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Electronic Structures and Conformations of Polyoxymethylene and Polyoxyethylene

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ABSTRACT: The CNDO/2 method using the tight-binding approximation for polymers was applied to hexagonal (HPOM), orthorhombic (OPOM), and trans zigzag (ZPOM) polyoxymethylenes and to helical (HPOE) and trans zigzag (ZPOE) polyoxyethylenes. The CNDO/2 calculations were also carried out for a model molecule of POE, $CH_3OCH_2CH_2OCH_3$. One of the main factors to stabilize HPOE was demonstrated clearly by the examinations of the model molecule. The relative stabilities among HPOM, OPOM, and ZPOM, and between HPOE and ZPOE, were reasonably reproduced by the present calculations. Contribution of the intrasegment and intersegment energies to the total energy were discussed in connection with the relative stabilities of the various conformations. The O···O electrostatic repulsions in the treated molecules were also discussed in terms of the electronic structures of the molecules. The band structures of POM and POE were proposed.

Normal form polyoxymethylene, hexagonal (HPOM),[2] is obtained under the γ-ray irradiation polymerization of trioxane or tetraoxane in the solid phase.[3] On the other hand under special conditions, the polymer appears in the orthorhombic form (OPOM).[4] Both in HPOM and OPOM each molecule stays in the G conformation about a C–O or O–C bond. The planar zigzag form (ZPOM) can also be accepted for consideration. Among these three forms, the relative stability can be considered in the order, HPOM > OPOM > ZPOM. Polyoxyethylene (POE) forms crystalline complexes for example with urea[5] and $HgCl_2$[6,7] in which a POE molecule has various conformations. The planar zigzag conformer (ZPOE) is stable under tension.[8b] Under the ordinary condition, the helical conformer (HPOE), in which the conformation around the bonds O–C–C–O is TGT, is the stable form.[8] Therefore, the stability between HPOE and ZPOE is considered to be in the order, HPOE > ZPOE.

With the model molecules such as $CH_3OCH_2OCH_3$ and/or $CH_3OCH_2OCH_2OCH_3$ for POM, dipole moment,[9] electron diffraction,[10] and semiempirical MO[11] studies have been reported previously. Vibrational analyses of a model molecule for POE $CH_3OCH_2CH_2OCH_3$ have been extensively investigated,[12] and CNDO/2 calculations[13] have also been carried out. Furthermore, the results of statistical mechanical treatments on polyethylene (PE), POM, and POE have been adequately reviewed by Flory.[14]

POM can be considered to have a similar chemical unit to PE substituted by oxygen instead of one methylene group, while POE has a unit in which an O atom combines to a PE residue. Accordingly, it is worth mentioning that there seems to be intimate relations between the electronic structures for PE, POM, and POE.

The electronic structures of polymers have been extensively examined by Imamura and his co-workers.[15-17] Their methods were applied to PE,[15,16] polyglycine,[16,17] poly-L-alanine,[17] $(SN)_x$ and $(SCH)_x$,[18] and later to poly-L-proline I and II.[19]

In the present study, we have investigated the electronic structures of POM and POE with the aid of the CNDO/2 method[20] in terms of the tight-binding approximation.[21] Actual numerical calculations were carried out on the basis of the method reported by Imamura and Fujita.[17] The CNDO/2 calculations were also carried out for a model molecule of POE, $CH_3OCH_2CH_2OCH_3$.

I. Method of Calculations

The total energy of a polymer can be expressed as follows:[17]

$$E_{\text{total}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A}} \sum_{\text{A}<\text{B}} E_{\text{A,B}}^{(0,0)} + \sum_{j} \sum_{\text{A}} \sum_{\text{B}} E_{\text{A,B}}^{(0,j)} \quad (1)$$

One-center term:

$$E_{\text{A}} = \sum_{t}^{\text{on A}} P_{tt}[-\tfrac{1}{2}(I_t + A_t) - (Z_{\text{A}} - \tfrac{1}{2})\gamma_{\text{A,A}}^{(0,0)}] + \tfrac{1}{2}\sum_{t}^{\text{on A}} \sum_{t_1}^{\text{on A}} [P_{tt}P_{t_1t_1} - \tfrac{1}{2}(P_{tt_1})^2]\gamma_{\text{A,A}}^{(0,0)} \quad (2)$$

Intrasegment two-center term:

$$E_{\text{A,B}}^{(0,0)} = 2\beta_{\text{AB}}^{0} \sum_{t}^{\text{on A}} \sum_{t_1}^{\text{on B}} P_{tt_1}S_{tt_1}^{(0,0)} - \tfrac{1}{2}\sum_{t}^{\text{on A}} \sum_{t_1}^{\text{on B}} (P_{tt_1})^2\gamma_{\text{A,B}}^{(0,0)} + [P_{\text{AA}}P_{\text{BB}}\gamma_{\text{A,B}}^{(0,0)} - P_{\text{AA}}Z_{\text{B}}\gamma_{\text{A,B}}^{(0,0)} - P_{\text{BB}}Z_{\text{A}}\gamma_{\text{A,B}}^{(0,0)} + (Z_{\text{A}}Z_{\text{B}}e^2/R_{\text{AB}})] \quad (3)$$

