1052 *J. Phys. Chem. A* **2006,** *110,* 1052−1059

Quantum Chemical Study of the Interaction of the Short-Chain Poly(oxyethylene)s $CH_3(OCH_2CH_2)_mOCH_3$ ($C_1E_mC_1$; $m = 1$ and 2) with a Water Molecule in the Gas Phase and in Solutions

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Received: September 7, 2005; In Final Form: November 16, 2005

It is well-known that the role of the oxygen atom of the hydrophilic unit of poly(oxyethylene) (POE) is one of the important factors of the high solubility of POE in water. In the present study, we focused on the hydration of the oxyethylene OCH_2CH_2O unit of POE, $CH_3(OCH_2CH_2)_mOCH_3$ ($C_1E_mC_1$), and theoretically examined the role of the water molecule on the stability of POE using the short-chain POE, 1,2-dimethoxyethane (DME) $CH_3(OCH_2CH_2)OCH_3$ ($C_1E_1C_1$) and diglyme $CH_3(OCH_2CH_2)_2OCH_3$ ($C_1E_2C_1$). The relative energies of the important conformers of the model POE with and without a water molecule in the gas phase and the solvent have been calculated by the second-order Møller−Plesset perturbation (MP2) method using the 6-311G** basis set. We found three types of H-bonding of a water molecule with the POE chain for the TTT and the TGT conformers of $C_1E_1C_1$ and for the TTTTTT, the TGTTGT, and the TGTTG′T conformers of $C_1E_2C_1$, which are classified into the monodentate and the bidentate H-bonding. The conformers including the gauche form of the OCH_2CH_2O unit without the intramolecular electrostatic interaction are less stable in energy than the trans conformers in the gas phase for both $C_1E_1C_1$ and $C_1E_2C_1$. However, this order in the stability is reversed by the hydration. It is also found that the H-bond between POE and a water molecule is strengthened in the solvent. The stability of the conformers of POE in the gas phase and in the solvent is discussed in detail.

1. Introduction

Poly(oxyethylene) (POE) is one of the important polymers from the biotechnical and the biomedical points of view.[1,2] In light of the significant behavior of POE polymer in water, a lot of experimental and theoretical studies have been performed for the peculiar properties of POE in water.[3,4] POE is an excellent candidate for both experimental and theoretical studies aimed at gaining a better understanding of the polymer−water interactions. It is the general consensus that hydration is one of the key factors for the high solubility of POE in water and is induced by the hydrophilic nature of POE. The solubility of POE in the aqueous solution is considered to arise from the interaction of the ether oxygen atom of the hydrophilic unit of POE and the incoming water molecule.[5]

The experimental[6−8] and the theoretical[9−16] studies on the conformation of POE have shown the preference of the gauche form of the OCH_2CH_2O segment in water and in other solvents that can form the H-bond with the POE chain. These studies suggest that the H-bonding with the solvent molecule plays an important role on the stability of POE in the solution, because the trans conformer is more stable in energy in the gas phase than the gauche conformer without the intramolecular electrostatic interaction.

The existence of the short chain POE, $CH_3(OCH_2CH_2)OCH_3$ ($C_1E_1C_1$), as a mixture of the several principal conformers has been experimentally revealed in the gas phase, in water, and in other various solvents by the IR, the Raman, and the electron diffraction measurements.[7,17−23] The principal conformers of $C_1E_1C_1$ is TTT, TGT, TTG, TGG, and TGG′, where T and G denote the trans and the gauche form of the POE segments, respectively. It is also experimentally shown that the TTT conformer has the lowest-energy in the gas phase.[20] Yoshida et al.[18] has suggested using the IR spectroscopic technique that the TTT conformer is the most prominent species in the argon matrix. The energies of the conformers become higher in the gas phase in the order, TTT < TGT < TGG′. However, in the solution, the TGT conformer is the lowest in energy.[19] To understand the stability of the conformers in the solvent, it is necessary to clarify the essential nature of the H-bonding of the POE chain with the solvent molecule.

On the basis of a lot of previous experimental works for $C_1E_mC_1$ ($m = 1−3$),[24,25] three types of H-bonding of a water molecule with the POE chain with the different conformations, types I, II and III, can be proposed as shown in Figure 1. Type I is the H-bonding by the monodentate mode, where only one O−H bond of the water molecule participates in the H-bonding. On the other hand, types II and III are the H-bonding by the bidentate mode, where both O−H bonds of the water molecule participate in H-bonding. Two O−H bonds attach to the oxygen atoms on the O2,O5-position in type II and to the oxygen atoms on the O2,O8-posotion in type III. These modes of the H-bonding of the POE chain with a water molecule and the stability of the hydrated conformers of POE is not completely clarified, although there are some speculations in the relevant previous experimental studies. The systematic and quantitative understanding of the stability of the conformers of POE in the

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10.1021/jp055054f CCC: $33.50

