# Conformational Characteristics of Poly(ethylene sulfide) and Poly(ethylene oxide): Solvent Dependence of Attractive and Repulsive Gauche Effects

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ABSTRACT: Conformational characteristics of poly(ethylene sulfide) (PES), poly(ethylene oxide) (PEO), and their oligomeric model compounds have been investigated by the rotational isomeric state (RIS) analysis of ab initio molecular orbital (MO) calculations, NMR vicinal coupling constants, characteristic ratios, and dipole moment ratios. Conformational energies of PES were determined from <sup>1</sup>H and <sup>13</sup>C NMR vicinal constants of its monomeric model compound, 1,2-bis(methylthio)ethane (BMTE), and ab initio MO calculations for BMTE at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and MP2/6-311+G-(3df,2p)//HF/6-31G(d) levels. By the NMR analysis, the firs-order interaction energies for the gauche states around the C–C and C–S bonds, designated as  $E_{\sigma}$  and  $E_{\rho}$  respectively, were evaluated as follows: in benzene,  $E_{\sigma} = 0.41$  kcal mol<sup>-1</sup> and  $E_{\rho} = -0.74$  kcal mol<sup>-1</sup>; in chloroform,  $E_{\sigma} = 0.31$  kcal mol<sup>-1</sup> and  $E_{\rho} = -0.74$  kcal mol<sup>-1</sup>; in chloroform,  $E_{\sigma} = 0.31$  kcal mol<sup>-1</sup> and  $E_{\rho} = -0.74$  kcal mol<sup>-1</sup>. -0.41 kcal mol<sup>-1</sup>. The C-C and C-S bonds were shown to prefer the trans and gauche conformations, respectively. These tendencies are consistent with the MO calculations: B3LYP,  $E_{\sigma} = 1.39$  kcal mol<sup>-1</sup> and  $E_{\rho} = -0.24$  kcal mol<sup>-1</sup>; MP2,  $E_{\sigma} = 0.89$  kcal mol<sup>-1</sup> and  $E_{\rho} = -0.41$  kcal mol<sup>-1</sup>. Inasmuch as the MO calculations represent gaseous BMTE, the conformational energies were indicated to have large solvent dependence. Ab initio MO calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and MP2/6-311+G-(3df,2p)//HF/6-31G(d) levels and by the complete basis set (CBS-Q) method were carried out for 1,2dimethoxyethane (DME), a model compound of PEO. All of the MO calculations showed the presence of the (C-H)...O attraction in the  $g^{\pm}g^{\mp}$  conformations for the C-C/C-O bond pairs. The MP2 calculations gave the first-order interaction energies ( $E_{\sigma}$  and  $E_{\rho}$ ) for the gauche states around the C–C and C–O bonds as 0.32 and 1.22 kcal mol<sup>-1</sup>, respectively. The conformational energy  $E_{\omega}$  representing the (C–H)···O interaction was evaluated as -1.12 kcal mol<sup>-1</sup>. In the RIS scheme, bond conformations of PEO in 1,4-dioxane and dipole moment ratios of PEO in benzene were simultaneously simulated, and the conformational energies of PEO in nonpolar organic solvents were determined:  $E_a = -0.25$ ,  $E_b = -0.25$ 1.17, and  $E_{\omega} = -0.79$  kcal mol<sup>-1</sup>. Ours and Abe and Mark's data  $[E_{\sigma} = -0.5, E_{\rho} = 0.9, \text{ and } E_{\omega} = 0.4$  kcal mol<sup>-1</sup>, Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468] show that the  $E_{\sigma}$  and  $E_{\omega}$  values of PEO so widely vary with solvent as to change the signs. Configurational entropies of 200 mers of PES and PEO were calculated to be 5.8–6.3 and 5.0-5.1 cal mol<sup>-1</sup>  $K^{-1}$ , respectively. Thus, the difference in melting point between PES (216 °C) and PEO (68 °C) was indicated to come from that in enthalpy ( $\Delta H_{u}$ ) of fusion:  $\Delta H_u$  (PES) >  $\Delta H_u$  (PEO). The natural bond orbital analysis for BMTE and DME revealed the following facts. For BMTE and DME, vicinal bond-antibond interactions around the C-C bond cause the gauche preference. For BMTE, however, a steric S $\cdots$ S repulsion considerably reduces the gauche stability, and hence the trans preference appears in the C-C bond. Bond-antibond and lone pair-antibond interactions around the C-X bond (X = S or O) stabilize the gauche conformation for BMTE but the trans state for DME. Both MO calculations and NMR experiments for BMTE showed that the most stable states are  $g^{\pm}tg^{\mp}$ , in which electron delocalization in the S-C-C-S antibonds is maximized and a large antiparallel dipole-dipole interaction is formed. Thus, the  $g^{\pm}tg^{\mp}$  conformations have a smaller free energy than  $g^{\pm}tg^{\pm}$  by ca. 0.2 kcal mol<sup>-1</sup>, being found in BMTE and PES crystals.