Intersegment two-center term:

$$E_{\text{A,B}}^{(0,j)} = \beta_{\text{AB}}^{0} \sum_{t}^{\text{on A}} \sum_{t_1}^{\text{on B}} P_{t_1t}^{+j}S_{tt_1}^{(0,j)} - \tfrac{1}{4}\sum_{t}^{\text{on A}} \sum_{t_1}^{\text{on B}} P_{t_1t}^{+j}P_{tt_1}^{-j}\gamma_{\text{A,B}}^{(0,j)} + \tfrac{1}{2}[P_{\text{AA}}P_{\text{BB}}\gamma_{\text{A,B}}^{(0,j)} - P_{\text{AA}}Z_{\text{B}}\gamma_{\text{A,B}}^{(0,j)} - P_{\text{BB}}Z_{\text{A}}\gamma_{\text{A,B}}^{(0,j)} + (Z_{\text{A}}Z_{\text{B}}e^2/R_{\text{AB}})] \quad (4)$$

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Table I
Geometries of POM and POE

	HPOM[a]	OPOM[b]	ZPOM[c]	HPOE[d]	ZPOE[d]
r(C-H), Å	1.09	1.09	1.09	1.09	1.09
r(C-O), Å	1.43	1.43	1.43	1.43	1.43
r(C-C), Å				1.54	1.54
ϕ(COC)	110° 45′	112° 50′	109° 28′	112°	112°
ϕ(OCO)	110° 45′	112° 50′	109° 28′		
ϕ(CCO)				110°	110°
ϕ(OCH)	108° 48′	109° 13′	109° 28′	109.332°[c]	109.332°[c]
ϕ(HCH)	108° 48′	109° 13′	109° 28′	109.5°	109.5°
ϕ(CCH)				109.332°[c]	109.332°[c]
τ(C-O)	76° 14′	63° 50′	180°	188.3°	180°
τ(C-C)				65°	180°

[a] From ref 23. [b] From ref 4. [c] Assumed. [d] From ref 8b. (See also ref 24.)

where A or B denote atom, t or t_1 denote atomic orbital, j is the number of a certain segment, and 0 is the central segment.

P_{tt_1} and $P_{tt_1}{}^{\pm j}$ are given by eq 5 and 6, respectively:

$$P_{tt_1} = 2\sum_{k=0}^{2\pi}\sum_{s}^{\text{occ}} C_{ks,t}C^*_{ks,t_1} \tag{5}$$

$$P_{tt_1}{}^{\pm j} = 2\sum_{k=0}^{2\pi}\sum_{s}^{\text{occ}} \exp(\pm ikj)C_{ks,t}C^*_{ks,t_1} \tag{6}$$

where k is the number corresponding to the wavenumber vector. The other notations used in eq 1–6 are the same as those usually used.[17,20] In eq 3 and 4, the first term of the right-hand side is the core resonance term, the second the exchange term, and the third the electrostatic term, respectively.

The total energy of a small molecule (closed shell), now the model molecule, can be expressed[20] as follows by analogy with the polymer:

$$E_{\text{total}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A}}\sum_{\text{A}<\text{B}} E_{\text{A,B}} \tag{7}$$

One-center term:

$$E_{\text{A}} = \sum_{t}^{\text{on A}} P_{tt}[-\tfrac{1}{2}(I_t + A_t) - (Z_{\text{A}} - \tfrac{1}{2})\gamma_{\text{A,A}}] + \tfrac{1}{2}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on A}}[P_{tt}P_{t_1t_1} - \tfrac{1}{2}(P_{tt_1})^2]\gamma_{\text{A,A}} \tag{8}$$

Two-center term:

$$E_{\text{AB}} = \sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}} 2P_{tt_1}\beta_{tt_1} - \tfrac{1}{2}\sum_{t}^{\text{on A}}\sum_{t_1}^{\text{on B}}(P_{tt_1})^2\gamma_{\text{A,B}} + [P_{\text{AA}}P_{\text{BB}}\gamma_{\text{A,B}} - P_{\text{AA}}Z_{\text{B}}\gamma_{\text{A,B}} - P_{\text{BB}}Z_{\text{A}}\gamma_{\text{A,B}} + (Z_{\text{A}}Z_{\text{B}}e^2/R_{\text{AB}})] \tag{9}$$

where the notations are the same as those used in the polymer. In eq 8, the first term of the right-hand side is the core term, and the second the electron repulsion term, respectively. In eq 9, meanings of the right-hand side are the same as those in eq 3.