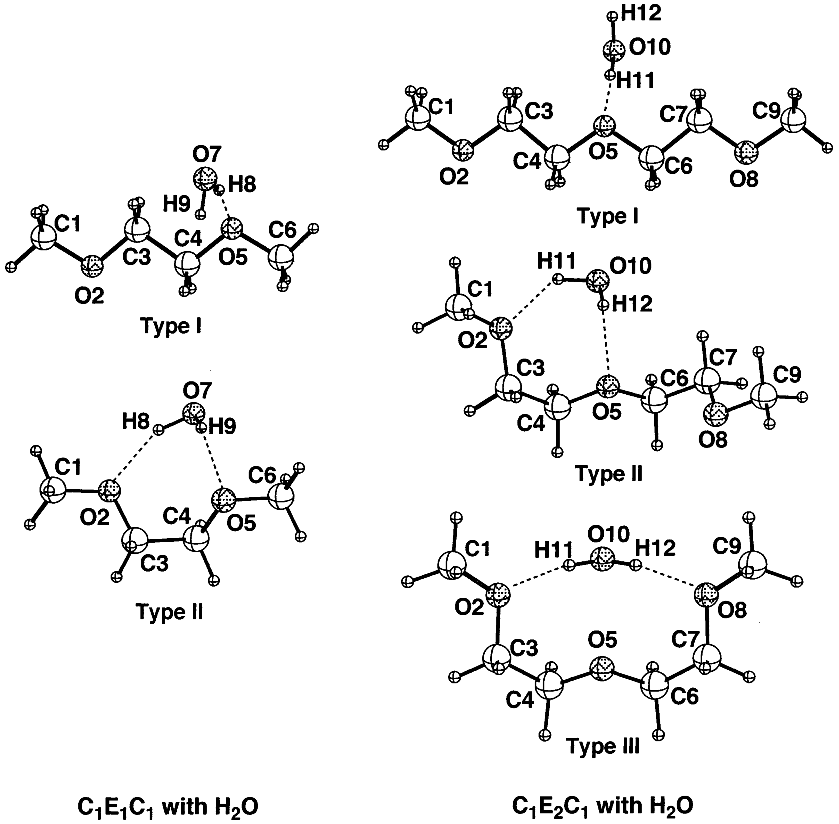


Figure 1. Three types of H-bonding of a water molecule with the ether oxygen atom of $C_1E_1C_1$ and $C_1E_2C_1$ with the various conformations. Type I: monodentate. Type II: bidentate on the O2,O5-position. Type III: bidentate on the O2,O8-position.

solution is really expected. The theoretical method is one of powerful tools to support the achievement of this purpose.

We therefore focused on the hydration of the oxyethylene OCH_2CH_2O unit of POE and theoretically examined the role of the water molecule on the stability of POE in attempt to gain a better understanding of the solubility of POE. Because it is known in experiment that the 1:1 POE−water adduct is dominantly formed by the hydration,[26] we investigated the interaction of POE with one water molecule. As a model of POE, we used the short-chain POE, $CH_3(OCH_2CH_2)_mOCH_3$ ($C_1E_mC_1$) ($m = 1, 2$). The quantum chemical calculations were performed for types I, II, and III H-bonding of a water molecule with the important conformers of the model POE presented in Figure 1 in the gas phase and in the several solvents with the various dielectric constants. Following the explanation of the Computational Methods in section 2, we will discuss in section 3.1 at first, $C_1E_1C_1$. In section 3.2, $C_1E_2C_1$ is discussed. Conclusions are summarized in the final section.

2. Computational Methods

All the calculations have been carried out using the GAUSSIAN03 program.[27] The geometry optimizations were performed by the second-order Møller−Plesset perturbation (MP2) method using the basis set at the 6-311G** level. The quadratic configuration interaction method with single and double substitutions (QCISD) in addition to the MP4 method was used to obtain more reliable energies. The thermochemical parameters, enthalpy, entropy and Gibbs free energy, were also calculated by the MP2 method with a scale factor of 0.9496[28] for calculated vibrational frequencies at the temperature of 298.15 K. For the entropy, we considered only the translational, rotational, and vibrational contributions. The solvent effects were investigated optimizing the geometries in the various solvents by the polarized-continuum-model (PCM) approximation.[29,30] As the solvents, water (H_2O), dimethyl sulfoxide ($(CH_3)_2SO$), methanol (CH_3OH), dichloromethane (CH_2Cl_2), chloroform (CH_3Cl), and carbon tetrachloride (CCl_4) with the dielectric constants, $\epsilon = 78.4, 46.7, 32.6, 8.9, 4.9$, and 2.2, were used. The natural bond orbital (NBO) analysis[31] was performed to examine the charge distribution of the POE molecule and its change by the interaction with a water molecule. The binding energy (BE) of a water molecule to the POE chain was calculated according to the following equation.

$$\mathrm{BE} = E(\mathrm{POE{-}water\ adduct}) - E(\mathrm{POE}) - E(\mathrm{water}) \qquad (1)$$

Here, the basis set superposition error (BSSE) in the binding energy was corrected by the counterpoise method.[32,33]

3. Results and Discussion

There exist 27 possible conformations even for $C_1E_1C_1$ that has the shortest chain as a model of POE. For $C_1E_2C_1$, the number of conformations increases to 729. However, only some conformations play an important role for the solubility in water. We therefore focused on these important conformations, i.e., TTT and TGT, for $C_1E_1C_1$, and TTTTTT, TGTTGT, and TGTTG′T for $C_1E_2C_1$.

3.1. $C_1E_1C_1$. The optimized geometrical parameters of the conformers, TTT and TGT, of $C_1E_1C_1$ are presented in Table 1. The geometries of TTT and TGT without a water molecule in the gas phase are quite similar to each other except for the dihedral angles. All the dihedral angles of TTT are 180°. On the other hand, the dihedral angle, ∠O2−C3−C4−O5, of TGT is reduced to 72° due to the gauche conformation of the OCH_2-CH_2O segment. Other dihedral angles, ∠O2−C3−C4−O5 and ∠O2−C3−C4−O5, are also reduced by 5°. We also optimized

TABLE 1: Optimized Geometrical Parameters (in Å and Degree) of the Conformers, TTT(I) and TGT(II), of $C_1E_1C_1$ with and without a Water Molecule in the Gas Phase and the CCl_4 Solvent and Free Water Molecule at the MP2/6-311G Level**[a]