# **1. Introduction**

Poly(ethylene oxide) (PEO,  $[-CH_2CH_2O-]_x$ ) is a unique polymer; it is soluble in a number of solvents such as ordinary organic solvents, water, and aqueous solutions of inorganic salts and innocuous to organisms, thus being widely used for antifoaming agents, cosmetics, and artificial organs. As found for crown ethers, the O-C-C-O bond sequence acts as an effective electron donor. These peculiar physicochemical properties, being due to the lone pair and electronegativity of oxygen, enable us to utilize PEO as ion conductors.  $^{1}\,$ 

Oxygen and sulfur belong to the group VIB in the periodic table. These atoms have analogous valenceshell configurations: O,  $2s^22p$ ;<sup>4</sup> S,  $3s^23p$ .<sup>4</sup> However, poly-(ethylene sulfide) (PES,  $[-CH_2CH_2S-]_x$ ) exhibits physical and chemical properties different from those of PEO. For example, PES is soluble in a few solvents at temperatures above 140 °C. The melting point of PEO, depending on molecular weight and terminal group, is, at the highest, 68 °C, whereas that of PES is as high as 216 °C. Despite the outstanding thermal properties, PES is too intractable to be used for industrial purposes.<sup>2</sup>

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**Figure 1.** Schematic representation of compounds treated in this study: (a) monomeric model compounds, 1,2-bis(methyl-thio)ethane (BMTE) and 1,2-dimethxyethane (DME); (b) polymers, poly(ethylene sulfide) (PES) and poly(ethylene oxide) (PEO). The bonds are numbered and the atoms are designated as indicated, and *x* is the degree of polymerization.

In the crystalline state, PES and PEO adopt different conformations. In the X-C-C-X (X = S or O) bond sequence, PES and its monomeric model compound, 1,2-bis(methylthio)ethane (BMTE, CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub>, Figure 1), have the g<sup>+</sup>tg<sup>-</sup> conformation,<sup>3,4</sup> whereas PEO can take either tgt or ttt conformation.<sup>5,6</sup> The latter conformation of PEO has been found only in stretched samples. 1,2-Dimethoxyethane (DME, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-OCH<sub>3</sub>), a monomeric model compound of PEO, also adopts the tgt conformation.<sup>7</sup>

It is well-known that the C–C bond in Y–C–C–Z bond sequences prefers the gauche conformation. Here, Y and Z stand for electronegative elements such as F, Cl, and O. This phenomenon was designated as the attractive gauche effect.<sup>8–10</sup> If both X and Y are sulfur, the C–C bond tends to take the trans conformation. This is called the repulsive gauche effect.<sup>8–10</sup> By vibrational spectroscopic measurements for gaseous and liquid BMTE, enthalpies of the gauche state around the C–C bond were estimated to be 1.1 and 0.1 kcal mol<sup>-1</sup>, respectively.<sup>11</sup> The solvent dependence is surprisingly large.

Of all synthetic polymers, PEO has been most extensively investigated in terms of conformation. From experimental characteristic ratio and dipole moment ratio of PEO, Mark and Flory determined the conformational energies,  $E_{\sigma}$  and  $E_{\rho}$ , for the gauche states of the C–C and C–O bonds as  $-0.43 \pm 0.07$  and  $0.90 \pm$ 0.07 kcal mol<sup>-1</sup>, respectively. <sup>12-14</sup> The conformational energy  $E_{\omega}$  for the second-order interaction (referred hereafter to as the  $(C-H)\cdots O$  interaction) between the methylene (methyl) group and oxygen atom occurring in the  $g^{\pm}g^{\mp}$  conformations for the  $\dot{C}$ -O/C-C bond pairs was estimated to be 0.35  $\pm$  0.20 kcal mol<sup>-1</sup>. The intramolecular interactions are illustrated in Figure 2. Abe and Mark<sup>15</sup> offered a minor modification of the energy parameters:  $E_{\sigma} = -0.5$ ,  $E_{\rho} = 0.9$ , and  $E_{\omega} = 0.4$  kcal mol<sup>-1</sup>. These data mean that the attractive gauche effect of PEO is due to the first-order  $\sigma$  interaction; that is, the C-C bond itself has a gauche preference. In recent years, however, ab initio MO calculations for DME have estimated the  $E_{\sigma}$  and  $E_{\omega}$  values to be 0.1– 0.5 kcal mol<sup>-1</sup> and -1.2 to -1.4 kcal mol<sup>-1</sup>, respectively.<sup>16,17</sup> The (C-H)····O interaction is suggested to be attractive and stabilize the gauche state of the C-C bond. The MO calculations reasonably reproduced experimental conformer fractions of gaseous DME.<sup>18,19</sup>

The intramolecular  $(C-H)\cdots O$  attractions were also suggested by ab initio MO calculations for 1,2-dimethoxypropane (1,2-DMP, CH<sub>3</sub>OCH<sub>2</sub>CH(CH<sub>3</sub>)OCH<sub>3</sub>), a monomeric model compound of poly(propylene oxide) (PPO,



**Figure 2.** Definition of intramolecular interactions (statistical weights) for PES and PEO.  $\rho$  and  $\sigma$  are the first-order interactions around the C–X and C–C bonds (X = S or O), respectively.  $\omega$  and  $\omega'$  are the second-order interactions occurring in the  $g^{\pm}g^{\mp}$  conformations for the X–C/C–C and C–X/X–C bond pairs, respectively.  $\chi$  and  $\kappa$  are the third-order interactions formed in the  $g^{\pm}g^{\pm}g^{\pm}$  and  $g^{\pm}tg^{\mp}$  conformations of the X–C–C–X bond sequence, respectively.

