

Determination of Glass Transition Temperature from Dielectric Analysis for a Series of Epoxide Oligomers

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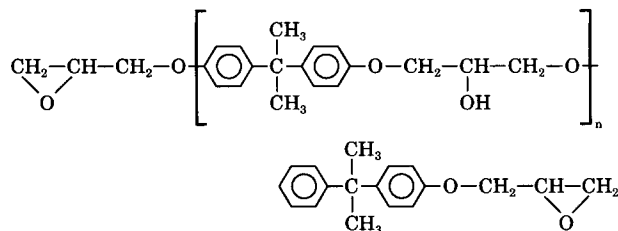
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SYNOPSIS

Dielectric properties have been investigated for a bisphenol-A type epoxide oligomer, whose weight average molecular weight (\bar{M}_w) was 9454. The dielectric α -relaxation of the oligomer was found to be governed by the Havriliak–Negami equation as well as the same series of oligomers with smaller \bar{M}_w s ($388 \leq \bar{M}_w \leq 3903$). The dielectric relaxation times (τ s) for the oligomers with different \bar{M}_w s ($1396 \leq \bar{M}_w \leq 9454$) can be expressed by the Williams–Landel–Ferry (WLF) equation as a function of the glass transition temperature (T_g) at fixed temperatures from 70 to 100°C. The finding indicates that the T_g of the epoxide oligomer is calculated from the τ through the WLF equation, providing the relation between T_g and τ . The same type of WLF equation was also successfully applied to describe the T_g dependence of the practical dielectric relaxation time (τ_p), which was obtained from the peak of the dielectric loss vs. frequency curve. The τ_p can be calculated more easily than the τ , based on the Havriliak–Negami equation, not only in the measurement of epoxide oligomer, but also in that of the reactive epoxy resin systems during curing. The T_g of an epoxy–aromatic amine system, which was determined from the τ_p nondestructively detected in the dielectric cure monitoring, was consistent with the T_g experimentally measured by differential scanning calorimetry (DSC).

INTRODUCTION

The diglycidyl ether of bisphenol-A (DGEBA), one of the epoxide oligomers, has been applied to various commercial uses after crosslinking with adequate curing agents depending on the purpose. The chemical structure of DGEBA is shown below.¹



The epoxide oligomer is composed of linear molecules with different molecular weights according to the variation of the repeated number, n , in the structural formula.

Dielectric analysis is widely used to monitor the curing process of epoxy resin systems, due to the effective nondestructive measurement, as reported by many workers.^{2–8} DGEBA oligomers are considered to have chemical structures similar to that of the reactive DGEBA–aromatic amine system before gelation during curing, because, in the early stage of curing, the reactive DGEBA system may have a large proportion of linear molecule caused by the difference in the reaction rate between the primary and the secondary amine to the epoxy resin, according to the study by Bell.⁹ Thus, the dielectric study on DGEBA oligomers may provide valuable information for a better understanding of the curing mechanism of epoxy resin. The dielectric properties

of epoxide oligomers have been studied by some researchers. Pochan et al.¹⁰ measured the dielectric properties of an epoxide oligomer below the glass transition temperature (T_g) and discussed the β - and γ -relaxation of the oligomer. Sheppard and Senturia¹¹ reported that dielectric α -relaxation processes for several DGEBA oligomers were described by the Kohlraush-Williams-Watts (KWW) relaxation function.¹² In a previous work,¹³ the authors studied dielectric properties for a series of DGEBA oligomers with different molecular weights and found that the dielectric α -relaxation of the oligomers fit the empirical model of the Havriliak-Negami equation.¹⁴

The dielectric data, collected on the temperature dependence of the dielectric relaxation time (τ) for several oligomers with different molecular weights, may be applicable to reveal the T_g dependence of τ for a group of oligomers at an isothermal condition taking T_g as a variable.^{13,15} In a previous work,¹⁵ the T_g of the reactive DGEBA-aromatic amine system was obtained from the τ by a procedure of reading the plot, which demonstrated the relations between τ and T_g for the oligomers at four fixed temperatures. This study focused on the detailed analysis of the relationship between τ and T_g for the nonreacting oligomer, in order to find a general expression of the T_g dependence of τ at the point of nondestructive determination of T_g from the τ detected for the reactive epoxy resin system in the dielectric cure monitoring.