geometrical parameter	gas phase: with a water	gas phase: without a water	CCl_4 solvent: with a water	CCl_4 solvent: without a water
TTT(I)				
d(C1−O2)	1.412	1.410	1.414	1.410
d(O2−C3)	1.411	1.410	1.412	1.412
d(C3−C4)	1.516	1.520	1.516	1.515
d(C4−O5)	1.418	1.410	1.419	1.412
d(O5−C6)	1.416	1.410	1.419	1.413
d(O7−H8)	0.965		0.966	
d(O7−H9)	0.958		0.961	
d(O5−H8)	1.941		1.916	
∠C1−O2−C3	110.7	111.0	111.0	111.0
∠O2−C3−C4	106.8	107.4	107.4	107.4
∠C3−C4−O5	107.8	107.4	107.4	107.4
∠C4−O5−C6	111.2	111.0	111.0	111.0
∠H8−O7−H9	102.1		102.3	
∠C1−O2−C3−C4	178.9	180.0	179.8	180.0
∠O2−C3−C4−O5	179.8	180.0	179.6	180.0
∠C3−C4−O5−C6	177.6	180.0	177.5	180.0
TGT(II)				
d(C1−O2)	1.418	1.410	1.419	1.412
d(O2−C3)	1.415	1.410	1.418	1.411
d(C3−C4)	1.510	1.509	1.510	1.509
d(C4−O5)	1.414	1.409	1.415	1.411
d(O5−C6)	1.414	1.410	1.415	1.412
d(O7−H8)	0.962		0.963	
d(O7−H9)	0.961		0.962	
d(O2−H8)	2.087		2.038	
d(O5−H9)	2.164		2.107	
∠C1−O2−C3	110.5	110.9	110.5	110.7
∠O2−C3−C4	108.9	108.7	109.1	108.9
∠C3−C4−O5	109.3	108.7	109.4	108.9
∠C4−O5−C6	111.2	110.9	111.1	110.7
∠H8−O7−H9	98.9		98.7	
∠C1−O2−C3−C4	178.3	175.4	179.3	176.9
∠O2−C3−C4−O5	72.3	72.8	72.2	72.5
∠C3−C4−O5−C6	176.3	175.4	175.3	175.5
Free Water				
d(O7−H8)		0.960		
d(O7−H9)		0.960		
∠H8−O7−H9		104.9		

[a] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

TABLE 2: Relative Potential Energy (Δ*E*), Enthalpy (Δ*H*), Entropy (*T*Δ*S*), and Gibbs Free Energy (Δ*G*)[a] (in kcal/mol) of the Conformers, TTT(I), TGT(II), and TGG′(I) of $C_1E_1C_1$ with and without a Water Molecule in the Gas Phase and the CCl_4 Solvent at the MP2/6-311G Level**

conformer[b]	with a water: Δ*E*	with a water: ΔH	with a water: *T*Δ*S*	with a water: Δ*G*	without a water: Δ*E*	without a water: Δ*H*	without a water: *T*Δ*S*	without a water: Δ*G*
Gas Phase								
TTT(I)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TGT(II)	−2.7	−2.6	−1.4	−1.2	0.5	0.3	0.2	0.1
TGG′(I)	−1.1	−1.0	−1.0	0.0	0.02	0.0	0.2	−0.2
CCl_4 Solvent								
TTT(I)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TGT(II)	−2.1	−2.0	−1.3	−0.7	0.3	0.1	0.2	−0.1
TGG′(I)	−0.4	−0.5	−0.7	0.2	0.1	0.0	0.2	−0.2

[a] $\Delta G = \Delta H - T\Delta S$ at 298.15 K. [b] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

the structures of these conformers in the CCl_4 solvent, because the H-bonding of a water molecule with the POE chain is experimentally examined in detail in the CCl_4 solvent.[34,35] The geometries of both TTT and TGT conformers were not so diffrent even in the CCl_4 solvent.

When a water molecule is added to the TTT and the TGT conformers, the hydration mode is different. One of the O−H bonds of the water molecule attaches to one of the ether oxygen atoms by the monodentate mode in the TTT conformer (see Figure 1). On the other hand, both O−H bonds of the water molecule attach to two ether oxygen atoms on the O2,O5-position by the bidentate mode in the TGT conformer. Both conformers have no other hydration mode. In the case of the TTT conformer, the O−H bond of the water molecule that attaches to the O5 atom is slightly shortened and the other O−H bond is lengthened by the formation of the H-bond. In the case of the TGT conformer, both O−H bonds of the water molecule are stretched and the ∠H−O−H angle is reduced to 98.9° due to the deformation of the structure caused by the H-bonding. It is also obvious that all the O−C distances of the $C_1E_1C_1$ chain are elongated by the hydration. These trends are not changed in the CCl_4 solvent. However, the O- - -H distance of the H-bond is shortened in the CCl_4 solvent, which suggests that the H-bond is strengthened by the solvent effect.

The stability of the conformers, TTT and TGT, in the gas phase is presented in Table 2. Yoshida et al.[18] have found by the IR spectroscopy that the three conformers, TTT, TGT, and TGG′, are the dominant species and the TTT conformer is the lowest in energy in the argon matrix for $C_1E_1C_1$. Our computational result agrees with this experimental result. Without the interaction with a water molecule, the TTT conformer is the most stable in the potential energy, although the TGG′ conformer with the intramolecular electrostatic interaction is the most stable in the Gibbs free energy as previously reported by Tsuzuki et al.[36] However, the H-bonding of a water molecule by the bidentate mode largely stabilizes the TGT conformer so that the TGT conformer becomes more stable in energy than the TTT conformer with the interaction with a water molecule. The difference in the potential energy between the TTT and the TGT conformers decreases to half in the Gibbs free energy, because the entropy term reduces the stability of the POE−water adduct by the bidentate mode. These tendencies found in the gas phase were not changed in the CCl_4 solvent. The previous computational works have also showed the similar result that the hydration more favorably occurs in the TGT conformer than in the TTT conformer.[37,38]

3.2. $C_1E_2C_1$. For $C_1E_2C_1$, we calculated three essentially important conformers, i.e., TTTTTT, TGTTGT, and TGTTG′T. Here, G′ means that the sign of the dihedral angle is opposite to that of G. For these three conformers, we have found the monodentate and the bidentate H-bonding of a water molecule, which lead to three hydration modes, types I, II, and III, shown in Figure 1. The geometries of three conformers of $C_1E_2C_1$ with and without a water molecule and in the gas phase and the CCl_4 solvent are presented in Table 3. Without the interaction with a water molecule, the bond distances and the angles of $C_1E_2C_1$ are nearly the same as those of $C_1E_1C_1$. The geometry of each conformer in the gas phase was not changed in the CCl_4 solvent.