 $[-CH_2CH(CH_3)O-]_x)^{20}$  The presence of the  $(C-H)\cdots O$ attraction in PPO and its oligomeric model compounds was demonstrated by comparison between calculations and observations of characteristic ratio  $(\langle r^2 \rangle_0 / nl^2)$  and dipole moment ratio ( $\langle \mu^2 \rangle / nm^2$ ) of isotactic PPO,<sup>21</sup> <sup>1</sup>H and <sup>13</sup>C NMR vicinal coupling constants of 1,2-DMP,<sup>20,22</sup> and <sup>13</sup>C NMR chemical shifts of six dimers having different configurational sequences.<sup>23</sup> Here, r is the end-to-end distance, *n* is the number of skeletal bonds, *l* is the bond length,  $\mu$  is the dipole moment, *m* is the bond dipole moment, the angular brackets represent the ensemble average, and the subscript 0 stands for the unperturbed state. For PEO, however, all experimental facts on the gauche effect are not consistent with each other and cannot be elucidated just by the (C-H)...O attraction. For example, not the  $tg^+g^-$  but the tgt conformation is formed in crystallized PEO and DME.5,7 The tgt conformation seems to be more stable than ttt, because the ttt form appears only in stretched samples.<sup>6</sup> The MO energies did not well reproduce the observed dipole moment ratio of PEO.24

Conformational analysis of PES was first carried out about 2 decades ago. Abe<sup>25</sup> calculated the conformational energies by semiempirical potential energy functions. The  $E_{\sigma}$  and  $E_{o}$  values were calculated to be +0.4 and -0.1 kcal mol<sup>-1</sup>, respectively. The second-order interaction energies,  $E_{\omega}$  and  $E_{\omega'}$ , arising in the  $g^{\pm}g^{\mp}$ conformations for the S-C/C-C and C-S/S-C bond pairs (see Figure 2), were estimated as 1.1 and 0.4 kcal mol<sup>-1</sup>, respectively. From these energy parameters, the  $\langle r^2 \rangle_0 / nl^2$  and  $\langle \mu^2 \rangle / nm^2$  values of PES were calculated to be 4.2 and 0.42, respectively. Because PES is soluble in a few solvents at high temperatures, the  $\Theta$  condition has not been found. Therefore, it is probably impossible to obtain the experimental  $\langle r^2 \rangle_0 / n l^2$  value. Riande and Guzmán<sup>26,27</sup> estimated the  $E_\sigma$  value indirectly from experimental dipole moments of an alternating copolymer of pentamethylene sulfide and ethylene sulfide as well as 1,2-bis(butylthio)ethane dissolved in benzene. The  $E_{\sigma}$  value was found to be in the range 0.4–0.7 kcal  $mol^{-1}$ .

In this study, the first-order and second-order interaction energies for the S-C-C-S bond sequence have been evaluated from <sup>1</sup>H and <sup>13</sup>C NMR vicinal coupling constants observed from BMTE dissolved in benzene and chloroform. The NMR method enabled us to determine bond conformations for the individual bonds. Ab initio molecular orbital (MO) calculations were carried out for BMTE and DME by the Hartree-Fock (HF) method including the second-order Møller-Plesset (MP2) electronic correlation and the density functional method of Becke's three-parameter functions using the Lee-Yang–Parr correlation function (B3LYP)<sup>28</sup> to calculate the free energies, dipole moments, and atomic charges of all possible conformers in the gas phase. For DME, MO calculations using the complete basis set (CBS-Q) method<sup>29</sup> were also carried out. Conformational energies of PES and PEO in the gas phase and solutions were determined from the MO calculations and NMR data. From the energy parameters thus established, the  $\langle r^2 \rangle_0/$  $nl^2$  and  $\langle \mu^2 \rangle / nm^2$  values and configurational entropies  $(S_{\text{conf}}$ 's) were calculated. In addition, the natural bond orbital (NBO) analysis 30-34 at the MP2 level with the 6-311+G(3df,2p) basis set was applied to BMTE and DME to interpret the gauche effects in terms of bondantibond ( $\sigma \rightarrow \sigma^*$ ) and lone pair-antibond ( $n \rightarrow \sigma^*$ ) interactions. In this paper, the results are reported in detail and discussed.

#### 2. Materials and Methods

**2.1. Sample Preparation. 2.1.1. 1,2-Bis(methylthio)ethane (BMTE).**<sup>35</sup> Aqueous solution of sodium thiomethoxide (0.51 mol, 220 mL) was heated to 60 °C in a four-necked flask with a condenser, a thermometer, and a dropping funnel. To the solution, trioctylmethylammonium chloride (1.0 g) and 1,2dibromoethane (0.23 mol, 20 mL) were added dropwise. The mixture was heated at 60 °C for ca. 6 h. After being cooled to room temperature, the reaction mixture was subjected to extraction with ether. The organic extract was dried over sodium sulfate for a day, filtered, condensed, and distilled under reduced pressure (80 °C and 20 mmHg) to yield BMTE (yield: 60%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C,  $\delta$ ): 2.33 (H<sub>A</sub> and H<sub>A</sub>), 2.61 (H<sub>B</sub> and H<sub>B</sub>), <sup>2</sup>J<sub>AA'</sub> = <sup>2</sup>J<sub>BB'</sub> = -7.85 Hz, <sup>3</sup>J<sub>AB</sub> = <sup>3</sup>J<sub>A'B</sub> = 10.50 Hz, <sup>3</sup>J<sub>AB</sub> = <sup>3</sup>J<sub>A'B'</sub> = 5.41 Hz. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$ ): 2.58 (H<sub>A</sub> and H<sub>A</sub>), 2.86 (H<sub>B</sub> and H<sub>B'</sub>), <sup>2</sup>J<sub>AA'</sub> = <sup>2</sup>J<sub>BB'</sub> = -7.63 Hz, <sup>3</sup>J<sub>AB'</sub> = <sup>3</sup>J<sub>A'B</sub> = 10.31 Hz, <sup>3</sup>J<sub>AB</sub> = <sup>3</sup>J<sub>A'B'</sub> = 5.52 Hz. For the designation of protons, see Figure 1.

