Dipole Moments of Polyethylene Glycol Diethyl Ethers

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The configurations of high polymer molecules can be studied in various ways; the measurement of their dipole moments is considered to be one of the important of these methods.

Studies have been made, therefore, of some high polymer compounds and, particularly, of the high polymer molecules with elementary dipoles along the polymer chain, for the molecules of the lower degree of polymerization are synthesized easily and the relation of their dipole moments with the degree of polymerization thus made manifest. The series of polyoxymethylene dimethyl ethers, polyethylene glycols and polyethylene glycol diethyl ethers have been studied for this purpose.

This report presents a study in detail of the dipole moments of the lower-membered polyethylene glycol diethyl ethers and to decide the configuration of their skeleton.

Experimental

Polyethylene glycol diethyl ethers are generally represented by the formula; C_2H_5-O-$(C_2H_4$-O$)_p$-C_2H_5.

We studied six compounds of which p were 1, 2, 3, 4, 5 and 6 respectively. They were prepared by the condensation reactions as follows: ethylene glycol diethyl ether ($p=1$), b. p. 121°C, from ethyl bromide and sodium salt of ethylene glycol monoethyl ether (cellosolve); diethylene glycol diethyl ether ($p=2$), b. p. 186°C, from ethyl bromide and sodium salt of diethylene glycol monoethyl ether (carbitol); triethylene glycol diethyl ether ($p=3$), b. p. 118°C/10 mmHg, from ethyl bromide and sodium salt of triethylene glycol monoethyl ether; tetraethylene glycol diethyl ether ($p=4$), b. p. 159°C/10 mmHg, from $\beta\beta'$-dichlorodiethyl ether and sodium salt of cellosolve; pentaethylene glycol diethyl ether ($p=5$), b. p. 175°C/3 mmHg, from ethylene glycol $\beta\beta'$-dichlorodiethyl ether and sodium salt of cellosolve; hexaethylene glycol diethyl ether ($p=6$), b. p. 157°C/0.15 mmHg, from $\beta\beta'$-dichlorodiethyl ether and sodium salt of carbitol.

The dielectric constants and the specific volumes of benzene solutions of these compounds were measured at 25°C and at 50°C.

For the calculation of the molecular polarization at infinite dilution, $P_{2\infty}$, the following equations presented by Halverstadt and Kumler1) were used;

$$P_{2\infty}=M\left\{(v_0+\beta)\frac{\varepsilon_0-1}{\varepsilon_0+2}+\frac{3\alpha v_0}{(\varepsilon_0+2)^2}\right\}$$

$$\alpha=\frac{\varepsilon-\varepsilon_0}{w},\ \beta=\frac{v-v_0}{w}$$

where M is the molecular weight, ε_0 and v_0 are the dielectric constant and the specific volume of solvent, ε and v are those of solution, and w is the weight fraction of the solute.

For the calculation of the dipole moments, we assume that the value of P_A+P_E is $1.1\,MR_D$, since it is so in diethyl ether2), while P_A and P_E are the atomic polarization and the electronic polarization, and MR_D is the molecular refraction for the D line.

The observed values and the resultant dipole moments are shown in Table I.

Marchal and Benoit3) measured the dipole moments of diethylene glycol diethyl ether and hexaethylene glycol diethyl ether at 20°C; they obtained 1.99 and 2.93 D respectively. But they used the equation:

$$\mu^2=4.92\times10^{-4}Tv_0M(\alpha-\gamma)/(\varepsilon_0+2)^2$$

where $\gamma=\lim\limits_{w=0}\partial n^2/\partial w$, and n is the refractive index of solution. That is, they assumed that P_A+P_E equals to MR_D. If they had adopted our assumption ($1.1\,MR_D$), they would have obtained 1.93 D and 2.86 D, respectively. These values are in good agreement with our results.

Discussion

Theoretical Treatment.—we define the following notations to examine the observed data, and to calculate the dipole moments for these compounds4);

$\overrightarrow{a_i}$: the unit vector representing the direction of the ith bond of the molecule ($i=0, 1, 2,\cdots 4+3p$). $\overrightarrow{a_{3h}}$, $\overrightarrow{a_{3h+1}}$ and $\overrightarrow{a_{3h+2}}$ represent C–C, C–O and O–C bonds respectively.

μ_i: the dipole moment of the hth bond.

$\overrightarrow{\mu_{3h}}=0,\ \overrightarrow{\mu_{3h+1}}=-\mu_{CO}\overrightarrow{a_{3h+1}},\ \overrightarrow{\mu_{3h+2}}=+\mu_{CO}\overrightarrow{a_{3h+2}}$

μ: the total dipole moment of a molecule.

