# Free Volume and Dipole Mobility in an Epoxide Oligomer Before Crosslinking

### TSUNEO KOIKE, NORITOSHI ISHIZAKI

Research and Development Laboratory, Yuka Shell Epoxy Company, Ltd., No. 1 Shiohama-cho, Yokkaichi, Mie, 510–0851 Japan

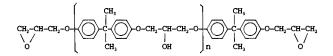
Received 2 February 1998; accepted 30 April 1998

ABSTRACT: The free volume of a bisphenol-A-type epoxide oligomer (DGEBA) was studied using Williams–Landel–Ferry parameters and thermal expansion coefficients above and below the glass transition temperature  $(T_g)$ . The values of the free-volume fraction at the  $T_g$  are around 0.02 for the DGEBA oligomers having weight-average molecular weights  $(\bar{M}_w$ 's) from 1396 to 2640. The dipole mobility, which was obtained from the analysis of the temperature dependence of the dielectric relaxation time, was compared with the segment mobility in terms of the critical volume for the transport of each moving unit. The critical volume for the segment transport increases with increase of the  $\bar{M}_w$  of the oligomer. The critical volume for the dipole movement, on the other hand, is not different between the oligomers studied (1396  $\leq \bar{M}_w \leq 2640$ ), which leads to that the dipole mobility in the epoxide oligomer is smaller than is the segment mobility. The low mobility of the dipole is considered to result from the molecular interaction restricting the dipole movement, especially in a smaller  $\bar{M}_w$  oligomer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 207–214, 1999

**Key words:** epoxy resin; free volume; thermal expansion; glass transition temperature; WLF equation

# INTRODUCTION

The epoxide oligomer has been widely used in many applications after crosslinking with adequate curing agents depending on the purpose.<sup>1</sup> A typical epoxide oligomer is the diglycidyl ether of bisphenol-A (DGEBA), whose structural formula is shown below:



The epoxide oligomer has different molecular weights according to the variation in the repeated number (n) in the structural formula.<sup>1</sup>

Journal of Applied Polymer Science, Vol. 71, 207-214 (1999)

The macroscopic free volume is an important parameter closely related to the rheological behavior of an amorphous material.<sup>2,3</sup> It is generally believed that the glass transition is regarded as an iso-free volume state and the free-volume fraction  $(f_{\sigma})$  at the glass transition temperature  $(T_g)$  is around 0.025 for many monomers and polymers.<sup>2,3</sup> The Williams-Landel-Ferry (WLF) method is widely used for determining the  $f_g$  value.<sup>4</sup> Crosslinked epoxy resin networks have been analyzed according to the WLF equation.<sup>5-9</sup> Several researchers have determined the fractional free volume of the crosslinked epoxy network using the WLF  $C_1$  or  $C_2$  parameter that was obtained from different measuring methods, such as the dynamic mechanical<sup>7,8</sup> or the direct current (dc) conduction<sup>10,11</sup> measurements. As for the epoxide oligomer before crosslinking, the freevolume content has not been yet experimentally determined by the WLF method.<sup>12–18</sup>

Correspondence to: T. Koike.

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/020207-08

DGEBA Oligomer	$\mathop{T_g}_{(^\circ\mathrm{C})}$	$ar{M}_w$	${ar M}_w/{ar M}_n$	$n = 0^{a}$ (%)	$\alpha_l^{\rm b}$ (°C <sup>-1</sup> )	${lpha_g}^{ m c}$ (°C <sup>-1</sup> )	$lpha_l - lpha_g \ (^{\circ}\mathrm{C}^{-1})$
Epikote 1001	30	1396	1.55	11.5	$5.54 imes10^{-4}$	$1.30 imes10^{-4}$	$4.24 imes10^{-4}$
Epikote 1002	39	1891	1.63	7.0	$5.34 imes10^{-4}$	$1.35 imes10^{-4}$	$3.99 imes10^{-4}$
Epikote 1003	45	2078	1.66	5.8	$5.34 imes10^{-4}$	$1.36 imes10^{-4}$	$3.98 imes10^{-4}$
Epikote 1004	54	2640	1.72	3.7	$5.44 imes10^{-4}$	$1.50 imes10^{-4}$	$3.94 imes10^{-4}$

Table I Thermal Expansion Behavior of DGEBA Oligomers

<sup>a</sup> The content of the n = 0 component by area % in gel permeation chromatogram.

