of light, d the length of sample cell, g the characteristic conductance between the line and sample section, ω the angular frequency and ε^*_s the complex permittivity of standard sample.

The detailed procedure and operation of TDR technique were already reported elsewhere[7-9]. We used 3 kinds of cables with different radius and length to cover the large frequency windows. Air, ethanol and n-propanol were used as the standard samples, of which complex dielectric permittivities were already reported[10-11]. The temperature of a sample was monitored by an alumel-chromel thermocouple.

The samples used were propylene glycol monomer (PG) and its five oligomers (poly propylene glycol, PPG) which have the molecular weights 192 (tPG), 425 (PPG-425), 725 (PPG-725), 2000 (PPG-2000) and 4000 (PPG-4000). All the samples are the organic fragile glass-forming liquids with two -OH groups. The PG was purchased from Wako Pure Chemical Industries, Ltd. It was distilled and desiccated by molecular sieves 3Å prior to use. The tPG was purchased from Tokyo Chemical Industry Co., Ltd. and the others were from Aldrich Chemical Company, Inc.

RESULTS AND DISCUSSION

On cooling a glass-forming material from liquid to glass state, the characteristic relaxation frequency decreases dramatically. The high sensitivity and large frequency range are the main reasons why the dielectric measurement becomes the powerful technique for studying the dynamics of glass-forming liquid, especially slowing dynamics.

We give, in Figure 2, the observed dielectric loss of the PPG-4000 at several temperatures. The Harvrilliak-Negami (HN) expression[12] in frequency domain and a stretched exponential Kohlrausch-Williams-Watts (KWW)[13] function in time domain are the popular forms to analyze the complex dielectric permittivity, $\varepsilon^*(\omega)$. These dielectric losses have well been reproduced by the HN empirical relaxation function,

$$\varepsilon^*_{HN}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1 + (i\omega\tau_{HN})^\alpha]^\gamma, \qquad (3)$$

$$(0 < \alpha,\ \gamma \leqq 1)$$

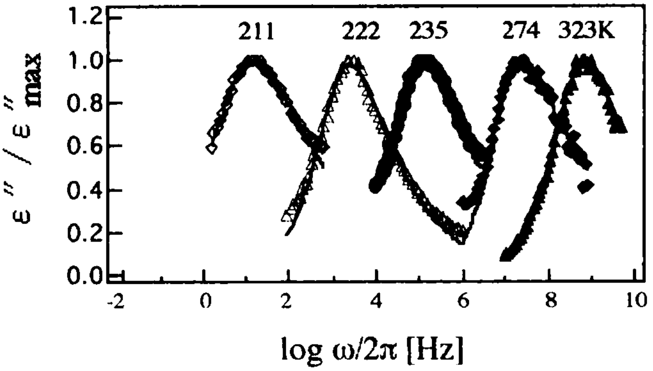

FIGURE 2 Normalized dielectric loss spectra of the PPG-4000 at several temperatures. The solid lines are the fitted curves by the Harvrilliak-Negami expression.

where τ_{HN} is a characteristic relaxation time, and ε_∞ and ε_s are the dielectric constant in the high and low frequency limits, respectively.

The Arrhenius plot of the relaxation frequency for PG, tPG and PPG-4000 are shown in Figure 3. The Vogel-Tammann-Fulcher(VTF) fits[14], $f_{max} = A \exp[-DT_0/(T-T_0)]$, provide good description of the loss peak positions in all the experimental temperature windows for all the samples. In this equation, the D means the fragility and T_0 Vogel-Fulcher temperature. We employed the method of temperature derivative analysis[15] to determine its dependence precisely, $[d\ln f_{max}/d(1/T)]^{-1/2} = (1-T_0/T)(DT_0)^{-1/2}$ for the VTF dependence. In all the temperatures, we can obtain an expression of linear dependence of f_{max} against 1/T.

This VTF behavior is derived from the model in which the intermolecular cooperativity was discussed by the concept of conformer which is the smallest segmental unit of rotation[16]. This model assumed that the conformer must move in cooperation with its neighbors to complete a rotational relaxation. The marked decrease of f_{max} causes the increase of the conformer size in each domain which reveals a tendency to increase the cooperativity.

To identify T_0, theoretical arguments with a percolation singularity based on the free volume approach for the particle dynamics are referred[17]. Recently,

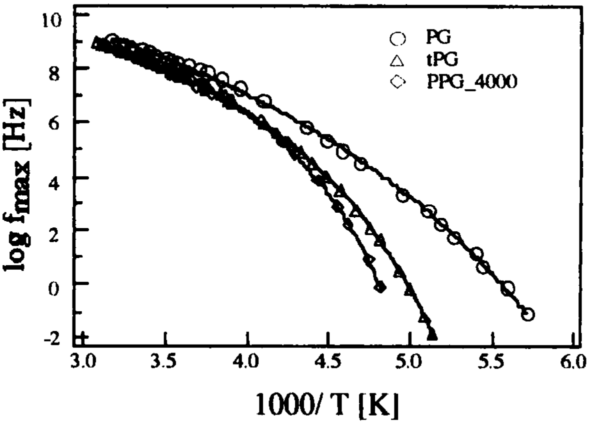

FIGURE 3 Arrhenius plots, i.e., log f_{max} vs. 1000/T for PG, tPG and PPG-4000. The data are fitted by the Vogel-Tammann-Fulcher relation (solid lines)

