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ORIGINAL PAPER

Conformational analysis for hydrated ethylene oxide oligomer models by quantum chemical calculations

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Abstract Hydrate effects on the conformations of ethylene oxide oligomers (EO-x, $x = 1$–8 mers) were examined using quantum chemical calculations (QCC). Conformational analyses were carried out by RHF/6-31G. The models were constructed by locating a water molecule to each ether–oxygen in the structures optimized for non-hydrate oligomers. Hydrate ratio, h ($h = \mathrm{H_2O_{mol}/O_{mol\ in\ oligomer}}$), was set from 0 to 1.0. The six type conformations with repeated units of O–C, C–C and C–O bonds were examined. Conformational energy, E_c (HF), was calculated as difference between the energy of oligomer with water molecules and that of non-hydrogen and/or hydrogen bonding water molecules. Hydrate energies for each conformer, $\Delta\mu_h$ (kcal/m.u., based on E_c in non-hydrate state), were negative and linearly decreased with the increase of h values, and such effects with the increase of h values were weaken with increasing x values. These results were consistent with our previous results calculated using the permittivity, ε ($\varepsilon = 0$–80.1), by QCC. In non-hydrate ($h = 0$), the $(\mathrm{ttt})_x$ conformers were the most stable independent of x. However, in hydrate states ($h = 0.44$–0.67), the $(\mathrm{tg^+t})_x$ conformers were the most stable independent of x values, and in $h = 1$, the $(\mathrm{tg^+t})_8$ conformer (8-mer) was most stable [$\Delta E_{c(g)} = -1.3$ kcal/m.u., $\Delta E_{c(g)}$: energy difference between a given oligomer and the $(\mathrm{ttt})_x$ oligomer]. These results supported the experimental those based on NMR analyses using dimethoxyethane and triglyme solutions. Molecular lengths (l) of $(\mathrm{tg^+t})_x$, $(\mathrm{tg^+g^-})_x$ and $(\mathrm{g^+g^+g^+})_x$ conformers having higher x values significantly decreased with increasing h values. Such contraction with hydration, however, was independent of $\Delta E_{c(g)}$ values of each conformer.

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Introduction

Poly(ethylene oxide) (PEO) has unique properties because it possesses electron-releasing heteroatom (O) in the skeletal chain. Such properties, including specific affinity to substrate and solubility of inorganic salt, have been employed in the advancement of biomaterials and solid polymer electrolytes [1], etc. These properties are often affected by conformational characteristics such as trans/gauche preferences, which depend on environmental factors such as temperature, solvent, etc. The conformational analyses of these polymers, therefore, are essential in the molecular design towards various applications.

X-ray diffraction (XRD) analyses [2, 3] have shown that the structure of a PEO crystal in the original un-stretched state is a 7/2 helix [2], with a repeating tgt (t: trans, g: gauche) conformation for the O–C, C–C, and C–O bonds, respectively. In the stretched state, the structure transforms into a planar zigzag ttt conformation [3]. In the case of the PEO solutions, based on NMR analyses using dimethoxyethane (DME) [4, 5] and triglyme (TGL) [6] as models of PEO, it has been reported that the preferences to adopt a gauche-conformation (gauche preference) of the C–C bonds increases with higher permittivity (ε) of solvents. The conformation of PEO, in this manner, specifically depends on environmental factors. Unfortunately, detailed understandings of these environmental effects are complex and have yet to be clarified.

To complement the experimental observations in the conformational analyses of PEO, computational chemistry is employed. Pioneering works, involving a rotational isomeric state model (RIS), was reported by Mark et al. [7, 8]. More recently, studies using molecular mechanics (MM) and molecular dynamics (MD) have been reported [9, 10]. Furthermore, in contrast to the RIS, MM, and MD methods, recent studies involve quantum chemical calculations method (QCC). Conformational analysis in the gaseous phase using QCC has been reported for DME [5, 11, 12] and its oligomers [5, 6] (as models of PEO). Comparable studies in the liquid phase, however, are little. Smith et al. [13] have reported the potential study of DME in aqueous solution (mono-hydrate model) using QCC.

We have reported the conformational analyses of EO oligomers, as a model of PEO, in the gaseous [14] and liquid phases [15] using QCC. In the case of liquid phases [15], the conformational energies of 1 to ~4-mers were estimated by IPCM method [16] using the permittivity: ε ($\varepsilon = 0$–80.1: water) of solvents, and the results were in good agreement with experimental those. In this paper, in order to estimate in more detail with the conformations in hydrate state, the hydrate models for EO oligomers (1 to ~8-mers) were investigated. The energies and structures optimized for these hydrate models were examined using QCC, and the conformational characteristics of hydrated EO oligomers were discussed.

Quantum chemical calculations (QCC)

Designations of non-hydrated oligomer models (EO-*x*)

For the oligomer models (single chain) of PEO, EO *x*-mers ($x = 1$–8 monomer units) capped with methoxy and methyl groups were used. The specified structures are given in Table 1. The structural example designated for EO-1 is given in Fig. 1. For each oligomer, the conformation $(\tau_n\tau_{n+1}\tau_{n+2})_x$ (τ: dihedral angles, n: sequential number of atoms along a skeletal chain) are designated as $(\mathrm{ttt})_x$, $(\mathrm{ttg}^+)_x$, $(\mathrm{tg}^+\mathrm{t})_x$, $(\mathrm{tg}^+\mathrm{g}^+)_x$, $(\mathrm{tg}^+\mathrm{g}^-)_x$, and $(\mathrm{g}^+\mathrm{g}^+\mathrm{g}^+)_x$ (t, trans; g^+ and g^-, gauche) as the combination of τ that are repeated for the units of O–C, C–C, and C–O bonds. Every dihedral angle was independently assigned along the skeletal chains, and the values of 180° (t), +60° (g^+), or −60° (g^-) were used.