<sup>b</sup> Thermal expansion coefficient above  $T_g^{r}$ 

Microscopic analysis of the free volume has also been applied to epoxy resin systems. Positron annihilation spectroscopy (PAS) provides useful information on the microstructural properties of the free volume, such as free-volume hole sizes and distributions.<sup>19-25</sup> Deng et al.<sup>20</sup> attempted to calculate the fractional free volume in the crosslinked epoxy network from the *ortho*-positronium lifetime and corresponding intensity. Wang et al.<sup>23</sup> estimated the fractional free volume of a crosslinked epoxy resin from PAS measurement on the assumption that the  $f_g$  is 0.025.

The free volume generally has a size distribution. The macroscopic average free volume, however, is still a useful parameter for discussing the rheological behavior of epoxy resin systems. This article focuses on the experimental determination of the macroscopic average free volume in an uncrosslinked DGEBA oligomer. The free-volume data were applied to analyze the dipole mobility in comparison with the segment and ion mobility in the epoxide oligomer.

# **EXPERIMENTAL**

#### Materials

The DGEBA oligomers used in this study were Epikote 1001, 1002, 1003, and 1004, which were supplied by Yuka Shell Epoxy (Yokkaichi, Japan). The four oligomers are amorphous solids at room temperature. The weight-average molecular weights  $(M_w$ 's) and the glass transition temperatures  $(T_{\sigma}$ 's) for the four oligomers are from 1396 to 2640 and from 30 to 54°C, respectively (Table I). Bisphenol-A-type epoxide oligomers generally have molecular weight distributions. A gel permeation chromatogram of Epikote 1002 is given in Figure 1. The measurement of the gel permeation chromatography was described elsewhere.<sup>26</sup> The ratio of  $\bar{M}_w$  and the number-average molecular weight  $(M_n)$ ,  $M_w/M_n$ , is an indication of the molecular weight distribution. In Table I, the  $M_w/$  $\overline{M}_n$  value is listed for each oligomer along with the content of the n = 0 component in the structural formula of the oligomer previously shown.

### **Measurements**

The density  $(\rho)$  of the solid sample was calculated from the buoyancy of the sample in silicon oil (KF96-5, Shinetsu Silicon). The thermal expansion coefficient  $(\alpha)$  of the sample is determined from the relationship between the specific volume  $(V = 1/\rho)$  and the temperature (T) in the following way:

$$\alpha = (1/V)(dV/dT) \tag{1}$$

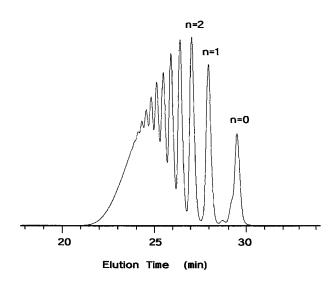
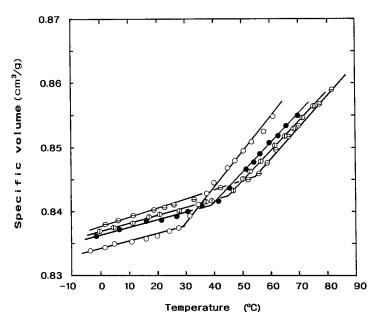


Figure 1 Gel permeation chromatogram of Epikote 1002.



**Figure 2** Specific volume as a function of temperature for DGEBA oligomers: ( $\bigcirc$ ) Epikote 1001; ( $\bigcirc$ ) Epikote 1002; ( $\bigcirc$ ) Epikote 1003; ( $\ominus$ ) Epikote 1004.

# **RESULTS AND DISCUSSION**

### Thermal Expansion Behavior of Epoxide Oligomer

Figure 2 shows the specific volume of four DGEBA oligomers, Epikote 1001, 1002, 1003, and 1004, as a function of temperature. Thermal expansion coefficients above and below the  $T_g$ ,  $\alpha_l$  and  $\alpha_g$ , are summarized in Table I. The  $\alpha_l$  and  $\alpha_g$  values for these DGEBA oligomers (1396  $\leq M_w \leq 2640$ ) are from  $5.34 \times 10^{-4}$  to  $5.54 \times 10^{-4}$  °C<sup>-1</sup> and from  $1.30 \times 10^{-4}$  to  $1.50 \times 10^{-4}$  °C<sup>-1</sup>, respectively. The value of  $\alpha_l - \alpha_g$  decreases with increase of the  $T_g$  of the oligomer.

