Relationship Between Melt Viscosity and Dielectric Relaxation Time for a Series of Epoxide Oligomers

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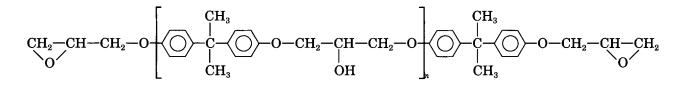
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SYNOPSIS

Melt viscosity has been investigated for a series of bisphenol-A type epoxide oligomers with different weight-average mol wts (\bar{M}_w) , ranging from 388 to 2640. The temperature dependence of the melt viscosity is described by the Williams-Landel-Ferry (WLF) equation. The melt viscosity η is correlated with both the direct current (dc) conductivity σ and the dielectric relaxation time τ . The two relationships between these three properties, $\sigma \cdot \eta^* = \text{const} (0.63 \le \kappa \le 1.12)$ and $\eta/\tau^{\ell} = \text{const} (0.73 \le \ell \le 1.06)$, are experimentally derived. Both exponents, κ and ℓ , depend on the \bar{M}_w of the oligomer. The lower \bar{M}_w oligomer has the larger value of κ . The κ value is close to unity for the low \bar{M}_w oligomer, which agrees with Walden's rule, $\sigma \cdot \eta = \text{const}$, applicable to most low mol wt liquids. The ℓ value is near unity for the epoxide oligomer with higher \bar{M}_w than 2000, which means that the melt viscosity is proportional to the dielectric relaxation time. The low \bar{M}_w oligomer (\bar{M}_w < 2000), on the other hand, has a smaller value of ℓ below unity. The result indicates that the melt viscosity is not proportional to the dielectric relaxation time for the low \bar{M}_w epoxide oligomer, whose dielectric α -relaxation is not governed by the Debye equation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The diglycidyl ether of bisphenol-A (DGEBA) is usually manufactured by the direct addition of epichlorohydrin to bisphenol-A in the presence of sodium hydride, which is called a conventional process or a solvent finishing one. Another process, the advancement or fusion one, involves the reaction of low mol wt DGEBA with bisphenol-A. The chemical structure of DGEBA is shown below.¹



The epoxide oligomer has different mol wts according to the variation of the repeated number n in the structural formula. The epoxide oligomer at room temperature is a viscous liquid or amorphous solid, according to the mol wt.

Flow properties of epoxide oligomers were reported by several workers. Aleman^{2,3} discussed shear-rate effects on the shear viscosity measured by an Instron rheometer and found that each epoxide oligomer studied had Newtonian behavior up to the shear rate of 2000 s⁻¹. Ghijsels et al.⁴ reported that the temperature dependence of the zero-shear viscosity was well described by the Vogel equation. Utracki and Ghijsels⁵ analyzed the melt viscosity for several epoxide oligomers according to the equation, which combined Doolittle's emperical formula⁶

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with the statistical thermodynamics theory of a liquid.

In a previous work,⁷ the authors studied the dielectric relaxation and the direct current (dc) conduction for a series of DGEBA oligomers and found that the dielectric α -relaxation for each oligomer fit the Havriliak-Negami equation⁸ and that the temperature dependences of both the dielectric relaxation time τ and the dc conductivity σ above the glass transition temperature (T_g) were described by the Williams-Landel-Ferry (WLF) equation.⁹ In addition, the relation between τ and σ , $\sigma \cdot \tau^m = \text{const}$ ($0.62 \leq m \leq 0.82$), was experimentally derived. The exponent m of the empirical formula was found to depend on the weight-average mol wt (\overline{M}_w) of the oligomer.

It is generally recognized that the relaxation time is proportional to the melt viscosity for a simple liquid whose dielectric α -relaxation is governed by the Debye equation.¹⁰ As for an oligomer, the relationship between the relaxation time and the melt viscosity is still not clear. According to the previous work,⁷ an epoxide oligomer, whose dielectric α -relaxation is not fitted to the Debye model, is supposed to exhibit viscoelastic behavior different from a simple liquid or a polymer. This article focused on the analysis of the relationship between the dielectric relaxation time and the melt viscosity for a series of DGEBA oligomers with different mol wts.