With the TTTTTT conformer, a water molecule interacts only by the monodentate mode. The bifurcate H-bonding where both O−H bonds of the water molecule interact with one oxygen atom did not exist. The geometrical parameters of the hydrated TTTTTT conformer where the O−H bond of the water molecule forms the H-bond with the O5 atom of the POE chain is presented in Table 2 (for the geometry, see Figure 1). The C4−O5 and the O5−C6 bonds are affected by the H-bonding and are stretched by 0.008 Å.

TABLE 3: Optimized Geometrical Parameters (in Å and Degree) of the Conformers, TTTTTT(I), TGTTGT(II), TGTTGT(III), and TGTTG′T(III), of $C_1E_2C_1$ with and without a Water Molecule in the Gas Phase and the CCl_4 Solvent at the MP2/6-311G Level**[a]

	gas phase		CCl_4 solvent			gas phase		CCl_4 solvent
geometrical parameter	with a water	without a water	with a water	without a water	geometrical parameter	with a water	without a water	with a water
				TTTTTT(I)				
d(C1−O2)	1.412	1.411	1.414	1.413	∠C1−O2−C3	110.9	111.0	110.8
d(O2−C3)	1.409	1.411	1.410	1.411	∠O2−C3−C4	107.0	107.3	107.1
d(C3−C4)	1.516	1.515	1.516	1.515	∠C3−C4−O5	107.3	107.2	107.3
d(C4−O5)	1.421	1.413	1.422	1.414	∠C4−O5−C6	112.0	111.5	111.9
d(O5−C6)	1.421	1.413	1.422	1.414	∠O5−C6−C7	107.3	107.2	107.3
d(C6−C7)	1.516	1.515	1.516	1.515	∠C6−C7−O8	107.0	107.3	107.1
d(C7−O8)	1.409	1.411	1.411	1.411	∠C7−O8−C9	110.9	111.0	110.8
d(O8−C9)	1.412	1.411	1.414	1.413	∠H11−O10−H12	102.2		102.1
d(O10−H11)	0.966		0.966		∠C1−O2−C3−C4	177.9	180.0	178.4
d(O10−H12)	0.958		0.961		∠O2−C3−C4−O5	178.5	180.0	178.7
d(O5−H11)	1.889		1.890		∠C3−C4−O5−C6	177.4	180.0	178.1
					∠C4−O5−C6−C7	177.3	180.0	179.3
					∠O5−C6−C7−O8	178.5	180.0	178.3
					∠C6−C7−O8−C9	177.9	180.0	177.7
				TGTTGT(II)				
d(C1−O2)	1.413	1.410	1.141	1.412	∠C1−O2−C3	111.2	110.9	111.0
d(O2−C3)	1.414	1.410	1.415	1.412	∠O2−C3−C4	109.0	108.6	109.0
d(C3−C4)	1.510	1.510	1.509	1.509	∠C3−C4−O5	108.6	108.5	108.7
d(C4−O5)	1.415	1.410	1.418	1.413	∠C4−O5−C6	110.9	111.4	110.8
d(O5−C6)	1.420	1.410	1.521	1.413	∠O5−C6−C7	108.5	108.5	108.8
d(C6−C7)	1.508	1.510	1.508	1.509	∠C6−C7−O8	108.8	108.6	109.0
d(C7−O8)	1.409	1.410	1.411	1.412	∠C7−O8−C9	110.8	110.9	110.5
d(O8−C9)	1.410	1.410	1.412	1.412	∠H11−O10−H12	99.1		99.1
d(O10−H11)	0.964		0.965		∠C1−O2−C3−C4	173.8	175.4	173.9
d(O10−H12)	0.960		0.961		∠O2−C3−C4−O5	72.1	72.6	71.5
d(O2−H11)	2.290		2.265		∠C3−C4−O5−C6	176.6	174.7	177.5
d(O5−H12)	2.015		2.000		∠C4−O5−C6−C7	177.2	174.7	176.2
					∠O5−C6−C7−O8	69.9	72.6	69.9
					∠C6−C7−O8−C9	177.0	175.4	178.3
				TGTTGT(III)				
d(C1−O2)	1.418		1.418		∠C1−O2−C3	110.8		110.7
d(O2−C3)	1.413		1.416		∠O2−C3−C4	108.2		108.3
d(C3−C4)	1.512		1.511		∠C3−C4−O5	106.3		106.4
d(C4−O5)	1.409		1.411		∠C4−O5−C6	115.0		114.6
d(O5−C6)	1.409		1.411		∠O5−C6−C7	106.3		106.5
d(C6−C7)	1.512		1.511		∠C6−C7−O8	108.2		108.3
d(C7−O8)	1.413		1.415		∠C7−O8−C9	110.8		110.7
d(O8−C9)	1.418		1.418		∠H11−O10−H12	99.8		99.9
d(O10−H11)	0.962		0.963		∠C1−O2−C3−C4	170.3		172.7
d(O10−H12)	0.963		0.964		∠O2−C3−C4−O5	63.3		62.5
d(O2−H11)	2.187		2.151		∠C3−C4−O5−C6	173.7		172.8
d(O8−H12)	2.193		2.157		∠C4−O5−C6−C7	172.0		171.3
					∠O5−C6−C7−O8	63.0		62.2
					∠C6−C7−O8−C9	170.4		172.8
				TGTTG′T(III)				
d(C1−O2)	1.412	1.409	1.414	1.412	∠C1−O2−C3	111.7	110.9	111.6
d(O2−C3)	1.414	1.408	1.415	1.410	∠O2−C3−C4	108.3	109.0	108.3
d(C3−C4)	1.510	1.510	1.510	1.510	∠C3−C4−O5	107.8	109.0	107.8
d(C4−O5)	1.413	1.411	1.414	1.413	∠C4−O5−C6	111.7	110.9	111.7
d(O5−C6)	1.413	1.411	1.414	1.413	∠O5−C6−C7	107.8	109.0	107.8
d(C6−C7)	1.510	1.510	1.510	1.510	∠C6−C7−O8	108.3	109.0	108.3
d(C7−O8)	1.414	1.408	1.415	1.410	∠C7−O8−C9	111.6	110.7	111.6
d(O8−C9)	1.412	1.409	1.415	1.411	∠H11−O10−H12	101.8		102.0
d(O10−H11)	0.963		0.964		∠C1−O2−C3−C4	175.5	175.2	175.4
d(O10−H12)	0.963		0.963		∠O2−C3−C4−O5	70.2	73.0	69.4
d(O2−H11)	2.001		1.973		∠C3−C4−O5−C6	172.2	178.2	172.7
d(O8−H12)	2.000		1.972		∠C4−O5−C6−C7	172.1	178.1	172.5
					∠O5−C6−C7−O8	70.2	73.0	69.5
					∠C6−C7−O8−C9	175.2	175.2	175.3