EXPERIMENTAL

Materials

The DGEBA oligomer used in this study was Epikote 1009, which was supplied by Yuka Shell Epoxy. The weight-average molecular weight (\bar{M}_w) and the number-average molecular weight (\bar{M}_n) of the oligomer was 9454 and 4746, respectively, which was larger than those of the oligomers studied in previous works.^{13,15} The T_g of the oligomer was 82°C, using differential scanning calorimetry (DSC). The characterization of the oligomer was performed by the same method as reported before.¹³

Measurements

Dielectric measurements were performed using an inductive-ratio-arm bridge type apparatus (TR-1100; Ando Electric). The measuring frequency was 50 Hz–1 MHz, in the temperature range of 82–

150°C. The measuring cell, a parallel plate type based on the three terminal method, was the same one used in previous works.^{13,15}

The direct current (dc) conductivity measurements were performed in the temperature range of 82–170°C, using an apparatus system that consisted of a dc power supply (TR300C; Takeda Riken), a vibrating reed electrometer (TR84M; Takeda Riken), and a pen recorder (EPR-200A; Toa Dempa). The measuring cell was the same one used for the dielectric measurements.

T_g was measured by a duPont 9000 differential scanning calorimeter.

RESULTS AND DISCUSSION

Relationship between T_g and Dielectric Properties for a Series of Epoxide Oligomers

Epoxide oligomers studied in previous works^{13,15} have relatively small \bar{M}_w s ($388 \leq \bar{M}_w \leq 3903$) when considering the application of the dielectric data of the nonreacting oligomer to the analysis of the reactive epoxy resin system, which may include larger \bar{M}_w components. In this work, Epikote 1009 ($\bar{M}_w = 9454$), one of the commercially available DGEBA oligomers with large \bar{M}_w s, was investigated for obtaining further information needed in the dielectric cure analysis. The dielectric α -relaxation of Epikote 1009 was found to fit the following Havriliak-Negami equation,¹⁴ as well as those of the low \bar{M}_w oligomers ($388 \leq \bar{M}_w \leq 3909$) studied in previous works.^{13,15}

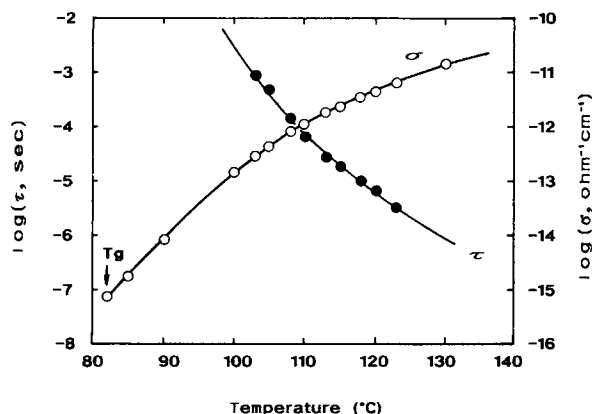


Figure 1 Temperature dependence of dielectric relaxation time τ and dc conductivity σ for Epikote 1009: (●) relaxation time; (○) dc conductivity.

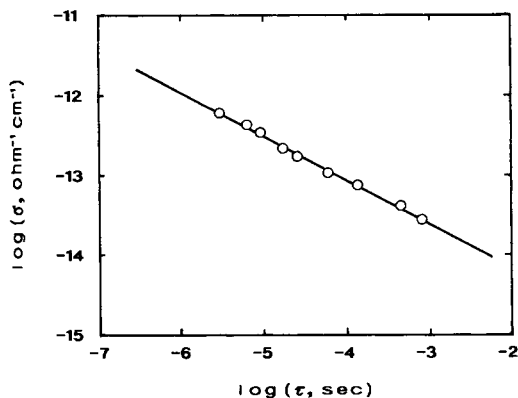


Figure 2 Relationship between $\log \tau$ and $\log \sigma$ for Epikote 1009.

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (1)$$

where $\epsilon^*(\omega)$ = the complex dielectric constant, ϵ_∞ = high-frequency limit to the dielectric constant, ϵ_0 = low-frequency limit to the dielectric constant, i = square root of -1 , ω = angular frequency, τ = dielectric relaxation time, α = distribution parameter, and β = skewness parameter.