EXPERIMENTAL

Materials

The samples used in this study were five commercially available oligomers of the diglycidyl ether of bisphenol-A (DGEBA) with different \bar{M}_w s (388 $\leq \bar{M}_w \leq 2640$), which were the same materials investigated in a previous work.⁷ The values of the repeated number n for the epoxide oligomers range

Table I Properties of Epoxide Oligomers

Oligomer	T_{g} (°C)	$ar{M}_n{}^{\scriptscriptstyle \mathrm{B}}$	$ar{M_w}^{ ext{b}}$	$ar{M}_w/ar{M}_n$	n°
Epikote 828	-16	366	388	1.06	0.1
Epikote 834	0	479	590	1.23	0.5
Epikote 1001	30	898	1396	1.55	2.0
Epikote 1002	39	1147	1891	1.63	2.8
Epikote 1004	54	1538	2640	1.72	4.2

^a Number-average mol wt.

^b Weight-average mol wt.

^c Repeated number.

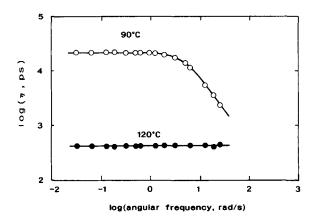


Figure 1 Angular frequency dependence of melt viscosity η for Epikote 1002 at 90°C and 120°C: (\bigcirc) 90°C; (\bigcirc) 120°C.

from 0.1 to 4.2. The five oligomers, Epikote 828, 834, 1001, 1002, and 1004, were manufactured by a conventional process at Yuka Shell Epoxy. The characteristics of the samples are given in Table I.

Measurements

Viscosity measurements were performed using a cone and plate viscometer (MR-3; Rheology Engineering), equipped with a cone having a diameter of 3.2 cm and an angle of 2 degrees, operating in the angular frequency range from 6.28×10^{-3} to 6.28 \times 10 rad/s. The temperature range studied was from 10 to 170°C. The temperature variations during the measurements were less than ± 0.1 °C. Two typical viscosity-angular frequency curves for Epikote 1002 at 90 and 120°C are shown in Figure 1. The epoxide oligomer was found to exhibit Newtonian behavior up to relatively high angular frequency (high shear stress), as reported by Aleman^{2,3} and Ghijsels et al.⁴ Similar Newtonian behavior was observed for each oligomer studied. The melt viscosity for the oligomer was determined by the value in the Newtonian region as seen in Figure 1.

Dielectric measurements were performed in the same way as mentioned before.⁷

RESULTS AND DISCUSSION

Comparison of Melt Viscosity with Dielectric Relaxation Time

In a previous work,⁷ the authors experimentally derived the following equation between the dielectric relaxation time τ and the dc conductivity σ for the same DGEBA oligomers as those used in this work.

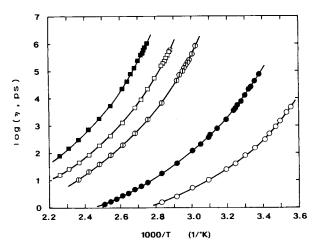


Figure 2 Temperature dependence of melt viscosity for five oligomers: (\bigcirc) Epikote 828; (\bigcirc) Epikote 834; (\bigcirc) Epikote 1001; (\Box) Epikote 1002; (\blacksquare) Epikote 1004.

$$\sigma(T) [\tau(T)]^{m} = \text{const}$$
(1)

where $\sigma(T)$ is the dc conductivity at temperature $T, \tau(T)$ is the dielectric relaxation time at T, and m is the exponent $(0.62 \le m \le 0.82)$. The exponent m was reported to depend on the \overline{M}_w of the oligomer.

The melt viscosity η is closely associated with the dielectric relaxation time. The temperature dependence of the melt viscosity for each oligomer was evaluated and was compared to both the dielectric relaxation time and the dc conductivity. Figure 2 shows the melt viscosity of five oligomers as a function of the reciprocal Kelvin temperature. Figures 3 and 4 demonstrate the temperature dependences

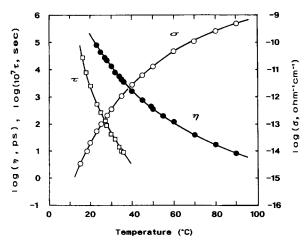


Figure 3 Temperature dependence of melt viscosity η , dc conductivity σ , and dielectric relaxation time τ for Epikote 834: (\bullet) melt viscosity; (\bigcirc) dc conductivity; (\Box) dielectric relaxation time.

