

## Rotational Isomeric State Analysis of Poly(oxyethylene). Conformational Energies and the Random-Coil Configuration

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**ABSTRACT:** Configuration-dependent properties of the poly(oxyethylene) (POE) chain were calculated within the framework of the rotational isomeric state (RIS) approximation. Conformational energies of the chain have been determined by the  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies on 1,2-dimethoxyethane (DME) and POE as described in our recent paper as well as in the present work. The unperturbed chain dimension  $C (= \langle r^2 \rangle_0 / nl^2)$ , the dipole moment  $\langle \mu^2 \rangle / nm^2$ , and the molar Kerr constant  $\langle {}_m K \rangle / x$  were calculated as a function of RIS parameters such as bond angles, rotational angles, and conformational energies. The value of  $C (= 5.2)$  determined in organic solutions by Beech and Booth was found to be favorably reproduced by these calculations. The SANS result ( $C = 6.9$ ) recently reported by Kugler *et al.* on the melt exceeds the limit of a probable range estimated from uncertainties involved in each of the RIS parameters. Within the limit mentioned above, a set of RIS parameters was chosen so as to give an optimum agreement with observed values of the configurational properties of POE. Conformational energies thus estimated are as follows:  $E_g = -0.5 \text{ kcal mol}^{-1}$  for the C-C bond and  $E_o = 0.8 \text{ kcal mol}^{-1}$  for the C-O bond, both representing the energy of the *gauche* form expressed relative to the *trans* state. Use of the conformational energies ( $E_g = -1.2$  and  $E_o = 1.1 \text{ kcal mol}^{-1}$ ) determined in  $\text{D}_2\text{O}$  leads to a value of  $C = 3.2$ , suggesting that the end-to-end dimension of the chain for the state unperturbed by long-range interactions may be considerably small in pure water.

**KEY WORDS** Poly(oxyethylene) / Rotational Isomeric State Analysis /  
Conformational Energies / Unperturbed Dimension / Dipole Moment /  
Molar Kerr Constant /

One of the most characteristic features of the poly(oxyethylene) (POE) chain is its strong preference for the *gauche* state about the constituent OC-CO bond, which makes the chain highly flexible.<sup>1-3</sup> As is well-known, the polymer is soluble in water as well as in certain organic solvents. In aqueous salt solutions, POE exhibits a lower critical solution temperature. The unperturbed dimension of the POE chain has been determined in a variety of solvents: the results are usually expressed as the characteristic ratio  $C = \langle r^2 \rangle_0 / nl^2$ , where  $r$  is the end-to-end distance,  $n$  the number of skeletal bonds, and  $l^2$  the average of the square of their lengths. The

most reliable values may be obtained from measurements under the  $\Theta$  condition. Beech and Booth<sup>4</sup> carried out viscosity measurements on the fractionated POE samples in isobutyl methyl ketone, diethylene glycol diethyl ether, and 0.45 M aqueous potassium sulfate. The results obtained around the  $\Theta$  temperature lead to a value of  $C = 5.2$  in all these three solvents when the hydrodynamic constant  $\phi$  is taken to be  $2.6 \times 10^{23} \text{ mol}^{-1}$ .<sup>1,2</sup> Recently, Kugler *et al.*<sup>5</sup> quoted a larger value,  $C = 6.8 - 7.5$ , from Peuscher's unpublished work. They simply stated that this value was obtained from viscosity measurements on highly purified salt free samples in some

organic solvents. Values of  $C$  determined in aqueous salt solutions (under the  $\Theta$  condition) by the other groups<sup>6</sup> scatter over a rather wide range from 4.1 to 5.6.

In our recent paper<sup>3</sup> (hereafter referenced as paper I), conformational characteristics of 1,2-dimethoxyethane (DME) and POE were studied by the NMR method, supplemented with conformational energy calculations. The observed temperature dependence of the vicinal coupling constants was analyzed on the basis of the rotational isomeric state (RIS) scheme. For the C–C bond, conformational energy  $E_\sigma$ , representing the energy of the *gauche* form expressed relative to the *trans* state, was found to vary over a range from  $-0.5$  to  $-1.2$  kcal mol<sup>-1</sup>, depending on the solvent system. For the rotation about the C–O bond, values of  $E_\rho = 0.8$  to  $1.1$  kcal mol<sup>-1</sup> were obtained for the energy difference between the *gauche* and *trans* states. In these analyses, conformational energy  $E_\omega$  for the four-bond interaction C–O–(C)–C–O was set equal to the value ( $0.53$  kcal mol<sup>-1</sup>) estimated by the calculation.<sup>3</sup> It should be important to note that values of  $E_\sigma$  and  $E_\rho$  derived from the monomer model (DME) and the polymer are comparable with each other when compared for the same solvent system. The values of  $E_\sigma$ ,  $E_\rho$ , and  $E_\omega$  derived in this manner are generally in agreement with those adopted previously<sup>2</sup> in the analysis of the unperturbed dimension ( $C = 5.2$ ). Thus, the NMR measurements have provided a support to the theoretical calculation presented in our previous paper.<sup>2</sup>

Allen and Maconnachie<sup>7</sup> were the first to report the small angle neutron scattering (SANS) data on POE in the molten state. They obtained a value of  $C = 9.7$ , which is exceedingly larger than those estimated in solution. Lately, Kugler, Fischer, Peuscher, and Eisenbach<sup>5</sup> reported a substantially smaller value (6.9) from their SANS experiments. The latter value is, however, still considerably higher than those generally estimated in solution except the one obtained by Peuscher *et*

*al.* as quoted in Kugler's paper.<sup>5</sup> Chain dimensions in the melt or in the amorphous bulk state are usually the same as those in  $\Theta$  solvents.<sup>8</sup> In view of the aforementioned experimental results, Kugler *et al.*<sup>5</sup> stated that the theoretical calculations should be checked to decide if they can confirm the SANS curves by using appropriate set of parameters.