The temperature dependence of the dielectric relaxation time (τ) is compared with that of the dc conductivity (σ) for Epikote 1009 in Figure 1. The relation between τ and σ is plotted in Figure 2. A linear plot between $\log \tau$ and $\log \sigma$, observed in Figure 2, indicates that the following empirical formula proposed in a previous work¹³ is also applicable to Epikote 1009.

$$\sigma(T)[\tau(T)]^m = \text{const.} \quad (2)$$

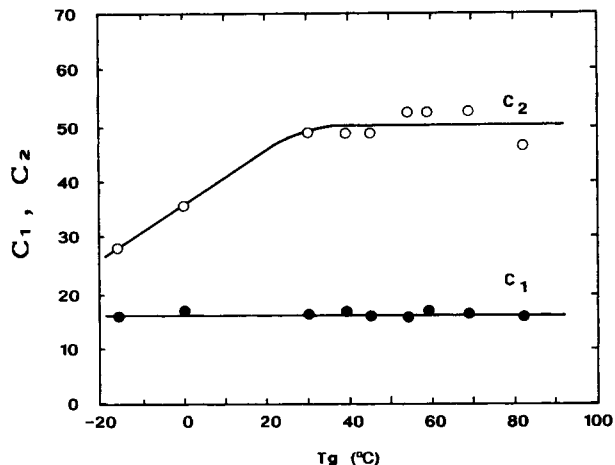


Figure 3 WLF parameters, C_1 and C_2 , of the dielectric relaxation time, as a function of T_g for DGEBA oligomers: (●) C_1 ; (○) C_2 .

where T is the temperature and m is an exponent. The m value for Epikote 1009 is listed together with those for low \bar{M}_w oligomers in Table I. The m value of Epikote 1009 is 0.54, which is consistent with the result obtained in a previous study¹³; the larger \bar{M}_w oligomer has the smaller value of m (Table I).

It is generally recognized for most amorphous polymers that the temperature dependence of τ above the T_g is governed by the Williams-Landel-Ferry (WLF) equation [Eq. (3)].¹⁶

$$\log \frac{\tau(T)}{\tau(T_g)} = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (3)$$

where T is the temperature ($T_g \leq T \leq T_g + 100^\circ\text{C}$), T_g is the glass transition temperature, and C_1 and

Table I Parameters for Temperature Dependence of Dielectric Relaxation Time of DGEBA Oligomers

DGEBA Oligomer	T_g ($^\circ\text{C}$)	\bar{M}_w	m	WLF Parameters		Relaxation Time at T_g (s)
				C_1	C_2	
Epikote 1001	30	1396	0.69	16.14	48.9	20
Epikote 1002	39	1891	0.68	16.54	48.8	69
Epikote 1003	45	2078	0.62	15.71	48.8	24
Epikote 1004	54	2640	0.62	15.46	52.6	12
Epikote 1005	59	2757	0.60	16.70	52.6	66
Epikote 1007	69	3903	0.58	16.11	52.9	54
Epikote 1009	82	9454	0.54	15.48	46.4	52

C_2 are parameters. The temperature dependence of τ for Epikote 1009 was analyzed and found to fit the WLF equation. The WLF parameters, C_1 and C_2 , for Epikote 1009 ($T_g = 82^\circ\text{C}$) were plotted as a function of T_g along with those for low T_g oligomers ($-16^\circ\text{C} \leq T_g \leq 69^\circ\text{C}$) in Figure 3. Both Epikote 1009 and other oligomers have similar C_1 values around 16. The C_2 value increases with the increase in the T_g for the low T_g oligomers ($-16^\circ\text{C} \leq T_g \leq 30^\circ\text{C}$), while the value appears to level off for the high T_g ones ($30^\circ\text{C} \leq T_g \leq 82^\circ\text{C}$). In Table I, two WLF parameters are summarized for seven oligomers whose T_g s are in the range of 30–82°C. The mean values of C_1 and C_2 parameters for seven oligomers are 16.02 and 50.1, respectively, which are close to the universal values of the WLF equation, 17.44 and 51.6. An epoxide oligomer (or polymer), with a higher T_g than 82°C, may have almost the same values of WLF parameters as those for the oligomers listed in Table I, judging from the behavior of the parameter vs. T_g curve in the high T_g region of Figure 3. According to eq. (2), expressing the relation between $\tau(T)$ and $\sigma(T)$, the τ at T_g [$\tau(T_g)$] can be calculated from the σ at T_g , whose typical value is marked by an arrow for Epikote 1009 in Figure 1. As shown in Table I, the $\tau(T_g)$ value is in the range of 12–69 sec, which is regarded as a similar value within experimental error taking into account the accuracy of the measurement of T_g ($\pm 1^\circ\text{C}$).