Table 1 Non-hydrate models

No.	Monomer unit number: *x*	Molecular models	Molecular weights
EO-1	1	$CH_3O–(CH_2CH_2O)_1–CH_3$[a]	90.14
EO-2	2	$CH_3O–(CH_2CH_2O)_2–CH_3$	134.20
EO-3	3	$CH_3O–(CH_2CH_2O)_3–CH_3$[b]	178.26
EO-4	4	$CH_3O–(CH_2CH_2O)_4–CH_3$	222.32
EO-5	5	$CH_3O–(CH_2CH_2O)_5–CH_3$	266.38
EO-8	8	$CH_3O–(CH_2CH_2O)_8–CH_3$	398.56

[a] Dimethoxyethane (DME)

[b] Triglyme (TGL)

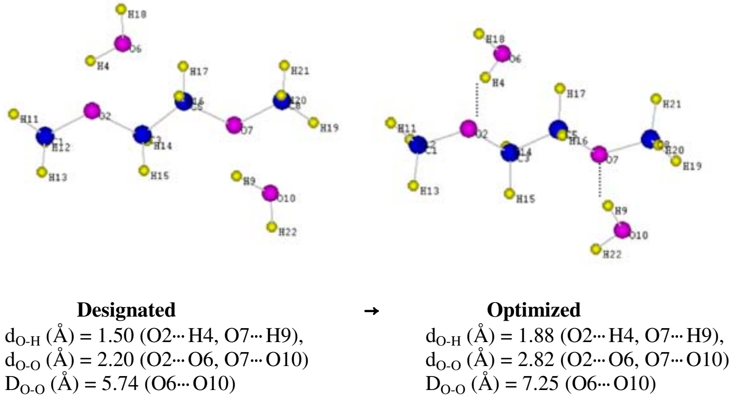

Fig. 1 Structure examples designated and optimized for EO-1 (conformation: $(\mathrm{ttt})_1$, $h = 1$, by RHF/6-31G). The conformations were defined by $(\tau_n\tau_{n+1}\tau_{n+2})_x$, where τ_n, τ_{n+1}, and τ_{n+2} are the dihedral angles (°) for O–C, C–C, and C–O bonds, respectively, and x is monomer unit number. For example, in the figure, the value of 180° was designated as the dihedral angles for O2–C3, C3–C5, and C5–O7 bonds. The hydrate distance, $d_{\mathrm{O–H}}$ (Å), was defined by the distance of hydrogen bond in O···HOH′; for examples, O2···H4 and O7···H9 in the figure

Designations of hydrate oligomer models

For the hydrate models, EO-*x* hydrated to the structure optimized for non-hydrate model were used. The optimizations of non-hydrate models were carried out firstly by RHF/STO-3G, and then RHF/6-31G method which is the same method as used in optimizations of hydrate models; for more detail, refer following section. Each water molecule was located to an ether–oxygen. The specified models are given in Table 2. Hydrate ratio (h) was defined by $H_2O_{mol}/O_{mol\ in\ oligomer}$, and the values of 0–1 were used. The structural example ($h = 1$) designated for EO-1 is given in Fig. 1. Hydrate distance: $d_{O–H}$ (Å) was defined by the un-bonded distance between the ether–oxygen (O) and the hydrogen (H) in water molecule (HOH′), in which H atom is closer than H′ atom to the ether–oxygen as shown in Fig. 1. The value of 1.5 Å was used as $d_{O–H}$, except for otherwise noted.

Conformational analyses

Conformational analyses were carried out for each model using QCC via the Gaussian 03 W (Gaussian Inc.) program [17]. For structural optimizations, RHF/6-31G was used as the calculation method. The energy of hydrated oligomer with waters, E_h (Hartree, 1 Hartree = 627.51 kcal/mol) was calculated for the optimized structure. The conformational energy (E_c) of hydrated oligomer was calculated via Eqs 1 and 2.

$$E_c = E_h - \sum E_w \tag{1}$$

Table 2 Hydrate models

Oligomers	Hydrate models[a]	Number of ether–oxygen: a	Number of waters: b	Hydrate ratio: h (b/a)
EO-1	–$\underline{\mathrm{O}}$–O–	2	1	0.500
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	2	2	1.000
EO-2	–O–$\underline{\mathrm{O}}$–O–	3	1	0.333
	–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–	3	2	0.667
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	3	3	1.000
EO-3	–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–	4	2	0.500
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	4	4	1.000
EO-4	–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–	5	2	0.400
	–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$	5	3	0.600
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	5	5	1.000
EO-5	–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–	6	3	0.500
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	6	6	1.000
EO-8	–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–$\underline{\mathrm{O}}$–O–	9	4	0.444
	–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–$\underline{\mathrm{O}}$–	9	9	1.000

[a] O and $\underline{\mathrm{O}}$ show non-hydrated and hydrayted units (OCH_2CH_2), respectively

$$\sum E_{\mathrm{w}} = N_{\mathrm{w}(n)}E_{\mathrm{w}(n)} + N_{\mathrm{w}(h)}E_{\mathrm{w}(h)}\left(N_{\mathrm{w}(n)} + N_{\mathrm{w}(h)} = N_{\mathrm{w}}\right) \tag{2}$$

where $\sum E_{\mathrm{w}}$ is total energy of the hydrated water molecules. $N_{\mathrm{w}(n)}$ and $N_{\mathrm{w}(h)}$ are number of non-hydrogen bonded (longer than 3 Å of O···O distance, $D_{\mathrm{O–O}}$) and hydrogen bonded (shorter than 3 Å of $D_{\mathrm{O–O}}$) water molecules estimated for optimized structures, respectively. $E_{\mathrm{w}(n)}$ and $E_{\mathrm{w}(h)}$ are energies calculated for non-hydrogen and hydrogen bonded water molecules by RHF/6-31G, respectively. $E_{\mathrm{w}(n)}$ and $E_{\mathrm{w}(h)}$ values are given in Table 3.

