The Attractive Gauche Effect of Ethylene Oxides

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ABSTRACT: Conformational energies of monomeric (1,2-dimethoxyethane, DME) and trimeric (triglyme) model compounds of poly(ethylene oxide) have been evaluated by accurate *ab initio* molecular orbital (MO) calculations at the MP2/6-311++G(3df, 3pd)//HF/6-31G(d) level. The first-order interaction energies (E_{σ} 's) for gauche states around the C–C bonds of DME and the terminal repeating unit of triglyme are *ca.* +0.1 kcal mol⁻¹, whereas the central unit of triglyme has a slightly negative E_{σ} value of *ca.* -0.1 kcal mol⁻¹. For the C–C bond conformations of triglyme, the MO calculations exactly agree with NMR observations using a nonpolar solvent of cyclohexane- d_{12} . The attractive gauche effect of the ethylene oxides has been shown to exist independently of intramolecular (C–H)···O hydrogen bonds. [doi:10.1295/polymj.PJ2006018]

KEY WORDS Poly(ethylene oxide) / Conformation / Ab Initio Molecular Orbital Calculation / NMR / Attractive Gauche Effect / Weak Hydrogen Bond /

The attractive gauche effect has been found in X-C-C-X bond sequences, where X stands for electronegative atoms such as F, Cl, and O;^{1,2} the central C-C bond has been considered to have the inherent gauche preference. In a previous paper,³ we have proposed a concept of the competitive balance between intramolecular and intermolecular attractions of ethylene oxides. The isolated (i.e., gaseous) ethylene-oxide chains form the intramolecular hydrogen bonds, which cause an apparent gauche stability of the C-C bond. In polar solvents, however, the O-C-C-O segment tends to prefer the tgt conformation because of attractive interactions with solvents (for the bond sequence, see Figure 1). These phenomena may be observed as variations in two conformational energies: E_{σ} and E_{ω} (for the interactions, see Figure 2). The former energy corresponds to the energy difference between trans and gauche states, and the latter represents the (C–H)···O interaction. The E_{σ} and E_{ω} values, depending on the polarity of environment, shift in the



Figure 1. (a) Monomeric (1,2-dimethoxyethane: DME) and (b) trimeric (triglyme) model compounds of poly(ethylene oxide) (PEO). As indicated, the skeletal bonds are numbered.

opposite directions: $E_{\sigma} = +0.32$ and $E_{\omega} = -1.12$ kcal mol⁻¹ for 1,2-dimethoxyethane (DME) in the gas phase;³ $E_{\sigma} = -0.25$ and $E_{\omega} = -0.79$ kcal mol⁻¹ for poly(ethylene oxide) (PEO) in weakly polar solvents such as 1,4-dioxane and benzene;³ $E_{\sigma} = -0.5$



Figure 2. Intramolecular interactions defined for the ethylene oxides: (a) σ and (b) ρ : the first-order interactions around the C–C and C–O bonds, respectively; (c) ω : the second-order interaction occurring in $g^{\pm}g^{\mp}$ conformations for the C–O/C–C bond pair; (d) χ : the third-order interaction formed in $g^{\pm}g^{\pm}g^{\pm}$ conformations of the O–C–C–O bond sequence. The ω and χ interactions represent intramolecular hydrogen bonds. The model here is DME.

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and $E_{\omega} = +0.4 \text{ kcal mol}^{-1}$ for PEO in the Θ solutions, e.g., 0.45 M K₂SO₄ at 34.5 °C.⁴⁻⁶ In a good solvent, water, PEO shows a very small E_{σ} value of -1.2kcal mol^{-1.7} The interdependence of the two conformational energies has so far been pointed out.⁸⁻¹⁰

The natural bond orbital (NBO) analysis¹¹ on DME indicated that the attractive gauche effect comes mainly from C–H bond \rightarrow C–O antibond ($\sigma_{C-H} \rightarrow \sigma^*_{C-O}$) delocalizations,³ suggesting that the tgt state is more stable than ttt. Here, the designation tgt indicates that bonds 2, 3, and 4 take t, g, and t states, respectively (see Figure 1a). To our knowledge, however, all ab initio molecular orbital (MO) calculations performed so far for DME have suggested that the ttt conformation is more stable than tgt. In the crystalline state, PEO is allowed to adopt either tgt or ttt state in the O-C-C-O bonds. The former and latter conformations form a distorted (7/2) helix^{12,13} and a planar zigzag structure,¹⁴ respectively. It is expected that PEO prefers the tgt state to ttt, because the ttt conformation is formed only in stretched samples.^{14,15} The four (7/2) helical chains form a $P2_1/a$ monoclinic cell,¹³ in which we can not find any clue to the specific interactions such as O···H close contacts to stabilize the tgt conformation.