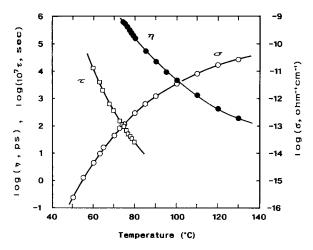


Figure 4 Temperature dependence of melt viscosity η , dc conductivity σ , and dielectric relaxation time τ for Epikote 1002: (•) melt viscosity; (\bigcirc) dc conductivity; (\Box) dielectric relaxation time.

of three properties, η , σ , and τ , for Epikote 834 and Epikote 1002, respectively. The data for σ in Figures 3 and 4 were cited from the results of a previous work.⁷ Log-log plots of melt viscosity vs. dc conductivity for three oligomers, Epikote 828, 1001, and 1004, are shown in Figure 5. The following relation was obtained from the linear plots in Figure 5.

$$\sigma(T)[\eta(T)]^{*} = \text{const}$$
(2)

where $\sigma(T)$ is the dc conductivity at temperature $T, \eta(T)$ is the melt viscosity at T, and κ is the exponent. Similar relations were obtained for other two oligomers. The exponent κ (0.63 $\leq \kappa \leq 1.12$) is also dependent on the \bar{M}_w of the oligomer as well as m in eq. (1). Figure 6 shows the \bar{M}_w dependence of

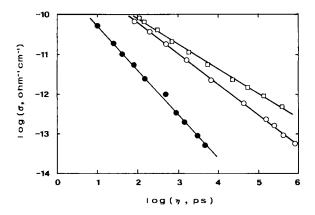


Figure 5 Relation between $\log \eta$ and $\log \sigma$ for three epoxide oligomers: (\bullet) Epikote 828; (\bigcirc) Epikote 1001; (\Box) Epikote 1004.

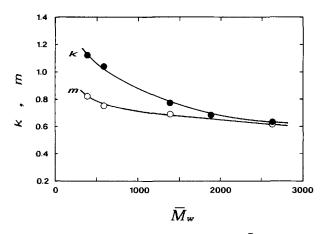


Figure 6 Plot of exponents κ and m vs. \overline{M}_w of the epoxide oligomer: $(\bullet) \kappa$; $(\bigcirc) m$.

the κ value along with m. The κ value is decreasing with the increase in \overline{M}_w of the oligomer, and is close to the m value for the high \overline{M}_w oligomers. The κ value for the low \overline{M}_w oligomer is around unity, which is consistent with Walden's rule¹¹ [eq. (3)] for low mol wt liquids.

$$\sigma(T)[\eta(T)] = \text{const} \tag{3}$$

Sasabe and Saito¹² investigated the relationship between the dielectric relaxation time and the dc conductivity for several amorphous polymers, such as poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVDC), and reported that the same relationships as in eq. (1) were applicable to those polymers. In addition, the exponent m for the polymers was found to have a linear dependence on the T_g below 60°C. In order to obtain the relationship between two exponents, κ and m, and T_g for the epoxide oligomer, the two exponents were plotted as a function of T_g in Figure 7. Each exponent has a linear dependence on the T_g of the oligomer, which leads to the following relations.

$$\kappa = 1.01 - 7.6 \times 10^{-3} T_g \tag{4}$$

$$m = 0.77 - 2.6 \times 10^{-3} T_{e}$$
 (5)

These relations may offer useful information for analyzing the curing process of an epoxy resin system by the on-line dielectric measurement, ¹³⁻¹⁸ which can provide the conductivity of the reactive system, because the viscosity or the relaxation time of the system can be calculated through these relations [eqs. (1) and (5), or eqs. (2) and (4)] from the conductivity directly detected during curing of the epoxy resin system before gelation. The relationship between the melt viscosity and the dielectric relaxation time can be derived from the former two relations [eqs. (1) and (2)] and is expressed in the following form.

$$\frac{\eta(T)}{[\tau(T)]^{m/\kappa}} = \text{const}$$
(6)

where m/κ is the exponent $(0.72 \le m/\kappa \le 1.00)$. As shown in Figures 3 and 4, the direct comparison of the melt viscosity with the dielectric relaxation time is possible in a relatively narrow range of temperatures for each oligomer. Figure 8 demonstrates log-log plots of melt viscosity vs. dielectric relaxation time for five oligomers. The relation between log η and log τ for each oligomer is also linear, which gives the following empirical formula between η and τ .

$$\frac{\eta(T)}{[\tau(T)]^{\ell}} = \text{const}$$
(7)

where ℓ is the exponent $(0.73 \leq \ell \leq 1.06)$. This equation is the same type as eq. (6), which is derived from eqs. (1) and (2). In Figure 9, the value of the exponent ℓ was plotted vs. the \bar{M}_w of the oligomer in comparison with the value of the exponent m/κ in eq. (6). Good agreement is observed between the experimentally obtained value ℓ and the calculated value m/κ (Fig. 9). The ℓ values for five oligomers are summarized in Table II, as well as for the other exponents, κ , m, and m/κ .