2.1.2. 2-(1,1-Dimethylethyl)-1,4-dithiane (DMEDT).36,37 2,2'-Azobis(isobutyronitrile) (5.3 g) was dissolved under dry nitrogen in toluene (370 mL) in a four-necked flask with a condenser, a thermometer, and a dropping funnel. 3,3-Dimethyl-1-butyne (0.044 mol, 3.7 mL) and 1,2-ethanedithiol (0.049 mol, 6.0 mL) were added dropwise to the flask, which was cooled with ice water. The mixture was stirred at room temperature for 4 days with the condenser being cooled at ca. 1 °C by circulating aqueous solution of ethylene glycol. The reaction mixture was solidified by removing the liquid components. The crude product was recrystallized with *n*-hexane and dried under reduced pressure to yield DMEDT (2.6 g, 53%). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 25 °C,  $\delta$ ): 2.77 (H<sub>A</sub>), 2.60 (H<sub>B</sub>), 2.82 (H<sub>C</sub>), 2.86 (H<sub>D</sub>), 2.18 (H<sub>E</sub>), 2.44 (H<sub>F</sub>), 2.64 (H<sub>G</sub>)  ${}^{2}J_{AB} =$ -13.50 Hz,  ${}^{3}J_{AC} = 10.87 \text{ Hz}$ ,  ${}^{3}J_{BC} = 1.89 \text{ Hz}$ ,  ${}^{3}J_{DE} = 2.41 \text{ Hz}$ ,  ${}^{2}J_{DE} = -13.78 \text{ Hz}$ ,  ${}^{3}J_{DG} = 12.00 \text{ Hz}$ ,  ${}^{3}J_{EF} = 4.09 \text{ Hz}$ ,  ${}^{2}J_{EG} = 2.41 \text{ Hz}$ , -13.59 Hz,  ${}^{3}J_{FG} = 2.44$  Hz.  ${}^{1}$ H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta){:}~~2.90~(H_A),~2.84~(H_B),~2.89~(H_C),~3.11~(H_D),~2.66~(H_E),~2.93$ (H<sub>F</sub>), 2.89 (H<sub>G</sub>)  ${}^{2}J_{AB} = -13.59$  Hz,  ${}^{3}J_{AC} = 10.89$  Hz,  ${}^{3}J_{BC} = 1.84$  Hz,  ${}^{3}J_{DE} = 2.43$  Hz,  ${}^{2}J_{DF} = -13.83$  Hz,  ${}^{3}J_{DG} = 12.06$  Hz,  ${}^{3}J_{EF} = 4.09$  Hz,  ${}^{2}J_{EG} = -13.67$  Hz,  ${}^{3}J_{FG} = 2.47$  Hz. The long-range couplings  ${}^{4}\mathcal{J}s$  were also included in the simulations to be described below, being estimated to be smaller than 1 Hz. For the designation of protons, see Figure 3.

**2.1.3.2** (1,1-Dimethylethyl)-1,4-dithiane-5,5,6,6-*d*<sub>4</sub> (DMEDT-*d*<sub>4</sub>). Aqueous solution of sodium hydrosulfide hydrate (205 mL)



**Figure 3.** (a) 2-(1,1-Dimethylethyl)-1,4-dithiane (DMEDT) and (b) 2-(1,1-dimethylethyl)-1,4-dithiane-5,5,6,6- $d_4$  (DMEDT- $d_4$ ). The hydrogen atoms are designated as indicated.

was heated to 60 °C in a four-necked flask with a condenser, a thermometer, and a dropping funnel. To the solution, trioctylmethylammonium chloride (1.0 g) and 1,2-dibromoethane- $d_4$  (Isotec, 0.26 mol) were added dropwise. The mixture was heated at 60 °C for ca. 10 h. After being cooled to room temperature, the precipitate was removed by filtration. The filtrate was subjected to extraction using ether, and the ethereal solution was dried over sodium sulfate for a day, filtered, condensed, and distilled under reduced pressure (64 °C and 46 mmHg) to yield 1,2-ethandithiol-1,1,2,2- $d_4$  (4.2 g, 16%). As described in the preceding section, 2-(1,1-dimethyl-ethyl)-1,4-dithiane-5,5,6,6- $d_4$  was prepared from 1,2-ethanedithiol-1,1,2,2- $d_4$ . The yield was 53% (2.9 g).

