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Conformational analysis of ethylene oxide and ethylene imine oligomers by quantum chemical calculations: solvent effects

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Summary

Conformational analyses using quantum chemical calculations were carried out for 1- to 4-mers of ethylene oxide (EO) and ethylene imine (EI) oligomer models (EO-x and EI-x, x = 1 - 4) in the liquid phase using four solvents (permittivity: $\varepsilon = 2.0 \sim 80.1$). The results were compared against those obtained in the gaseous phase. The calculations involved either RHF/6-31+G(d,p) or B3LYP/6-31G(d) // SCRF/IPCM, based on the observed and calculated results for the energy difference between *trans*- and *cis*-dichloroethane. The conformations repeated for a unit of X-C, C-C and C-X bonds (X: O or N) were examined. For both oligomers, the energies of every conformer decreased with increasing ε values, and were linear against the Kirkwood function ($K_f = (\varepsilon-1)/(2\varepsilon+1)$). For the EO oligomers, the $(ttt)_x$ conformer was most stable in the gaseous phase. In liquid phases, however, the preference for the gauche-conformation (gauche preference) of the C-C bonds increased with higher values of ε. In the case of EO-3, the $(tg^+t)_x$ conformer was most stable above an ε value of 8.9, which were in good agreement with those observed for triglyme solutions using NMR analysis. For the EI oligomers, the $(tg^+t)_x$ conformer was most stable in either gaseous or liquid phase, and the gauche preference of the C-C bonds in both phases were comparable. These results were in good agreement with those observed for di-MEDA solutions using NMR analysis. It was estimated that such small solvent effects on gauche preferences of the EI oligomers result in weakening for hydrogen bonds (NH-N) of neighboring imino groups by solvents.

Introduction

Poly(ethylene oxide) (PEO) and poly(ethylene imine) (PEI) share common properties because both possess electron-releasing heteroatoms (O or N) in the skeletal chain. Such properties, including solubility of inorganic salt and specific affinity to substrate, have been employed in the advancement of solid polymer electrolytes (PEO [1], PEI [2]), gene delivery polymers (PEI [3]), 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 [4,5] have shown that the structure of a PEO crystal in its original state exists as a 7/2 helix, 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. In the case of the PEO solutions, based on NMR analyses using dimethoxyethane (DME) [6,7] and triglyme (TGL) [8] 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. XRD and other analyses [9-12] have confirmed that the structure of a linear dehydrated PEI crystal exists as a 5/1 double stranded helix, with a repeating tgt conformation for the HN-C, C-C, and C-NH bonds, respectively. In the hydrated state, the structure transforms to the planar zigzag ttt conformation. Unlike the PEO solutions, the trans-fractions of the C-C bonds of the PEI solutions increase with greater values of ε, based on NMR analyses of N, N'-dimethylethylenediamine (di-MEDA) as a model of PEI [13]. Although both crystals adopt the tgt conformation in their original states (C-C bonds: gauche preference), intermolecular interactions and solvent effects differ significantly. Unfortunately, detailed understandings of these differences are complex and have yet to be clarified.

To complement the experimental observations in the conformational analyses of PEO and PEI, computational chemistry is employed. Pioneering works on PEO, involving a rotational isomeric state model (RIS), was reported by Mark *et al.*[14,15]. More recently, studies of PEO and PEI using molecular mechanics (MM) and molecular dynamics (MD) have been reported [16-18]. Furthermore, in contrast to the RIS, MM, and MD methods, recent studies involve quantum chemical calculations method (QCC). Although conformational analysis in the gaseous phase using QCC has been reported for DME [7,19-21] and its oligomers [7,8] (as models of PEO) and for di-MEDA [13,22] (as a model of PEI), comparable studies in the liquid phase have yet to be reported.

In a previous paper [23], we reported on the conformational analyses of EO and EI oligomers that have various molecular weights (1- to 11-mers) in the gaseous phase using QCC, with comparisons to the experimental results for the polymers in the crystal state. Our report, however, did not adequately explain a few points, including: i) disagreement between the most stable ttt conformation that was calculated for the EO oligomers and the tgt conformation that was observed for the normal state of the PEO crystal, and ii) driving force behind the transition from the tgt to the ttt conformation in the hydrated PEI crystal. Herein, to address these points, systematic conformational analyses were carried out for EO and EI oligomers (1- to 4-mers) in liquid phases using QCC, and the results were compared against those obtained in the gaseous phase. Conformational energies were calculated in four solvents using the Isodensity Polarizable Continuum Model (IPCM) [24] as a calculation model. Based on comparisons between the calculated and observed results, the conformational characteristics of both polymers are discussed.