To meet their request, we first performed a conformational analysis of DME in the neat liquid to elucidate values of  $E_\sigma$  and  $E_\rho$  appropriate for the treatment of POE in the molten state. We then examined by calculation how sensitively the  $C$  value changes with various parameters employed in the RIS scheme. On this basis, the controversial subject raised by Kugler *et al.*<sup>5</sup> will be discussed in detail. The dipole moments and molar Kerr constants are also calculated as a function of the chain length by using the same RIS parameters and compared with the corresponding experimental results.<sup>9–13</sup>

## DETERMINATION OF CONFORMATIONAL ENERGIES $E_\sigma$ AND $E_\rho$ FOR DME IN THE NEAT LIQUID

### *Experimental*

Reagent grade sample of DME is commercially available and was used without further purification.

The <sup>13</sup>CH satellite side band spectra were recorded on a JEOL-FX-100 spectrometer equipped with an FT system operating at 100 MHz. The FT spectra contain 8192 data points for 300 Hz spectral width. In the measurements, about 100 transients were accumulated with a 90° rf pulse of 14 μs duration. The pulse repetition time was 10 s. NMR sample tube with a diameter of 5 mm was used.

The <sup>13</sup>C natural abundance undecoupled NMR spectra were recorded on the same spectrometer operating at 25.15 MHz. The FT spectra contain 8192 data points for 500 Hz spectral width: 300 transients were accumu-

lated with a 90° rf pulse of 20 μs duration, the pulse repetition time being 10 s. NMR sample tube with 10 mm diameter was used.

A capillary filled with DMSO-*d*<sub>6</sub> for <sup>2</sup>D field-frequency lock was inserted in the NMR sample tube both in the <sup>1</sup>H and <sup>13</sup>C NMR measurements. The temperatures were maintained within ± 1°C during the measurements.

#### Analysis of the Experimental Results

Vicinal coupling constants customarily expressed as <sup>3</sup>*J*<sub>HH</sub> and <sup>3</sup>*J*'<sub>HH</sub> were determined from the <sup>13</sup>CH satellite side band spectra by using LAOCOON III program, and the results are listed in Table I. Also given in the table are values of the vicinal <sup>13</sup>C-<sup>1</sup>H coupling constants <sup>3</sup>*J*<sub>CH</sub> obtained from the proton-coupled <sup>13</sup>C spectra for the terminal methoxyl group.

As may be expected from similarity in the chemical compositions between DME and 1,4-dioxane, the <sup>3</sup>*J*<sub>HH</sub> vs. <sup>3</sup>*J*'<sub>HH</sub> plot prepared for the neat liquid closely resembles that obtained previously for DME in 1,4-dioxane-*d*<sub>8</sub>.<sup>3</sup> Following the previous treatment,<sup>3</sup> we assume that the relation

$${}^3J_{HH} = -(1/2){}^3J'_{HH} + (1/2)J_T + J_G \quad (1)$$

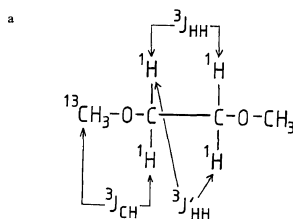
is valid. Here *J*<sub>T</sub> and *J*<sub>G</sub> denote the vicinal coupling constants for the *trans* and *gauche* arrangements, respectively. Statistical weight parameters σ, ρ, and ω required in the RIS treatment may be expressed in terms of the corresponding conformational energies:

$$\begin{aligned} \sigma &= 0.99 \exp(-E_\sigma/RT) \\ \rho &= 0.61 \exp(-E_\rho/RT) \\ \omega &= 0.88 \exp(-E_\omega/RT) \end{aligned} \quad (2)$$

where the pre-exponential factors are the same as those adopted in paper I.<sup>3</sup> In the following calculations, the value of *E*<sub>ω</sub> was set equal to 0.53 kcal mol<sup>-1</sup>, otherwise noted.<sup>3</sup> The least-squares treatment of the experimental data was performed as set forth in paper I.<sup>3</sup> The value of *E*<sub>ρ</sub> was thus estimated to be -0.6 kcal

**Table I.** Experimental values of <sup>3</sup>*J*<sub>HH</sub>, <sup>3</sup>*J*'<sub>HH</sub>, and <sup>3</sup>*J*<sub>CH</sub> for DME in the neat liquid<sup>a</sup>

<i>T</i> °C	<sup>3</sup> <i>J</i> <sub>HH</sub> Hz	<sup>3</sup> <i>J</i> ' <sub>HH</sub> Hz	<sup>3</sup> <i>J</i> <sub>CH</sub> Hz
20.0	6.02	3.90	1.83
40.0	6.00	4.01	
50.0	5.96	4.05	1.83
60.0	5.91	4.10	1.79
70.0			1.89
80.0			1.90



mol<sup>-1</sup>, being comparable to that (-0.5 kcal mol<sup>-1</sup>) obtained previously in 1,4-dioxane-*d*<sub>8</sub>.<sup>3</sup> The observed temperature dependence of <sup>3</sup>*J*<sub>HH</sub> and <sup>3</sup>*J*'<sub>HH</sub> (cf. Table I) was found to be well reproduced by calculation with the *E*<sub>a</sub> value given above. The values of *J*<sub>T</sub> and *J*<sub>G</sub> determined concomitantly are as follows: *J*<sub>T</sub> = 11.1, and *J*<sub>G</sub> = 2.4, both being in Hz.