In the previous study,³ we calculated conformer free energies of monomer (DME) and trimer (triglyme) of PEO at the B3LYP/6-311+G(3df, 2p)// B3LYP/6-31G(d) level. The gauche energy of the central C-C bond seems to depend on the chain length: DME, $0.76 \text{ kcal mol}^{-1}$; triglyme, $0.15 \text{ kcal mol}^{-1}$. It is known that more expensive MO calculations based on the MP2 theory yield more reliable energy data than the B3LYP computations. Therefore, accurate MO calculations at the MP2/6-311++G(3df, 3pd)// HF/6-31G(d) level have been carried out here for triglyme as well as DME. In addition, we have analyzed ¹H NMR spectra observed from triglyme to evaluate the bond conformations and compare the MO calculations. If gaseous triglyme has E_{σ} values significantly smaller than hydrocarbon chains such as *n*-alkanes and polyethylene, the attractive gauche effect would be proved to exist independently of the $(C-H) \cdot \cdot \cdot O$ hydrogen bonds as predicted by the NBO analysis.

COMPUTATIONS AND EXPERIMENTS

Ab Initio MO Calculations

Ab initio MO calculations were carried out for DME and triglyme with the Gaussian03 program¹⁶ installed on an HPC Silent-SCC T2 computer. For each conformer, the geometrical parameters were fully optimized at the HF/6-31G(d) level, and the thermal correction to the Gibbs free energy (at 25 °C and 1 atm) was calculated with a calibration factor of

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0.9135.¹⁷ With the optimized geometry, the selfconsistent field (SCF) energy was computed at the MP2/6-311++G(3df, 3pd) level. All the SCF calculations were performed under the tight convergence. The Gibbs free energy was calculated from the SCF and thermal-correction energies, being given here as the difference from that of the all-trans conformer and denoted as ΔG_k (*k*: conformer number).

NMR Measurements of Triglyme

Commercially available triglyme was used without further purification. Cyclohexane- d_{12} , chloroform-d, methanol- d_4 , dimethyl sulfoxide- d_6 , and deuterium oxide were used as the solvents, and the solute concentration was *ca*. 5 vol %. The proton NMR spectra were measured at 500 MHz on a JEOL JNM-LA500 spectrometer equipped with a variable temperature controller in the Chemical Analysis Center of Chiba University. During the measurement the probe temperature was maintained within ± 0.1 °C fluctuations. The $\pi/2$ pulse width, data acquisition time, and recycle delay were 5.6 µs, 13.1 s, and 3.7 s, respectively. Before the Fourier transform, zero filling was performed so that the digital resolution would be close to 0.01 Hz.

RESULTS AND DISCUSSION

MO Calculations

Statistical weight matrices U_i (*i*: bond number) of DME and triglyme are given by

$$U_2 = \begin{bmatrix} 1 & \rho_2 & \rho_2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(1)

$$U_{3} = \begin{bmatrix} 1 & \sigma_{3} & \sigma_{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \sigma_{3} & \sigma_{3}\omega_{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & \sigma_{3}\omega_{3} & \sigma_{3} \end{bmatrix}$$
(2)

| U_4 | = l | $J_7 =$ | U_{10} | = | | | | | | |
|-------|-----|----------|----------|---|----------------|------------------|---|------------------|-----------------|-----|
| | Γ1 | ρ_i | ρ_i | 0 | 0 | 0 | 0 | 0 | 0 7 | |
| | 0 | 0 | 0 | 1 | $ ho_i$ | $ ho_i \omega_i$ | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 1 | $ ho_i \omega_i$ | $ ho_i$ | |
| | 1 | ρ_i | ρ_i | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 1 | $ ho_i \chi_i$ | $ ho_i \omega_i$ | 0 | 0 | 0 | (3) |
| | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | $ ho_i$ | |
| | 1 | ρ_i | ρ_i | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 1 | $ ho_i$ | 0 | 0 | 0 | 0 | |
| | | 0 | 0 | 0 | 0 | 0 | 1 | $ ho_i \omega_i$ | $\rho_i \chi_i$ | |
| | | | | | | | | | | |