ρ_{ij}: the angle between $\overrightarrow{a_i}$ and $\overrightarrow{a_j}$. $\rho_{i-1,i}$ is the supplement of the bond angle of the ith atom, and was assumed to be 70.5° in this paper, that is, $\langle\cos\rho_{i-1,i}\rangle=1/3\equiv c$.

φ_i: the rotation angle around the ith bond; $=0$ when $\overrightarrow{a_{i+1}}$ is parallel to $\overrightarrow{a_{i-1}}$.

b_i: the average value of $\cos\varphi_i$, i. e. $\langle\cos\varphi_i\rangle$;

$b_0=b_3=b_6=\cdots\equiv b_C$ around the C–C bond.

$b_1=b_2=b_4=\cdots\equiv b_O$ around the C–O bond.

TABLE I. THE OBSERVED VALUES OF THE COMPOUNDS

p	Temp. °C	ε_0	v_0 cc./g	α	β	$P_{2\infty}$ cc.	MR_D cc.	μ* D
1	25	2.273	1.146	2.141	0.058	90.0	33.5	1.61
	50	2.223	1.182	1.855	0.058	86.0	33.5	1.61
2	25	2.273	1.146	2.292	−0.041	124.0	44.5	1.91
	50	2.223	1.182	2.078	−0.061	119.7	44.5	1.94
3	25	2.273	1.146	2.400	−0.088	158.1	55.5	2.18
	50	2.223	1.182	2.187	−0.105	153.8	55.5	2.21
4	25	2.273	1.144	2.464	−0.124	192.0	66.6	2.41
	50	2.223	1.181	2.233	−0.124	187.2	66.6	2.46
5	25	2.273	1.144	2.491	−0.135	226.9	77.7	2.63
	50	2.223	1.180	2.268	−0.151	220.5	77.7	2.67
6	25	2.273	1.144	2.505	−0.141	260.5	88.7	2.82
	50	2.223	1.180	2.313	−0.156	255.8	88.7	2.89

* For the calculations of the dipole moments we assumed that P_A+P_E equals to $1.1\,MR_D$.

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1) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

2) R. J. W. Le Fèvre, "Dipole Moments", Methuen & Co., London (1953).

3) J. Marchal and H. Benoit, *J. Chim. Phys.*, **52**, 818 (1955); *J. Polymer Sci.*, **23**, 223 (1957).

4) The theory is previously proposed by one of the authors, K. Suzuki, This Bulletin, **20**, 19 (1947).

μ_{CO} was assumed to be 1.04 D, because of the value 1.22 D of diethyl ether in benzene and because of the valency angle of the oxygen atom, 108°.

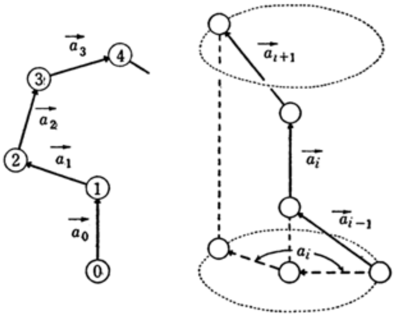

Fig. 1. The feature of the bond vectors.

The total dipole moment of a molecule is expressed by the elementary dipole moments as follows:

$$\langle\mu^2\rangle=\sum_i\mu_i{}^2+2\sum_{i<j}\sum\mu_i\mu_j\langle\cos\rho_{i,j}\rangle \tag{1}$$

Assuming that the bond angle of an oxygen atom is equal to that of a carbon atom, i. e.,

$$\langle\cos\rho_{i-1,i}\rangle=c \tag{2}$$

we have the equations,

$$\langle\cos\,\rho_{i-2,i}\rangle=c^2(1+b_{i-1})-b_{i-1} \tag{3}$$

$$\langle\cos\,\rho_{h,i}\rangle=c(1+b_{i-1})\langle\cos\rho_{h,i-1}\rangle$$
$$-b_{i-1}\langle\cos\rho_{h,i-2}\rangle \qquad \text{for } i\rangle h+2 \tag{4}$$

Because $\langle\cos\rho_{3i+m,\,3i+m+k}\rangle$ are independent of i ($m=0$, 1, 2), Eq. 1 leads to

$$\langle\mu^2\rangle=2\mu_{CO}{}^2\{(p+1)(1-c)+\sum_{i=1}^{p}(p+1-i)$$
$$(\langle\cos\rho_{1,3i+1}\rangle-\langle\cos\rho_{2,3i+1}\rangle-\langle\cos\rho_{1,3i+2}\rangle$$
$$+\langle\cos\rho_{2,3i+2}\rangle)\} \tag{5}$$

in which $\langle\cos\rho_{1,3i+1}\rangle$ etc. can be given by Eq. 4 step by step.