Simha and Boyer found the following relation between  $\alpha_l - \alpha_g$  and  $T_g$  for many amorphous polymers<sup>27,28</sup>:

$$(\alpha_{\ell} - \alpha_{g})T_{g} \approx \text{const} \approx 0.113 \tag{2}$$

where  $T_g$  is in K. This relationship is also considered applicable to oligomers.<sup>27</sup> The product,  $(\alpha_l - \alpha_g) T_g$ , for the epoxide oligomer ranges from 0.124 to 0.129 and is similar among the oligomers studied. Several aromatic backbone polymers, such as polystyrene, have the  $(\alpha_l - \alpha_g) T_g$  values in the range from 0.101 to 0.179 (the average value: 0.128).<sup>27,28</sup> The thermal expansion coefficients for the epoxide oligomers are considered reasonable.

# Relationship Between Free-Volume Fraction at $T_g$ and WLF Parameters

In previous studies  $^{29-33}$  the WLF parameters for the four DGEBA oligomers were obtained by three measuring methods, the dielectric relaxation time ( $\tau$ ), the melt viscosity ( $\eta$ ), and the direct current (dc) conductivity ( $\sigma$ ) measurements as summarized in Table 2. Each measuring method measures a moving unit that is the dipole, the molecular segment, or the ionic charge carrier in the oligomer investigated. The WLF  $C_1$  and  $C_2$ parameters are generally described in the following forms according to the free-volume theory developed by Cohen and Turnbull.<sup>34–36</sup>

$$C_1 = \gamma \nu^* / (2.303 f_g \bar{\nu}_m) \text{ and } C_2 = f_g / \alpha_f$$
 (3)

where  $\gamma$  is a numerical factor introduced to correct for the overlap of the free volume;  $\nu^*$ , the critical volume large enough to permit a molecule (a moving unit) to jump in after the displacement;  $\bar{\nu}_m$ , the average molecular volume;  $f_g$ , the free-volume fraction at the  $T_g$ ; and  $\alpha_f$ , the thermal expansion coefficient of the free volume.

Equation (3) 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 mobility of the moving unit, which is expressed by the critical volume ( $\nu^*$ ) for the transport of the dipole, the oligomer segment, or the ionic charge carrier.

### Determination of Free-Volume Fraction at $T_g$

The free-volume fraction  $(f_g)$  at the  $T_g$  can be obtained from either the WLF  $C_1\,{\rm or}\,C_2$  parameter

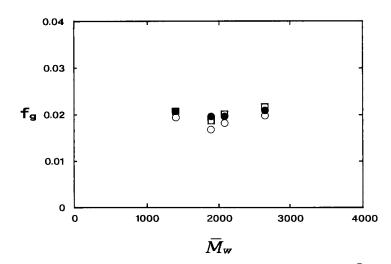


Figure 3 Relationship between free-volume fraction  $f_g$  at  $T_g$  and  $M_w$  of DGEBA olig<br/>mer: (O)  $f_g$  by melt viscosity measurement; ( $\bullet$ )<br/>  $f_g$  by dielectric relaxation time measurement; ( $\Box$ )  $f_g$  by dc conduction measurement.

as indicated in eq. (3). The WLF  $C_1$  parameter has two unknown factors,  $\gamma$  and  $\nu^*$ . The other WLF parameter,  $C_2$ , was then used to determine the  $f_{\sigma}$ value of the DGEBA oligomer. Equation (3) shows that  $f_{\sigma}$  can be calculated using the  $C_2$  parameter in the following way:

$$f_g = C_2 \alpha_f \tag{4}$$

where  $\alpha_f$  is the thermal expansion coefficient of the free volume. The  $\alpha_f$  value is usually approximated by the value of  $\alpha_l - \alpha_g$  because the thermal expansion coefficient of the free volume is difficult to directly measure. Table III lists the three  $f_{g}$  values,  $f_{g\tau}, f_{g\nu}$ , and  $f_{g\sigma}$ , which were obtained from the dielectric relaxation time, the melt viscosity, and the dc conduction measurements for each oligomer. In Figure 3, the three  $f_g$  values are plotted as a function of  $\bar{M}_w$  for the oligomers. The  $f_g$  values for these oligomers are around 0.02, which is smaller than the universal value (0.025) of  $f_g$ .