As shown in Figure 1, the skeletal conformations for PE, POM, and POE are described by two, two, and three torsional angles, respectively. Now we can assume that the τ_1 and τ_2 of PE and POM and τ_1 and τ_3 of POE are equal. Then we can describe the conformations of PE and POM by only one torsional angle and those of POE by two angles. The X-ray analyses of POM[3,4,22,23] and POE[8,24] have been reported. The geometries used in the calculations were determined from the data of X-ray analyses; they are presented in Table I. For HPOE, Tadokoro et al. have reported a newly revised crystal structure.[24] However, when we use this newly revised model, the calculations become very complicated, since a repetition unit presented

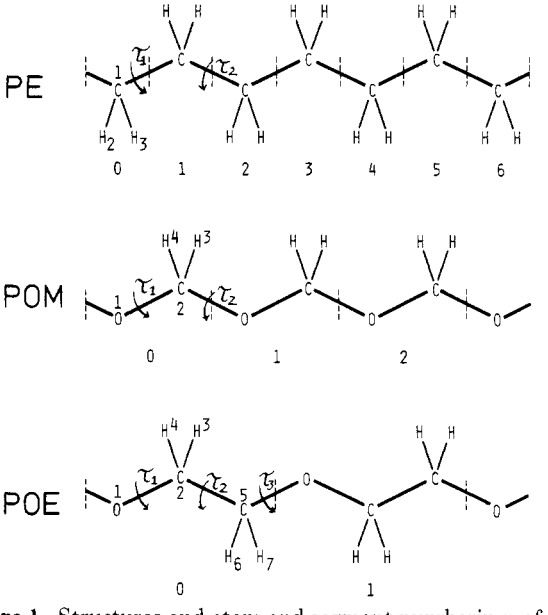

Figure 1. Structures and atom and segment numberings of PE, POM, and POE.

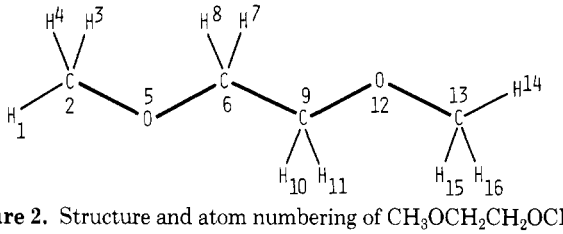

Figure 2. Structure and atom numbering of $CH_3OCH_2CH_2OCH_3$.

is too long to treat. Therefore, we have used the crystal structure model composed of $^7/_2$ uniform helices for HPOE.[8b] Geometries used for $CH_3OCH_2CH_2OCH_3$ were the same as those used in the polymer. Atom numberings of this molecule are shown in Figure 2.

In order to compare the electronic structures among POM, POE, and PE, the calculations were also carried out for PE. Geometries used for PE are as follows: r(C–C) = 1.54 Å, r(C–H) = 1.10 Å, and configurations around a carbon atom were assumed to be tetrahedral. As for the torsional angles of PE, we have used the same angles as those of POM and POE, respectively. (See Table I.)

II. Results and Discussion

A. Polyoxymethylene (POM). Let us start with a discussion of the conformational stability of POM. By an analysis of the dipole moment of the model molecules of POM such as $CH_3OCH_2OCH_3$ and $CH_3OCH_2OCH_2OCH_3$, Uchida et al. have concluded that the G conformation is preferred over the T conformation,[9b] and they deduced an

Table II
Total Energy (eV) of POM

energy	HPOM	OPOM	ZPOM
total	−738.26	−738.24	−738.19
total intrasegment	−710.53	−710.52	−710.42
total one center	−642.13	−642.06	−642.01
total two center	−68.39	−68.46	−68.40
total intersegment	−27.73	−27.71	−27.77
total two center			
0-1[a]	−13.85	−13.85	−13.84
0-2			−0.03

[a] For simplicity, 0-1 (segments) means the central and the first nearest neighbor segments, 0-2, 0-3, ..., refers to the central and the second, third, ..., nearest neighbor segments. In the present article, up to 0-4 segments were taken into consideration for all polymers under study. Energy terms: absolute values less than 0.01 eV are not cataloged (energy, see eq 1-4).

energy difference of 1.74 kcal/mol between the G and T conformations. A gas phase electron diffraction study of $CH_3OCH_2OCH_3$ reports a G conformation around the C–O bond with a value of $\tau = 66.3°$.[10] MO calculations of this molecule also suggest that the G state is the lowest energy conformation.[11,36] Moreover, Flory et al. have analyzed the POM polymer with the statistical mechanical method and concluded that the dispersion and coulombic interactions between O and CH_2 are responsible for the preference for the G form.[25]

The total energies calculated for POM are summarized in Table II. From the total energy of this polymer the relative stabilities are estimated to be in the order, HPOM > OPOM > ZPOM. This shows that the G conformation is more stable than the T conformation about a C–O bond. The energy differences between HPOM and ZPOM and between OPOM and ZPOM are 1.64 and 1.04 kcal/mol, respectively. These differences correspond very well with the value of 1.5 kcal/mol reported by Flory et al. for the G and T states.[25] Furthermore, a trans-gauche energy difference of 1.2–1.5 kcal/mol has been deduced from light scattering and viscosity measurements.[26] This is also in excellent agreement with our calculated energy differences. The energy difference between HPOM and OPOM is only 0.60 kcal/mol. Zamboni et al. stated that OPOM is less stable than HPOM and that OPOM is converted into ordinary HPOM by heating (75–80 °C) by an endothermic and monotropic transition.[27] The energy difference obtained in the present work is consistent with this experimental result.