Quantum chemical calculations (QCC)

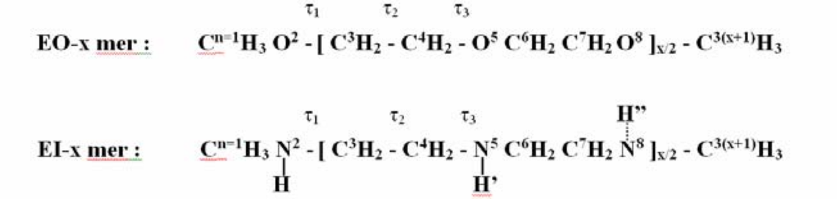
Oligomer models

For the oligomer models (single chain) of PEO, EO x-mers (x = 1 - 4 monomer units) capped by methoxy and methyl groups were used. Similarly, for those of PEI, EI

Table 1. Molecular models

No.	Monomer unit number: x	Molecular models	Molecular weights
EO-1	1	$CH_3O\text{-}(CH_2CH_2O)_1\text{-}CH_3$ [a]	90.14
EO-2	2	$CH_3O\text{-}(CH_2CH_2O)_2\text{-}CH_3$	134.20
EO-3	3	$CH_3O\text{-}(CH_2CH_2O)_3\text{-}CH_3$ [b]	178.26
EO-4	4	$CH_3O\text{-}(CH_2CH_2O)_4\text{-}CH_3$	222.32
EI-1	1	$CH_3NH\text{-}(CH_2CH_2NH)_1\text{-}CH_3$ [c]	88.18
EI-2	2	$CH_3NH\text{-}(CH_2CH_2NH)_2\text{-}CH_3$	131.26
EI-3	3	$CH_3NH\text{-}(CH_2CH_2NH)_3\text{-}CH_3$	174.34
EI-4	4	$CH_3NH\text{-}(CH_2CH_2NH)_4\text{-}CH_3$	217.42

[a] Dimethoxyethane (DME); [b] Triglyme (TGL); [c] N, N'-Dimethylethylenediamine (di-MEDA).



$$\textbf{EO-x mer :}\quad C^{n=1}H_3\,O^2\text{-}[\,\overset{\tau_1}{C^3H_2}\text{-}\overset{\tau_2}{C^4H_2}\text{-}\overset{\tau_3}{O^5}\,C^6H_2\,C^7H_2\,O^8\,]_{x/2}\text{-}C^{3(x+1)}H_3$$

$$\textbf{EI-x mer :}\quad C^{n=1}H_3\,\underset{\displaystyle H}{\underset{|}{N^2}}\text{-}[\,\overset{\tau_1}{C^3H_2}\text{-}\overset{\tau_2}{C^4H_2}\text{-}\overset{\tau_3}{\underset{\displaystyle H'}{\underset{|}{N^5}}}\,C^6H_2\,C^7H_2\,\overset{H''}{\overset{\vdots}{N^8}}\,]_{x/2}\text{-}C^{3(x+1)}H_3$$

Figure 1. Structures of EO and EI oligomer models, where x is the number of monomer units. 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 X-C, C-C', and C-X' (X, X': O, or N), respectively. Pseudoasymmetry in EI x-mer was defined by the following: N—H and N---H bonds in each of the NH groups in the Figure are on either side of the paper, respectively, and for example, the pseudoasymmetry for the N^2—H and the N^5—H' bonds is meso, and that for the N^5—H' and the N^8---H" bonds is racemo.

x-mers (x =1 - 4) capped by N-methylimino and methyl groups were used. The specified structures are given in Table 1 and Figure 1. For each oligomer, the conformation $(\tau_n\tau_{n+1}\tau_{n+2})_x$ (n, sequential number of atoms along a skeletal chain) are designated as $(ttt)_x$, $(ttg^+)_x$, $(tg^+t)_x$, $(tg^+g^+)_x$, $(tg^+g^-)_x$, and $(g^+g^+g^+)_x$ (t, trans; g^+ and g^-, gauche) as the combination of the dihedral angles (τ) that are repeated for the units of X-C, C-C, and C-X bonds (X = O or N, refer to Figure 1). Every dihedral angle was independently assigned along the skeletal chains. For EO-x, values of 180° (t), +60° (g^+), or -60° (g^-) were used. In the previous paper [23], the authors reported that the energies and pseudoasymmetries (racemo or meso) of the conformers of the EI oligomers in the gaseous phase were affected by the designation values for trans. Designations of the trans values of EI-x were carried out accordingly, in which the most stable conformers were optimized as follow: $\tau_n/\tau_{n+1}/\tau_{n+2}$ was -175°/-175°/-175° for $(ttt)_x$ conformations (the optimized pseudoasymmetry: meso), and was -175°/-175°/180° for other conformations. For the gauche values of EI-x, +60° (g^+) and -60° (g^-) were used.

Conformational analyses in gaseous phase

Conformational analyses in the gaseous phase were carried out for each model using QCC via the Gaussian 03W (Gaussian Inc.) program [25]. For structural optimizations, RHF/6-31+G(d,p) or B3LYP/6-31G(d) was used as the calculation method. The conformational energies, E (Hartree, 1 Hartree = 627.51 kcal/mol, hereinafter referred to as energy), and dipole moments, μ, Debye), were modified for the optimized structures. The conformations were specified based on IUPAC [26] as follow: τ_n of trans ($t^{\pm}$) and gauche ($g^{\pm}$) are ±120° to ±180° and ±0° to ±120°, respectively.

Conformational analyses in liquid phases

For each optimized structure in the gaseous phase, conformational analyses were carried out in the liquid phase using QCC. To assess the model and the method used in the calculations, the energies of *trans*- and *cis*-1, 2-dichloroethane were calculated and compared to the observed values. According to the results (details will be discussed in the following section), the IPCM [24] was used as the calculation model with permittivity (ε) of the solvents, and RHF/6-31+G(d,p) or B3LYP/6-31G(d) was used for the calculating method. The ε values of the four solvents (cyclohexane, dichloromethane, acetonitrile and water) were based on their reference data [26], as listed in Table 3. The calculating methods were consistent with those used in the gaseous phase. The energies (E) and dipole moments (μ) were modified for the converged structures.