### Critical Volume for the Transport of Moving Unit

The critical volume  $(\nu^*)$  for the transport of a moving unit is a measure of the mobility of the moving unit in the epoxide oligomer. The  $\nu^*$  value is difficult to obtain through eq. (3) because  $\gamma$ , a constant accounting for the overlap of the free volume, is undetermined for the epoxide oligomer. Cohen and Turnbull reported that  $\gamma$  took the value from 0.5 to unity for some simple liquids.<sup>34,35</sup> The product of  $\gamma$  and  $\nu^*$ ,  $\gamma\nu^*$ , is also used as one of the indicators for the mobility of each moving unit in the epoxide oligomer. Equation (3)shows that the  $\gamma \nu^*$  value can be calculated using  $f_g$ ,  $\bar{\nu}_m$ , and the  $C_1$  parameter in the following way:

$$\gamma \nu^* = 2.303 f_\sigma \bar{\nu}_m C_1 \tag{5}$$

The  $f_g$  and  $C_1$  values were already obtained as listed in Tables II and III. The vaue for the average molecular volume  $(\bar{\nu}_m)$  is not available. Equa-

DGEBA Oligomer	$T_g$ (°C)	Viscosity <sup>a</sup>		Relaxation Time <sup>a</sup>		$Conductivity^{a}$	
		$C_1$	$C_2$	$C'_1$	$C_2'$	$C_1''$	$C_2''$
Epikote 1001	30	13.89	45.7	16.14	48.9	10.99	48.3
Epikote 1002	39	15.36	42.2	16.54	48.8	11.05	47.1
Epikote 1003	45	14.54	45.7	15.71	48.8	9.82	50.3
Epikote 1004	54	14.99	50.0	15.46	52.6	9.76	54.6

Table II WLF Parameters of DGEBA Oligomers

<sup>a</sup> WLF parameter values are cited from refs. 26, 29, and 30.

DCEDA	Visco	osity	Relaxati	on Time	Conductivity	
DGEBA Oligomer	$f_{g\eta}$	$\gamma { u}^*_\eta$	$f_{g\tau}$	$\gamma \nu_{ au}^*$	$f_{g\sigma}$	$\gamma  u_{\sigma}^{*}$
Epikote 1001	0.0194	0.512	0.0207	0.637	0.0205	0.430
Epikote 1002	0.0168	0.496	0.0195	0.619	0.0188	0.398
Epikote 1003	0.0182	0.510	0.0194	0.587	0.0200	0.378
Epikote 1004	0.0197	0.570	0.0207	0.617	0.0215	0.404

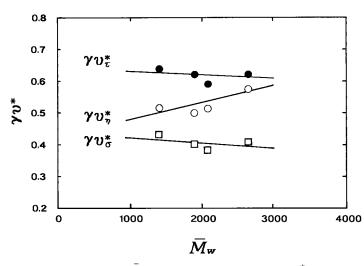
Table III Free-Volume Fractions at  $T_g$  and  $\gamma \nu^*$  Values of DGEBA Oligomers

tion (5) is based on the WLF-type equation that is valid in the temperature range from  $T_g$  and  $T_g$  + 100°C. The  $\bar{\nu}_m$  value was then calculated using the specific volume at  $T_g$  + 50°C and the thermal expansion coefficient of the free volume.