The conformations were specified based on IUPAC [18] as follow: τ_{n} of trans ($\mathrm{t}^{\pm}$) and gauche ($\mathrm{g}^{\pm}$) are ±120 to ±180° and ±0 to ±120°, respectively. Lengths of oligomer molecules were defined by l (Å), where l is un-bonded distance between the terminal oxygen atoms. In Fig. 1, for example, l is given as that between O2 and O7.

Results and discussion

Effects of designations on the optimized structures

The influences of the designated hydrate distance on the optimized structures were examined using EO 1-mer models [EO-1, conformation: $(\mathrm{ttt})_1$]. The structural optimizations were carried out using the RHF/6-31G method with structures that were optimized in each non-hydrate model. The results for hydrate ratio: $h = 1$ are shown in Table 4. As shown in Table 4, the hydrate distances ($d_{\mathrm{O–H}}$, and $d_{\mathrm{O–O}}$: un-bonding distance between ether–oxygen and water's oxygen) optimized for some models were constant independent of the designated $d_{\mathrm{O–H}}$ values (1.5–2.3 Å). The locations of water molecules in the optimized structure were almost same as those in the designated structure (refer Fig. 1). As shown in Table 4, the optimized $d_{\mathrm{O–O}}$ values fell within those which has been reported as distances of oxygen atoms in water dimer with hydrogen bonding (2.74 in regular ice [19], 2.85 in liquid [19], and 2.98 Å in vapor [20, 21]). Therefore, it will be confirmed that all water molecules are hydrated to each ether–oxygen with hydrogen bonding as shown in Fig. 1. The

Table 3 Energies (E_{w}, HF) calculated for water molecules by RHF/6-31G

n^{a}	$E^{\mathrm{b}}_{\mathrm{w}(n)}$	$E^{\mathrm{c}}_{\mathrm{w}(h)}$	n^{a}	$E^{\mathrm{b}}_{\mathrm{w}(n)}$	$E^{\mathrm{c}}_{\mathrm{w}(h)}$	n^{a}	$E^{\mathrm{b}}_{\mathrm{w}(n)}$	$E^{\mathrm{c}}_{\mathrm{w}(h)}$
1	−75.9854		4	−303.9416	−303.9850	7	−531.8978	−531.9939
2	−151.9708	−151.9826	5	−379.9274	−379.9876	8	−607.8832	−607.9973
3	−227.9562	−227.9830	6	−455.9128	−455.9907	9	−683.8686	−684.0007

[a] Units number of water molecules

[b] Energies of non-hydrogen bonded water molecules

[c] Energies for linear hydrogen bonded structures which are consisted of n units of sequential water molecules

Table 4 Effects of designated hydrate distances on the structures optimized for hydrate models (EO-1: CH_3–O1–CH_2CH_2–O2–CH_3, conformation: $(ttt)_1$, $h = 1$. Waters: H1O1H1 and H2O2H2. Calculations: RHF/6-31G)

Designated distances				Optimized				
Hydrated (d, Å)		Water–Water (D, Å)		Hydrated distances (d, Å)		Water–Water (D, Å)		E_c (HF)
$d_{O\text{–}H}$	$d_{O\text{–}O}$	$D^{a}_{O1\text{–}H2}$	$D_{O1\text{–}O2}$	$d_{O1\text{–}H1}/d_{O1\text{–}O1}$	$d_{O2\text{–}H2}/d_{O2\text{–}O2}$	$D^{a}_{O1\text{–}H2}$	$D_{O1\text{–}O2}$	
1.5	2.20	4.94	5.74	1.88/2.82	1.88/2.82	6.30	7.25	−306.8649
1.9	2.57	5.50	6.39	1.89/2.82	1.88/2.82	6.30	7.25	−306.8649
2.3	2.95	6.21	7.07	1.88/2.82	1.88/2.82	6.29	7.25	−306.8649

[a] "H2" in "O1-H2" shows a hydrogen atom neighboring to O1 atom

conformational energies (E_c) were constant independent of the designated $d_{O\text{–}H}$ values as shown in Table 4. Taking into account these results, the value of 1.5 Å was used as $d_{O\text{–}H}$ value in all designations herein after.

Hydrate effects on the energy of each conformer

The conformational analyses for the hydrated EO oligomer (EO-x, $x = 1$–8) models were carried out using the RHF/6-31G method with optimized structures in non-hydrate models. The conformational energies (E_c) were calculated via Eqs 1 and 2. The difference of energy between the $(ttt)_x$ conformer in non-hydrate states and the other conformers, ΔE_c (kcal/m.u., m.u.: monomer units), were calculated for all models. The results are given in Table 5. In Table 6, the examples of calculations for E_c using the $(tg^{+}t)_1$ conformer models (EO-1, $h = 0$–1) are shown. In Fig. 2, the example of structure optimized for $(tg^{+}t)_1$ conformer (EO-1, $h = 1$) is shown. The two water molecules in the $(tg^{+}t)_1$ conformer were in hydrogen bonding with each other ($D_{O\text{–}O} = 2.90$ Å) as shown in Fig. 2, while those in the $(ttt)_1$ conformer were not in hydrogen bonding ($D_{O\text{–}O} = 7.25$ Å, Fig. 1).