Results and discussion

Examination of the calculation model and calculating methods

Concerning the calculation model for the liquid phase using QCC, the SCRF theory [24] was investigated, in which the solvent was treated as a reaction field having homogeneously distributed permittivity. The basic model based on the SCRF theory is the Onsager reaction field model [27], in which the reaction field is treated as a functional approximated cavity. Recently, the Polarizable Continuum Model (PCM) [28], along with its improved version, IPCM [24], have been developed, in which the reaction fields are treated as a continuous cavity of sequential atomic balls. To examine the applicability of the calculation model and calculating methods for the conformational analyses in the liquid phases, conformational energies of *trans*- and *cis*-1,2-dichloroethane in gaseous and liquid phases were calculated using IPCM with some calculating methods. As shown in Table 2, the calculated energy differences ($\Delta E = E_{cis} - E_{trans}$, kcal/mol) between the *trans*- and *cis*-forms were compared to those observed [29-31]. With the exception of the results for RHF/6-31G(d) and RHF/6-31+G(d), the energy differences ("(ΔE)" in Table 2) between the gaseous and liquid phases were in good agreement. Based on these results, the RHF/6-31+G(d,p) or B3LYP/6-31G(d) // SCRF/IPCM methods were adopted.

Table 2. Comparison of energy differences (ΔE, kcal/mol)[a] between calculated and observed for *trans*- and *cis*-1,2-dichloroethane

	Calculation methods (calculation model: SCRF/IPCM[b])					
Phase	RHF/ 6-31G(d)	RHF/ 6-31+G(d)	RHF/ 6-31+G(d,p)	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d,p)	Observed[c]
Gas	1.88 (0.00)	2.01 (0.00)	1.95 (0.00)	1.69 (0.00)	1.69 (0.00)	1.20 (0.00)
Cyclohexane	1.76 (-0.12)	1.82 (-0.19)	1.57 (-0.38)	1.32 (-0.37)	1.44 (-0.25)	0.91 (-0.29)
Liquid	1.51 (-0.37)	1.57 (-0.44)	1.07 (-0.88)	0.75 (-0.94)	0.75 (-0.94)	0.31 (-0.89)
Acetonitrile	1.44 (-0.44)	1.51 (-0.50)	0.94 (-1.01)	0.56 (-1.13)	0.75 (-0.94)	0.15 (-0.95)

[a] $\Delta E = E_{cis} - E_{trans}$; [b] Permittivities (ε) used in calculations: gas, 1.0; cyclohexane, 2.0; liquid, 10.4; acetonitrile, 36.6 [26]; [c] [29-31].

Solvent effects on the energy of each EO conformer

The conformational analyses for the EO oligomer models (EO-x, x = 1 - 4) in liquid phases were carried out using the RHF/6-31+G(d,p) // SCRF/IPCM method with structures that were optimized in the gaseous phase.

As shown in Table 3, the dipole moments (μ) generally increased with greater values of ε; overall, the values for μ and ε seem to correlate positively. However, the μ values of $(ttt)_x$ of EO-1 and -3 were independent of ε, and those of $(tg^+t)_x$ and $(g^+g^+g^+)_x$ of EO-4 correlated negatively with ε. These results indicated that solvent effects on the dipole moments of the conformers are intricately affected by both the conformation and the degree of polymerization.

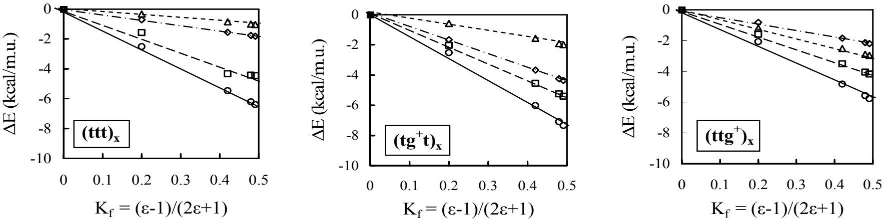


Figure 2. Plots of energies (ΔE) of some conformers against Kirkwood functions (K_f) in EO oligomers. △E values are differences to E in gaseous phase of each conformer ($\Delta E = E_{liquid} - E_{gas}$). ○: 1 mer, □: 2 mer, ◇: 3 mer, Δ: 4 mer.

As shown in Table 3, the energy differences (ΔE per monomer unit, kcal/m.u.) of each conformer, with respect to the $(ttt)_x$ conformer in the gaseous phase, decreased with increasing values of ε. Next, the relationships between ΔE and the Kirkwood function [32] ($K_f = (\varepsilon-1)/(2\varepsilon+1)$, refer Table 3), based on the electrostatic energy of the solvent, were examined. As shown in the relations for typical conformers (Figure 2), the relationships for all conformers were negative and linear, in which the negative effects decreased with increasing values of x. These results indicate that electrostatic interactions with solvents contribute to the stabilities of the conformers, and such inter actions are diluted with increasing monomer units. As shown in Table 3, the ΔE values of the conformers generally decreased with increasing μ values; overall, the ΔE and μ values are negatively related. However, the ΔE values of the $(ttt)_x$ conformers of EO-1 and 3 decreased with greater values of ε, whereas their μ values were independent of ε. Furthermore, both the ΔE and μ values of the $(tg^+t)_x$ and $(g^+g^+g^+)_x$ conformers for EO-4 decreased with increasing ε values. These results indicate that the dipole moment of the conformers is not a primary factor in determining the conformational energies.