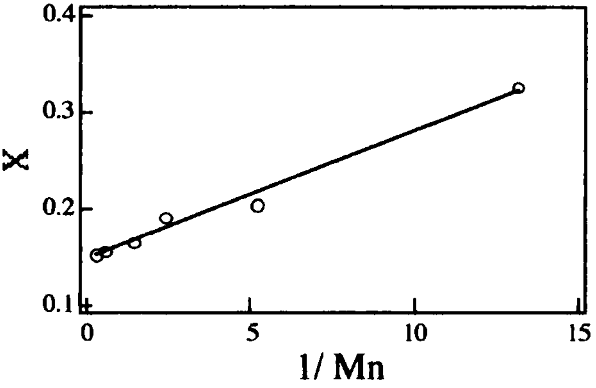

FIGURE 4 The molecular weight dependence of the measure of non-linearity.

the meaning of T_0 is argued with the view-point of cooperativity[16]. This is the low-temperature limit at which every conformer becomes meshed with all others and the entire body becomes one huge meshed domain when an electric field is impulsed. The conformational entropy is, therefore, zero at this temperature.

On the other hand, there are several methods to determine the glass transition temperature T_g from the calorimetric, viscosity and dielectric measurements. We determined the T_g at which the dielectric relaxation time of fitted results by the VTF relation is 60sec.

From these analysis, we determined the parameters such as T_0 and T_g. The ratio T_0/T_g is directly related to the measure of non-linearity, x, in the Narayanaswamy-Moynihan expression[18,19] with the relation $x \approx (1 - T_0/T_g)$ [19,20]. The x increases linearly with 1/Mn as shown in Figure 4. It is clear that the x increase with the decrease of molecular weight as indicated the decrease of T_0/T_g with it. It agrees to the fact that the PG monomer is more fragile liquid than its oligomer. The detailed analysis will be published later.

Acknowledgments

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References

[1.] W. Götze in *Liquid, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque and J. Zinn-Justin (North-Holland, Amsterdam, 1991).

[2.] K. L. Ngai, G. R. Wright, Eds., *Relaxation in Complex System* (North-Holland, Amsterdam, 1991).

[3.] A. J. Dianoux, W. Petry, D. Richter, Eds., *Dynamics of disordered materials* (Elsevier Science Publishers, Amsterdam, 1993).

[4.] R. Richert and A. Blumen, Eds., *Disorder Effects on Relaxational Process* (Springer, Berlin, 1994).

[5.] Y. B. Mel'nichenko, J. Schüller, R. Richert, B. Ewen and C. K. Loong, *J. Chem. Phys.*, **103**, 2016 (1995).

[6.] G. P. Johari, A. Hallbrucker and E. Mayer, *J. Poly. Sci.: Part B : Poly. Phys.*, **26**, 1923 (1988).

[7.] R. H. Cole, S. Mashimo, and P. Winsor IV, *J. Phys. Chem.*, **84**, 786 (1980).

[8.] T. Umehara, S. Kuwabara, S. Mashimo and S. Yagihara, *Biopolymers*, **30**, 649 (1990).

[9.] R. Nozaki and T. K. Bose, *IEEE Trans. Instrum. Meas.*, **39**, 945 (1990).

[10.] R. C. Weast, M. J. Astle and W. H. Beyer, Eds., *CRC handbook of* *chemistry and physics*, 77th Ed. (Chemical rubber, Cleveland, Ohio, 1996).

[11.] F. Stickel, E. W. Fischer, and R. Richert, *J. Chem. Phys.*, **104**, 2043 (1996).

[12.] S. Harvnilliak and S. Negami, *J. Polym. Sci. C*, **14**, 99 (1966).

[13.] F. Kohlrausch, *Pogg. Ann. Phys.*, **119**, 352 (1663); G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970).

[14.] H. Vogel, *Phys. Z.*, **22**, 645(1921); G.S. Fulcher, *J. Am. Ceram. Soc.*, **8**, 339 (1923); G. Tamman and W. Hesse, *Z. Anorg. Alleg. Chem.*, **156**, 245 (1926).

[15.] F. Stickel, E. W. Fischer and R. Richert, *J. Chem. Phys.*, **104**, 2043 (1996).

[16.] S. Matsuoka and X. Quan, *Macromolecules*, **24**, 2770, (1991).

[17.] M. H. Cohen and G. S. Grest, *Phys. Rev. B*, **20**, 1077 (1979).

[18.] O. S. Narayanaswamy, *J. Am. Ceram. Soc.*, **54**, 491 (1971); C. T. Moynihan, A. J. Easteal, M. A. DeBolt and T. Tucker, *J. Am. Ceram. Soc.*, **59**, 12 (1976)

[19.] I. M. Hodge, *J. Non-Cryst. Solids*, **169**, 211 (1994).

[20.] I. M. Hodge, *Macromolecules*, **20**, 2897, (1987).