[a] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

On the other hand, a water molecule interacts with the TGTTGT and the TGTTG′T conformers only by the bidentate mode. The H-bonding by the bidentate mode is possible at the oxygen atoms on the O2,O5-position (type II in Figure 1) and at the oxygen atoms on the O2,O8-position (type III in Figure 1). However, only type III was found for the TGTTG′T conformer. The geometrical parameters for the hydrated TGTTGT and TGTTG′T conformers with type II and III H-bonding are presented in Table 2. In the hydrated TGTTGT conformer with type II H-bonding, two O- - -H distances of the H-bonds

TABLE 4: Relative Potential Energy (ΔE), Enthalpy (ΔH), Entropy ($T\Delta S$), and Gibbs Free Energy (ΔG)[a] (in kcal/mol) of the Conformers, TTTTTT(I), TGTTGT(II), TGTTGT(III), and TGTTG′T(III), of $C_1E_2C_1$ with and without a Water Molecule in the Gas Phase at the MP2/6-311G Level**

	with a water				without a water			
conformer[b]	ΔE	ΔH	$T\Delta S$	ΔG	ΔE	ΔH	$T\Delta S$	ΔG
TTTTTT(I)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TGTTGT(II)	−2.5	−2.6	−1.7	−0.9	0.7	0.4	−0.4	0.8
TGTTGT(III)	−5.4	−5.3	−2.0	−3.3				
TGTTG′T(III)	−5.3	−5.2	−2.6	−2.6	1.2	0.8	−0.3	1.1

[a] $\Delta G = \Delta H - T\Delta S$ at 298.15 K. [b] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

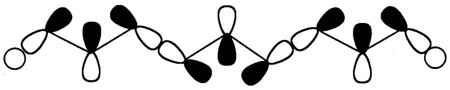
TABLE 5: Relative Potential Energies (in kcal/mol) Calculated at the Various Levels for the Important Three Conformers, TTTTTT, TGTTGT, and TGTTG′T, of $C_1E_2C_1$ Optimized at the MP2/6-311G Level in the Gas Phase and the CCl_4 Solvent**

conformer	MP2/ 6-311G**	MP4SDQ/ 6-311G**	QCISD(T)/ 6-311G**	B3LYP/ 6-311G**
		Gas Phase		
TTTTTT	0.0	0.0	0.0	0.0
TGTTGT	0.7	1.0	0.9	1.0
TGTTG′T	1.2	1.6	1.4	1.5
		CCl_4 Solvent		
TTTTTT	0.0	0.0	0.0	0.0
TGTTGT	0.5	0.9	0.7	0.8
TGTTG′T	0.9	1.3	1.2	1.2

are obviously different. The O2- - - -H11 distance is longer by 0.275 Å than the O5- - - -H12 distance in the gas phase. The space between the two oxygens on the O2,O5-position is too small to form two H-bonds. Therefore, one of the H-bonds is strengthened and the other is weakened. In contrast, both H-bonds formed on the O2,O8-position are strong as shown by the short O2- - - -H11 and O8- - -H12 distances, because there is enough space between the O2 and the O8 atoms to form two H-bonds by the bidentate mode. The O2- - - -H11 and the O8- - -H12 distances of the H-bonds are shorter by 0.18−0.19 Å for the TGTTG′T conformer than for the TGTTGT conformer, which suggests that the hydration more strongly occurs in the TGTTG′T conformer than in the TGTTGT conformer.

Especially the terminal bonds, C1−O2 and O8−C9, are stretched by type III H-bonding in the case of the TGTTGT conformer. As reflected in the bond angles and the dihedral angles, the structure of the POE chain and the bound water molecule are largely deformed by the H-bonding. The angle ∠H11−O10−H12 of the bound water molecule is reduced to 99.8° and all the dihedral angles of the POE chain are also reduced by 1.0−9.6°. In contrast, the deformation of the POE chain and the bound water by the formation of the H-bond is significantly reduced in the TGTTG′T conformer, which suggests that the space provided between the O2 and the O8 atoms of the TGTTG′T conformer (O2- - -O8 distance is 4.954 Å) is moderate for the bidentate H-bonding compared to that of the TGTTGT conformer (O2- - -O8 distance is 5.638 Å). Only the dihedral angles, ∠C3−C4−O5−C6 and ∠C4−O5−C6−C7, of the POE chain notably change. Four bonds of the POE chain, C1−O2, O2−C3, C7−O8, and O8−C9, are slightly elongated. The deformation of the POE chain of the TGTTGT and the TGTTG′T conformers by the H-bonding in the gas phase increases in the CCl_4 solvent. The O- - -H distances of the H-bonds become shorter in the CCl_4 solvent for each conformer except for TTTTTT, which is similar to the case of $C_1E_1C_1$. This fact suggests that the H-bond is strengthened in the solvent. The O- - -H distances of the H-bonds were similarly shortened in other solvents with the larger dielectric constant such as H_2O.

The conformation energies of $C_1E_2C_1$ with and without a water molecule are presented in Table 4. Without a water molecule, the TTTTTT conformer is more stable in energy than the TGTTGT and the TGTTG′T conformers, which is consistent with the experimental results previously reported.[26] This tendency is more obvious compared to the case of $C_1E_1C_1$. The TTTTTT conformer can get much stability by the electron delocalization though the molecular orbital displayed below. When the TTTTTT conformer is transformed to the TGTTGT or the TGTTG′T conformers, this electron delocalization is broken and the stability decreases. The order in the stability, TTTTTT > TGTTGT > TGTTG′T, and the energy difference among the conformers were not changed even at the higher calculation level, as shown in Table 5, which suggests that the MP2 level we selected is good enough.