Solvent effects on trans/gauche preferences of the EO conformers

As shown in Figure 3, for the EO oligomers, the energy differences (ΔE_G, kcal/m.u.) of each conformer with respect to the $(ttt)_x$ conformer were plotted against the number of monomer units (x) in some phases; above an ε value of 8.9, the relations were almost same as those in ε value of 8.9. In the gaseous phase (ε = 1), the ΔE_G values of

Table 3. Conformational analyses for EO oligomers using RHF/6-31+G (d, p) // SCRF/IPCM

Phases		Dipole moments (μ, Debye)[a]				Energies (ΔE, kcal/m. u.)[b]			
(ε, K_f)[c]	Conformers	EO-1	EO-2	EO-3	EO-4	EO-1	EO-2	EO-3	EO-4
Gas	$(ttt)_x$	0.00	0.60	0.00	0.60	0.00[d]	0.00[e]	0.00[f]	0.00[g]
(1.0, 0)	$(tg^{+}t)_x$	0.63	0.13	0.46	0.68	1.38	1.26	1.21	1.19
	$(tg^{+}g^{-})_x$	0.68	1.16	1.48	1.93	1.76	1.69	1.63	1.58
	$(ttg^{+})_x$	0.72	0.27	0.40	0.75	1.88	1.85	1.82	1.80
	$(tg^{+}g^{+})_x$	1.13	1.65	2.23	2.85	3.33	3.48	3.28	3.11
	$(g^{+}g^{+}g^{+})_x$	0.64	0.09	0.53	0.68	4.33	4.27	4.23	4.22
Cyclohexane	$(ttt)_x$	0.00	0.69	0.00	0.67	-2.51	-1.57	-0.71	-0.33
(2.0, 0.2)	$(tg^{+}t)_x$	0.74	0.11	0.57	0.62	-1.13	-0.41	-0.82	0.61
	$(tg^{+}g^{-})_x$	0.75	1.30	1.58	2.00	-0.25	-0.16	0.84	0.78
	$(ttg^{+})_x$	0.81	0.29	0.36	0.92	-0.19	0.25	1.00	0.61
	$(tg^{+}g^{+})_x$	1.28	1.84	2.45	3.13	0.56	1.85	2.03	1.96
	$(g^{+}g^{+}g^{+})_x$	0.74	0.05	0.74	0.63	1.63	2.76	2.01	3.34
Dichloro-methane	$(ttt)_x$	0.00	0.84	0.00	0.77	-5.46	-4.33	-1.55	-0.85
	$(tg^{+}t)_x$	0.91	0.07	0.68	0.52	-4.64	-2.42	-3.33	-0.38
(8.9, 0.42)	$(tg^{+}g^{-})_x$	0.84	1.48	1.72	2.11	-2.64	-2.60	-0.19	-0.56
	$(ttg^{+})_x$	0.94	0.46	0.34	1.11	-2.95	-1.66	-0.02	-0.71
	$(tg^{+}g^{+})_x$	1.50	2.13	2.76	3.54	-3.26	-0.44	0.40	0.39
	$(g^{+}g^{+}g^{+})_x$	0.89	0.35	0.94	0.53	-1.95	0.85	-0.59	2.18
Acetonitrile	$(ttt)_x$	0.00	0.84	0.00	0.80	-6.21	-4.33	-1.76	-1.00
(36.6, 0.48)	$(tg^{+}t)_x$	0.96	0.06	0.70	0.49	-5.71	-2.98	-4.04	-0.72
	$(tg^{+}g^{-})_x$	0.86	1.53	1.75	2.17	-3.33	-3.33	-0.46	-1.04
	$(ttg^{+})_x$	0.99	0.53	0.35	1.17	-3.70	-2.20	-0.31	-1.08
	$(tg^{+}g^{+})_x$	1.57	2.23	2.87	3.68	-4.46	-1.16	-0.08	-0.09
	$(g^{+}g^{+}g^{+})_x$	0.94	0.50	0.49	1.00	-3.07	0.38	-1.30	1.84
Water	$(ttt)_x$	0.00	0.84	0.00	0.80	-6.40	-4.46	-1.82	-1.04
(80.1, 0.49)	$(tg^{+}t)_x$	0.97	0.06	0.70	0.48	-5.96	-3.11	-4.18	-0.78
	$(tg^{+}g^{-})_x$	0.86	1.54	1.76	2.18	-3.45	-3.48	-0.52	-1.13
	$(ttg^{+})_x$	0.99	0.54	0.35	1.18	-3.89	-2.32	-0.38	-1.16
	$(tg^{+}g^{+})_x$	1.59	2.25	2.89	3.72	-4.64	-1.32	-0.21	-0.82
	$(g^{+}g^{+}g^{+})_x$	0.95	0.53	1.00	0.48	-3.26	0.28	-1.44	1.76