Comparison of WLF Parameters

In a previous work,⁷ the authors found that the temperature dependences of both the dielectric relaxa-

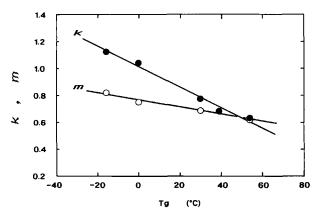


Figure 7 Plot of exponents κ and m vs. T_{g} of the epoxide oligomer: (\bullet) κ ; (\bigcirc) m.

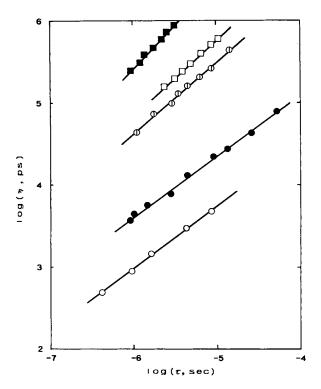


Figure 8 Relation between $\log \eta$ and $\log \tau$ for five epoxide oligomers: (\bigcirc) Epikote 828; (\bigcirc) Epikote 834; (\bigcirc) Epikote 1001; (\Box) Epikote 1002; (\blacksquare) Epikote 1004.

tion time τ and the dc conductivity σ for five DGEBA oligomers fit the WLF equation^{9,19} and they experimentally derived the relation between τ and σ as given in eq. (1). Furthermore, each oligomer was found to have the following relations between the WLF parameters and the exponent m in eq. (1).

$$C_1' \neq C_1'' \tag{8}$$

$$C'_2 \approx C''_2$$
 (9)

$$m \approx \frac{C_1''}{C_1'} \tag{10}$$

where C'_1 and C'_2 are WLF parameters for τ , and C''_1 and C''_2 are those for σ .

These relations for the oligomers agreed with the results of Sasabe and Saito's work¹² on amorphous polymers, such as PVC and PVDC. The meaning of m for the oligomer was explained according to both the WLF equation and the free volume theory developed by Cohen and Turnbull;^{20,21}

$$C_1 = \frac{\gamma v^*}{2.303 f_g v_m} \quad \text{and} \quad C_2 = \frac{f_g}{\alpha_f} \qquad (11)$$

 C_1 , C_2 = WLF parameters,

- γ = a numerical factor introduced to correct for overlap of free volume,
- v* = the critical volume large enough to permit a molecule to jump in after the displacement,
- $v_{\rm m}$ = the average molecular volume,
- f_g = the free volume fraction at the T_g ,
- α_f = the thermal expansion coefficient of the free volume.

Equation (11) implies that the C_2 parameter reflects the characteristics of an oligomer matrix or a host oligomer matrix only. The C_1 parameter is determined not only by the characteristics of an oligomer (a host oligomer) matrix, but also by the size of the moving unit, which is expressed by the critical volume v^* for the transport of the oligomer segment or the ionic charge carrier. Consequently, the exponent *m* in eq. (10) is regarded as a measure of the size of the dipole.

The temperature dependences of the melt viscosity for the same five oligomers as those previously used⁷ were analyzed in this work. The following WLF equation was found to be applicable to the melt viscosity.

$$\log \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T - T_g)}{C_2 + T - T_g}$$
(12)

where η is the melt viscosity and C_1 and C_2 are parameters. The best fit parameters for the melt viscosity are summarized in Table III. The WLF parameters, given in Table III, are plotted as a function of \overline{M}_w of the epoxide oligomer along with other WLF

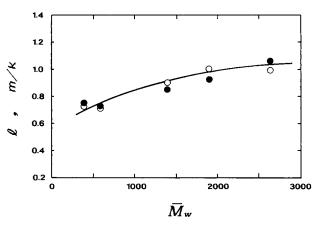


Figure 9 Plot of exponents ℓ and m/κ vs. M_w of the epoxide oligomer: (\bullet) ℓ ; (\bigcirc) m/κ .