Discussion of Results.—It is well known that the potential minima around each bond in the molecules are close to the trans position ($\varphi=180°$, $b=-1$) or the gauche positions ($\varphi=60°$ or $-60°$, $b=0.5$). Hence, we can assume that the various models having the various trans and gauche forms for each bond in the molecule. The values of the dipole moments of these models, as calculated by Eq. 5, are plotted in Fig. 2.

As shown in Fig. 2, the calculated dipole moments of these compounds do not coincide with the observed ones.

In Fig. 2, when b_C is equal to b_O, it means that the potential values around the C–C bond and the C–O bond are the same; i. e., when $b_C=b_O=-1$, the model of the bonds is a series of trans forms, and similarly, when $b_C=b_O=0.5$ and $b_C=b_O=O$, the models are series of gauche forms and free rotation forms respectively. And in the case $b_C \neq b_O$, the models of the bonds consist of a mixture of the trans, gauche and free rotation forms.

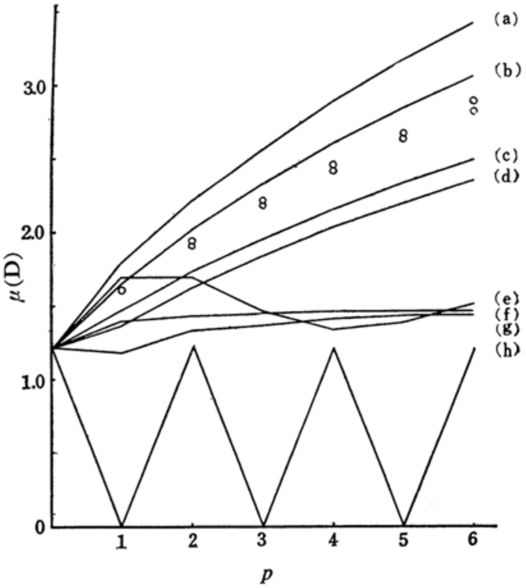

Fig. 2. The calculated moments of the compounds.

(a)	$b_C=0.5$	$b_O=0$	(f)	$b_C=0$	$b_O=-1$
(b)	0	0		−1	0
(c)	0.5	0.5	(g)	−1	0.5
(d)	0	0.5	(h)	−1	−1
(e)	0.5	−1	○	Observed values	

Furthermore, as shown in Fig. 2, when b_C or b_O is equal to -1, the calculated values of the dipole moments of the models are plotted in a zigzag manner with the increase of p, the degree of polymerization. This fact is in disagreement with the tendency that the observed moments increase in a simple way with the increase of p.

The following hypothesis about the configuration of these polyethylene glycol diethyl ethers may therefore be possible:

1) These compounds consist of a mixture of the various rotational isomers, as shown in Fig. 2. By this hypothesis, the temperature dependence of the observed moments can be explained by the assumption that the mixture ratio of the rotational isomers changes.

In the case of polyoxymethylene dimethyl ethers, it was concluded that their configurations consist of a mixture of various rotational isomers, the predominant ones of which are herical or almost herical structures arising from the gauche minima[5].

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[5] T. Uchida, Y. Kurita and M. Kubo, *J. Polymer Sci.* 22, 365 (1956).

2) The value of the angle φ in the stable position slightly differs from 180° (trans position), 60° and $-60°$ (gauche positions).

About the configurations of polyethylene glycols, Uchida et al.[6] concluded that these compounds are in a free rotational state in dioxane solutions; on the other hand, about the configurations of polyethylene glycols and polyethylene glycol diethyl ethers in benzene solutions, Marchal and Benoit[3] concluded that the value of b, which is identical with b_C and b_O in this report, is ± 0.3. Although Marchal and Benoit do not make any distinction between the value of b_C and that of b_O, these values are generally different. Let us therefore study the relation between the value of b_C and that of b_O to explain the observed dipole moment sufficiently.

When the value of μ in Eq. 5 is taken as the observed value, Fig. 3 can be obtained by plotting the values of b_C and b_O as calculated from Eq. 5.