[a] $\mu = (\mu_X^2 + \mu_Y^2 + \mu_Z^2)^{1/2}$; [b] Calculated based on E of each $(ttt)_x$ in gas phases; [c] ε: permittivity [26], K_f: Kirkwood function [32], $K_f = (\varepsilon-1)/(2\varepsilon+1)$; [d] E = -307.0041(Hartree); [e] E = -459.9296; [f] E = -612.8550; [g] E = -765.7804.

each conformer were independent of x. The $(ttt)_x$ conformer was the most stable, followed by the $(tg^{+}t)_x$ conformer. The ΔE_G of the $(tg^{+}t)_x$ conformer ($E_{(tg+t)x}$ - $E_{(ttt)x}$, hereinafter referred to as ΔE_σ) was 1.2 ~ 1.4 kcal/m.u, which indicated that the C-C bond of the EO conformer prefers the trans conformation in the gaseous phase. Our results were in good agreement with those previously reported [7,8,21]. From an energetic aspect, our results do not correspond to the conformation of PEO crystals in the normal state (tgt), but to that in the stretched state (ttt). As discussed in our previous report [23], details of the calculated results remain unclear.

As shown in Figure 3, the ΔE_G values of some conformers in liquid phases change with increasing x and ε values. In the cases of the $(tg^{+}t)_x$ and $(g^{+}g^{+}g^{+})_x$ conformers of EO-3, significant decreases in ΔE_G were observed with increasing ε. Above an ε value of 8.9, the $(tg^{+}t)_x$ conformer of EO-3 was the most stable (ΔE_σ = -1.8 ~ -2.4 kcal/m.u.), in which the C-C bond exhibited a strong preference for the gauche-conformation. The relationship between x and ΔE_G can presumably result in a non-linear relation between the monomer unit number and structural symmetry, which were shown in the dipole moments. As shown in Figure 4, the ΔE_σ values of all $(tg^+t)_x$ conformers exhibited a linear relationship to the K_f values, while corresponding to the electrostatic property of solvent. The slopes of these linear plots were nearly negative (-7.2 ~ 0), and the ΔE_σ values (except for EO-2) were less than or nearly equal to the energies of the $(ttt)_x$ conformer with increasing values of ε, as shown in Figure 4. These results indicate that the gauche preference of the C-C bonds of the EO conformers increases with greater values of ε, resulting in intramolecular interactions that are intensified by electrostatic interactions with the solvent.

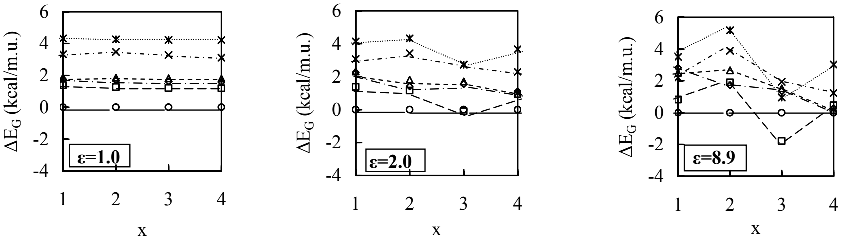


Figure 3. Plots of energies (ΔE_G) of conformers against monomer unit number (x) in some phases of EO oligomers. ΔE_G values were calculated based on E of $(ttt)_x$ of each oligomer. ○: $(ttt)_x$, □: $(tg^+t)_x$, ◇: $(tg^+g^-)_x$, Δ: $(ttg^+)_x$, ×: $(tg^+g^+)_x$, ∗: $(g^+g^+g^+)_x$.

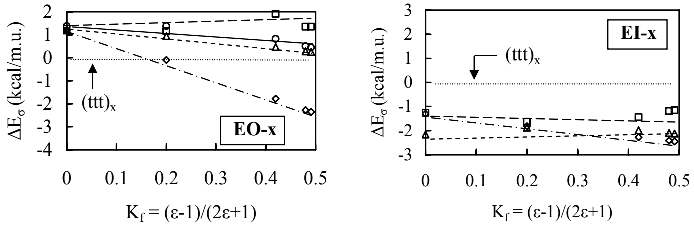


Figure 4. Plots of ΔE_σ against Kirkwood function (K_f) in EO and EI oligomers, where $\Delta E_\sigma = E(tg^+t)_x - E(ttt)_x$; ○: 1 mer, □: 2 mer, ◇: 3 mer, Δ: 4 mer.

For conformational studies in liquid phases using NMR studies, studies have been carried out by Tasaki *et al.* [6] and Sasanuma *et al.* [7] using DME, and by Sasanuma *et al.* [8] using triglyme (TGL). As shown in Table 4, our results were compared to those of these NMR studies. Estimated trans-fractions ($f_t^{(C\text{-}C)}$ or $f_t^{(C\text{-}O)}$) to the C-C or C-O bond were calculated via equations (1) ~ (4) using ΔE_G in each phase:

$$C_A = \exp\left(\frac{-\Delta E_G}{RT}\right) \quad \textbf{(1)}$$

$$f_t^{(C-C)} = \frac{C_A^{(ttt)x}}{C_A^{(ttt)x} + C_A^{(tg+t)x}} \quad \textbf{(2)}$$

$$f_t^{(C-O)} = \frac{C_A^{(ttt)x}}{C_A^{(ttt)x} + C_A^{(ttg+)x}} \quad (3)$$

$$f_t + f_g = 1, \quad (4)$$

where C_A, R, T, and f_g are the conformation average, gas constant, temperature (298.15 °K, 1 atm), and gauche-fractions, respectively. In the case of DME (= EO-1), although the calculated $f_t^{(C\text{-}C)}$ values for each phase differed with those observed, the tendency of increased gauche preference with increasing values of ε was consistent with that observed, as shown in Table 4. In the case of TGL (= EO-3), the calculated $f_t^{(C\text{-}C)}$ values for each phase was in good agreement with those observed. These results indicated that our calculation model is applicable toward the conformational analyses of EO oligomers in liquid phases.