Oligomer	к	C_{1}''/C_{1}	l	C_1/C'_1	m	C_{1}''/C_{1}'	<i>т к</i>
Epikote 828	1.12	1.15	0.75	0.72	0.82	0.82	0.73
Epikote 834	1.04	1.00	0.73	0.73	0.75	0.73	0.72
Epikote 1001	0.77	0.79	0.85	0.86	0.69	0.68	0.90
Epikote 1002	0.68	0.72	0.92	0.93	0.68	0.67	1.00
Epikote 1004	0.63	0.65	1.06	0.97	0.62	0.63	0.99

Table II Comparison of Exponents and the Ratios between the WLF C_1 Parameters for Epoxide Oligomers

parameters for τ and σ in Figures 10 and 11. The C_1 parameters, C_1 , C'_1 , and C''_1 , each have different values, while the C_2 parameters, C_2 , C'_2 , and C''_2 , have similar values for the same oligomer.

As indicated in eq. (11), the C_2 parameters are determined by the nature of the epoxide oligomer, or that of the host oligomer in the measurement of dc conduction, which is caused by the ion movement closely related to the segment movement. Therefore, it appears reasonable that Figure 11 demonstrates a good agreement between three C_2 parameters for the same oligomer.

Three C_1 parameters, on the other hand, differ from each other for the same oligomer (Fig. 10). According to eq. (11), the C_1 parameters are affected not only by the nature of the oligomer, but also by the size of the moving unit, such as oligomer segment, dipole, or ion charge carrier. The C_1 parameter includes some unknown factors based on the oligomer's nature, for example, a correction factor for overlap of free volume γ , which is supposed to be dependent on the \bar{M}_w of the oligomer. Dividing one C_1 parameter by another, however, makes it possible to eliminate the effect caused by the nature of the oligomer, and to compare the mobilities of three moving units; oligomer segment, dipole, and ion charge carrier. Equation (10) shows that the exponent m has almost the same value as the ratio of the parameter C''_1 to C'_1 . Similar relations can be

Table IIIWLF Parameters for EpoxideOligomers

		Melt Viscosity		
Oligomer	T_g (°C)	C_1	<i>C</i> ₂	
Epikote 828	-16	11.27	25.8	
Epikote 834	0	12.23	36.0	
Epikote 1001	30	13.89	45.7	
Epikote 1002	39	15.36	42.2	
Epikote 1004	54	14.99	50.0	

seen between the other two exponents (κ and ℓ), as summarized in Table II. These relations are written in the following forms.

$$m \approx \frac{C_1''}{C_1'}, \quad \kappa \approx \frac{C_1''}{C_1} \quad \text{and} \quad \ell \approx \frac{C_1}{C_1'}$$
 (13)

where m, κ , and ℓ are exponents in eqs. (1), (2), and (7), respectively, and C_1 , C'_1 , and C''_1 are the WLF parameters for the melt viscosity, the dielectric relaxation time, and the dc conductivity, respectively. Figure 9 shows that the exponent m/κ has almost the same value as ℓ for the same oligomer, which supports these relations in eq. (13).

Meanings of Exponents

The exponent κ is considered to be a measure of the ratio of the ionic mobility to the segmental one which is detected as the melt viscosity. Figure 6 shows that the κ value is around unity for the low \overline{M}_w oligomer, which is consistent with Walden's rule [eq. (3)] for low mol wt liquids, as mentioned before.

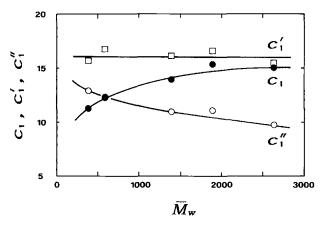


Figure 10 Plot of WLF C_1 constants for η , σ , and τ versus \overline{M}_{ω} of the epoxide oligomer: (•) C_1 for η ; (□) C'_1 for τ ; (○) C''_1 for σ .

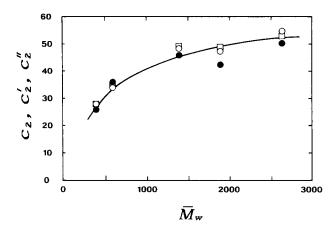


Figure 11 Plot of WLF C_2 constants for η , σ , and τ versus \overline{M}_w of the epoxide oligomer: (•) C_2 for η ; (□) C'_2 for τ ; (○) C''_2 for σ .