The hydrate effects on the energy of each conformer were examined. The hydrate energy, $\Delta\mu_h$ (kcal/m.u.), was defined as the difference of the conformational energy (E_c) of hydrated oligomer and non-hydrated oligomer. In Fig. 3, the $\Delta\mu_h$ values (based on the values in non-hydrates) are plotted against the hydrate ratios (h). The plots fell on a straight line with a negative slope and the slope became less steep with increasing values of x. These results indicate that the hydrate effect with hydrogen bonding contributes to the stability of conformer, and such effects are diluted with increasing monomer units. In our previous paper [15], in which the conformational analyses for the solutions of EO oligomers (1–4 mers) were carried out by QCC using the permittivities of solvents (IPCM method [16]), the energy of each conformer decreased with increasing values of the permittivities: ε ($\varepsilon = 0$–80.1 of water), and such effects appeared to relate to the electrostatic effect with solvents. It can be estimated that the results in present study using hydrate ratios ($h = 0$–1) are corresponding to those calculated using the permittivity ($\varepsilon = 0$–80.1), and all conformers stabilize by electrostatic effect with increases of hydrate ratios.

Table 5 Conformational energy differences (ΔE_c) of EO 1 to ~8-mers (by RHF/6-31G)

Conformers	h	EO-1		EO-2		EO-3		EO-4		EO-5		EO-8	
		$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]	$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]	$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]	$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]	$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]	$N_{\mathrm{w}(n)}/N_{\mathrm{w}(h)}$	ΔE_c[a]
$(\mathrm{ttt})_x$	0	0/0	0[b]	0/0	0[c]	0/0	0[d]	0/0	0[e]	0/0	0[f]	0/0	0 [g]
	0.4–0.7	1/0	−7.66	2/0	−7.28	2/0	−4.83	3/0	−5.74	3/0	−4.28	4/0	−3.43
	1	2/0	−14.4	3/0	−10.5	4/0	−9.22	5/0	−9.30	6/0	−8.21	9/0	−7.51
$(\mathrm{tg^+t})_x$	0	0/0	2.57	0/0	2.38	0/0	2.18	0/0	2.32	0/0	2.31	0/0	2.29
	0.4–0.7	1/0	−7.53	2/0	−9.07	2/0	−5.00	3/0	−6.37	3/0	−5.65	4/0	−3.84
	1	0/2	−11.8	0/3	−7.81	1/3	−8.55	5/0	−9.15	6/0	−7.39	9/0	−8.84
$(\mathrm{tg^+g^-})_x$	0	0/0	1.38	0/0	1.26	0/0	1.19	0/0	1.13	0/0	1.09	0/0	1.69
	0.4–0.7	1/0	−6.34	0/2	−6.12	0/2	−3.41	1/2	−4.52	0/3	−2.91	0/4	−2.20
	1	2/0	−16.1	1/2	−11.0	2/2	−10.1	3/2	−8.85	6/0	−7.39	4/5	−8.31
$(\mathrm{ttg^+})_x$	0	0/0	1.88	0/0	1.73	0/0	1.72	0/0	1.71	0/0	1.69	0/0	1.69
	0.4–0.7	1/0	−7.91	2/0	−6.40	2/0	−4.71	3/0	−4.77	3/0	−3.79	4/0	−3.84
	1	2/0	−16.0	3/0	−10.8	4/0	−9.58	5/0	−8.97	4/2	−7.83	9/0	−8.97
$(\mathrm{tg^+g^+})_x$	0	0/0	4.77	0/0	4.67	0/0	4.27	0/0	3.98	0/0	4.67	0/0	3.29
	0.4–0.7	1/0	−6.34	0/2	−6.24	0/2	−3.37	–[h]	–[h]	–[h]	–[h]	–[h]	–[h]
	1	–[i]	–[i]	0/3	−7.94	–[h]	–[h]	–[h]	–[h]	–[h]	–[h]	–[h]	–[h]
$(\mathrm{g^+g^+g^+})_x$	0	0/0	4.58	0/0	4.30	0/0	4.25	0/0	4.22	0/0	4.19	0/0	4.16
	0.4–0.7	1/0	−4.89	2/0	−5.84	2/0	−2.15	3/0	−3.18	3/0	−1.52	4/0	−0.60
	1	2/0	−15.1	3/0	−10.7	2/2	−9.12	5/0	−7.98	4/2	−8.31	5/2,2	−6.43

[a] Unit: kcal/m.u., Calculated based on the energies (E_c) of $(\mathrm{ttt})_x$ conformers in $h = 0$

[b] $E_\mathrm{c} = -306.8419$ (HF)

[c] $E_\mathrm{c} = -459.6888$ (HF)

[d] $E_\mathrm{c} = -612.5358$ (HF)

[e] $E_\mathrm{c} = -765.3827$ (HF)

[f] $E_\mathrm{c} = -918.2296$ (HF)

[g] $E_\mathrm{c} = -1376.7704$ (HF)

[h] Optimizations could not been carried out because of the “close contacts” of distances between un-bonded atoms in each designation

[i] Non-converged in structural optimization

Table 6 Examples of calculations for conformational energy (E_c) (Model: EO-1 $(tg^+t)_1$. Calculation: RHF/6-31G)

h	N_w	E_h (HF)[a]	Water molecules					E_c (HF, $E_c = E_h - \sum E_w$)
			Non H-bonded		H-bonded		$\sum E_w$	
			$N_{w(n)}$	$E_{w(n)}$ (HF)	$N_{w(h)}$	$E_{w(h)}$ (HF)		
0	0	−306.8378	0	0	0	0	0	−306.8378
0.5	1	−382.8393	1	−75.9854	0	0	−75.9854	−306.8539
1	2	−419.2077	0	0	2[b]	−151.9826[b]	−151.9826	−306.8608