Table 4. Comparison of trans-fractions (f_t) between calculated and observed for EO oligomers

		Calculated		Observed	
Oligomers	Solvents	$f_t^{(C\text{-}C)}$	$f_t^{(C\text{-}O)}$	$f_t^{(C\text{-}C)}$	$f_t^{(C\text{-}O)}$
DME (EO-1)	Cyclohexane	0.912	0.980	0.30[a]	0.79[a]
	Water	0.678	0.986	0.12[a]	0.87[a]
TGL(EO-3)	Cyclohexane	0.458	0.948	0.20[b]	-
	Water	0.018	0.919	0.05[b]	-

[a] Estimated from $E_\sigma^{(C\text{-}C)}$ and $E_\rho^{(C\text{-}O)}$ values observed by NMR studies (Tasaki *et al.* [6]), using equations (1)~(4); [b] Observed by NMR studies (Sasanuma *et al.* [8]).

Solvent effects on the energy of each EI conformer

Conformational analyses for the EI oligomers (EI-x, x = 1 - 4) in liquid phases were carried out using the structures that were optimized in the gaseous phase. Although the RHF/6-31+G(d,p) // SCRF/IPCM method was used for EI-1 ~ EI-3 (similarly as for the EO oligomers), the B3LYP/6-31G(d) // SCRF/IPCM method was used for EI-4 because the calculations did not converge using the former method.

As shown in Table 5, μ and ε for all conformers, in general, exhibited a positive relationship. In the cases of the $(tg^+g^-)_x$ conformer for EI-3 and the $(ttg^+)_x$ conformer for EI-4, however, the μ value decreased with increasing ε. As for the EO oligomers, solvent effects on the dipole moments of the conformers are influenced by both the conformation and the number of the monomer units.

As shown in Table 5, the energy differences (ΔE) of each conformer, with respect to the $(ttt)_x$ conformer in the gaseous phase, decreased with increasing values of ε. The plots of ΔE against the Kirkwood functions exhibited a negative linear relation (Figure 5). The stabilities of the conformers were dominated by the electrostatic interactions with the solvents, which were diluted with increasing number of monomer units. Such results are comparable to those of the EO oligomers, and explain the similarity between both molecular structures. In general, as shown in Table 5, ΔE decreased with increasing μ. In the cases of $(tg^+g^-)_x$ in EI-3 and $(ttg^+)_x$ in EI-4, however, ΔE and μ decreased with increasing ε, which indicated that the dipole moment of conformer is not a primary factor in the conformational energy, which is similar to the EO oligomers.

Table 5. Conformational analyses for EI oligomers using RHF/6-31+G (d, p) // SCRF/IPCM[a]

Phases		Dipole moments (μ, Debye)				Energies (ΔE, kcal/m. u.)[b]			
(ε, K_f)	Conformers	EI-1	EI-2	EI-3	EI-4	EI-1	EI-2	EI-3	EI-4
Gas (1.0, 0)	$(ttt)_x$	0.73	0.39	0.07	0.91	0.00[c]	0.00[d]	0.00[e]	0.00[f]
	$(tg^+t)_x$	0.47	0.91	1.27	1.78	1.88	-1.26	-1.30	-2.16
	$(tg^+g^-)_x$	0.65	0.58	1.12	1.91	2.32	2.51	2.61	1.40
	$(ttg^+)_x$	0.58	0.59	0.84	1.05	1.00	0.94	0.92	0.83
	$(tg^+g^+)_x$	0.61	-[g]	-[g]	-[g]	-0.50	-	-	-
	$(g^+g^+g^+)_x$	-[h]	0.66	0.85	0.96	-	2.26	2.01	0.47
Cyclohexane (2.0, 0.2)	$(ttt)_x$	0.82	0.39	0.07	1.32	-2.26	-0.69	-1.00	-1.10
	$(tg^+t)_x$	0.60	1.03	1.52	2.00	-0.13	-2.32	-2.82	-2.98
	$(tg^+g^-)_x$	0.73	0.70	1.08	2.20	1.00	0.85	2.36	0.00
	$(ttg^+)_x$	0.65	0.74	0.86	1.02	-0.69	-0.44	0.27	0.55
	$(tg^+g^+)_x$	0.69	-	-	-	2.26	-	-	-
	$(g^+g^+g^+)_x$	-	0.75	1.08	1.00	-	0.75	0.06	0.31
Dichloro-methane (8.9, 0.42)	$(ttt)_x$	0.97	0.40	0.30	2.07	-5.33	-2.10	-2.36	-2.31
	$(tg^+t)_x$	0.81	1.20	1.82	2.36	-3.07	-3.55	-4.64	-4.30
	$(tg^+g^-)_x$	0.87	0.90	1.01	2.54	-1.00	-1.54	1.90	-1.85
	$(ttg^+)_x$	0.76	0.95	0.92	0.97	-2.95	-2.23	-0.69	0.09
	$(tg^+g^+)_x$	0.81	-	-	-	-4.52	-	-	-
	$(g^+g^+g^+)_x$	-	0.88	1.39	1.07	-	-1.19	-2.22	0.03
Acetonitrile (36.6, 0.48)	$(ttt)_x$	1.03	0.42	0.38	2.34	-6.21	-2.67	-2.78	-2.62
	$(tg^+t)_x$	0.88	1.25	1.91	2.48	-4.02	-3.86	-5.19	-4.72
	$(tg^+g^-)_x$	0.93	0.97	0.99	2.64	-1.69	-2.29	1.76	-2.42
	$(ttg^+)_x$	0.80	1.01	0.94	0.95	-3.64	-2.76	-0.98	-0.08
	$(tg^+g^+)_x$	0.85	-	-	-	-5.21	-	-	-
	$(g^+g^+g^+)_x$	-	0.92	1.47	1.10	-	-1.79	-2.82	-0.06
Water (80.1, 0.49)	$(ttt)_x$	1.04	0.43	0.40	2.40	-6.40	-2.79	-2.87	-2.68
	$(tg^+t)_x$	0.89	1.26	1.93	2.51	-4.20	-3.95	-5.31	-4.80
	$(tg^+g^-)_x$	0.94	1.01	0.98	2.66	-1.82	-2.45	1.72	-2.53
	$(ttg^+)_x$	0.81	1.02	0.95	0.95	-3.77	-2.86	-1.05	-0.11
	$(tg^+g^+)_x$	0.86	-	-	-	-5.33	-	-	-
	$(g^+g^+g^+)_x$	-	0.93	1.49	1.11	-	-1.88	-2.95	-0.08