$$U_5 = U_8 =$$

| - 5 | - | 0 | | | | | | | | |
|-----|-----|----------|----------|---|----------|-------------------|---|-------------------|----------|-----|
| | [1] | ρ_i | ρ_i | 0 | 0 | 0 | 0 | 0 | 0] | |
| | 0 | 0 | 0 | 1 | $ ho_i$ | $ ho_i \omega_i'$ | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 1 | $ ho_i \omega_i'$ | ρ_i | |
| | 1 | $ ho_i$ | $ ho_i$ | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 1 | ρ_i | $ ho_i \omega_i'$ | 0 | 0 | 0 | (4) |
| | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | ρ_i | |
| | 1 | ρ_i | $ ho_i$ | 0 | 0 | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 1 | $ ho_i$ | 0 | 0 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 1 | $ ho_i \omega_i'$ | ρ_i | |
| | | | | | | | | | | |

and

$$U_6 = U_9 =$$

Here, the conformational energies, E_{ξ_i} , $(\xi_i = \rho_i, \sigma_i, \omega_i,$ and $\chi_i)$, have been defined for each bond to examine their position dependence. The intramolecular interactions are illustrated in Figure 2. Tables I and II show the SCF and Gibbs free energies of the individual conformers of DME and triglyme, respectively. In the rotational isomeric state (RIS) scheme,^{5,18} the ΔG_k values of DME are represented as a function of E_{ξ_i} 's. For example, the g⁺g⁺g⁺ conformation has a weight

Table I. SCF (\triangle SCF) and free ($\triangle G_k$) energies of conformers of DME^a

| k | conformation | M_k | statistical weight ^b | ΔSCF^c (kcal mol ⁻¹) | ΔG_k^{c} (kcal mol ⁻¹) |
|----|-------------------------|-------|------------------------------------|---|--|
| 1 | ttt | 1 | 1 | 0.00 | 0.00 |
| 2 | ttg^{\pm} | 4 | ρ_2 | 1.49 | 1.31 |
| 3 | tg±t | 2 | σ_3 | 0.20 | 0.19 |
| 4 | $tg^{\pm}g^{\pm}$ | 4 | $\rho_2 \sigma_3$ | 1.61 | 1.28 |
| 5 | $tg^{\pm}g^{\mp}$ | 4 | $\rho_2 \sigma_3 \omega_3$ | 0.38 | 0.26 |
| 6 | $g^{\pm}tg^{\pm}$ | 2 | $ ho_2^2$ | 3.05 | 2.74 |
| 7 | g±tg∓ | 2 | ρ_2^2 | 3.00 | 2.61 |
| 8 | $g^{\pm}g^{\pm}g^{\pm}$ | 2 | $ ho_2^2 \sigma_3 \chi_4$ | 1.73 | 2.27 |
| 9 | $g^{\pm}g^{\pm}g^{\mp}$ | 4 | $\rho_2^2 \sigma_3 \omega_3$ | 1.97 | 1.88 |
| 10 | $g^{\pm}g^{\mp}g^{\pm}$ | 2 | $\rho_2^2 \sigma_3 \omega_3^2$ | 2.32 | 1.77 |

^aRelative to the all-trans conformation. At 25 °C and 1 atm. ^bFor the statistical weights, see eqs 1–5 and Figure 2. °At the MP2/6-311++G(3df, 3pd)//HF/6-31G(d) level.

| Table II. | SCF (\triangle SCF) and free ($\triangle G_k$) energies |
|-----------|--|
| | of conformers of triglyme ^a |