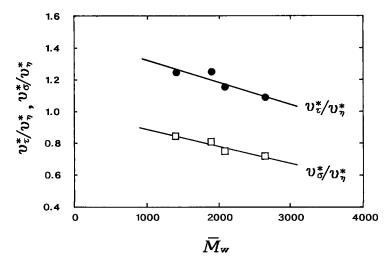
The three  $\gamma \nu^*$  values,  $\gamma \nu_{\eta}^*$ ,  $\gamma \nu_{\tau}^*$ , and  $\gamma \nu_{\sigma}^*$ , which were calculated through eq. (5), are summarized for each oligomer in Table III. The relationship between  $\gamma \nu^*$  and the  $M_w$  of the oligomer is plotted in Figure 4. Although  $\gamma$  is an undetermined factor, the  $M_w$  dependence of  $\gamma\nu^*$  provides useful information on the mobility of each moving unit. The  $\gamma \nu_n^*$  value for the segment mobility increases with increase of the  $\overline{M}_w$  of the oligomer. If the difference in  $\gamma$  is small between the same kinds of oligomers (1396  $\leq M_w \leq$  2640), the  $M_w$  dependence of  $\gamma \nu_n^*$  for the segment mobility in Figure 4 is considered reasonable; a lower  $M_w$  oligomer needs a smaller critical volume for the transport of a chain segment. The behavior of  $\gamma \nu_{\alpha}^{*}$  for the ion mobility is also explained in the following way: The four epoxide oligomers were produced from

the same raw materials by the same production process, which is a conventional one.<sup>26,30</sup> These oligomers are considered to have the same kinds of ions. The major ions in the epoxide oligomers are Na<sup>+</sup> and Cl<sup>-</sup> due to the manufacturing process. The concentrations of Na<sup>+</sup> and Cl<sup>-</sup> are very low and similar among these oligomers as described in a previous study.<sup>26</sup> The size of the ion is much smaller than that of the oligomer molecule. The critical volume for the ion transport is considered similar among the oligomers having different  $\overline{M}_w$ 's from 1396 to 2640.

As for the dipole mobility, the  $\gamma \nu_{\tau}^*$  value is not different among the oligomers and slightly decreases with increase of the  $\bar{M}_w$  of the oligomer as shown in Figure 4. A larger  $\bar{M}_w$  oligomer has a larger dipole and may need a larger critical volume for the transport of the moving unit. The  $\bar{M}_w$ -dependent behavior of  $\gamma \nu_{\tau}^*$  in Figure 4 is difficult to explain by the size of the moving unit only.



**Figure 4** Dependence of  $\gamma \nu^*$  on  $\overline{M}_{\nu\nu}$  of DGEBA oligomer: (O)  $\gamma \nu_{\eta}^*$  for segment mobility; ( $\bullet$ )  $\gamma \nu_{\tau}^*$  for dipole mobility; ( $\Box$ )  $\gamma \nu_{\sigma}^*$  for ion mobility.



**Figure 5** Dependence of the ratio between critical volumes for two moving units on  $\overline{M}_w$  of DGEBA oligomer: ( $\bullet$ ) the ratio between critical volumes for dipole and segment mobility  $(\nu_{\tau}^*/\nu_{\eta}^*)$ ; ( $\Box$ ) the ratio between critical volumes for ion and segment mobility  $(\nu_{\sigma}^*/\nu_{\eta}^*)$ .

# Dipole Mobility in Comparison with Segment Mobility

The relationship between  $\gamma \nu_{\tau}^*$  and  $\gamma \nu_{\eta}^*$  was studied in order to understand the mobility of the dipole. The ratio of the two  $\gamma \nu^*$  values eliminates the undetermined  $\gamma$  factor and is a direct comparison of the mobility of two moving units in the same oligomer. The ratio of the segment mobility and the dipole mobility,  $\nu_{\gamma}^{*}/\nu_{\eta}^{*}$ , is plotted as a function of the  $M_w$  of the oligomer in Figure 5. The mobility of the dipole is lower than that of the chain segment when the value of  $\nu_{\tau}^*/\nu_{\eta}^*$  is greater than unity. Figure 5 indicates that the  $\nu_{\tau}^* / \nu_{\eta}^*$  value is above unity and decreases with increase of the  $M_w$  of the oligomer. An epoxide oligomer having  $ar{M}_w$  around 3000 has the  $u_\eta^*\!/
u_\eta^*$  value near unity. The mobility of the dipole in the epoxide oligomer  $(M_w < \text{ca. 3000})$  is then smaller than the segment mobility. The difference in mobility between the two moving units is large for a low  $M_w$  oligomer because of a large  $\nu_{\tau}^* / \nu_{\eta}^*$  value as shown in Figure 5.