The WLF equation [eq. (3)] can be rearranged in the following form by taking T_g as a variable and temperature T as a constant for a given oligomer.

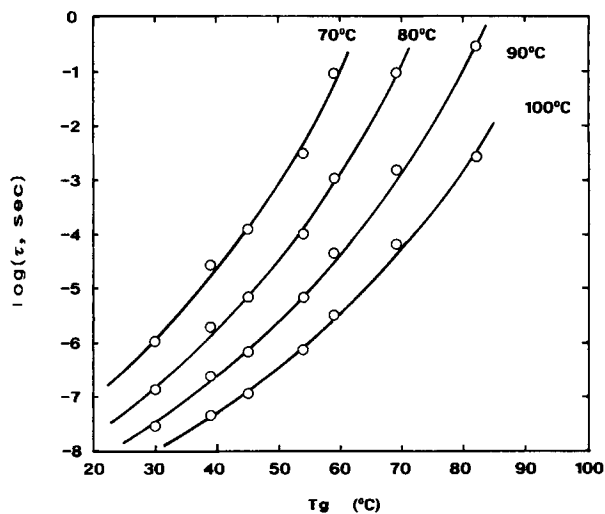


Figure 4 Relationship between relaxation time τ and T_g for DGEBA oligomers at four temperatures.

Table II WLF Parameters for T_g Dependence of Dielectric Relaxation Time of DGEBA Oligomers at Four Temperatures

Temperature (°C)	C_1	C_2	C_1''	C_2''
70	20.35	67.8	21.67	73.3
80	20.10	68.9	21.82	76.3
90	18.72	63.8	19.44	66.3
100	18.54	64.2	19.57	68.3

$$\log \frac{\tau(T)}{\tau(T_g)} = \frac{-C_1(T_g - T)}{-C_2 + T_g - T} \quad (4)$$

Assuming that three parameters, C_1 , C_2 , and $\tau(T_g)$, have almost the same value, respectively, for seven oligomers, eq. (4) can be rewritten in a more general form applicable to a series of oligomers with different T_g s.

$$\log \frac{\tau(T)}{\tau_0} = \frac{-C_1'(T_g - T)}{-C_2' + T_g - T} \quad (5)$$

where $\tau(T)$ is τ at the fixed temperature T for the oligomer, C_1' and C_2' are parameters, and τ_0 is τ at the T_g that is taken as a mean of τ values for seven oligomers. Since the $\tau(T)$ in eq. (5) is defined as the τ at a fixed temperature T for a given oligomer, the $\tau(T)$ is not a function of T , but a function of the characteristic of the oligomer, such as \bar{M}_w or T_g , on which the τ depends in an isothermal condition. Therefore, eq. (5) is rewritten in the following form as a function of T_g at a temperature T for the behavior of a group of oligomers with similar chemical structure.

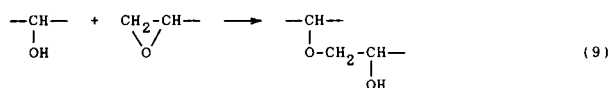
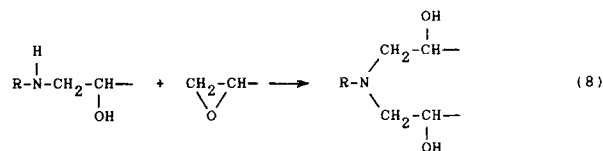
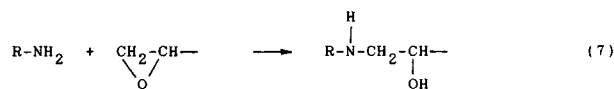
$$\log \frac{\tau_n(T_g)}{\tau_0} = \frac{-C_1'(T_g - T)}{-C_2' + T_g - T} \quad (6)$$