We now discuss the origin of the energy difference between the three forms. Among these three forms, the total intrasegment energy is in the order, HPOM ≃ OPOM < ZPOM. On the other hand, the total intersegment energy is in the order, ZPOM < HPOM < OPOM.

B. Intrasegment and Intersegment Energies in POM. ZPOM has the lowest energy of the three forms in the intersegment part, but in this form the intrasegment energy is the highest of the three. In this form, therefore, the gained energy in the intersegment is not enough to compensate the intrasegment energy. As a result, as a balance of these two energy terms ZPOM becomes the most unstable of the three forms. However, for HPOM and OPOM, the differences in the one-center and two-center contributions to the intrasegment part largely cancel. Therefore, the difference in conformational stability between HPOM and OPOM is mainly due to the difference of the interactions between the different segments.

Now we analyze the contribution of each atom or bond to the energy difference between, for example, ZPOM and HPOM in the two-center interaction in the central segment using Table III. From this table, we can see that the resonance and exchange terms of (H3,O1) and the electrostatic terms of (H3,C2) and (H4,C2) stabilize ZPOM, while the resonance term of (H4,O1) and the electrostatic term of (C2,O1) stabilize HPOM.

Table III
The Difference in Two-Center Interaction Energy (eV) in the Central Segment between ZPOM and HPOM[a]

	O1[b]	C2	H3	total
resonance term				
C2[b]	−0.02		symmetric	
H3	−0.03	0.01		
H4	0.04	0.02		0.03
exchange term				
H3	−0.03		symmetric	−0.03
electrostatic term				
C2	0.05		symmetric	
H3	0.01	−0.04		
H4	0.02	−0.05		
total				
C2	0.02		symmetric	
H3	−0.04	−0.02		
H4	0.05	−0.02	0.01	

[a] Digits show energy difference: ZPOM − HPOM. Energy terms: absolute values less than 0.01 eV are not cataloged. (See text and eq 3 for more details.) [b] Atom numberings are shown in Figure 1.

Table IV
The Difference in Two-Center Interaction Energy (eV) in the 0-1 Segments between ZPOM and HPOM[a]

	^{1}O1[b,c]	^{1}C2	^{1}H3	^{1}H4	total
resonance term					
^{0}O1[b,c]	−0.01	−0.03		0.01	
^{0}C2	−0.01	−0.05	0.05	−0.01	
^{0}H3	0.02	−0.01			
^{0}H4	−0.01	0.05			−0.04
exchange term					
^{0}O1	0.02				
^{0}H4	−0.01				0.01
electrostatic term					
^{0}O1	−0.03	0.04			
^{0}C2	0.02	0.02		−0.01	
^{0}H3		−0.01			0.04
total					
^{0}O1	−0.02				
^{0}C2		−0.04	0.05	−0.02	
^{0}H3	0.02	−0.02			
^{0}H4	−0.02	0.05			0.01

[a] See footnote *a* of Table III. (See text and eq 4 for more details.) [b] See footnote *b* of Table III. [c] For example, (^{0}O1,^{1}O1) refers to the interaction term between the O1 oxygen atom in the central segment and the O1 oxygen atom in the first nearest neighbor segment.

We now again discuss the intersegment energy. There is not such a very clear difference in the interactions between the central segment and the first nearest neighbor segments, 0–1 term, among the three. For example, in Table IV, the difference of the two-center interaction energy between ZPOM and HPOM is summarized. The resonance terms of (^{0}C2,^{1}H3) and (^{0}H4,^{1}C2) mainly contribute to stabilize HPOM. In the case of ZPOM, the contribution of the 0–2 segment interaction term is somewhat larger than those of the other two. (See Table II.) This is characteristic for ZPOM.