**2.2. NMR Measurements.** <sup>1</sup>H (<sup>13</sup>C) NMR spectra were measured at 500 MHz (125.65 MHz) on a JEOL JNM-LA500 spectrometer equipped with a variable temperature controller. During the measurement the probe temperature was maintained within  $\pm 0.1$  °C fluctuations. In the measurements, free induction decays were accumulated 8 (ca. 6000) times. The  $\pi/2$  pulse width, data acquisition time, and recycle delay were 5.6 (4.8)  $\mu$ s, 13.1 (10.4) s, and 3.7 (2.5) s, respectively. The solvents were benzene- $d_6$  and chloroform- $d_1$ , the internal standard was tetramethylsilane, and the solute concentration was 5 vol %. Here, the values in the parentheses represent the corresponding <sup>13</sup>C NMR parameters. The gated decoupling technique was used in the <sup>13</sup>C NMR measurements.

2.3. Ab Initio MO Calculations. Ab initio MO calculations were carried out for BMTE and DME using the Gaussian98 program<sup>38</sup> installed on a Compaq XP1000 workstation. At the HF/6-31G(d) level, the geometrical parameters were fully optimized, and the zero-point energies, thermal energies, and entropies were also calculated. Then a scale factor of 0.9135 was used to correct the overestimated thermodynamic quantities.<sup>39,40</sup> With the geometries thus determined, the selfconsistent field (SCF) energies were calculated at the MP2/6-311+G(3df,2p) level (abbreviated as MP2/6-311+G(3df,2p)// HF/6-31G(d)), atomic charges and dipole moments were computed by the Merz–Singh–Kollman method,  $^{41,42}$  and the NBO analysis  $^{30-34,43}$  was concomitantly performed. Conformational free energies of the individual conformers at 298.15 K and 1.0 atm were evaluated from the SCF energy and thermodynamic quantities. The free energies, atomic charges, and dipole moments were also calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level;<sup>28</sup> however, the thermal correction at the HF/6-31G(d) level, obtained as above, was used. For DME, the conformer free energies were also calculated by the CBS-Q method.<sup>29</sup> Supplementary computations for the oligomers were carried out to investigate the chain length effects, etc. The details are described in later sections.

# 3. Results and Discussion

**3.1.** <sup>1</sup>H NMR from BMTE and DMEDT. Figure 4 shows satellite spectra observed from BMTE dissolved in  $C_6D_6$  at 15 °C. As illustrated in Figure 4a, naturally abundant <sup>13</sup>C atoms yield two groups of satellite peaks, which are separated from each other by the direct C–H



**Figure 4.** <sup>1</sup>H NMR spectra of BMTE in  $C_6D_6$  at 15 °C: (a) methylene peak portion and (b) observed and (c) simulated satellite peaks.





trans gauche

**Figure 5.** Newman projections for (a) C–C and (b) C–S bonds of BMTE with definitions of vicinal coupling constants.

coupling constant  ${}^{1}J_{CH}$  and symmetrical with respect to the intense methylene peak. In Figure 4b, the upfield group is enlarged.

Newman projections for the trans and gauche states around the C–C bond of BMTE are shown in Figure 5a. With the rotational isomeric state (RIS) approximation, the observed vicinal  ${}^{1}\text{H}{-}{}^{1}\text{H}$  coupling constants,  ${}^{3}J_{\text{HH}}$  and  ${}^{3}J_{\text{HH}}$ , can be expressed as<sup>44,45</sup>

$${}^{3}J_{\rm HH} = {}^{3}J_{\rm AB} = {}^{3}J_{\rm A'B'} = {}^{3}J_{\rm G}\,p_{\rm t}^{\rm CC} + \frac{{}^{3}J_{\rm T} + {}^{3}J_{\rm G'}}{2}p_{\rm g}^{\rm CC} \quad (1)$$

and

$${}^{3}J'_{\rm HH} = {}^{3}J_{\rm AB'} = {}^{3}J_{\rm A'B} = {}^{3}J_{\rm T} p_{\rm t}^{\rm CC} + {}^{3}J'_{\rm G} p_{\rm g}^{\rm CC}$$
 (2)

where  ${}^{3}J_{T}$ ,  ${}^{3}J_{T}$ ,  ${}^{3}J_{G}$ ,  ${}^{3}J_{G}$ , and  ${}^{3}J_{G}'$  are defined in Figure



**Figure 6.** (a) Observed and (b) calculated <sup>1</sup>H NMR spectra of DMEDT in CDCl<sub>3</sub> at 35 °C and (c) observed and (d) calculated <sup>1</sup>H NMR spectra of DMEDT- $d_4$  in CDCl<sub>3</sub> at 35 °C. The capital letters (A–G) indicate chemical shift positions of the corresponding protons (see Figure 3).

Table 1. Observed Vicinal <sup>1</sup>H-<sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H Coupling Constants of BMTE

solvent	dielectric constant of solvent <sup>a</sup>	temp (°C)	<sup>3</sup> J <sub>HH</sub> (Hz)	<sup>3</sup> J' <sub>HH</sub> (Hz)	<sup>3</sup> <i>J</i> <sub>CH</sub> (Hz)
benzene- <i>d</i> 6	2.28	$15.0 \\ 25.0 \\ 35.0 \\ 45.0 \\ 55.0$	5.36 5.41 5.41 5.46 5.48	10.72 10.50 10.50 10.40 10.28	4.60 4.59 4.56 4.53 4.50
chloroform-d <sub>1</sub>	4.81	15.0 25.0 35.0 45.0 55.0	5.50 5.52 5.56 5.56 5.60	10.37 10.31 10.20 10.12 10.08	4.39 4.35 4.35 4.34 4.26

<sup>a</sup> At 20 °C.