where $\tau_n(T_g)$ is the τ for a series of oligomers as a function of T_g at the temperature T , C_1' and C_2' are WLF parameters, and τ_0 is a mean (42 sec) of τ values at the T_g for the oligomers. Figure 4 shows the plots of τ vs. T_g for the oligomers at temperatures of 70, 80, 90, and 100°C in comparison with the solid curve drawn according to the WLF equation [eq. (6)] for each temperature. The best fit WLF parameters in the T_g range of 30–82°C are listed for four temperatures in Table II. The C_1' and C_2' parameters have a similar value, respectively, for each

isothermal temperature. A good agreement between the actual plot and the calculated solid curve in Figure 4 shows that the behavior of τ for a group of epoxide oligomers at the temperature T can be well described by the WLF type equation as a function of T_g . Accordingly, the T_g of the epoxide oligomer ($30^\circ\text{C} \leq T_g \leq 82^\circ\text{C}$) can be estimated from the τ of the oligomer for each isothermal temperature from 70 to 100°C through the WLF type equation [eq. (6)].

Determination of T_g for Reactive Epoxy Resin System during Curing

The isothermal curing behavior of an epoxy resin with an aromatic amine has been studied in a previous work.¹⁵ The curing system consisted of the DGEBA and 4-4'-diamino diphenyl methane (DDM). The DGEBA-DDM system before gelation may have a chemical structure similar to that of the epoxide oligomer, because the system is considered to be a mixture of linear molecules with or without branches, according to the studies by Schechter et al.¹⁷ and by Bell.⁹ Schechter et al.¹⁷ suggested that there were three possible reactions [(7)–(9)] in the epoxy resin with diamines as shown below.



Bell⁹ reported that in the reaction between DGEBA and DDM, the primary amine reaction (7) was approximately 7–12 times as fast as the secondary amine reaction (8), due to steric hindrance, and that reaction (9) was negligible, which resulted in a large proportion of linear molecule in the reactive DGEBA-DDM system before gelation. Accordingly, in the early stage of curing, the behavior of the DGEBA-DDM system can be approximately predicted from that of a nonreacting DGEBA oligomer, consisting of linear molecules.

In a previous work,¹⁵ the T_g of the DGEBA-DDM system during isothermal curing was obtained from the τ by a procedure of reading the plot, which gave the relationship between T_g and τ at the isothermal temperature for a series of oligomers. As mentioned above, the T_g dependence of τ for the oligomer was found to fit the WLF type equation by investigating the relation between T_g and τ in the isothermal condition. From the viewpoint of developing the method to predict the T_g of the reactive epoxy resin system from the parameter measured in the dielectric cure monitoring, the parameter is not always limited to the dielectric relaxation time based on the Havriliak-Negami equation. Many workers calculated the dielectric relaxation time from the peak of dielectric loss (ϵ'') vs. frequency curve in the dielectric analysis.^{4,18-20} This practical dielectric relaxation time (τ_p), which is defined in eq. (10), is easily obtained in comparison with the τ calculated through the Havriliak-Negami equation [eq. (1)].

$$\tau_p = 1/\omega_{\max} \quad (10)$$

where τ_p = the practical dielectric relaxation time, and ω_{\max} = the angular frequency at which the ϵ'' is a maximum.

If the τ_p has a certain relation with the T_g of the oligomer, the τ_p becomes another parameter determining the T_g of the reactive epoxy-aromatic amine system from the dielectric analysis. The relation between $\log \tau$ and $\log \tau_p$ is plotted for seven oligomers in Figure 5. The slope of the straight line, observed in Figure 5, is close to unity, which indicates that the τ_p has good correlation with the T_g of the oligomer as well as the τ . In Figure 6, the τ_p is plotted as a function of T_g for the oligomers at temperatures

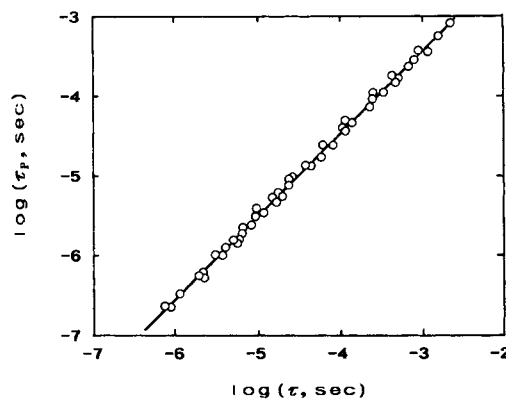


Figure 5 Relationship between $\log \tau$ and $\log \tau_p$ for DGEBA oligomers.