[a] E_h: gross energy calculated for hydrated oligomers with waters

[b] Estimated for linear hydrogen bonded structure which are consisted of sequential water molecules (2 units). Refer Table 3

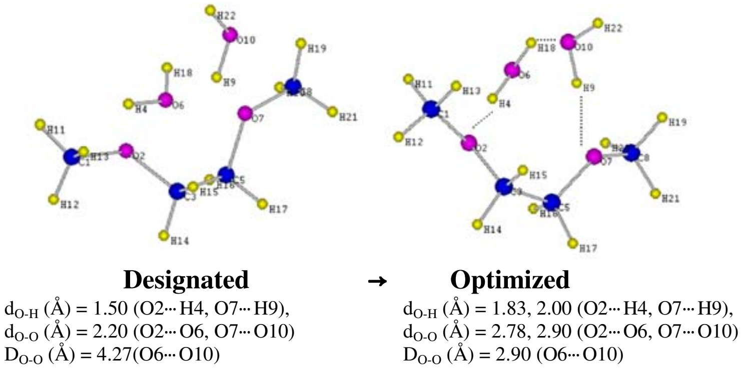

Fig. 2 Structures designated and optimized for $(tg^+t)_1$ conformer: EO-1, $h = 1$ (calculation: RHF/6-31G: hydrogen bonds)

As shown in Table 5, the calculations for almost all $(tg^+g^+)_x$ conformers, except for the cases of $h = 0$, could not be carried out because of the “close contacts” in designations or the “non-converged”. It seems to be that the $(tg^+g^+)_x$ conformers have unfavorable structure to the crowding effect by hydration.

Hydrate effects on trans/gauche preferences

The hydrate effects on the trans/gauche preferences of each conformer were examined. The gauche preference energy, $\Delta E_{c(g)}$ (kcal/m.u.), was defined as the difference of ΔE_c between a given oligomer and the $(ttt)_x$ oligomer. In Fig. 4, the $\Delta E_{c(g)}$ values are plotted against the number of monomer units (x). In non-hydrate ($h = 0$), the $(ttt)_x$ conformer was the most stable independent of x. This result means that the C–C bond of EO conformer prefers the trans conformation (trans preference) in non-hydrate. This result was in agreement with the other calculation results reported previously [5, 6, 12]. From an energetic aspect, this result does not

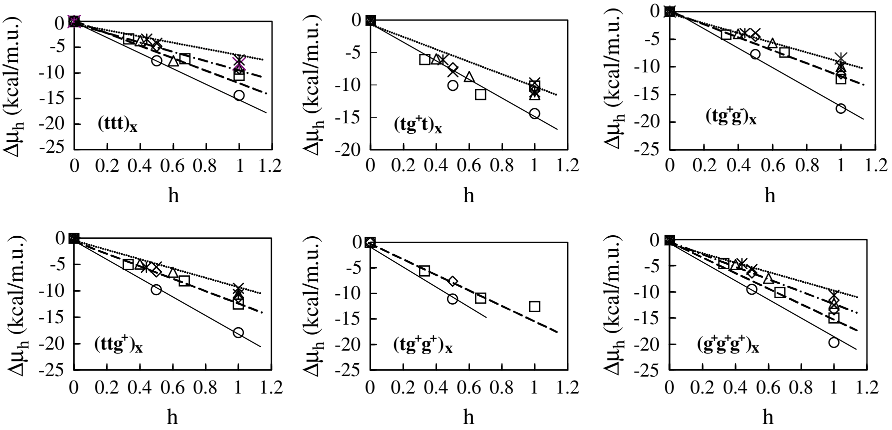

Fig. 3 Plots of hydrate energies ($\Delta\mu_h$, kcal/m.u.) against hydrate ratios (h) in EO oligomers. *Open circle* 1 mer, *open square* 2 mer, *open diamond* 3 mer, *open triangle* 4 mer, *multiple symbol* 5 mer, *asterisk* 8 mer

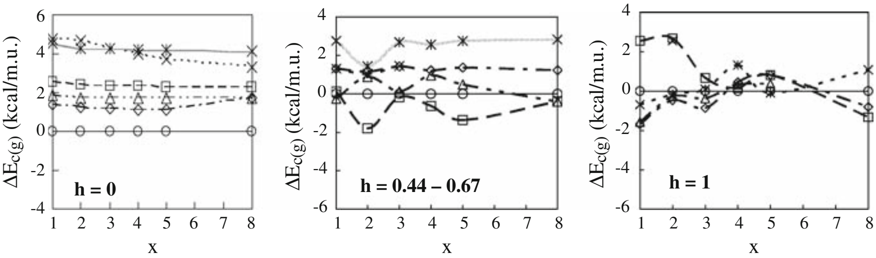

Fig. 4 Plots of gauche preference energies ($\Delta E_{c(g)}$, kcal/m.u.) against number of monomer units (x) in EO oligomers. *Open circle* $(ttt)_x$, *open square* $(tg^+t)_x$, *open diamond* $(tg^+g^-)_x$, *open triangle* $(ttg^+)_x$, *multiple symbol* $(tg^+g^+)_x$, *asterisk* $(g^+g^+g^+)_x$

correspond to the conformation (tgt) observed for PEO crystals in the normal state [2] but correspond to that (ttt) in the stretched state [3]. The details of the calculated results remain still unclear.