5a, and  $p_{\rm t}^{\rm CC}$  and  $p_{\rm g}^{\rm CC}$  are trans and gauche fractions of the C–C bond, respectively. Therefore, we have

$$p_{\rm t}^{\rm CC} + p_{\rm g}^{\rm CC} = 1 \tag{3}$$

As shown in Figure 4, the simulation based on an AA'BB'X spin system satisfactorily reproduced the observed spectrum. For other spectra, the simulation always gave good agreement with experiment. The  ${}^{3}J_{\rm HH}$  and  ${}^{3}J_{\rm HH}$  values thus determined are listed in Table 1. All NMR parameters for the C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> solutions at 25 °C are given in section 2.1.1.

To solve eqs 1–3, the vicinal coupling constants,  ${}^{3}J_{T}$ ,  ${}^{3}J_{G}$ ,  ${}^{3}J_{G}$ , and  ${}^{3}J'_{G}$ , are required. We attempted to derive these coupling constants from a cyclic compound DMEDT, which has the same S–CH<sub>2</sub>–CH<sub>2</sub>–S bond sequence as BMTE. The bulky *tert*-butyl substituent prevents the DMEDT ring from changing the conformation. Figure 6a shows methine and methylene part of a <sup>1</sup>H NMR spectrum observed from DMEDT in CDCl<sub>3</sub> at 35 °C. In the region, signals of seven protons A–G

 Table 2. Observed Vicinal <sup>1</sup>H-<sup>1</sup>H Coupling Constants of DMEDT<sup>a</sup>

solvent	temp	<sup>3</sup> <i>J</i> <sub>DG</sub> <sup><i>b</i></sup>	<sup>3</sup> J <sub>DE</sub>	<sup>3</sup> <i>J</i> <sub>EF</sub> <sup><i>c</i></sup>	<sup>3</sup> J <sub>FG</sub>	<sup>3</sup> <i>J</i> <sub>G</sub> <sup><i>d</i></sup>	<sup>3</sup> <i>J</i> ' <sub>G</sub> <sup>e</sup>
	(°C)	(Hz)	(Hz)	(Hz)	(Hz)	(Hz)	(Hz)
benzene- <i>d</i> <sub>6</sub>	15.0	12.02	2.41	4.08	2.43	2.97	2.42
	25.0	12.00	2.41	4.09	2.44	2.98	2.43
	35.0	11.99	2.41	4.10	2.41	2.97	2.41
	45.0	11.98	2.42	4.11	2.44	2.99	2.43
	55.0	11.95	2.44	4.10	2.45	3.00	2.45
chloroform- $d_1$	15.0 25.0 35.0 45.0 55.0	12.09 12.06 12.05 12.03 11.99	2.42 2.43 2.44 2.45 2.46	$\begin{array}{c} 4.08 \\ 4.09 \\ 4.11 \\ 4.12 \\ 4.10 \end{array}$	2.46 2.47 2.50 2.49 2.52	2.99 3.00 3.02 3.02 3.03	2.44 2.45 2.47 2.47 2.49

<sup>a</sup> For designation of protons, see Figure 3. <sup>b</sup>  ${}^{3}J_{T} = {}^{3}J_{T} = {}^{3}J_{DG}$ . <sup>c</sup>  ${}^{3}J'_{G} = {}^{3}J_{EF}$ .  ${}^{d}{}^{3}J_{G} = ({}^{3}J_{DE} + {}^{3}J_{EF} + {}^{3}J_{FG})/3$ . <sup>e</sup>  ${}^{3}J'_{G} = ({}^{3}J_{DE} + {}^{3}J_{FG})/2$ .

(Figure 3) overlap with one another. Using a commercially available computer program, gNMR,<sup>46</sup> we repeated simulations for the observed spectrum by reference to its homonuclear and heteronuclear COSY spectra, but did not reach satisfactory agreement with experiment.

Accordingly, we prepared DMEDT- $d_4$  and measured its <sup>1</sup>H NMR. Shown in Figure 6c is a spectrum observed from DMEDT- $d_4$  in CDCl<sub>3</sub> at 35 °C. The spectrum includes signals from only three protons A-C, being much simpler than that of DMEDT. The simulation using gNMR for DMEDT- $d_4$  showed good agreement with the experiment. In Figure 6d, the arrows indicate chemical shift positions of protons A-C. Using the chemical shifts and coupling constants determined for DMEDT- $d_4$ , we reattempted to analyze the spectrum of DMEDT and successfully reproduced the observation as shown in Figure 6b. For other spectra, we succeeded in the simulation by the same procedure. The NMR parameters determined for the benzene and chloroform solutions at 25 °C are given in section 2.1.2. The vicinal coupling constants between protons D–G are listed in Table 2.