The κ value decreases with an increase in the M_w of the oligomer, which exhibits a similar dependence on \overline{M}_w to the exponent m, indicating the ratio of the ionic mobility to the dipole one. This finding shows that the critical volume for the ion transport is not so different among the oligomers due to the similar size of ions contained in each oligomer,⁷ while the critical volume for the segment transport increases with an increase in \overline{M}_w .

The ratio of the segmental mobility to the dipole one is expressed by the exponent ℓ , whose value increases with an increase in the $\bar{M_w}$ of the oligomer and is close to unity for the oligomer with M_{μ} higher than 2000 (Fig. 9). As indicated in eqs. (11) and (13), the ℓ value below unity means that the critical volume for the dipole transport is large compared with that for the segment transport; in other words, the dipole mobility in the dielectric measurement is more strongly restricted than the segment mobility in the viscosity measurement. The behavior of ℓ in Figure 9 shows that the lower \bar{M}_w oligomer receives larger restriction in the dipole movement. According to the chemical structure shown before, each epoxide oligomer has a pair of strong polar end groups (epoxide ones) in the linear molecule. The molecular interaction, based on the terminal epoxide group, produces a larger influence on the low \overline{M}_w oligomer than the high \overline{M}_{w} one. The relatively large limitation of the dipole movement in the dielectric measurement is considered to be caused mainly by the interaction between epoxide groups. This type of molecular interaction appears to become negligible for the high \bar{M}_w oligomer ($\bar{M}_w > 2000$), judging from the behavior of ℓ in Figure 9.

If the exponent ℓ is near unity, the dielectric relaxation time τ is almost proportional to the melt viscosity η according to the relation between τ and η , $\eta/\tau^{\ell} = \text{const.}$ Figure 9 indicates that the dielectric relaxation time is almost proportional to the melt viscosity for the high \overline{M}_w oligomer ($\overline{M}_w > 2000$) and is not proportional for the low \overline{M}_w oligomer. Generally, the dielectric relaxation time is said to be proportional to the melt viscosity for a simple liquid whose dielectric α -relaxation is governed by the Debye model. The concept also implies that the dielectric relaxation time is not always proportional to the viscosity for the compound whose dielectric α -relaxation is not always proportional to the viscosity for the compound whose dielectric α -relaxation is not fitted to the simple Debye equation. The epoxide oligomer is considered to be one such example.

Dielectric analysis is widely used to monitor the curing process of epoxy resin system. The finding of this work, obtained on the relationship between the melt viscosity and dielectric properties for epoxide oligomers, may provide a new insight for the analysis of the reactive epoxy resin system in the early stage of curing.

CONCLUSIONS

Melt viscosity has been investigated for a series of bisphenol-A type epoxide oligomers with different weight-average mol wts (\overline{M}_w) , ranging from 388 to 2640. The following conclusions were obtained.

- 1. The temperature dependence of the melt viscosity is described by the Williams-Landel-Ferry (WLF) equation.
- 2. The melt viscosity η is correlated with both the direct current (dc) conductivity σ and the dielectric relaxation time τ . Two relationships, $\sigma \cdot \eta^{\kappa} = \text{const.}$ and $\eta/\tau^{\ell} = \text{const.}$ are experimentally derived. Both exponents κ and ℓ depend on the \overline{M}_w of the oligomer.
- 3. The exponent κ is considered to be a measure of the ratio of the segmental mobility to ionic mobility. The lower \overline{M}_w oligomer has the larger value of κ . The κ value is close to unity for the low \overline{M}_w oligomer, which agrees with Walden's rule, $\sigma \cdot \eta = \text{const.}$, applicable to most low mol wt liquids.
- 4. The ℓ value is near unity for the epoxide oligomer with higher \bar{M}_w than 2000, which shows that the melt viscosity is proportional to the dielectric relaxation time for the high \bar{M}_w oligomer. The low \bar{M}_w oligomer (\bar{M}_w < 2000), on the other hand, has a smaller value of ℓ below unity. The result indicates that the melt viscosity is not proportional to

the dielectric relaxation time for the low \overline{M}_{ω} oligomer, whose dielectric α -relaxation is not governed by the Debye equation.

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