In hydrate state, however, the $(tg^+t)_x$ conformers in $h = 0.44$–0.67 were the most stable independent of monomer units number as shown in Fig. 4. These results indicate that EO oligomer prefers gauche conformation of C–C bonds with hydration. Based on conformational studies of EO oligomers in solutions based on NMR analyses using dimethoxyethane (DME) [4, 5] and triglyme (TGL) [6], it has been reported that the gauche preference of the C–C bonds increases with higher permittivity (ε) of solvents. The results estimated in the present study support these experimental those. In $h = 1$, the $(tg^+t)_8$ conformer (EO-8) was the most stable ($\Delta E_{c(g)} = -1.3$ kcal/m.u.), but the $\Delta E_{c(g)}$ values of $(tg^+t)_x$ conformers having x values of 1 and 2 are significantly large as shown in Fig. 4. These results in $h = 1$ seem to be connect with or without the formation of hydrogen bond between water molecules around the $(tg^+t)_x$ conformers. In the $(tg^+t)_x$ conformers, as shown in

Table 5, such hydrogen bondings were not estimated in hydrate ratios of 0.4–0.7 independent of *x* values. On the other hand, in the hydrate ratio of 1, such hydrogen bondings were estimated in low *x* values ($x = 1$–3). The formation of hydrogen bond between the water molecules neighboring an ether–oxygen will result in weakening the hydrate effect because of increase of the hydrate distance.

Hydrate effects on the structures of conformers

The hydrate effects on the conformational structures optimized for EO 1–8 mers were examined. The dihedral angles (τ_n) of C–C bonds and molecular lengths (l) of each conformer are shown in Tables 7 and 8.

Table 7 Structures optimized for EO 1- and 2-mers by RHF/6-31G

Conformers	EO-1					EO-2					
	h	τ_n (°)[a]	l (Å)[b]	Hydrate distances: *d* (Å)[c]		*h*	τ_n (°)[a] (average)	l (Å)[b]	Hydrate distances: *d* (Å)[c]		
				d_{O-H}	$d_{O'-H}$				d_{O-H}	$d_{O'-H}$	$d_{O''-H}$
$(ttt)_x$	0	180.0	3.59	–	–	0	180.0	7.11	–	–	–
	0.5	180.0	3.59	1.88	–	0.67	180.0	7.14	1.88	–	1.89
	1	180.0	3.61	1.88	1.88	1	180.0	7.14	1.89	1.90	1.89
$(tg^+t)_x$	0	78.8	2.95	–	–	0	78.1	5.80	–	–	–
	0.5	74.2	2.91	1.87	–	0.67	67.4	5.17	1.86	–	1.86
	1	74.7	2.91	1.83	2.00[d]	1	70.2	5.31	2.11[d]	1.89	1.84
$(tg^+g^-)_x$	0	74.4	2.99	–	–	0	73.3	5.55	–	–	–
	0.5	74.4	2.99	1.86	–	0.67	71.7	5.07	2.13[d]	–	1.80
	1	74.9	3.01	1.85	1.84	1	68.8	4.88	2.10[d]	1.81	1.77
$(ttg^+)_x$	0	−179.5	3.63	–	–	0	179.9	6.81	–	–	–
	0.5	−179.0[e]	3.60	1.86	–	0.67	177.7	6.77	1.86	–	1.86
	1	180.0[e]	3.61	1.86	1.86	1	175.5	6.10	1.86	1.86	1.86
$(tg^+g^+)_x$	0	71.5	2.97	–	–	0	57.0	4.61	–	–	–
	0.5	68.2	2.94	2.04	–	0.67	69.6	4.65	1.99	–	3.42[d]
	1	–[f]	–[f]	–[f]	–[f]	1	66.2	5.39	1.98	4.08[d]	1.90
$(g^+g^+g^+)_x$	0	43.8	2.85	–	–	0	43.2	5.20	–	–	–
	0.5	45.8	2.86	1.84	–	0.67	45.5	5.39	1.82	–	1.82
	1	50.8	2.90	1.82	1.82	1	45.9	5.52	1.83	1.79	1.82

[a] Dihedral angles of C–C bonds

[b] Molecular lengths (un-bonded distances between the terminal oxygen atoms

[c] The un-bonded distances between the ether–oxygen atom (O, O′, or O″) and the water–hydrogen atom (H) neighboring ether–oxygen atom, Refer Fig. 2

[d] The formation of hydrogen bond (under 3 Å of D_{O-O}) between water molecules was estimated. Refer Table 5

[e] Transferred from $(ttg^+)_1$ into $(ttt)_1$ conformer by optimization

[f] The optimizations could not been carried out because of the "close contacts" of distances between un-bonded atoms in designation