C. Polyoxyethylene (POE). The calculated total energy is summarized in Table V. The total energy of HPOE is a little smaller than that of ZPOE. Flory et al. have concluded that the G state about the C–C bond is approximately 400 cal/mol lower than the T state.[28] Uchida et al. have measured the dipole moments of

Table V
Total Energy (eV) of POE

energy	HPOE	ZPOE
total	-974.48	-974.47
total intrasegment	-947.14	-947.07
total one center	-810.21	-810.21
total two center	-136.92	-136.86
total intersegment	-27.34	-27.39
total two center 0-1[a]	-13.65	-13.68

[a] See footnote *a* of Table II. (Energy, see eq 1-4.)

polyethylene glycols $HO(CH_2CH_2O)_nH$ (n = 1–7).[29] From the results, they have concluded that the free rotational model is suitable for a polyoxyethylene chain. Later from the dipole moment measurements of six lower members of the polyethylene glycol diethyl ethers, Kotera et al. have proposed two models:[30] one is a mixture of the several rotational isomers, and the other a model of the GGG form. Mean-square dipole moments of polyoxyethylene have been determined from dielectric constant measurements by Bak et al.[31] They have also obtained similar conclusions to those of Kotera et al.[30] The results of the present calculation are consistent with these experiments.[28-31] Recently an energy minimization method for seeking stable crystal structure with the use of the nonbonded repulsive energy was derived and applied to POE.[32] The result corresponds well with the present calculations.

D. Intrasegment and Intersegment Energies in POE. The comparison of the intrasegment energy with the intersegment energy in POE leads to the conclusion that the former is smaller in HPOE, while the latter is smaller in ZPOE. With regard to one- and two-center terms in the central segment, both forms have nearly equal values in the one center, and the two-center term of HPOE is smaller than that of ZPOE.

As we have discussed above, the total intrasegment energy of HPOE is smaller than that of ZPOE. This supports the experimental result in which the model molecule such as $CH_3OCH_2CH_2OCH_3$ is in the TGT form in the crystalline solid state.[12]

We now discuss the contribution of each atom or bond to the energy difference in some detail using Tables VI and VII. Table VI shows the energy difference distribution on each atom in the two-center term of the central segment. First of all, we consider the change in the resonance term between two methylene groups, in which the relative position changes most remarkably by the variation of τ_2 defined in Figure 1, that is, one methylene group consists of C2, H3, and H4, and another C5, H6, and H7. By summing up all the resonance terms between these two methylene groups, the interactions between them stabilize HPOE 0.02 eV more than ZPOE. Among the other terms, the resonance term of (H6,O1) is the largest of all. We may deduce that this term, therefore, governs the intrasegment conformational energy of POE. As a result, these two factors stabilize POE in the intrasegment in the TGT form but not in the TTT form. The atoms H6 and H7 have the same relation with respect to the O1 atom in ZPOE. But in HPOE, the situation is differnet and the distances H6···O1 and H7···O1 are 3.37 and 2.64 Å, respectively. In HPOE, the group O1–C2–C5–H6 is almost in the trans state, and the group O1–C2–C5–H7 is in the gauche state. By examining the density matrix elements, the element in relation to (H6,O1) is bonding; on the other hand, (H7,O1) is antibonding. That is, the term with the longer distance in the trans state is bonding and the term with the shorter distance in the gauche state is antibonding. This is very interesting, since it is not the distance but the configuration that determines whether the interaction is bonding or antibonding. An analogous situation will be discussed in the section on the model molecule.

We now discuss the intersegment interactions, using Table VII. ZPOE gets 0.03 eV more than HPOE in the interactions between the central and the first nearest neighbor segments. From this table, we can easily recognize that fairly large values appear in the interaction terms between each central segment atom and the oxygen atom of the first nearest neighbor segments. Here the term (^{0}H4,^{1}O1) is the same term which was defined as (H6,O1) in the central segment energy. (See Table VI.)

E. Electrostatic Terms in POM and POE. It is well known that PE is stable in the planar trans zigzag form, while with sulfur analogues such as $CH_3SCH_2SCH_3$,[33a] $RSCH_2SR$ (R = Et, Pr, and Bu),[33b] and polythiomethylene (PTM),[33a] it is stated that the lone pair–lone pair interactions between sulfur atoms dictate that the G state (rabbit-ear effect)[34] is preferred. The gauche tendency of the O–X–O (X = C or P) linkages has also been explained, for example, by an "anormeric" effect.[35,36] Moreover, the preference of the gauche form in fluorine compounds, for example in $CH_3CH_2CH_2F$, has been discussed from the experiment of the microwave spectra.[37] A similar situation is also explained in POM.[38] Figure 3 shows the dipole moment in POM. All the COC dipoles lie in the same direction in ZPOM. On the other hand in the helical structure, e.g., in OPOM, adjacent dipoles are opposed. Tadokoro concludes that such effects stabilize the helical structure.[38]

Table VI
The Difference in Two-Center Interaction Energy (eV) in the Central Segment between ZPOE and HPOE[a]

	O1[b]	C2	H3	H4	C5	H6	total
resonance term							
C2[b]	-0.02				symmetric		
H4	-0.02	0.01	0.01				
C5	-0.03	0.03		0.02			
H6	0.06	0.02	-0.08	0.01	0.01		
H7	-0.01		0.10	-0.08		0.01	0.06
exchange term							
H6	0.02		-0.02		symmetric		
H7			0.02	-0.02			
total							
C2	-0.02				symmetric		
H4	-0.02	0.02	0.01				
C5	-0.04	0.03		0.02			
H6	0.09	0.02	-0.11		0.02		
H7	-0.01		0.13	-0.11		0.01	0.06

[a] Digits show energy difference: ZPOE – HPOE. Energy terms: absolute values less than 0.01 eV are not catalogued. (See text and eq 3 for more details.) [b] See footnote *b* of Table III.