[a] For only EI-4, B3LYP/6-31G(d)//SCRF/IPCM was used; [b] Calculated based on E of $(ttt)_x$ in gas; [c] E = -267.3530 Hartree; [d] E = -400.4505; [e] E = -533.5480; [f] E = -671.0213; [g] Optimized from $(tg^+g^+)_x$ to $(tg^+g^+)(g^+g^+g^+)_{x-1}$ in gas; [h] Optimized from $(g^+g^+g^+)_x$ to $(tg^+t)_x$ in gas.

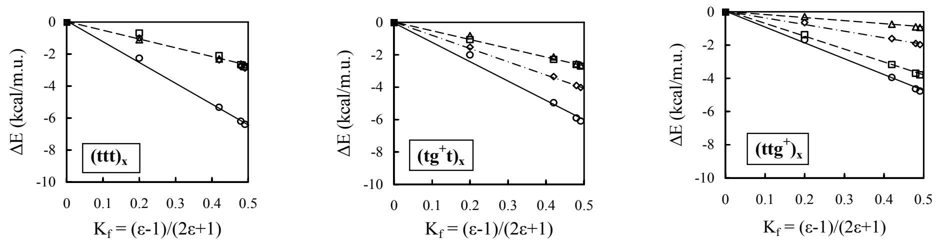


Figure 5. Plots of energies (ΔE) of some conformers against Kirkwood function (K_f) in EI oligomers. The ΔE values are differences to E in gaseous phase of each conformer ($\Delta E = E_{liquid} - E_{gas}$). ○: 1 mer, □: 2 mer, ◇: 3 mer, Δ: 4 mer.

Solvent effects on trans/gauche preferences of the EI conformers

As shown in Figure 6, the energy differences (ΔE_G) for the EI conformers were plotted against the number of monomer units (x) for each phase; above an ε value of 8.9, the relations were comparable to those in ε value of 8.9. In the gaseous phase, the $(tg^+t)_x$ conformer was the most stable, followed by the $(ttt)_x$ conformer. The significantly large ΔE_G value for the $(tg^+t)_x$ conformer of the monomer (x = 1) can be attributed to, as discussed in our previous report [23], structural differences between the monomer and the 2- to 11-mers; unfortunately, detailed explanation remains elusive. In the cases above 2-mer, the ΔE_σ values were -1.3 ~ -2.2 kcal/m.u. In contrast to the EO conformers, the negative ΔE_σ value indicates the gauche preference of the C-C bond, which corresponds to the conformation of the PEI crystal (tgt) [10,11], from an energetic aspect, and is in good agreement with the calculated results of other studies [13,22].

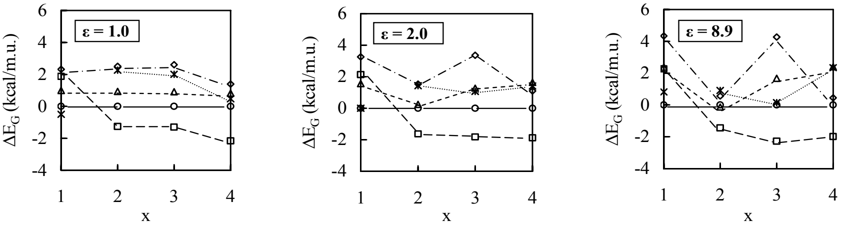


Figure 6. Plots of energies (ΔE_G) of conformers against monomer unit number (x) in some phases of EI oligomers. ΔE_G values were calculated based on E of $(ttt)_x$ of each oligomer. ○: $(ttt)_x$, □: $(tg^+t)_x$, ◇: $(tg^+g^-)_x$, △: $(ttg^+)_x$, ×: $(tg^+g^+)_x$, *: $(g^+g^+g^+)_x$.