Table 8 Structures optimized for EO 3 to ~5-mers and EO-8 mers by RHF/6-31G

Conformers	EO-3			EO-4			EO-5			EO-8		
	h	τ_n (°)[a]	l (Å)[b]	h	τ_n (°)[a]	l (Å)[b]	h	τ_n (°)[a]	l (Å)[b]	h	τ_n (°)[a]	l (Å)[b]
$(ttt)_x$	0	180.0	10.7	0	180.0	14.2	0	180.0	17.8	0	180.0	28.5
	0.5	180.0	10.7	0.6	179.5	14.3	0.5	180.0	17.8	0.44	180.0	28.4
	1	180.0	10.7	1	179.6	14.3	1	180.0	17.9	1	180.0	28.6
$(tg^{+}t)_x$	0	77.9	8.64	0	78.0	11.5	0	77.9	14.4	0	77.8	23.0
	0.5	72.7	8.37	0.6	66.4	9.81	0.5	70.6	12.8	0.44	71.1	18.4
	1	67.2	7.40	1	71.1	11.1	1	64.2	12.4	1	66.4	20.5
$(tg^{+}g^{-})_x$	0	73.0	8.38	0	72.8	11.1	0	72.7	13.9	0	72.5	22.1
	0.5	71.7	7.67	0.6	71.8	9.75	0.5	70.5	10.7	0.44	70.9	12.8
	1	73.2	7.62	1	72.8	10.3	1	78.3	14.3	1	73.9	6.28
$(ttg^{+})_x$	0	179.9	9.83	0	179.8	13.1	0	179.8	16.5	0	179.8	26.2
	0.5	179.2	10.1	0.6	179.4	13.0	0.5	178.8	15.3	0.44	70.5[c]	17.2
	1	176.2	8.99	1	179.8	13.1	1	173.3	14.0	1	63.1[c]	20.1
$(tg^{+}g^{+})_x$	0	57.8	4.89	0	57.6	5.50	0	57.6	7.29	0	57.6	10.8
	0.5	63.7	6.26	0.6	–[d]	–[d]	0.5	–[d]	–[d]	0.44	–[d]	–[d]
	1	–[d]	–[d]	1	–[d]	–[d]	1	–[d]	–[d]	1	–[d]	–[d]
$(g^{+}g^{+}g^{+})_x$	0	43.1	7.54	0	43.1	10.1	0	43.1	12.7	0	43.1	20.2
	0.5	44.9	7.80	0.6	45.2	10.4	0.5	44.9	12.9	0.44	44.9	20.5
	1	54.9	7.20	1	48.6	10.6	1	53.0	8.48	1	49.2	17.5

[a] Averages of τ_n values for C–C bonds

[b] Molecular length (un-bonded distance between the terminal oxygen atoms

[c] Transferred from $(ttg^{+})_8$ into $(tg^{+}t)_8$ conformer by optimization

[d] The optimizations could not been carried out because of the "close contacts" of distances between un-bonded atoms in designation

In Table 7 are shown the hydrate distances, $d_{O\text{–}H}$ (Å), of EO-1 and EO-2. As shown in Table 7, the $d_{O\text{–}H}$ values become larger by the formation of hydrogen bond between water molecules neighboring an ether–oxygen (see the subscript "*d*" data in Table 7, and refer Table 5). The values of $d_{O\text{–}H}$ changed from 1.8–2.0 to 2.1–4.1 Å by the formation of hydrogen bond. It can be considered that such formation results in weakening an inter-molecular interaction between oligomer and water molecule because of increase of the hydrate distance ($d_{O\text{–}H}$).

One of the structural changes by hydration must be a molecular length due to the changes of τ_n values. In Fig. 5, the ratio ($\Delta l/l_0$, %) of the change of the length (Δl) to the length of the non-hydrated oligomer (l_0) is plotted against h value. In Fig. 6, the examples of structures optimized for the hydrated $(ttt)_8$ and $(tg^{+}t)_8$ conformers of EO-8 ($h = 1$) are shown compared with each non-hydrate conformer, respectively. As shown in Fig. 5 and 6, the $(tg^{+}t)_x$ and $(tg^{+}g^{-})_x$ conformers having higher number of monomer units (x) significantly contracted with increases of h values, and the $\Delta l/l_0$ values of the $(tg^{+}t)_8$ and $(tg^{+}g^{-})_8$ conformers were -20% ($h = 0.44$) and -72% ($h = 1$), respectively. On the other hand, in the $(ttt)_x$ and $(ttg^{+})_x$ conformers, such contractions are small. These results indicate that the gauche

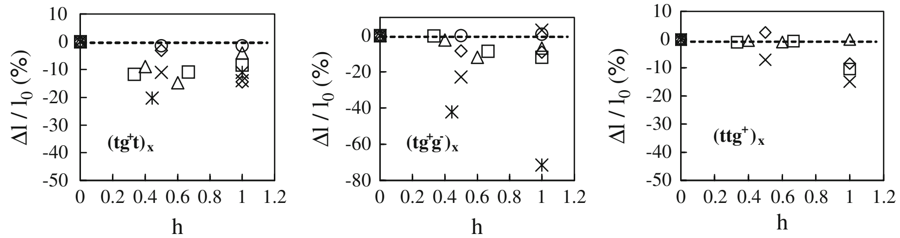

Fig. 5 Plots of the rates of molecular length's change ($\Delta l/l_0$, %) against hydrate ratios (*h*) in EO oligomers. *Open circle* 1 mer, *open square* 2 mer, *open diamond* 3 mer, *open triangle* 4 mer, *multiple symbol* 5 mer, *asterisk* 8 mer

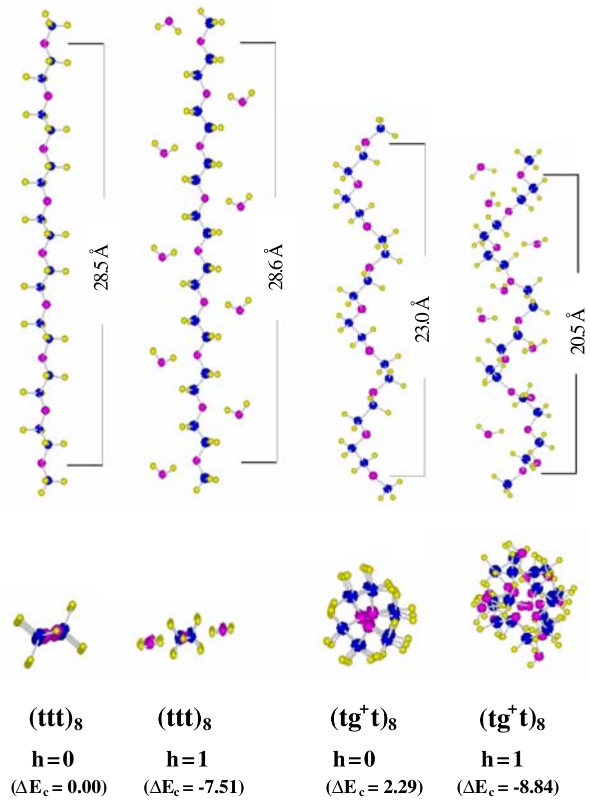

Fig. 6 Structures of (ttt)$_8$ and (tg$^+$t)$_8$ conformers optimized for EO-8 (non-hydrated or hydrated) by RHF/6-31G. Upper and lower figures show the stereo oblique and chain axis projections, respectively