| k | gauche bond(s) | statistical | ΔSCF^{c} | $\Delta G_k^{\ c}$ |
|----|---------------------------------------|---------------------------------|--------------------------|--------------------------|
| | gauene bond(s) | weight ^b | (kcal mol^{-1}) | (kcal mol^{-1}) |
| 1 | none (all-trans) | 1 | 0.00 | 0.00 |
| 2 | 2 | ρ_2 | 1.45 | 1.25 |
| 3 | 3 | σ_3 | 0.03 | 0.06 |
| 4 | 4 | $ ho_4$ | 1.27 | 1.09 |
| 5 | 5 | ρ_5 | 1.23 | 1.05 |
| 6 | 6 | σ_6 | -0.13 | -0.08 |
| 7 | $2 (g^{\pm}) 3 (g^{\mp})$ | $\rho_2 \sigma_3 \omega_3$ | 0.28 | 0.15 |
| 8 | $3 (g^{\pm}) 4 (g^{\mp})$ | $\sigma_3 \rho_4 \omega_4$ | 0.19 | -0.03 |
| 9 | $5 (g^{\pm}) 6 (g^{\mp})$ | $\rho_5 \sigma_6 \omega_6$ | 0.04 | -0.18 |
| 10 | $2 (g^{\pm}) 3 (g^{\pm}) 4 (g^{\pm})$ | $\rho_2 \sigma_3 \rho_4 \chi_4$ | 1.42 | 1.95 |
| 11 | $5~(g^{\pm})~6~(g^{\pm})~7~(g^{\pm})$ | $ ho_5^2 \sigma_6 \chi_7$ | 1.12 | 1.64 |

^aRelative to the all-trans conformation. At 25 °C and 1 atm. ^bFor the statistical weights, see eqs 1–5 and Figure 2. °At the MP2/6-311++G(3df, 3pd)//HF/6-31G(d) level.

of $\rho_2^2 \sigma_3 \chi_4$. Thus, the ΔG_k value may correspond to $2E_{\rho_2} + E_{\sigma_3} + E_{\chi_4}$. The statistical weight is related to the corresponding conformational energy through the Boltzmann factor; for example, $\rho = \exp(-E_{\rho}/RT)$, where *R* is the gas constant, and *T* is the absolute temperature. The E_{ξ} values were determined by minimizing the following function:

$$S(\mathbf{E}) = \frac{1}{K} \sum_{k} \left(\sum_{\xi} L(\xi) E_{\xi} - \Delta G_{k} \right)^{2} \times M_{k} \exp(-\Delta G_{k} / RT)$$
(6)

The function $L(\xi)$ gives the number of conformational energy E_{ξ} included in the conformation, K is the total number of conformers, and M_k is the number of equivalent conformers. The squared difference between ΔG_k and the sum of E_{ξ} 's was multiplied by the Boltzmann factor $\exp(-\Delta G_k/RT)$ so as to weight low-energy conformations. The temperature was set to 298.15 K. The E_{ξ} values were determined as shown in Table III. The positive E_{σ_3} value of DME indicates that the ttt state is slightly more stable than tgt. For tri-

Table III. Conformational energies of DME and triglyme^a

| | DME | triglyme |
|----------------|-------|----------|
| $E_{ ho_2}$ | 1.30 | 1.25 |
| $E_{ ho_4}$ | | 1.09 |
| $E_{ ho_5}$ | | 1.05 |
| E_{σ_3} | 0.08 | 0.06 |
| E_{σ_6} | | -0.08 |
| E_{ω_3} | -1.02 | -1.15 |
| E_{ω_4} | | -1.18 |
| E_{ω_6} | | -1.14 |
| E_{χ_4} | -0.42 | -0.44 |
| E_{χ_7} | | -0.37 |
| | | |

^aIn kcal mol⁻¹.

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Figure 3. Observed (above) and calculated (below) ¹H NMR spectra of triglyme dissolved in cyclohexane- d_{12} at 25 °C: (a) methylene group a (satellite peaks); (b) methylene groups a and b; (c) methylene group c. For the designation of protons, see Figure 1.

glyme, the MO calculations were so time-consuming as to be performed only for specific conformers. From the ΔG_k values, the E_{ξ_i} values were derived for the individual bonds as listed in Table III.

The results can be summarized as follows. (1) A narrow range (-1.02 to $-1.18 \text{ kcal mol}^{-1}$) of E_{ω} 's were obtained for the two model compounds, the strength of the intramolecular hydrogen bond may scarcely depend on the chain length and position. (2) The E_{σ_3} and E_{σ_6} values are slightly positive and negative, respectively; the terminal monomeric unit has an E_{σ} value larger than the inner one. This suggests the possibility that PEO can adopt the gauche conformation in the C-C bond without the aid of the intramolecular hydrogen bonds; therefore, as a single chain, PEO somewhat prefers the helical structure to the all-trans planar zigzag form. The all-trans PEO chains, whose zigzag planes are parallel to each other, are packed in a $P_{\bar{1}}$ triclinic lattice.¹⁴ Densities of the monoclinic (helix) and triclinic (zigzag) lattices are 1.228 and 1.197 g cm^{-3} , respectively; therefore, the helical chains are more densely packed than the planar zigzag ones. The small magnitude of E_{σ_6} suggests that PEO may change the C-C conformation between gauche and trans even in the crystal.