of 70, 80, 90, and 100°C. The T_g dependence of τ_p , shown in Figure 6, was analyzed for each temperature and was found to fit the same type of WLF equation [eq. (11)] as eq. (6).

$$\log \frac{\tau_p(T_g)}{\tau_{p0}} = \frac{-C_1''(T_g - T)}{-C_2'' + T_g - T} \quad (11)$$

where $\tau_p(T_g)$ is the τ_p of the oligomer as a function of T_g at the temperature T , C_1'' and C_2'' are WLF parameters, and τ_{p0} is a constant (16 sec), which is calculated from the mean value (42 sec) of τ at the T_g according to the relation between τ and τ_p given in Figure 6. The best fit parameters, C_1'' and C_2'' , are summarized for four temperatures in Table II.

The T_g , which was nondestructively predicted from the dielectric analysis, was compared with the one actually measured for a reacting epoxy resin system. The T_g for the reactive DGEBA-DDM system during an isothermal temperature (80°C) was calculated from the τ_p of that system through eq. (11) and was plotted as a function of curing time in Figure 7 together with the T_g experimentally measured by DSC in a previous work.¹⁵ A good agreement was observed between the calculated T_g and the experimental one. The finding indicates that the determination of T_g from the τ_p obtained in the dielectric analysis may become a practical method for the nondestructive cure monitoring of the DGEBA-DDM system.

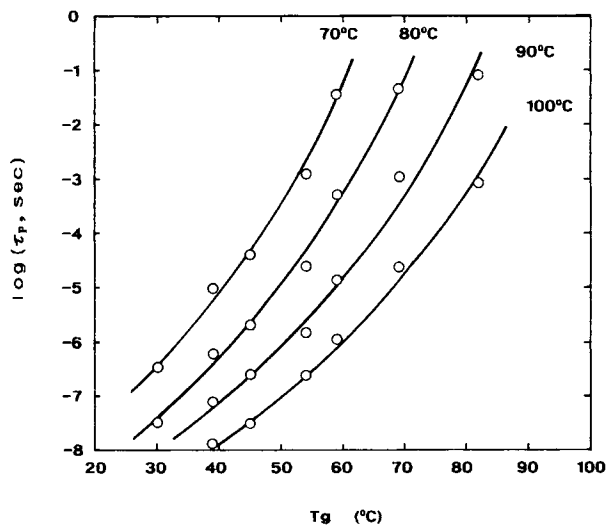


Figure 6 Relationship between relaxation time τ_p and T_g for DGEBA oligomers at four temperatures.

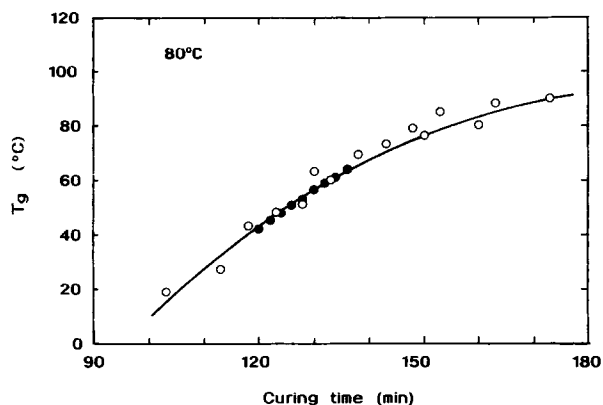


Figure 7 Glass transition temperature as a function of curing time at 80°C for DGEBA-DDM system: (○) experimental value; (●) calculated value.

CONCLUSIONS

Dielectric properties have been carefully analyzed for a series of epoxide oligomers ($1396 \leq \bar{M}_w \leq 9454$), whose dielectric α -relaxations fit the Havriliak-Negami equation. The following conclusions were obtained:

1. The dielectric relaxation times for this series of oligomers can be expressed by the Williams-Landel-Ferry (WLF) equation, as a function of the glass transition temperature (T_g) at fixed temperatures from 70 to 100°C.
2. The WLF type equation was also applied to the T_g dependence of the practical dielectric relaxation time (τ_p), which was obtained from the peak of the dielectric loss vs. frequency curve.
3. The T_g of an epoxy-aromatic amine system, which was calculated from the τ_p of the reactive epoxy system through the WLF type equation, was consistent with the T_g experimentally determined by differential scanning calorimetry (DSC).

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