In the liquid phases, as shown in Figure 6, the ΔE_σ values of the $(tg^+t)_x$ conformers (-1.2 ~ -2.4 kcal/m.u.) were comparable to those in the gaseous phase, in which the gauche preferences of the C-C bonds with increasing ε values were maintained. Furthermore, as shown in Figure 4, the ΔE_σ values were virtually proportional to the K_f values except in the case of the 3-mer, the slopes of the plots were nearly flat (0 ~ 0.8). In contrast to the EO conformers, therefore, the effect of ε on ΔE_σ is small for the EI conformers. Presumably, the hydrogen bond (NH-N) between the neighboring imino groups, which contribute to the gauche preference, is weakened by the polarity of the solvent, and then, the electrostatic contributions to the gauche preference of the solvent were compensated.

To the best of our knowledge, only a few reports describe the conformational examinations of EI oligomers in the liquid phase. Our results were compared against those of NMR analyses using solutions of di-MEDA and N,N,N'-tri-MEDA (tri-MEDA) as model compounds, as reported by Sasanuma *et al.* [13]. Estimations of the trans-fractions ($f_t^{(C\text{-}C)}$ or $f_t^{(C\text{-}O)}$) were calculated via equations (1) ~ (4) using the ΔE_G and C_A values in each phase. The f_t values for tri-MEDA were calculated using ΔE_G values that were obtained by the same method as for EI-1. As shown in Table 6, the calculated $f_t^{(C\text{-}C)}$ values for EI-2 were in good agreement with those observed for di-MEDA. Although the calculated $f_t^{(C\text{-}C)}$ values for EI-1 did not correlate with those observed for di-MEDA, the calculated values for tri-MEDA, in which the proton on one side of the imino groups was substituted by a methyl group, exhibited good correlation with experimental results. Based on this result, the significantly high energy for EI-1, in gaseous or liquid phases, can be attributed to the strong hydrogen bonding between the neighboring imino groups due to the reversed structure [23]. As shown in Table 6, the trans-fractions of C-C bonds increased with increasing ε values or with the substitution of a proton with a methyl group. Accordingly, as also mentioned by Sasanuma *et al.* [13], the molecular chains are presumably stretched due to decreased intramolecular hydrogen bonding.

Table 6. Comparison of trans-fractions (f_t) between calculated and observed for EI oligomers

		Calculated		Observed[a]	
Oligomers	Solvents	$f_t^{(C\text{-}C)}$	$f_t^{(C\text{-}N)}$	$f_t^{(C\text{-}C)}$	$f_t^{(C\text{-}N)}$
di-MEDA (EI-1)	Cyclohexane	0.973	0.933	0.07	0.78
	Water	0.977	0.988	0.29	0.72
tri-MEDA[b]	Cyclohexane	0.073[c]	0.859[c]	0.14	0.93
	Water	0.097[c]	0.830[c]	0.48	0.74
(EI-2)	Cyclohexane	0.060	0.600		
	Water	0.123	0.474		

[a] Observed by NMR studies by Sasanuma *et al.* [13]; [b] N,N,N'-Trimethylethylenediamine; [c] The calculations of ΔE_G for f_t were carried out using the same method as for EI-1.

As mentioned earlier, in the hydrated state, the tgt conformation of the linear PEI crystal (5/1 double stranded helix) transformed to the ttt conformation (plannar zigzag) [9-12]. For the EI conformers, as shown in Table 5, the energies of the $(ttt)_x$ conformer in the aqueous phase (ε = 80.1) were lower by 0.7 ~ 1.4 kcal/m.u. than those of the $(tg^+t)_x$ conformer in the gaseous phase. Furthermore, as shown in Table 6, the trans-fractions of the C-C bonds increased in the aqueous phase. Although these results offers insight into the transition of hydrated PEI crystals, details of such transitional behavior are complicated and have yet to be elucidated.

Because these polymers often exist in a solitary state, conformational analysis for a single oligomer chain in the liquid phase using QCC is effective in understanding the solvent effects on a polymer. The SCRF // IPCM used herein is applicable as a calculation model to estimate the conformations of PEO and PEI in liquid phases. Further investigations, however, would require a combination of QCC and other methods such as MM, MD, etc.; one such example has been reported by Smith *et al.* [33] in the adoption of QCC in MD simulation model for hydrated DME.

Conclusions

The conformational characteristics of EO and EI oligomers in liquid phases were studied using QCC, comparing with the experimental results. The energies (ΔE) of every conformer in both oligomers were linear against the Kirkwood function (K_f), and the electrostatic interactions with solvents contribute to the stabilities of the conformers. The gauche preference of the C-C bonds of the EO conformers increases with greater values of ε, resulting in intramolecular interactions that are intensified by electrostatic interactions with the solvent. The small solvent effects on gauche preferences of C-C bonds of EI oligomers result in weakening for hydrogen bonds (NH-N) of neighboring imino groups by solvents.

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