The value of *E*<sub>ρ</sub> for the C-O bond may be estimated from the <sup>3</sup>*J*<sub>CH</sub> data. Adoption of *J*<sub>G</sub> = 1.3 Hz for the *gauche* arrangement in the moiety <sup>13</sup>C-O-C-<sup>1</sup>H yields *E*<sub>ρ</sub> = 0.9 kcal mol<sup>-1</sup>, which is similar in magnitude to that (0.8 kcal mol<sup>-1</sup>) derived previously in 1,4-dioxane-*d*<sub>8</sub>.<sup>3</sup> In the neat liquid, therefore, DME takes conformations nearly identical with those in 1,4-dioxane-*d*<sub>8</sub>.

### THEORETICAL TREATMENT OF CONFIGURATION-DEPENDENT PROPERTIES AND COMPARISONS WITH EXPERIMENTAL RESULTS

#### *Geometrical Parameters and Conformational Energies Required for the Calculation*

Values of the geometrical parameters and

**Table II.** Values of the geometrical parameters and conformational energies assembled in the base set, adopted for a preliminary calculation (see the text)

Geometrical parameters <sup>a</sup>					
$l_{CC}$	$l_{CO}$	$\angle CCO$	$\angle COC$	$\phi_{CC}^g$	$\phi_{CO}^g$
Å	Å	deg	deg	deg	deg
1.53	1.43	111.5	111.5	$\pm 117.0$	$\pm 98.0$
Conformational energies					
$E_\sigma$	$E_\rho$		$E_\omega$		
kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>		kcal mol <sup>-1</sup>		
-0.60	0.90		0.53		

<sup>a</sup> The *trans* states were taken to occur at 0°, *i.e.*,  $\phi_{CC}^t = \phi_{CO}^t = 0^\circ$ .

conformational energies adopted as a base set are listed in Table II. In the following calculations, some of these parameters are varied around given values to examine how sensitively the configurational properties of the chain depend on such factors. The bond lengths and bond angles given in Table II were taken from our previous paper.<sup>2</sup> The rotational angles were chosen from the energy calculations presented in paper I.<sup>3</sup> The conformational energies listed are those established for pure DME in the preceding section.

As for the bond angles, experimental values determined by various spectroscopic methods<sup>14-16</sup> scatter within certain ranges:  $\angle CCO = 111.0^\circ \pm 2.0^\circ$  and  $\angle COC = 111.0^\circ \pm 1.0^\circ$ . The value of  $\phi_{CC}^g$  given in Table II is consistent with the experimental data reported on DME in the gas phase.<sup>16</sup> However, somewhat larger displacements from the regularly staggered position have also been suggested from the X-ray analysis of the most stable crystalline form (*tg<sup>±</sup>t*)<sup>17,18</sup>:  $\phi_{CC}^g = \pm 112.6^\circ$  and  $\pm 115.0^\circ$ . Conformational energy calculations indicate a displacement of *ca.* 20°

for the *gauche* minima around the C–O bond ( $\phi_{CO}^g$ ) as indicated in Table II. Displacements of similar magnitude in these rotational states have been suggested in the crystallographic studies on poly(alkyl vinyl ether)'s.<sup>19</sup>

The rotational isomeric state treatment of the POE chain  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$  was carried out according to the Flory scheme.<sup>1</sup> The statistical weight matrices were expressed in a  $3 \times 3$  form. The characteristic ratio for the unperturbed dimension  $C$ , the dipole moment ratio  $\langle \mu^2 \rangle / nm^2$ , and the molar Kerr constant  $\langle {}_m K \rangle / x$  were calculated<sup>1</sup> for chains with  $x = 1$  to 161. Values of the bond dipole moment  $m$  are the same as those adopted in our previous work<sup>2</sup>:  $m_{CO} = 1.07$  D and  $m_{CC} = 0$ . Bond polarizabilities were taken from Patterson and Flory's paper<sup>20</sup>:  $\Delta\alpha_{CC} = 0.95$ ,  $\Delta\alpha_{CO} = 0.58$ , and  $\Delta\alpha_{CH} = 0.21$ , units being Å.<sup>3</sup> Temperatures were properly chosen in each case so as to facilitate comparison with experimental results.