From the structural similarity between BMTE and DMEDT (cf. Figures 3 and 5), we have assumed the following relations:

$${}^{3}J_{\rm T} = {}^{3}J_{\rm T} = {}^{3}J_{\rm DG} \tag{4}$$

$${}^{3}J_{\rm G} = \frac{{}^{3}J_{\rm DE} + {}^{3}J_{\rm EF} + {}^{3}J_{\rm FG}}{3}$$
(5)

$${}^{3}J_{\rm G} = \frac{{}^{3}J_{\rm DE} + {}^{3}J_{\rm FG}}{2} \tag{6}$$

and

$${}^{3}J'_{G} = {}^{3}J_{EF}$$
(7)

In DMEDT, two sulfur atoms are in the gauche position and hence the  ${}^{3}J_{T}$  and  ${}^{3}J_{G}$  values cannot be obtained directly from DMEDT. Accordingly, the following assumptions were adopted:  ${}^{3}J_{T} = {}^{3}J_{T}$  and  ${}^{3}J_{G} = ({}^{3}J_{DE} + {}^{3}J_{EF} + {}^{3}J_{FG})/3$ .

Substitution of  ${}^{3}J_{\text{HH}}$  and  ${}^{3}J_{\text{HH}}$  of BMTE (in CDCl<sub>3</sub> at 35 °C) and  ${}^{3}J_{\text{T}}$ 's and  ${}^{3}J_{\text{G}}$ 's of DMEDT (in CDCl<sub>3</sub> at 35 °C) into eqs 1 and 2 gives  $p_{\text{t}}^{\text{CC}} = 0.76$  and  $p_{\text{g}}^{\text{CC}} = 0.40$ . However, the sum (1.16) of  $p_{\text{t}}^{\text{CC}}$  and  $p_{\text{g}}^{\text{CC}}$  slightly exceeds unity. This discrepancy comes from the fact that the number of equations is larger than that of variables.

**Table 3. Bond Conformations of BMTE** 

medium	temp (°C)	$p_{ m t}^{ m CC}$	$p_{ m g}^{ m CC}$	$p_{ m t}^{ m CS}$	$p_{ m g}^{ m CS}$					
	Ν	MR								
benzene	15.0	0.69	0.31	0.12	0.88					
	25.0	0.68	0.32	0.13	0.87					
	35.0	0.68	0.32	0.14	0.86					
	45.0	0.67	0.33	0.15	0.85					
	55.0	0.67	0.33	0.17	0.83					
chloroform	15.0	0.67	0.33	0.20	0.80					
	25.0	0.66	0.34	0.22	0.78					
	35.0	0.66	0.34	0.22	0.78					
	45.0	0.65	0.35	0.23	0.77					
	55.0	0.65	0.35	0.26	0.74					
	Ab Initio MO <sup>a</sup>									
gas (B3LYP)	25.0	0.91	0.09	0.25	0.75					
gas (MP2)	25.0	0.83	0.17	0.21	0.79					

 $^a\operatorname{Evaluated}$  from the conformer free energies shown in Table 4.



Figure 7. (a) Observed and (b) calculated  $^{13}C$  NMR spectra of the methyl carbon of BMTE in  $C_6D_6$  at 15 °C.

This problem has often been discussed in the NMR analysis of PEO and DME; <sup>44,47–49</sup> negative coupling constants were occasionally estimated. In this study, the  $p_t^{CC}$  and  $p_g^{CC}$  values obtained as above were divided by their sum so as to satisfy eq 3. Finally, we have  $p_t^{CC} = 0.66$  and  $p_g^{CC} = 0.34$ . The difference in  $p^{CC}$  between before and after normalization of eq 3 is at most 10%.<sup>50</sup> The bond conformations thus evaluated are listed in Table 3.

**3.2.** <sup>13</sup>C NMR from BMTE. Figure 7 shows a <sup>13</sup>C NMR spectrum observed from the methyl carbon of BMTE in  $C_6D_6$  at 15 °C. The signal is largely split into four by direct coupling with methyl protons. In Figure 7a, one of the quartet is enlarged. On the basis of AA'BB'X spin system, the spectrum was simulated by gNMR. In the calculated spectrum, even small peaks are exactly reproduced. The vicinal coupling constant between the methyl carbon and methylene protons,  ${}^{3}J_{CH}$ , was obtained as 4.60 Hz. The observed  ${}^{3}J_{CH}$  value may be expressed as<sup>44,45</sup>

$${}^{3}J_{\rm CH} = {}^{3}J_{\rm G}\,p_{\rm t}^{\rm CS} + \frac{{}^{3}J_{\rm T} + {}^{3}J_{\rm G}}{2}\,p_{\rm g}^{\rm CS} \tag{8}$$

Table 4. Free Energies ( $\Delta G_k$ ) of Conformers of BMTE and DME, Evaluated by Ab Initio Molecular Orbital Calculations