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The tendency in the stability of the conformers without a water molecule, TTTTTT > TGTTGT > TGTTG′T, is, however, reversed by the hydration, because both TGTTGT and TGTTG′T conformers are significantly stabilized by the H-bonding with a water molecule. The H-bonding by the bidentate mode is stronger than that by monodentate mode. The stability of the hydrated TGTTGT conformer with type III H-bonding is nearly the same as that of the hydrated TGTTG′T conformer with type III H-bonding. Here, it should be noted that type III H-bonding more strongly stabilizes the TGTTGT conformer compared to type II H-bonding. This suggests that the H-bonding on the O2,O8-position is stronger than that on the O2,O5-position. These computational results verified the speculation on the basis of the experimental results.[25] The tendency in the relative Gibbs free energy was similar to that in the relative potential energy. However, the difference in the Gibbs free energy among the hydrated conformers with the different H-bonding modes becomes small, because the destabilization by the entropy term increases in the order, type III > type II > type I.

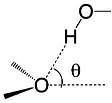
It was theoretically predicted by Morokuma and Pedersen in 1968[39] that the O−H···O H-bonding in the water dimer $H_2O\cdots H_2O$ is not bifurcated but linear. However, in the present system, the bidentate H-bonding is energetically preferred over the monodentate one. To compare the nature of the H-bond in the present system with that in the water dimer, we examined the component of the O−H···O H-bond in the present system using the energy decomposition analysis (EDA)[40] implemented in the GAMESS program.[41] The calculation was performed at the HF/6-311G** level using the CH_3OCH_3 molecule as the model of the POE segment. The calculation showed no significant difference in the component of the O−H···O H-bond between the present system and the water dimer.[42] The electrostatic component most largely contributes to the nature of the H-bond. The preference of the bidentate mode would be attributed to the geometry of the conformer (see below). The angle θ formed by the POE segment and the bound water

TABLE 6: Binding Energies (BE) (in kcal/mol) of a Water Molecule to the Important Conformers of $C_1E_1C_1$ and $C_1E_2C_1$

conformer[a]	BE[b]
$C_1E_1C_1$	
TTT(I)	−2.8 (−4.7)
TGT(II)	−4.9 (−7.6)
$C_1E_2C_1$	
TTTTTT(I)	−2.7 (−5.2)
TGTTGT(II)	−5.2 (−7.7)
TGTTGT(III)	−7.8 (−10.9)
TGTTG′T(III)	−8.1 (−10.6)

[a] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1). [b] The values in parentheses are the binding energies calculated without the counterpoise correction (see the Computational Methods).

molecule (see the illustration presented below) would affect the stability of the POE−water adduct.



In the case of the water dimer, the lowest energy has been found at the angle θ of about 30°. The hydrated TTTTTT conformer with type I H-bonding also showed the large value of 51.8°, which is considered to be the best angle for the H-bonding. On the other hand, the angle θ in the hydrated TGTTGT and TGTTG′T conformers with type II and III H-bonding largely deviates from this value.[43] Nevertheless, the hydrated TGTTGT and TGTTG′T conformers are more stable in energy than the hydrated TTTTTT conformer. The bridging H-bonding of types II and III in the TGTTGT and the TGTTG′T conformers would be strong enough to stabilize the structure even with those angle θ (see below).

We calculated the binding energy of the water molecule to examine the strength of the H-bond (Table 6). For $C_1E_1C_1$, the binding energy of the water molecule is larger in the TGT conformer where the water molecule binds by the bidentate mode than in the TTT conformer where the water molecule binds by the monodentate mode. This is reflected on the stability of the conformers, the hydrated TGT conformer being more stable in energy than the hydrated TTT conformer. For $C_1E_2C_1$, the binding energy was the smallest in the hydrated TTTTTT conformer with type I H-bonding. In the TGTTGT conformer, the binding energy is larger by 2.6 kcal/mol for type III H-bonding than for type II H-bonding. This is reflected on the trend in the stability that the hydrated TGTTG′T with type III H-bonding is 2.9 kcal/mol stable than the hydrated TGTTGT with type II H-bonding. Thus, type III H-bonding more strongly stabilizes the TGTTGT conformer compared to type II H-bonding. The type III H-bond in the TGTTG′T conformer was slightly stronger than the type III H-bond in the TGTTGT conformer.

It is generally well-known that the O−H stretching of the water molecule is affected by the formation of the H-bond. The vibrational frequency of the O−H bond of the bound water molecule would give us the information about the nature of the H-bond. We therefore calculated the vibrational frequencies of the O−H stretching of the water molecule bound to the conformers, TTTTTT, TGTTGT, and TGTTG′T (Table 7). The vibrational frequencies calculated at the MP2 level for each conformer agree well with those observed by the IR spectroscopy.[25,26] The number of the calculated vibrational frequency of the O−H stretching was in the range from 3592 to 3763 cm^{-1}. The vibrational frequencies of the bound water molecule showed a red shift, because the O−H bonds of the water molecule are weakened by the H-bonding. The calculated vibrational frequencies of the symmetric and the antisymmetric O−H stretching of the water molecule bound to the TGTTGT conformer by type III bidentate mode were 3661 and 3719 cm^{-1}, respectively, which are smaller by 38−92 cm^{-1} than the corresponding vibrational frequencies for free water. One can notice that the vibrational frequency of the antisymmetric stretching decreases with the increase in the strength of the H-bond.