#### Characteristic Ratios for the Unperturbed Dimension

Experimental values of the characteristic ratio  $C$  obtained from a literature survey are summarized in Table III, where the hydrodynamic constant  $\phi$  required in the treatment of viscometric data was assumed to be  $2.6 \times 10^{23}$  mol<sup>-1</sup> near the  $\Theta$  condition.<sup>1</sup> The pioneering data of Bailey and Callard<sup>21</sup> obtained on unfractionated samples may be superseded by the recent results of Boucher and Hines,<sup>6a</sup> and Ataman and Boucher,<sup>6b</sup> who also studied viscometric behaviors in aqueous salt solutions. Only the latter results are cited in the table. Values of  $C$  determined in aqueous salt solutions were mostly found in a range  $5.1 \pm 0.5$ , with an exception of the two low values ( $C = 4.1$ ) obtained in solutions of very high salt content (*cf.* Table III). As concluded by Beech *et al.*,<sup>4</sup> the unperturbed dimensions of POE in aqueous salt solutions are much the same as those in organic media. Values of the characteristic ratio deduced by an extrapolation from

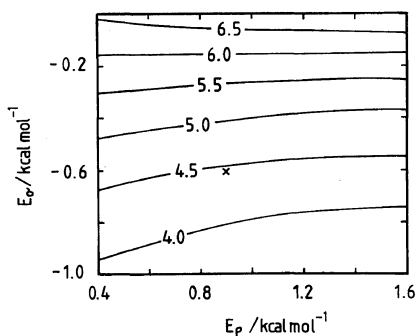
**Table III.** Observed values of the characteristic ratio  $C$ 

Method	Solvent	Temp	$C$	Ref
		°C		
Intrinsic viscosity measured under the $\Theta$ condition	0.45 M $K_2SO_4$	35	5.2	4
	Methyl isobutyl ketone	50	5.2	
	Diethylene glycol diethyl ether	50	5.2	
	2.4 M NaCl	54	4.1	6a
	2.4 M KCl	48	4.1	
	0.30 M $K_2CO_3$	56	4.7	
	0.30 M $Na_2SO_4$	52	4.7	
	0.30 M $K_2SO_4$	52	4.6	
	0.39 M $MgSO_4$	43	5.4	
	0.45 M $MgSO_4$	32	5.2	
	0.50 M $MgSO_4$	26	5.3	
	0.80 M KF	49	5.0	
	0.30 M $ZnSO_4$	54	5.4	
	0.35 M $ZnSO_4$	48	5.4	6b
	0.45 M $ZnSO_4$	35	5.6	
0.30 M $K_3PO_4$	45	5.2		
Extrapolation from intrinsic viscosities in a good solvent	Acetone	25	5.2	4
	Water	45.5	3.9	22
SANS on molten POE		80	6.9	5

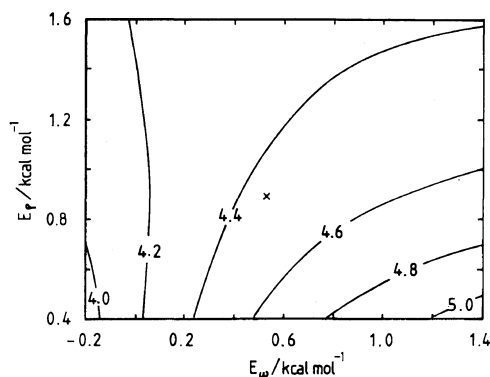
viscometric results obtained in a thermodynamically good solvent are often less reliable. (e.g., as pointed out by Beech *et al.*,<sup>4</sup> an extrapolation from benzene solution tends to give an overestimate of  $C$ .) In Table III, the results obtained in acetone and water are quoted. While the value derived from the former (acetone) is consistent with those found under the  $\Theta$  condition,<sup>4</sup> somewhat lower values were obtained by the extrapolation method in pure water.<sup>22</sup> Peuscher *et al.*'s values (6.8 to 7.5 in non-aqueous media at 20–74°C, as cited in Kugler *et al.*'s paper<sup>5</sup>) are omitted since details of the experimental conditions are not described. The SANS results<sup>5,7</sup> obtained on molten samples tend to give higher values. The newer value (6.9) reported by Kugler *et al.*<sup>5</sup> exceeds those estimated in solution by about 30%.

As stated in the introductory section, one of the purposes of the present investigation is to see whether the  $C$  value deduced from the

SANS studies<sup>5</sup> on the melt can be reproduced by the RIS calculation. Conformational energy parameters  $E_\sigma$ ,  $E_\rho$ , and  $E_\omega$  established for DME in the neat liquid are adopted in the base set given above (Table II). With this set of parameters, we obtain  $C=4.45$  for a chain of  $x=161$ , the temperature being set equal to 60°C. In Figures 1 and 2, variation of  $C$  was indicated by contour curves in the  $E_\sigma$ – $E_\rho$  and  $E_\rho$ – $E_\omega$  plane, respectively. In these calculations, the RIS parameters other than those shown here were kept invariant. The characteristic ratio ( $C=4.45$ ) corresponding to the aforementioned base set is indicated by  $\times$ . The value of  $C$  varies most sensitively with  $E_\sigma$ . For a range of  $E_\sigma = -0.6 \pm 0.1$  kcal mol<sup>-1</sup>, the value of  $C$  alters from 4.3 to 4.8 (*cf.* Figure 1). As the *gauche* fraction increases around the C–C bond, the value of  $C$  decreases. In contrast, the unperturbed end-to-end dimension varies quite insensitively with  $E_\rho$  (*cf.* Figure 1). Changes of  $C$  with  $E_\omega$  are also small around