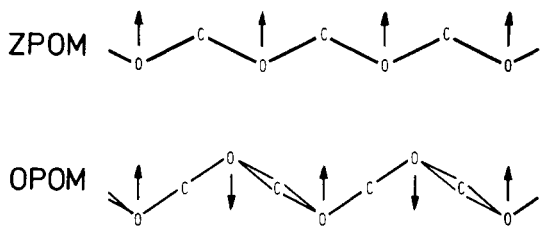

Figure 3. Dipole moment in POM.

Table VII
The Difference in Two-Center Interaction Energy (eV) in the 0-1 Segments between ZPOE and HPOE[a]

	$^1O1^{b,c}$	total
resonance term		
$^0O1^{b,c}$	−0.01	
$^0C2$	−0.01	
$^0H4$	0.03	
$^0C5$	−0.01	
$^0H6$	−0.01	−0.02
exchange term		
$^0O1$	−0.01	
$^0H4$	0.01	
electrostatic term		
$^0O1$	−0.01	−0.01
total		
$^0O1$	−0.04	
$^0C2$	−0.02	
$^0H4$	0.04	
$^0C5$	−0.01	
$^0H6$	−0.01	−0.03

[a] See footnote *a* of Table VI. (See text and eq 4 for more details.) [b] See footnote *b* of Table III. [c] See footnote *c* of Table IV.

It is acceptable that these electrostatic interactions are intimately combined with the electrostatic term now of interest.[39] (See eq 4.) Using Tables VIII and IX, we will explain these situations. In these tables, one of the methylene groups in two or three methylene units in PE:POM or PE:POE is considered as a group substituted for an O atom. The upper part of Table VIII shows the O···O repulsion term of POM and the corresponding CH_2···CH_2 term of PE, and the lower part shows the total electrostatic term between the different segments. From this table, we can easily recognize that the O···O electrostatic repulsion in POM is much stronger than the corresponding CH_2···CH_2 repulsions in PE. As for the 0–2 segment interactions the term of PE becomes almost zero, but in POM fairly large values are still retained.

In the case of total terms, the term becomes almost zero for the 0–3 segment interactions in PE. As has been shown above, it is found that the O···O repulsions in POM are larger than the CH_2···CH_2 repulsions in PE. However, this term alone does not govern conclusively the conformational stability of POM. That is, each term of ZPOM which is the most unstable form of the three considered is rather smaller than that of more stable forms of HPOM and OPOM.

We now discuss POE. As expected, the electrostatic terms of POE in Table IX are about half as large as those of POM. In the case of POE, ZPOE is smaller in the electrostatic term than HPOE, as is the case for POM. As for the 0–1 segment interactions of PE, the value is already zero. This shows that in other words the electrostatic interactions between the central segment and the third nearest neighbor segments in the case of the segment numbering in PE is already almost zero. (See Figure 1.) On the contrary both in HPOE and ZPOE, the O···O electrostatic repulsions are still retained in the 0–4 segment interactions.

With the intersegment total terms, the electrostatic terms become very small in the 0–2 segment interaction both in PE and POE.

F. Model Molecule $CH_3OCH_2CH_2OCH_3$. In order to explain the (H6,O1) and (H7,O1) interactions shown in POE and to examine electronic structures of POE in more detail, we now have taken up the model molecules which have the structures with a methyl and a methoxy group attached to the POE residue, $CH_3OCH_2CH_2OCH_3$. The CNDO/2 calculations were carried out for this molecule. The total energies calculated are summarized in table X. The order of the total energy between the TGT and TTT forms is in good agreement with that of the intrasegment energy of HPOE and ZPOE, although the differences in the energy between the two forms is fairly small. The terms (O5,H10) and (O5,H11) in the model molecules correspond to (H6,O1) and (H7,O1) of POE, respectively. As is shown in Table XI, the TGT form is stabilized by about 0.08 eV from the TTT form by these interactions. This result corresponds very well with that of POE, that is, the interaction between oxygen and trans hydrogen stabilizes the molecule, while the interaction between oxygen and gauche hydrogen destabilizes. From the O···O interaction (O5,O12), the TGT form is destabilized by about 0.08 eV from the TTT form.