¹H NMR of Triglyme

Figure 3 shows an example of ¹H NMR spectra observed from methylene protons of triglyme. Simu-

lations using the gNMR program¹⁹ yielded vicinal coupling constants, ${}^{3}J_{\rm HH}$ (= ${}^{3}J_{\rm AB} = {}^{3}J_{{\rm A'B'}}$) and ${}^{3}J'_{\rm HH}$ (= ${}^{3}J_{\rm AB'} = {}^{3}J_{{\rm A'B}}$), as listed in Table IV. The observed coupling constants can be expressed as

$${}^{3}J_{\rm HH} = {}^{3}J_{\rm G}p_{\rm t} + \frac{{}^{3}J_{\rm T}' + {}^{3}J_{\rm G}''}{2}p_{\rm g}$$
(7)

and

$${}^{3}J'_{\rm HH} = {}^{3}J_{\rm T}p_{\rm t} + {}^{3}J'_{\rm G}p_{\rm g}$$
 (8)

where ${}^{3}J_{T}$'s and ${}^{3}J_{G}$'s are defined in Figure 4, and p_{t} and p_{g} are trans and gauche fractions of the C–C bond, respectively; therefore, $p_{t} + p_{g} = 1$. Here, we have adopted ${}^{3}J$ values optimized for DME: ${}^{3}J_{T} = {}^{3}J'_{T} = 11.4$ Hz and ${}^{3}J_{G} = {}^{3}J'_{G} = {}^{3}J''_{G} = 2.3$ Hz.⁷ The sum of p_{t} and p_{g} values derived from eqs 7 and 8 was only slightly different from unity, thus being divided by the sum. In Table IV, the p_{t} and p_{g} values of bonds 3 and 6 are compared with those evaluated from the MO calculations. In general, the trans fraction decreases with increasing permittivity of the environment. This tendency agrees with that found previously for DME.⁷

As outlined in the Introduction, E_{σ_i} 's and E_{ω_i} 's tend to vary cooperatively with the medium. Increases in E_{ω_i} 's with increaseing permittivity of the medium are compensated by decreases in E_{σ_i} 's. Consequently, the bond conformations do not show large variations, and hence the three kinds of energy parameters, E_{σ_i} 's, E_{ω_i} 's, and E_{ρ_i} 's, can not be determined only from p_t

| | | bond 3 | | | bond 6 | | | | |
|-----------------------------------|--------------|-----------------------|------------------|-----------------|---------|-----------------------|--------------------------|------------------|---------|
| solvent | permittivity | $^{3}J_{\mathrm{HH}}$ | ${}^3J'_{ m HH}$ | $p_{\rm t}$ | p_{g} | $^{3}J_{\mathrm{HH}}$ | $^{3}J_{ m HH}^{\prime}$ | p_{t} | p_{g} |
| | | | MO ca | lc ^a | | | | | |
| (gas) | 1.0 | | | 0.21 | 0.79 | | | 0.17 | 0.83 |
| | | | NMR e | xptl | | | | | |
| cyclohexane- d_{12} | 2.0 | 6.01 | 4.30 | 0.21 | 0.79 | 6.10 | 4.03 | 0.18 | 0.82 |
| chloroform-d | 4.8 | 6.25 | 3.30 | 0.11 | 0.89 | 6.30 | 3.43 | 0.12 | 0.88 |
| methanol-d4 | 32.7 | 6.27 | 3.31 | 0.11 | 0.89 | 6.21 | 3.27 | 0.11 | 0.89 |
| dimethyl sulfoxide-d ₆ | 46.7 | 6.30 | 3.48 | 0.13 | 0.87 | 6.24 | 3.44 | 0.13 | 0.87 |
| deuterium oxide | 78.5 | 6.42 | 2.66 | 0.05 | 0.95 | 6.36 | 2.62 | 0.05 | 0.95 |

Table IV. Vicinal ¹H–¹H coupling constants and bond conformations of triglyme at 25 °C

^aEvaluated from the conformational energies shown in Table III.