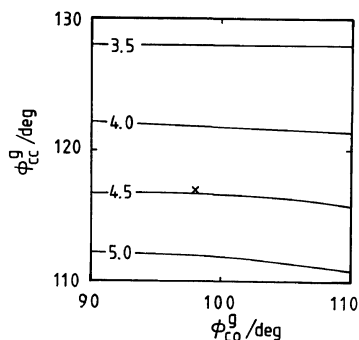


**Figure 1.** Contour diagram for the characteristic ratio  $C$  ( $=\langle r^2 \rangle_0/nl^2$ ) as a function of conformational energies  $E_\sigma$  and  $E_\rho$ . Values of the other parameters were taken from Table II. Calculations were carried out with a chain of  $x=161$  for the temperature of  $60^\circ\text{C}$ . The  $\times$  denotes the value (4.45) obtained from parameters assembled in the base set (Table II).

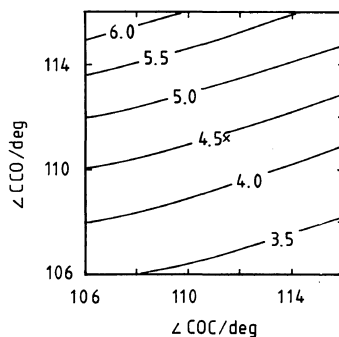


**Figure 2.** Contour diagram for the characteristic ratio  $C$  as a function of  $E_\rho$  and  $E_\omega$ . See legend to Figure 1.

$E_\rho=0.9$  kcal mol $^{-1}$  (cf. Figure 2): over a range of  $E_\omega=0.5\pm 0.1$  kcal mol $^{-1}$ ,  $C$  increases merely from 4.4 to 4.5. Experimental values of  $C$  (ca. 5.0) can be reproduced by adopting a value of  $E_\sigma=-0.4$  kcal mol $^{-1}$ , which is slightly smaller in magnitude than the one ( $-0.5$  kcal mol $^{-1}$ ) obtained for DME in a nonpolar solvent such as cyclohexane- $d_{12}$  or 1,4-dioxane- $d_8$ .<sup>3</sup> According to Figures 1 and 2,  $E_\sigma$  should be nearly zero for the SANS value (6.9).<sup>5</sup> This is apparently inconsistent with the NMR results on DME described in the previous section.

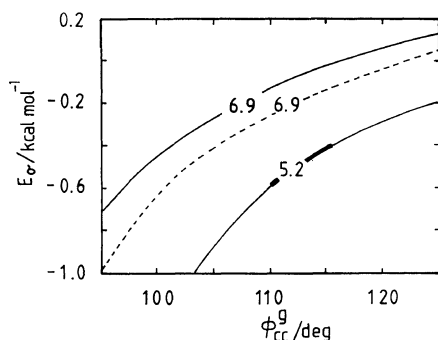


**Figure 3.** Contour diagram for the characteristic ratio  $C$  as a function of rotation angles  $\pm\phi_{CC}^g$  and  $\pm\phi_{CO}^g$ . See legend to Figure 1.



**Figure 4.** Contour diagram for the characteristic ratio  $C$  as a function of bond angles  $\angle\text{CCO}$  and  $\angle\text{COC}$ . See legend to Figure 1.

The effect arising from variations in the rotational angles about the C-C and C-O bond is indicated in Figure 3, where the rotational states for the *trans* form are taken to be zero, i.e.,  $\phi_{CC}^t=\phi_{CO}^t=0^\circ$ . As shown by the contour curves, the characteristic ratio  $C$  varies considerably with  $\pm\phi_{CC}^g$ . An increase in the magnitude of  $\phi_{CC}^g$  by ca.  $5^\circ$  suffices to bring  $C$  in the range of the value (ca. 5.0) observed in solution. According to the energy contour diagram shown in paper I,<sup>3</sup> the *gauche* minima occur at  $\phi_{CC}^g=\pm 117.0^\circ$ , but the associated potential well is rather shallow in the vicinity of the minimum. These calculations therefore suggest that rotational angles within the range  $|\phi_{CC}^g|=115^\circ\pm 5^\circ$  are allowable, being consistent with experimental observations.<sup>16-18</sup> In



**Figure 5.** Contour curves for the characteristic ratio  $C$  as a function of  $E_\sigma$  and  $\pm\phi_{CC}^g$ . The curves are drawn for the results derived from SANS for the melt (6.9), and from viscosity measurements in solution (5.2). For the two solid curves, values of the parameters required in the calculation were taken from Table II. The dotted curve indicates the result obtained when bond angle  $\angle CCO$  was tentatively widened ( $113.2^\circ$ ).

our previous treatment,<sup>2</sup> a value of  $\phi_{CC}^g = \pm 110.0^\circ$  was adopted. As manifestly shown in Figure 3, the value of  $C$  is insensitive to displacements in  $\phi_{CC}^g$  in contrast to the case for  $\phi_{CC}^g$ .

Bond angles  $\angle CCO$  and  $\angle COC$  were also altered. As shown in Figure 4, the value of  $C$  increases with an increase in  $\angle CCO$ , and less sensitively with a decrease in  $\angle COC$ . The  $C$  value corresponding to the base parameter set (*i.e.*,  $\angle CCO = \angle COC = 111.5^\circ$ ) is indicated by  $\times$  in the figure. The range of uncertainty involved in bond angles may be a few degrees at most. As is seen in the figure, variation in  $C$  attributable to this source should be quite small. Similarly, the effect arising from a small change in the bond length is trivial. The bond lengths are therefore kept invariant in the present calculations.