Now we must notice that there are two pairs of interactions (O5,H10) and (O12,H8) in a molecule, but there is only one term (O5,O12) in a molecule. Therefore even if a pair of, e.g., (O5,H10)–(O5,H11) and (O5,O12) is cancelled with each other, there is still one more stabilization term remaining, (O12,H8)–(O12,H7). The fact that the TGT form is more stable than the TTT form may, therefore, mainly originate from this O···H interaction. Consequently, as far as the total energy of the molecule is concerned, the change of the O···O interaction as well as the O···H interaction energy by the change of the conformation should be taken into account. The situation is also analogous in the high polymer POE.

Table VIII
Comparison of the Electrostatic Interaction Energy (eV) between POM and PE[a]

	HPOM	OPOM	ZPOM	PE:HPOM[e]	PE:OPOM[f]	PE:ZPOM[g]
$0\text{-}1^{b,c}$	0.19	0.18	0.16	0.06	0.05	0.06
0-2	0.11	0.12	0.07			
0-3	0.07	0.07	0.05			
0-4	0.05	0.06	0.03			
$0\text{-}1^{b,d}$	3.23	3.21	3.27	3.01	3.02	2.99
0-2				0.02	0.05	

[a] Two methylene units (e.g., segments 0 and 1 of PE in Figure 1) are now considered as one segment. Energy terms: absolute values less than 0.01 eV are not cataloged. (See eq 4.) [b] See footnote *a* of Table II. [c] O···O or corresponding CH_2···CH_2 interaction between the central and the neighbor segments. [d] Total interaction between the central and the neighbor segments. [e] PE with the same conformation as HPOM. [f] PE with the same conformation as OPOM. [g] PE with the same conformation as ZPOM.

Table IX
Comparison of the Electrostatic Interaction Energy (eV) between POE and PE[a]

	HPOE	ZPOE	PE: HPOE[e]	PE: ZPOE[f]
0-1[b,c]	0.11	0.09		
0-2	0.05	0.04		
0-3	0.04	0.03		
0-4	0.03	0.02		
0-1[b,d]	3.28	3.26	3.05	2.99

[a] Three methylene units (e.g., segments 0, 1, and 2 of PE in Figure 1) are now considered as one segment. Energy terms: absolute values less than 0.01 eV are not catalogued. (See eq 4.) [b] See footnote *a* of Table II. [c] See footnote *c* of Table VIII. [d] See footnote *d* of Table VIII. [e] PE with the same conformation as HPOE. [f] PE with the same conformation as ZPOE.

Table X
Total Energy[a] (eV) of $CH_3OCH_2CH_2OCH_3$

energy	TGT	TTT
total	-1987.67	-1987.66
total one center	-1645.36	-1645.35
total core	-2868.58	-2869.49
total electron repulsion	1223.21	1224.13
total two center	-342.30	-342.31
total resonance	-347.01	-347.00
total exchange	-82.58	-82.56
total electrostatic	87.29	87.25

[a] Energy, see eq 7-9.

G. Energy Band Structures of POM and POE. Figures 4 and 5 show the LUMO, HOMO, and NHOMO (next HOMO) energy levels of POM and POE, respectively, vs. the wavenumber vector k. The curvatures of HPOM and OPOM resemble each other as expected from their conformational structures. LUMO energy variations of ZPOM and ZPOE in relation to the wavenumber vector $k = 0$–π are larger than those of the other forms. This means that the distribution of the state density of LUMO is more widely spread in the cases of ZPOM and ZPOE than the others. In comparison with the curvatures of POM and POE, the bottom of the vacant band of, for example, ZPOM is minimum at $k = 0$. On the other hand that of ZPOE is minimum at $k = \pi$. From the bottom of the vacant band, we can easily see that POE is a better insulator than POM. We can also make use of these curvatures to explain spectroscopic data such as ESCA. For example with HPOM and OPOM, the HOMO's state density is high in a narrow region. Therefore, the spectrum becomes a sharp band in these cases. On the other hand that of ZPOM is widely spread, and the band becomes broad.

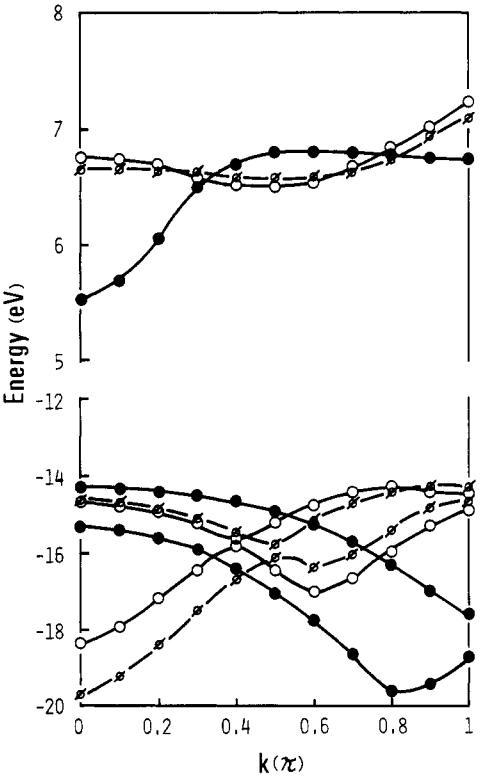

Figure 4. LUMO, HOMO, and NHOMO energy level vs. wavenumber vector in POM: ●, ZPOM; ϕ; OPOM; ○; HPOM.