The dielectric relaxation time is defined as the time required for the polarization to decay to 1/*e* of the original equilibrium value. The dielectric relaxation time will become longer when the dipole movement is restricted by some force, such as molecular interaction.<sup>37,38</sup> According to the chemical structure of the epoxide oligomer previously shown, each oligomer has a pair of strong polar end groups (epoxide ones) in the linear molecule. The molecular interaction, based on the terminal

epoxide group, may produce a greater influence on the low  $\bar{M}_w$  oligomer than on the high  $\bar{M}_w$  one; the movement of a small-size dipole is more easily restricted than is that of a large-size dipole by the molecular interaction. This kind of molecular interaction on the dipole mobility is considered very small in large  $\bar{M}_w$  oligomers or polymers.

The molecular interaction may also have influence on the segment mobility that is obtained from a macroscopic melt viscosity measurement for the epoxide oligomer. A low  $\bar{M}_w$  epoxide oligomer exhibits a Newtonian flow behavior up to a relatively high shear rate, as reported by several researchers.<sup>13–15,30</sup> The zero shear melt viscosity of the epoxide oligomer is usually obtained from the measurement under some degree of shear stress. The influence of molecular interaction on the melt viscosity measurement under shear stress is considered small compared with the influence on the dielectric relaxation time measurement under no stress environment. A low  $M_w$ oligomer accepts a larger effect by the molecular interaction in the dielectric relaxation time measurement in comparison with a high  $M_w$  oligomer having larger dipoles. The difference in the molecular interaction is reflected in the  $M_w$ -dependent behavior of  $\nu_{\tau}^* / \nu_{\eta}^*$  in Figure 5.

# Relationship Between Ion and Chain Segment Mobility

The behavior of the ion in the epoxide oligomer was taken into account as a reference for better understanding of the dipole and the chain segment mobility in terms of the free volume. The relationship between the chain segment mobility and the ion mobility in the epoxide (DGEBA) oligomer was already discussed by several researchers.<sup>16-18</sup> The ratio of the chain segment mobility and the ion mobility,  $\nu_o^*/\nu_n^*$ , is plotted as a function of the  $\bar{M}_w$  of the oligomer in Figure 5. Each oligomer takes a  $\nu_{\sigma}^*/\nu_{\eta}^*$  value below unity, which indicates that the ion in the oligomer needs a smaller critical volume for the transport compared with the chain segment. Figure 5 shows that the  $\nu_{a}^{*}/\nu_{n}^{*}$  value decreases with increase of the  $M_w$  of the oligomer. The  $\nu_o^*/\nu_\eta^*$  value is about unity by an exploratory plot to zero  $\overline{M}_w$  of the oligomer, which means that the mobility of the ion will be almost equal to that of a segment in a very small molecule. As already mentioned, each oligomer has similar ions that are much smaller than the chain segment. The size of the chain segment, on the other hand, increases with increase of the  $M_{\mu\nu}$ of the oligomer. Therefore, the ratio of the two critical volumes,  $\nu_{\sigma}^*/\nu_{\eta}^*$ , is below unity and decreases with increase of the  $\bar{M}_w$  of the oligomer. The  $M_w$ -dependent behavior of  $\nu_{\sigma}^*/\nu_n^*$  for the epoxide oligomer is consistent with results of other investigations.<sup>16–18</sup>

# **CONCLUSIONS**

The free volume of a bisphenol-A-type epoxide oligomer (DGEBA) was studied using the WLF parameters and the thermal expansion coefficients above and below the glass transition temperature  $(T_g)$ . The values of the free-volume fraction at the  $T_g$  were found to be around 0.02 for the oligomers having weight-average molecular weights  $(\bar{M}_w)$ 's) from 1396 to 2640.

The free-volume data were used to compare the dipole and the chain segment mobility in the epoxide oligomer. The following results were obtained:

- 1. The critical volume for the transport of the dipole is large compared with that of the chain segment in the oligomers, which means that the mobility of the dipole is smaller than that of the chain segment.
- 2. The mobility difference decreases with increase of the  $\bar{M}_w$  of the oligomer and may be negligible for higher  $\bar{M}_w$  oligomers ( $\bar{M}_w >$  ca. 3000).
- 3. The difference in mobility is considered to

be caused by the molecular interaction restricting the movement of a smaller oligomer dipole.