From the analysis described above, we may conclude that factors  $E_\sigma$  and  $\phi_{CC}^g$  are the major candidates for the possible source of enhancement in the theoretical values of  $C$ . The rest of the factors should give rise to comparatively minor changes in  $C$  within their experimental uncertainties. Shown in Figure 5 is the variation of  $C$  as a function of  $E_\sigma$  and  $\pm\phi_{CC}^g$ . The

contour curves for  $C=6.9$  represent combinations of  $E_\sigma$  and  $\pm\phi_{CC}^g$  which reproduce Kugler *et al.*'s results.<sup>5</sup> Calculations were carried out for two values of  $\angle CCO$ , *i.e.*,  $111.5^\circ$  and  $113.2^\circ$ , otherwise the same set of parameters being used. The latter value ( $113.2^\circ$ ) was reported by Astrup<sup>16</sup> from the electron diffraction studies on DME in the gas phase. This figure is exceptionally large among those usually adopted for  $\angle CCO$  in some ordinary compounds.<sup>14,15</sup> The result of calculations with  $\angle CCO = 113.2^\circ$ , which is indicated by the dotted curve, should therefore be regarded as only tentative. Experimental evidences<sup>3,14-18</sup> derived from the NMR, X-ray, and electron diffraction studies suggest that the range specified by  $E_\sigma > -0.2$  kcal mol<sup>-1</sup> and  $|\phi_{CC}^g| < 110^\circ$  may be safely excluded. The dimension of the polymer chain reported by Kugler *et al.*<sup>5</sup> from SANS is incompatible with the other observations mentioned above.

Also shown in Figure 5 is the result adjusted to reproduce  $C=5.2$ , calculations being carried out for the temperature of  $50^\circ\text{C}$ . The heavy-line portion of the curve represents a range corresponding to  $E_\sigma \leq -0.4$  kcal mol<sup>-1</sup> and  $|\phi_{CC}^g| \geq 110^\circ$ . Experimental results obtained in solution under the  $\theta$  condition (5.2 in organic media and  $5.1 \pm 0.5$  in salted water)<sup>4,6</sup> are favorably reproduced by adopting parameters in a range of  $E_\sigma = -0.5 \pm 0.1$  kcal mol<sup>-1</sup> and  $|\phi_{CC}^g| = 112 \pm 3^\circ$ . The temperature coefficient  $d \ln \langle r^2 \rangle_0 / dT$  varies from  $0.69$  to  $1.38 \times 10^{-3} \text{ K}^{-1}$  over this range. The values of  $E_\sigma$  and  $\phi_{CC}^g$  deduced above will be used for the calculation of the dipole moment and molar Kerr constant in the following section.

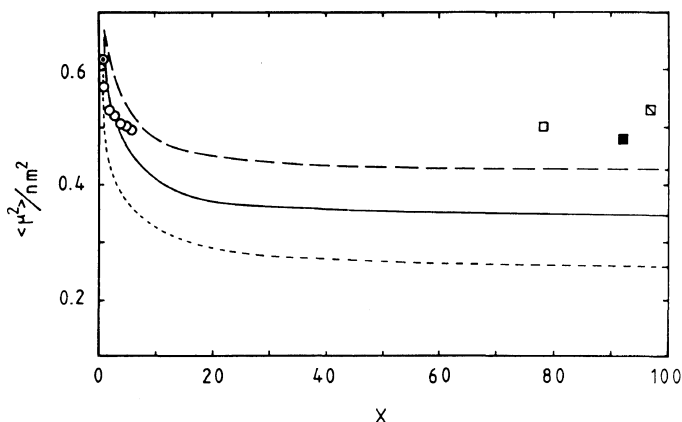
The unperturbed dimension of the POE chain estimated from the viscosity data in pure water by the extrapolation method is somewhat small (see Table III). For POE, water is a good solvent below the lower critical solution temperature. From the previous NMR studies<sup>3</sup> on DME and POE, the value of  $E_\sigma$  is known to be negative and large ( $-1.2$  kcal mol<sup>-1</sup>) in  $\text{D}_2\text{O}$ . It may be interesting to note

that adoption of this value for  $E_\rho$  leads to a suppression in the characteristic ratio (3.2 at 45°C) in accord with experimental observations (*ca.* 3.9).<sup>22</sup>

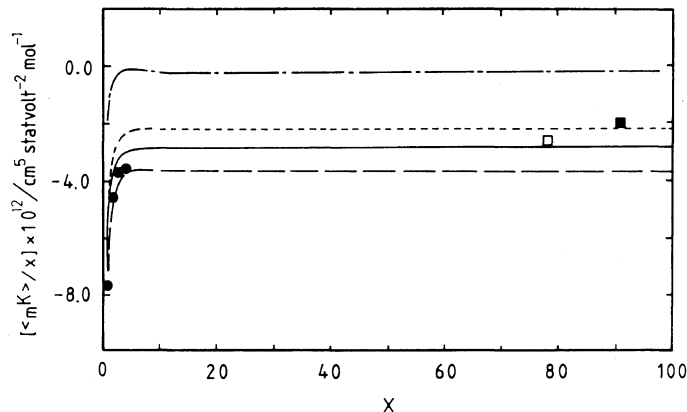
#### Dipole Moment Ratios and Molar Kerr Constants