III. Concluding Remarks

Relative stability among HPOM, OPOM, and ZPOM is explained reasonably by the CNDO/2 method on the basis of the tight-binding approximation.

Relative stability between HPOE and ZPOE is also well reproduced by this method.

Conformational stability among HPOM, OPOM, and ZPOM is mainly due to the total energy of each intrasegment.

Conformational stability between HPOE and ZPOE is governed by the balance of the total intrasegment and intersegment energies.

The O···O electrostatic repulsions in POM are somewhat larger than the corresponding CH_2···CH_2 repulsions in PE. These electrostatic interactions are one of the main factors to stabilize POM; however, these terms are not large enough to govern conclusively the conformations of the molecule.

The O···O electrostatic repulsions in POE are almost half of those in POM.

The intrasegment energy of POE is explained in terms of (H6,O1)-trans and (H7,O1)-gauche interactions. (See

Table XI
O···H and O···O Two-Center Interaction Energy (eV) in $CH_3OCH_2CH_2OCH_3$[a]

	TGT			TTT		
	H10[b,c]	H11[d]	O12[e]	H10[f]	H11[f]	O12[g]
resonance term						
O5[b]	-0.03	0.04	0.01	0.03	0.03	
exchange term						
O5	-0.02					-0.02
electrostatic term						
O5	0.01	0.01	0.22	0.01	0.01	0.18
total						
O5	-0.04	0.05	0.23	0.04	0.04	0.15

[a] Digits with minus sign show bonding, and those with plus sign antibonding. Energy terms: absolute values less than 0.01 eV are not catalogued. (See eq 9.) [b] Atom numberings are shown in Figure 2. [c] Distance O···H = 3.37 Å. [d] Distance O···H = 2.64 Å. [e] Distance O···O = 2.90 Å. [f] Distance O···H = 2.68 Å. [g] Distance O···O = 3.68 Å.

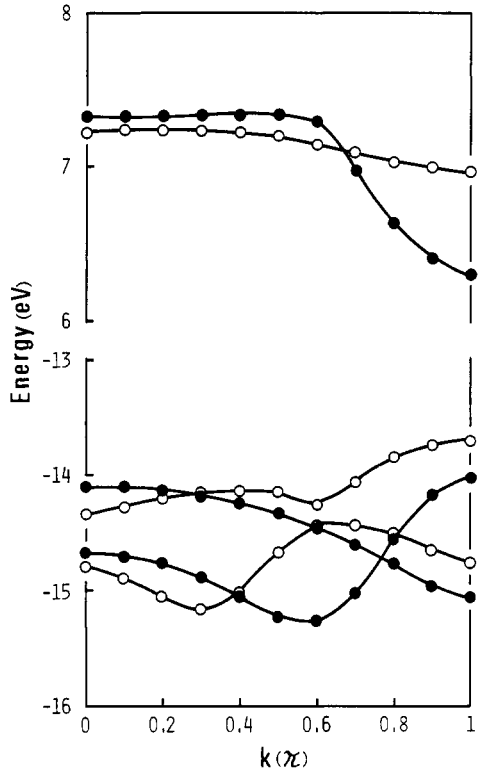

Figure 5. LUMO, HOMO, and NHOMO energy level vs. wavenumber vector in POE: ●; ZPOE; ○; HPOE.

text and Tables VI, XI, and XII.)

The energy band structures of POM and POE reveal a physical property of these molecules.

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References and Notes

(1) (a) Hiroshima University; (b) Shiga University of Medical Science.
(2) In the present article, the following abbreviations are used: POM, polyoxymethylene; POE, polyoxyethylene; PE, polyethylene; HPOM, hexagonal polyoxymethylene; OPOM, orthorhombic polyoxymethylene; ZPOM, planar zigzag polyoxymethylene; HPOE, helical polyoxyethylene; ZPOE, planar zigzag polyoxyethylene.
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(39) In order to check the validity of the CNDO approximation, we have calculated the Coulombic integral between oxygen lone-pair orbitals located at the distance 2.335 Å, which is identical to the O···O distance in ZPOM, two ways: (a) CNDO approximation (use of 2s atomic orbitals), and (b) without approximation (use of sp^3 hybridized orbitals). From these calculations, we have obtained the values for methods (a) and (b) to be 6.1631 and 6.1304 eV, respectively. From this, it seems that the CNDO approximation is enough to explain the situations quantitatively in these cases under study.