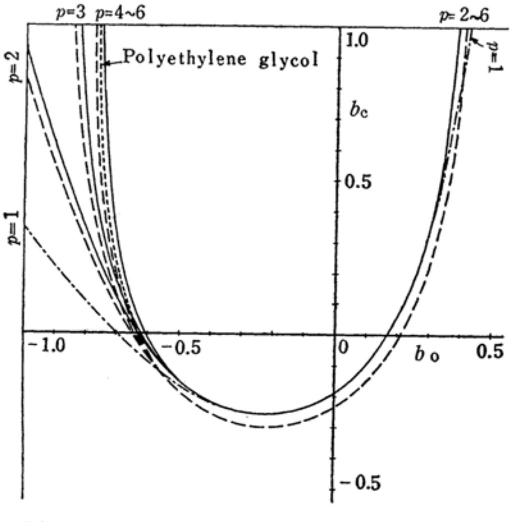

Fig. 3. The relations between the value of b_C and that of b_O.
———; at 25°C ($p=2\sim6$)
———; at 50°C ($p=2\sim6$)
—·—·; at 25°C and at 50°C ($p=1$)
------; at 20°C (polyethylene glycol, $p=79$ and 227)

As shown in Fig. 3, the curve which explains the relation between the value of b_C and that of b_O at 50°C passes the points nearer to the place of origin, where $b_C=b_O=0$, than the curve at 25°C. This fact is considered to show that with the increase in temperature the internal rotations about each bond get more like the free rotation. Moreover, the $b_C\sim b_O$ curves for the case of $p=1$ at 25°C are identical with that at 50°C, and this curve for $p=1$ coincides with the curve for $p=2\sim6$ at 50°C.

When p is very large, it is expected that the value of the dipole moment per oxygen atom of polyethylene glycol diethyl ether will be the same as that of polyethylene glycol. Marchal and Benoit[3] measured the value of $\mu^2/p+1$ in a series of polyethylene glycols at 20°C in benzene solutions and got 1.16 when p is 79 and 1.15 when p is 227. They assumed that P_A+P_E is equal to MR_D, but if we assume that P_A+P_E is equal to $1.1MR_D$, the above-mentioned values are 1.11 and 1.10 respectively. The $b_C\sim b_O$ curve from these values is almost in full agreement with the curve for polyethylene glycol diethyl ethers at 25°C, as is shown in Fig. 3.

In Fig. 3, if we compare the $b_C\sim b_O$ curves for the compounds, the curves for $p=1$, 2 and 3 are fairly different from the curves for $p=4\sim6$ under the condition $b_O<-0.5$. Therefore, the value of b_O for the compounds should be larger than -0.5, if it is assumed that the degree of the internal rotation around the each bond is independent of the degree of polymerization of the compounds. In fact, under the condition of $b_O<-0.5$, the calculated dipole moments of the compounds are plotted in a zigzag manner when p becomes large. This tendency of the relation between the calculated moments and p disagrees with that of the observed moments and p. Furthermore, as shown in Fig. 3, the value of b_O lies within the range of $-0.5\sim0.4$, and in this range we can select a pair of b_C and b_O satisfying the relation between the observed moments and p.

It is considered that the interaction between two C–O dipoles connected with both sides of the C–C bond is fairly large, while the interaction between the C–O dipole and the C–C bond, without the moment, each at one end of the C–O bond, is fairly small. The interactions between the elementary dipoles of each above-mentioned bond make it necessary that the value of b_O be nearer to zero than that of b_C. Taking the above condition, the range of the value of b_O is obtained from Fig. 3; $b_O=-0.3\sim0.13$ and $b_O>0.28$. However, since the range $b_O=-0.3\sim0.13$ corresponds to the range $b_C=-0.3\sim-0.1$ and since these ranges show that each bond takes the positions of the potential maxima, it is considered that these ranges are unreasonable as a basis for explaining the configurations of these compounds, considering the intramolecular potential.

On the other hand, if each bond in the molecule is at the fixed position near the potential minima, the value of b_C should be

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[6] T. Uchida, Y. Kurita, N. Koizumi and M. Kubo, ibid., 22, 313 (1956).

closer to -1 (trans) or to 0.5 (gauche) than the value of b_O, since interaction between the elementary dipoles exists. The case of $b_C=-1$ cannot then exist, as is shown in Fig. 3; consequently the value of b_C is close to 0.5. Therefore, (1) when the value of b_C is equal to 0.5, the values of b_O are 0.36 (25°C) and 0.33 (50°C), and (2) when the value of b_C is relatively closer to 0.5 than the value of b_O, the range of the value of b_C is $0.3\sim0.65$.

From what we have seen, it can be concluded that two C–O bonds around the C–C bond approximately take the gauche positions with regard to each other.

Summary

The dipole moments of six lower members of the polyethylene glycol diethyl ethers have been measured, and their configurations have been studied.

As the configurations of these compounds the two models have been considered; one is a mixture of the various rotational isomers, and the other a model in which the positions of the internal rotations of two C–O bonds around the C–C bond approximately take the gauche positions with regard to each other, and the positions of the C–O bond and the C–C bond around the C–O bond take positions similar to those mentioned above with regard to each other.

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