Analyses similar to those presented in

Figures 2—4 were carried out to see how values of  $\langle \mu^2 \rangle / nm^2$  and  $\langle {}_m K \rangle / x$  depend on the individual RIS parameters. The results, although not shown here, indicate that both  $\langle \mu^2 \rangle / nm^2$  and  $\langle {}_m K \rangle / x$  vary most sensitively with  $E_\rho$ . The effect of the other parameters was found to be moderate. Shown in Figures 6 and 7 are the asymptotic curves with  $x$  for the



**Figure 6.** Variation of the dipole moment ratio  $\langle \mu^2 \rangle / nm^2$  as a function of  $x$  (20°C). Calculations were carried out for  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$  at three values of  $E_\rho$ : ---, 1.0; —, 0.8; - · -, 0.6; all units being kcal mol<sup>-1</sup>. The other RIS parameters used in calculation are as follows:  $\angle \text{CCO} = \angle \text{COC} = 111.5^\circ$ ;  $\phi_{\text{CC}}^{\text{E}} = \pm 112.0^\circ$ ;  $\phi_{\text{CO}}^{\text{E}} = \pm 98.0^\circ$ ;  $E_\sigma = -0.5$ ,  $E_\rho = 0.53$  (units in kcal mol<sup>-1</sup>). Experimental results for a series of oligomers  $\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{C}_2\text{H}_5$  are indicated by  $\circ$  ( $\text{C}_6\text{H}_6$ , 25°C).<sup>9</sup> Those for polymers  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$  are shown by  $\square$  ( $\text{C}_6\text{H}_6$ , 25°C),<sup>10</sup>  $\square$  ( $\text{C}_6\text{H}_6$ , 20°C),<sup>11</sup> and  $\blacksquare$  ( $\text{CCl}_4$ , 23°C).<sup>13</sup> The value indicated by  $\odot$  (*c*- $\text{C}_6\text{H}_{12}$ , 25°C) was obtained in this work.<sup>23</sup>



**Figure 7.** Variation of the molar Kerr constant  $\langle {}_m K \rangle / x$  as a function of  $x$  (23°C). Calculations were performed for  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$  at three values of  $E_\rho$ : ---, 1.0; —, 0.8; - · -, 0.6; all units being in kcal mol<sup>-1</sup>. For the other parameters, see legend to Figure 6. The experimental results for oligomers  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$  are illustrated by  $\bullet$  ( $\text{CCl}_4$ , 23°C).<sup>13</sup> Those for polymers  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$  are shown by  $\square$  ( $\text{C}_6\text{H}_6$ , 25°C)<sup>12</sup> and  $\blacksquare$  ( $\text{CCl}_4$ , 23°C).<sup>13</sup>



dipole moment ratio and for the molar Kerr constant, respectively. Calculations were performed for three values of  $E_\rho$  as illustrated by the solid, broken and dotted curves in the figure. To be consistent with the results obtained in the preceding section, the values of  $E_\sigma$  and  $\phi_{CC}^g$  were taken to be  $-0.5 \text{ kcal mol}^{-1}$  and  $\pm 112.0^\circ$ , respectively. The other parameters used in these calculations are given in the legend to Figure 6. Experimental values included for comparison in Figures 6 and 7 were mostly taken from literatures.<sup>9-13</sup> The dipole moment of DME indicated by  $\odot$  was determined in cyclohexane in this work.<sup>23</sup> Experimental data for the oligomers are those obtained from samples end-capped with methoxyl or ethoxyl groups.

In Figure 6, the solid curve drawn for  $E_\rho = 0.8 \text{ kcal mol}^{-1}$  gives the best fit for the experimental data in the oligomer region, but it appreciably underestimate  $\langle \mu^2 \rangle / \text{nm}^2$  for the polymer as compared with the experimental value determined in  $\text{C}_6\text{H}_6$ <sup>10,11</sup> and  $\text{CCl}_4$ .<sup>13</sup> The height of the curve may be raised by adopting a smaller value of  $E_\rho$ . The broken curve ( $E_\rho = 0.6 \text{ kcal mol}^{-1}$ ) represents an intermediate behavior; while the curve overestimates the dipole moment ratio in the oligomer region, it gives an underestimate for the polymer. A similar trend is observed in the  $\langle {}_mK \rangle / x$  vs.  $x$  plot (Figure 7), where the magnitude of  $\langle {}_mK \rangle / x$  increases with an decrease in  $E_\rho$ . The solid curve drawn for  $E_\rho = 0.8 \text{ kcal mol}^{-1}$  most

favorably represents the experimental results reported by Kelly, Patterson and Tonelli<sup>13</sup> over the entire range of  $x$ . The broken curve ( $E_\rho = 0.6 \text{ kcal mol}^{-1}$ ) is preferable in the low molecular weight region, but it underestimates  $\langle {}_mK \rangle / x$  for the polymer. The uppermost curve (chain) in Figure 7 indicates the asymptotic behavior calculated by Kelly *et al.*<sup>13</sup> In this calculation, they assigned a value of  $\phi_{CO}^g = \pm 120^\circ$  to the C-O bond. Adoption of a more realistic value ( $\phi_{CO}^g \approx \pm 100^\circ$ ) is the major cause of improvement in the agreement with experimental results. The values used for the bond dipole moment are also substantially different between Kelly *et al.*'s (0.99 D)<sup>13</sup> and ours (1.07 D). The effect arising from this source was found to be minor (*ca.* 20%), however.