The atomic charge of the POE chain is remarkably affected by the hydration. The NBO charges of the oxygen atoms of $C_1E_2C_1$ with and without a water molecule in the gas phase are shown in Table 8. The conformers of $C_1E_2C_1$, TTTTTT, TGTTGT, and TGTTG′T, without a water molecule have similar negative charges on the ether oxygen atoms, O2, O5, and O8. The negative charge on the O5 atom, which is located on the center of the POE molecule, is slightly larger compared to those on the O2 and the O8 atoms. For the TTTTTT conformer, the negative charge of the O5 atom obviously increases by the hydration, because the water molecule forms the H-bond at the O5 atom as mentioned earlier. The electron moves from the H11 atom to the O10 atom by the effect of the incoming negatively charged O5 atom so that the positive charge of the H11 atom and the negative charge of the O10 atom increase. By this enhanced positive charge of the H11 atom, the negative charge of the O5 atom is also increased. It should be noted here that the positive charge of the H12 atom does not change by the formation of the H-bond. Thus, the polarization by the hydration locally occurs in the O10−H11- - -O5 region. Only the negative charges on the O2 and the O5 atoms increase in type II hydration for the TGTTGT conformer where the water

TABLE 7: Calculated Vibrational Frequencies (in cm^{-1}) of the Water Molecule Bound to the Conformers of $C_1E_2C_1$ and Free Water Molecule at the MP2/6-311G Level[a]**

conformer[b]	symmetric/bonded O−H stretching	antisymmetric/unbonded O−H stretching
TTTTTT(I)	3592 (3495−3515)	3763 (3685−3688)
TGTTGT(II)	3657	3752
TGTTGT(III)	3661 (3520−3535)	3719 (3590−3600)
TGTTG′T(III)	3646 (3520−3535)	3712 (3590−3600)
Free water	3709 (3615)	3811 (3707)

[a] The experimentally observed vibrational frequencies are shown in the parentheses.(see ref 26). [b] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

TABLE 8: NBO Charges on the Selected Atoms of the Conformers, TTTTTT, TGTTGT, and TGTTG′T, of $C_1E_2C_1$ with and without a Water Molecule and Free Water Molecule in the Gas Phase at the HF/6-311G Level**

conformer[a]	O2	O5	O8	O10	H11	H12
With a Water						
TTTTTT(I)	−0.631	−0.678	−0.631	−0.924	0.479	0.437
TGTTGT(II)	−0.650	−0.655	−0.626	−0.941	0.471	0.462
TGTTGT(III)	−0.642	−0.657	−0.641	−0.954	0.474	0.474
TGTTG′T(III)	−0.648	−0.646	−0.648	−0.963	0.476	0.476
Without a Water						
TTTTTT	−0.632	−0.652	−0.632			
TGTTGT	−0.625	−0.635	−0.625			
TGTTG′T	−0.621	−0.634	−0.621			
free water				−0.882	0.441	0.441

[a] The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

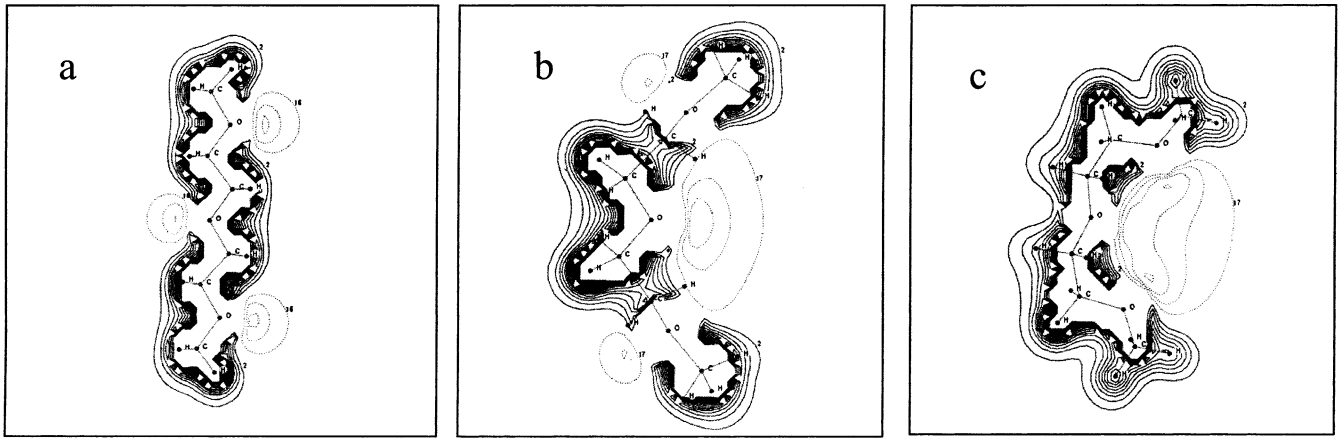


Figure 2. Contour maps of the electrostatic potential for the conformers of $C_1E_2C_1$ without a water molecule: (a) TTTTTT; (b) TGTTGT; (c) TGTTG′T. The positive and the negative potentials are given by the solid and the dotted lines, respectively, with increments of 0.025 au.

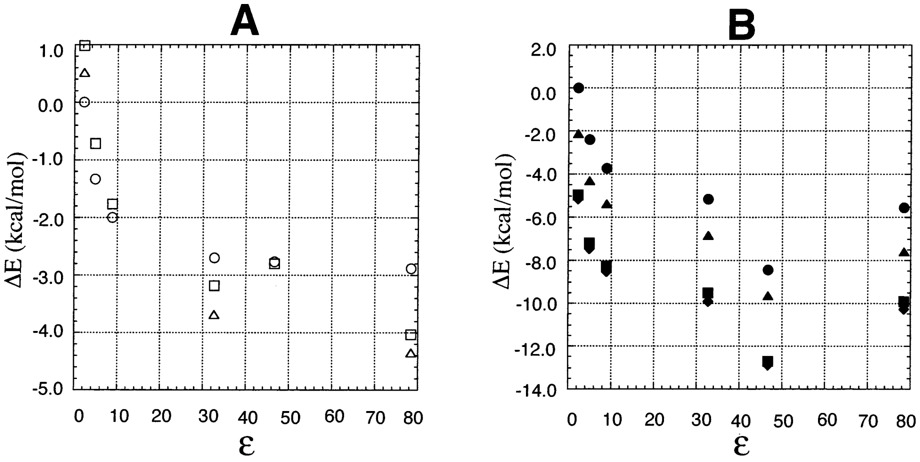


Figure 3. Plots of the relative energies (ΔE) of the conformers of $C_1E_2C_1$ versus the dielectric constants (ϵ) of the various solvents: (A) without a water molecule (○, TTTTTT; △, TGTTGT; □, TGTTG′T); (B) with a water molecule (●, TTTTTT(I); ▲, TGTTGT(II); ■, TGTTGT(III); ◆, TGTTG′T(III)). The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).

molecule interacts with the oxygen atoms on the O2,O5-position. On the other hand, in the hydrated TGTTGT conformer with type III H-bonding, not only the negative charge of the oxygen atoms on the O2,O8-position interacting with a water molecule but also the negative charge of the O5 atom increases. The positively charged H11 and H12 atoms of the water molecule that are relatively close to the O5 atom (d(O5−H11) = 2.342 Å, d(O5−H12) = 2.345 Å) would enhance the negative charge of the O5 atom.