The authors would like to express their thanks to Prof. M. Ochi of Kansai University for his valuable advice and suggestions.

# REFERENCES

- Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
- Ferry, J. D. Viscoelastic Properties of Polymers; Wiley: New York, 1970.
- Van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers; Elesvier, Amsterdam, 1976.
- Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
- 5. Shito, N. J Polym Sci Part C 1968, 23, 569.
- Gupta, V. B.; Drzal, L. T.; Rich, M. J Appl Polym Sci 1985, 30, 4467.
- Gupta, V. B.; Brahatheeswaran, C. Polymer 1991, 32, 1875.
- Ogata, M.; Kinjyo, N.; Kawata, T. J Appl Polym Sci 1993; 48, 583.
- Ochi, M.; Kotera, K. Nippon Setchaku Gakkaishi 1992, 28, 272.
- Miyamoto, T; Shibayama, K. Kobunshi Kagaku 1972, 29, 463.
- 11. Miyamoto, T.; Sugano, T.; Shibayama, K. Kobunshi Kagaku 1973, 30, 155.
- Hata, N.; Kumanotani, J. J Appl Polym Sci 1973, 17, 3545.
- 13. Aleman, J. V. Polym Eng Sci 1978, 18, 1160.
- Aleman, J. V. J Polym Sci Polym Chem Ed 1980, 18, 2567.
- Ghijsels, A.; Groesbeek, N.; Raadsen, J. Polymer 1980, 25, 463.
- Senturia, S. D.; Sheppard, Jr., N. F. Adv Polym Sci 1986, 80, 1.
- Sheppard, Jr., N. F.; Senturia, S. D. J Polym Sci Part B Polym Phys 1989, 27, 753.
- Simpson, J. O.; Bidstrup, S. A. J Polym Sci Part B Polym Phys 1993, 31, 609.
- Jean, Y. C.; Sandreczki, T. C.; Ames, D. P. J Polym Sci Part B Polym Phys 1986, 24, 1247.
- Deng, Q.; Sundar, C. S.; Jean, Y. C. J Phys Chem 1992, 96, 492.
- Deng, Q., Zandiehnadem, F., Jean, Y. C. Macromolecules 1992, 25, 1090.
- 22. Deng, Q.; Jean, Y. C. Macromolecules 1993, 26, 30.
- Wang, Y. Y.; Nakanishi, H.; Jean, Y. C.; Sandreczki, T. C. Polym Sci Part B Polym Phys 1990, 28, 1431.
- Suzuki, T.; Oki, Y.; Numajiri, M.; Miura, T.; Kondo, K.; Shiomi, Y.; Ito, Y. J Appl Polym Sci 1993, 49, 1921.

- 25. Suzuki, M.; Oki, Y.; Numajiri, M.; Miura, T.; Kondo, K.; Ito, Y. Polymer, 1993, 34, 1361.
- Koike, T.; Tanaka, R. J Appl Polym Sci 1991, 42, 1333.
- 27. Simha, R.; Boyer, R. F. J Chem Phys 1962, 37, 1003.
- 28. Boyer, R. F.; Simha, R. J Polym Sci Polym Lett Ed 1973, 11, 33.
- 29. Koike, T. J Appl Polym Sci 1992, 45, 901.
- 30. Koike, T. J Appl Polym Sci 1993, 47, 387.

- 31. Koike, T. Polym Eng Sci 1993 33, 1301.
- 32. Koike, T. J Appl Polym Sci 1995, 56, 1183.
- 33. Koike, T. J Appl Polym Sci 1993, 50, 1943.
- Cohen, M. H.; Turnbull, D. J Chem Phys 1959, 31, 1164.
- 35. Turnbull, D.; Cohen, M. H. J Chem Phys 1961, 34, 120.
- 36. Berry, G. C.; Fox, T. G. Adv Polym Sci 1968, 5, 261.
- 37. Porter, D. Polymer 1987, 28, 1051.
- 38. Porter, D. Polymer 1987, 28, 1056.