## CONCLUDING REMARKS

In the POE chain, the *gauche* O...O arrangement is known to be stabilized by the so-called "*gauche* oxygen effect."<sup>24</sup> Characteristics of the internal bond rotation have been investigated by NMR in paper I.<sup>3</sup> The conformational energies thus established were utilized in the present analysis of the configuration-dependent properties of these chains. In this work, values of the RIS parameter were adjusted to attain agreement with various experimental observations. The final set of parameters optimized in this manner is

**Table IV.** Comparison of the calculated and observed values of some configurational dependent properties of POE

	$\langle r^2 \rangle_0 / \text{nl}^2$	$[\text{d} \ln \langle r^2 \rangle_0 / \text{dT}] \times 10^3$	$\langle \mu^2 \rangle / \text{nm}^2$	$[\text{d} \ln \langle \mu^2 \rangle / \text{dT}] \times 10^3$	$\langle {}_mK \rangle / x \times 10^{12}$
		$\text{K}^{-1}$		$\text{K}^{-1}$	$\text{cm}^5 \text{ statvolt}^{-2} \text{ mol}^{-1}$
Calcd <sup>a</sup>	5.2	0.74	0.35	3.0	-2.9
Obsd	5.2 <sup>b</sup>	0.23 <sup>c</sup>	0.53 <sup>e</sup>	2.6 <sup>e</sup>	-2.0 <sup>f</sup>
		0.2 ( $\pm 0.2$ ) <sup>d</sup>	0.48 <sup>f</sup>		

<sup>a</sup> Calculated by adopting a parameter set such as  $\angle \text{CCO} = \angle \text{COC} = 111.5^\circ$ ;  $\phi_{CC}^g = \phi_{CO}^g = 0^\circ$ ,  $\phi_{CC}^g = \pm 112.0^\circ$ ,  $\phi_{CO}^g = \pm 100.0^\circ$ ;  $E_\sigma = -0.5$ ,  $E_\rho = 0.8$ ,  $E_\omega = 0.53$ , units for energies being  $\text{kcal mol}^{-1}$ .

<sup>b</sup> Reference 4. <sup>c</sup> Reference 1. <sup>d</sup> Reference 25. <sup>e</sup> Reference 11. <sup>f</sup> Reference 13.

given as follows:  $\angle \text{CCO} = \angle \text{COC} = 111.5^\circ$ ;  $\phi_{\text{CC}}^l = \phi_{\text{CO}}^l = 0^\circ$ ,  $\phi_{\text{CC}}^g = \pm 112.0^\circ$ ,  $\phi_{\text{CO}}^g = \pm 100.0^\circ$ ;  $E_\sigma = -0.5$ ,  $E_\rho = 0.8$ ,  $E_\omega = 0.53$ , units for energies being given in kcal mol<sup>-1</sup>. Results of calculations for the polymer are compared with those observed in Table IV. A somewhat larger discrepancy may be noted between the calculated and observed values for  $d \ln \langle r^2 \rangle_0 / dT$  as well as for  $\langle \mu^2 \rangle / nm^2$ . In both cases, agreement can be improved by adopting a lower value of  $E_\rho$  (0.4 to 0.6 kcal mol<sup>-1</sup>). As is shown in Figures 6 and 7, however, a value of  $E_\rho$  less than 0.6 kcal mol<sup>-1</sup> is incompatible with other experimental observations. The temperature coefficient  $d \ln \langle r^2 \rangle_0 / dT$  is also susceptible to changes in  $\phi_{\text{CC}}^g$ .

The characteristic ratio  $C$  was shown to vary quite sensitively with the parameters associated with the C-C bond, *i.e.*,  $E_\sigma$  and  $\phi_{\text{CC}}^g$ . As is demonstrated in Figure 5, however, the characteristic ratio ( $C=6.9$ ) derived from the SANS studies on the molten POE sample cannot be reproduced with reasonable values of  $E_\sigma$  and  $\phi_{\text{CC}}^g$ . At the present moment, we have no plausible explanation for such a large enhancement in  $C$  in the melt.

Stability of the *gauche* conformation for the OC-CO moiety changes significantly with types of the solvent used.<sup>3,26</sup> Such a change in the short-range interaction should be reflected in the unperturbed end-to-end dimension. Although values of  $C$  determined in aqueous salt solutions scatter over quite a wide range, the average, 5.1 ( $\pm 0.5$ ), is close to those obtained in organic solvents.<sup>4,6</sup> As mentioned in the previous section, use of the  $E_\sigma$  value ( $-1.2$  kcal mol<sup>-1</sup>) observed in pure water (D<sub>2</sub>O) leads to a theoretical estimate of  $C=3.2$ . Then, a question arises whether the *gauche* conformation around the C-C bond becomes less stable in water by an addition of salt. An attempt to determine the  $E_\sigma$  value in aqueous salt solution was unsuccessful: NMR spectra obtained on DME in aqueous salt solutions are all broad and poorly resolved. Further investigation is needed on this subject.

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