Figure 4. Conformations around the C–C bond of the ethylene oxides with definitions of vicinal coupling constants.

values of bonds 3 and 6; therefore, we have assumed E_{ω_i} and E_{ρ_i} values as follows to derive E_{σ_3} and E_{σ_6} of triglyme.

The boiling point of triglyme is so high $(216 \,^{\circ}\text{C})$ that NMR measurement for gaseous triglyme could not be conducted. In the previous study on DME,²⁰ the ${}^{3}J_{\rm HH}$ and ${}^{3}J'_{\rm HH}$ versus temperature plots for the gas phase and the cyclohexane solution overlap with each other, and no discontinuity was found between the two kinds of data. In fact, as seen from Table IV, the $p_{\rm t}$ and $p_{\rm g}$ values for the cyclohexane solution at 25 °C agree with those of the MO calculations for gaseous triglyme at 25 °C. In Figure 5, the p_t values, calculated from E_{ξ_i} 's (Table III) of triglyme except for E_{σ_6} , are plotted as a function of E_{σ_6} (curve A). The curve intersects with the horizontal line for the cyclohexane solution around $E_{\sigma_6} = -0.1 \text{ kcal mol}^{-1}$. This value probably corresponds to E_{σ_6} of not only the cyclohexane solution but also the gas phase. From bond conformations of PEO dissolved in 1,4-dioxane and dipole moment ratios for the benzene solution, we determined $E_{\rho} = 1.17$ and $E_{\omega} = -0.79 \text{ kcal mol}^{-1.3}$ These energy parameters are considered to represent the ethylene oxides in weakly polar solvents. From E_{ρ_i} 's = 1.17, E_{ω_i} 's = -0.79 kcal mol⁻¹, and E_{σ_3} = E_{σ_6} , the p_t values were calculated and plotted against E_{σ_6} (curve B). Similarly, curve C was obtained from



Figure 5. Trans fraction (p_t) of bond 6 of triglyme as a function of E_{σ_6} . The horizontal lines represent the p_t values determined from the NMR experiments using the solvents indicated. Curves A, B, and C were obtained from the following energy parameters: curve A, conformational energies of triglyme in Table III, except for E_{σ_6} ; curve B, E_{ρ_i} 's = 1.17 and E_{ω_i} 's = $-0.79 \text{ kcal mol}^{-1}$; curve C, E_{ρ_i} 's = 0.9 and E_{ω_i} 's = 0.4 kcal mol⁻¹. For curves B and C, $E_{\sigma_5} = E_{\sigma_6}$ was assumed.

 E_{ρ_i} 's = 0.9 and E_{ω_i} 's = 0.4 kcal mol⁻¹ (the Θ solution of PEO, *i.e.*, 0.45 M K₂SO₄ at 34.5 °C). The horizontal lines for chloroform, dimethyl sulfoxide, and methanol intersect with curves B and C around $E_{\sigma_6} = -0.5$ and -0.8 to -0.9 kcal mol⁻¹, respectively. Therefore, the E_{σ_6} values of triglyme in these solvents probably stay within the range. From the intersection between curve C and the horizontal line of water, we can estimate the E_{σ_6} value of triglyme in water as ≤ -1.6 kcal mol⁻¹.

From the p_t versus E_{σ_3} plots (not shown), we similarly estimated the E_{σ_3} values of bond 3 of triglyme in the solvents: cyclohexane, +0.1 kcal mol⁻¹; chloroform, methanol, and dimethyl sulfoxide, -0.5 to -0.9 kcal mol⁻¹; water, ≤ -1.4 kcal mol⁻¹. Both MO calculations and NMR experiments indicate that E_{σ_6} of triglyme is negative even in the gas phase. How-

ever, the essential fact here is that E_{σ_6} is significantly smaller than E_{σ} (+0.5 kcal mol⁻¹) of hydrocarbon chains^{5,21} because this indicates the inherent gauche stability of the C–C bond adjacent to the ether linkage, *i.e.*, the attractive gauche effect independent of the (C–H)···O attraction.

Finally, the small differences in E_{ξ} 's between DME and triglyme (Table III) fairly justify conformational analyses of polymers using monomeric model compounds, unless very strict discussion is required.

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