The charge is more uniformly distributed in the POE chain of the hydrated TGTTG′T conformer with type III H-bonding than in that of the hydrated TGTTGT conformer with the same type H-bonding. The bound water molecule is also more strongly polarized in the TGTTG′T conformer than in the TGTTGT conformer, which suggests that the H-bond is stronger in the TGTTG′T conformer than in the TGTTGT conformer. The hydration at the oxygen atoms on the O2,O8-position is considered to produce the well-balanced distribution of the positive and the negative charges on the POE chain of $C_1E_2C_1$. The positive and the negative charges distributed in the cyclic form of the hydrated TGTTG′T (see type III in Figure 1) would strengthen the H-bond with a water molecule. In addition, the moderate space produced on the O2,O8-position would be preferred. The space allowed on the O2,O5-position is tight for the H-bonding by the bidentate mode. As a result, in the hydrated TGTTGT with type II H-bonding, one of the H-bonds becomes much weaker than the other H-bond and the deformation of the POE chain by the H-bonding is large as mentioned above.

The counter map of the electrostatic potential for the optimized geometries of three essential conformers of $C_1E_2C_1$ at the HF/6-311G** level is depicted in Figure 2. Figure 2 indicates that the possibility of the electrostatic interaction of the incoming water molecule with the ether oxygen atoms of the POE chain of $C_1E_2C_1$ increases in the order, TGTTG′T > TGTTGT > TTTTTT. The negative region that contains the oxygen atoms, O2, O5, and O8, of the POE chain is separated and is very small for the TTTTTT conformer (Figure 2a). For the TGTTGT conformer, the negative potential is expanded over the O2, O5, and O8 atoms (Figure 2b). Therefore, it can be reasonably understood that both type II and type III H-bonding are allowed in the TGTTGT conformer. The counter map of the TGTTG′T conformer (Figure 2c) shows that the negative potential is more largely expanded over the O2 and the O8 atoms. This suggests that the incoming water molecule would be trapped in the space produced between the O2 and the O8 atoms.

We examined the solvent effect on the stability of the conformers using the PCM approximation. The change in the stability of the conformers with the dielectric constant of the solvent is presented in Figure 3. The order in the stability of the conformers without a water molecule drastically changed with the dielectric constant of the solvent (Figure 3A). In the

CCl_4 solvent with the small dielectric constant ϵ of 2.2, the stability of the conformers increases in the order TTTTTT > TGTTGT > TGTTG′T. This tendency is the same as that in the gas phase. However, the conformers, TGTTGT and TGTTG′T, become more stable in energy than the conformer TTTTTT and the energy difference between TTTTTT and TGTTGT or TGTTG′T enlarges when the dielectric constant increases. This indicates that the TGTTGT and the TGTTG′T conformers are largely stabilized by the solvent with the large dielectric constant such as water. It is also interesting that the relative energies of the three conformers are not affected so much by the solvent when the conformers already hydrate with one water molecule as shown by Figure 3B. The stability of three conformers increases with the increase in the dielectric constant of the solvent, which is similar to the case without a water molecule.

4. Conclusion

In the present work, we examined the hydration and the stability of the short-chain POE, which are closely related to its solubility, using the model molecules, $C_1E_1C_1$ and $C_1E_2C_1$, in the gas phase and in the various solvents. We selected the important conformers that have trans and gauche conformations for the OCH_2CH_2O segment. The monodentate H-bond is formed in the hydration of the trans conformers, TTT and TTTTTT. On the other hand, the bidentate H-bond is formed in the hydration of the conformers including the gauche form of the OCH_2CH_2O segment, TGT, TGTTGT, and TGTTG′T. By the hydration, the gauche conformers are more largely stabilized in energy than the trans conformers. Therefore, the order in the stability of the conformers without the hydration, TTT > TGT for $C_1E_1C_1$ and TTTTTT > TGTTGT > TGTTG′T for $C_1E_2C_1$, is reversed by the hydration. Thus, the hydration plays an important role to determine the stability of the conformers. These trends in the stability of the hydrated conformers were not changed, even if the solvent effect is taken into account. Type III H-bonding more largely stabilizes the conformers compared to type II H-bonding in both gas phase and the solvent. Our computations verified this fact experimentally speculated. The H-bond formed in the gas phase is further strengthened in the solvent.

Acknowledgment. We thank Prof. H. Matsuura of Hiroshima University for providing us with helpful experimental data and for fruitful discussion. This study was partly supported by grants from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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(42) The component of the interaction energy (−8.86 kcal/mol) for the monodentate H-bond was as follows: the electrostatic energy (ES), −12.79 kcal/mol; the exchange repulsion energy (EX), 8.80 kcal/mol; the polarization energy (PL), −1.36 kcal/mol; the charge-transfer energy (CT), −3.02 kcal/mol; the high order coupling energy (MIX), −0.48 kcal/mol.

(43) The values of the angle θ of the hydrated conformers of $C_1E_2C_1$ with type I, II, and III H-bonding are as follows: TTTTTT(I), 51.8°; TGTTGT(II), 5.8° and 76.5°; TGTTGT(III), 76.1° and 75.4°; TGTTG′T(III), 11.2° and 11.4°. The numbers in parentheses for the conformers are the type of the H-bonding with a water molecule (see Figure 1).