structure of C–C bond becomes to be more contracted structure by hydration. In Fig. 7, the ratios ($\Delta l/l_0$, %) of all conformers except for (ttt)$_x$ are plotted against the gauche preference energies [$\Delta E_{c(g)}$]. Many conformers are contract with hydration independent of *h* values. These results seem to be related to that EO oligomer has not the strong intra-molecular interaction, for example, as NH···H hydrogen bonding

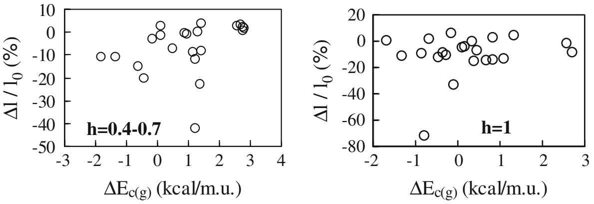

Fig. 7 Plots of the rates of molecular length's change ($\Delta l/l_0$, %) against gauche preference energies ($\Delta E_{c(g)}$) in hydrated EO oligomers (EO-1–EO-8)

in poly ethylene imine [22]. The values of $\Delta l/l_0$, however, are independent of $\Delta E_{c(g)}$. This result means that the contract structure with hydration is not necessarily stable from the aspect of its structural energy.

Conclusions

Hydrate effects on the conformations of ethylene oxide oligomers were examined using quantum chemical calculations (QCC). Hydrate energies ($\Delta\mu_h$) estimated from conformational energies (E_c) for each conformer were negative and linearly decreased with the increase of hydrate ratios (h), and all conformers were stabilized by hydrations. The $(ttt)_x$ conformers were most stable in non-hydrates. However, in hydrates, the $(tg^+t)_x$ conformers were the most stable in $h = 0.44$–0.67, and the $(tg^+t)_8$ conformer was most stable in $h = 1$. These results seemed to be connect to the gauche preference of EO oligomers with hydration, and supported the experimental those based on NMR analyses using dimethoxyethane and triglyme solutions. Molecular lengths of conformers having gauche structures of C–C bonds significantly decreased with increasing hydrate ratios and monomer unit number, and the gauche structures of C–C bonds became to be more contracted those by hydration. This result seems to be related to that EO oligomer has not the strong intra-molecular interaction as NH···H in ethylene imine oligomer. Such contractions by hydration, however, were independent of its conformational stability.

References

1. Ries ME, Brereton MG, Cruickshank JM, Klein PG, Ward IM (1995) Macromolecules 28:3282
2. Takahashi Y, Tadokoro H (1973) Macromolecules 6:672
3. Takahashi Y, Sumita I, Tadokoro H (1973) J Polym Sci Polym Phys Ed 11:2113
4. Tasaki K, Abe A (1985) Polym J 17:641
5. Sasanuma Y, Ohta H, Touma I, Matoba H, Hayashi Y, Kaito A (2002) Macromolecules 35:3748
6. Sasanuma Y, Sugita K (2006) The attractive Gauche effect of ethylene oxides. Polym J 38:983
7. Mark JE, Flory PJ (1965) The configuration of the polyoxyethylene chain. J Am Chem Soc 87:1415
8. Mark JE, Flory PJ (1966) Dipole moments of chain molecules. I. Oligomers and polymers of oxyethylene. J Am Chem Soc 87:3702
9. Geun G, Breitkreutz J (1994) Structures and molecular attributes of polyethylene glycols. Pharmazie 49:562

10. Dong H, Hyun JK, Durham C, Wheeler RA (2001) Polymer 42:7809
11. Tsuzuki S, Uchimaru T, Tanabe K, Hirano T (1993) J Phys Chem 97:1346
12. Smith GD, Yoon DY, Jaffe RL (1993) Macromolecules 26:5213
13. Smith GD, Borodin O, Bedrov D (2002) J Comput Chem 23:1480
14. Kobayashi M, Sato H (2008) Conformational analysis of ethylene oxide and ethylene imine oligomers by quantum chemical calculations. Polym J 40:343
15. Kobayashi M, Sato H (2008) Conformational analysis of ethylene oxide and ethylene imine oligomers by quantum chemical calculations: solvent effects. Polym Bull 61:529
16. Foresman JB, Keith TA, Wiberg KB, Snoonian J, Frisch MJ (1996) J Phys Chem 100:16098
17. Gaussian 03 User's Reference (2003) Gaussian Inc., PA, USA
18. Lide DR (2001) Handbook of chemistry and physics. 82nd edn. CRC Press LLC, London, pp 8–127
19. Ludwig R (2001) Water: from clusters to the bulk. Angew Chem Int Ed 40:1808
20. Dyke TR, Mack KM, Muenter JS (1977) J Chem Phys 66:498
21. Odutola JA, Dyke TR (1980) J Chem Phys 72:5062
22. Sasanuma Y, Hattori S, Imazu S, Ikeda S, Kaizuka T, Iijima T, Sawanobori M, Azam MA, Law RV, Steinke JHG (2004) Macromolecules 37:9169