			BMTE				DME	E	
			statistical	$\Delta G_k$ , a kca	$\Delta G_{k}$ , a kcal mol <sup>-1</sup>		$\Delta G_{k}$ , <sup>a</sup> kcal mol <sup>-1</sup>		
k	conformation	$M_k$	weight <sup>b</sup>	B3LYP <sup>c</sup>	$MP2^d$	weight <sup>b</sup>	B3LYP <sup>c</sup>	$MP2^d$	CBS-Q <sup>e</sup>
1	ttt	1	1	0.00	0.00	1	0.00	0.00	0.00
2	ttg±	4	ρ	-0.30	-0.46	ρ	1.34	1.28	1.25
3	t g <sup>≟</sup> t	2	σ	1.26	0.90	σ	0.66	0.61	0.75
4	$t g^{\pm} g^{\pm}$	4	ρσ	1.26	0.49	ρσ	1.47	1.31	1.40
5	t g± g∓	4	ρσω	1.33	0.77	ρσω	0.67	0.30	0.41
6	$g^{\pm} t g^{\pm}$	2	$\rho^2$	-0.45	-0.81	$\rho^2$	2.90	2.73	2.55
7	g± t g∓	2	$\rho^2 \kappa$	-0.68	-1.02	$\rho^2$	2.67	2.60	2.39
8	$g^{\pm} g^{\pm} g^{\pm}$	2	$\rho^2 \sigma \chi$	1.21	0.57	$\rho^2 \sigma \chi$	3.47	2.30	2.38
9	$\mathbf{g}^{\pm} \mathbf{g}^{\pm} \mathbf{g}^{\mp}$	4	$\rho^2 \sigma \omega$	1.46	0.63	$\rho^2 \sigma \omega$	2.45	1.93	1.94
10	$\overset{\circ}{\mathrm{g}^{\pm}}\overset{\circ}{\mathrm{g}^{\mp}}\overset{\circ}{\mathrm{g}^{\pm}}$	2	$\rho^2 \sigma \omega^2$	2.00	1.02	$\rho^2 \sigma \omega^2$	2.63	1.89	1.49

<sup>*a*</sup> Relative to the  $\Delta G_k$  value of the all-trans conformation. At 25 °C and 1 atm. <sup>*b*</sup> For definition of the statistical weights, see Figure 2. <sup>*c*</sup> At the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. <sup>*d*</sup> At the MP2/6-311+G(3df,2p)//HF/6-31G(d) level. <sup>*e*</sup> By the complete basis set (CBS-Q) method.

where  ${}^{3}J_{\rm G}$  and  ${}^{3}J_{\rm T}$  are defined in Figure 5b, and  $p_{\rm t}^{\rm CS}$  and  $p_{\rm g}^{\rm CS}$  are trans and gauche fractions of the C–S bond. The definition dictates that

$$p_{\rm t}^{\rm CS} + p_{\rm g}^{\rm CS} = 1 \tag{9}$$

In a previous study on poly(methylene sulfide),<sup>51</sup> we determined the  ${}^{3}J_{\rm G}$  and  ${}^{3}J_{\rm T}$  values for the  ${}^{13}{\rm C}{-}{\rm S}{-}{\rm C}{-}^{1}{\rm H}$  bond sequence from 2-methyl-1,3,5-trithiane (MTT). In the analysis for BMTE, the  ${}^{3}J_{\rm G}$  and  ${}^{3}J_{\rm T}$  values of MTT were used:  ${}^{3}J_{\rm T} = 7.13$  Hz and  ${}^{3}J_{\rm G} = {}^{3}J_{\rm G} = 2.62$  Hz (for C<sub>6</sub>D<sub>6</sub> solution);  ${}^{3}J_{\rm T} = 7.12$  Hz and  ${}^{3}J_{\rm G} = {}^{3}J_{\rm G} = 2.58$  Hz (for CDCl<sub>3</sub> solution). The  $p_{\rm t}^{\rm CS}$  and  $p_{\rm g}^{\rm CS}$  values thus derived are also listed in Table 3.

The trans fraction of the C–C bond, found within a range of 0.65–0.69, slightly decreases with temperature and dielectric constant ( $\epsilon$ ) of solvent. On the other hand, the C–S bond prefers the gauche conformation; the  $p_g^{CS}$  values are 0.74 (in CDCl<sub>3</sub> at 55 °C) – 0.88 (in C<sub>6</sub>D<sub>6</sub> at 15 °C).

3.3. Free Energies and Bond Conformations of BMTE, Obtained from MO Calculations. Free energies of 10 conformers of BMTE, obtained from the ab initio MO calculations, are listed in Table 4. From the table, the most stable conformations of BMTE are seen to be  $g^{\pm}tg^{\mp}$ , which have a free energy of -1.02 kcal mol<sup>-1</sup> at the MP2 level. Both BMTE and PES adopt this conformation in the crystalline state.<sup>3,4</sup> The MP2 and B3LYP calculations indicate that the  $g^{\pm}tg^{\mp}$  conformers have a lower free energy by ca.  $0.2 \text{ kcal mol}^{-1}$  than  $g^{\pm}tg^{\pm}$ . This difference may be significant, suggesting the existence of some bond correlation in the S-CH<sub>2</sub>-CH<sub>2</sub>–S sequence. The ttg<sup> $\pm$ </sup> and tg<sup> $\pm$ </sup>t states have  $\Delta G_k$ values of -0.46 and +0.90 kcal mol<sup>-1</sup> (MP2), respectively; the C-S and C-C bonds prefer the gauche and trans conformations, respectively. These results are qualitatively consistent with the above NMR analysis.

The conformer fraction  $f_k$  can be calculated from

$$f_k = \frac{\exp(-\Delta G_k/RT)}{\sum_{k}^{K} M_k \exp(-\Delta G_k/RT)}$$
(10)

where  $M_k$  is the multiplicity of the *k*th conformer, *R* is the gas constant, *T* is the absolute temperature, and *K* is the total number of conformers (= $\sum_k M_k$ ). From the  $f_k$  values, for example, the bond conformation  $p_t^{CC}$  is calculated according to

$$p_{\rm t}^{\rm CC} = \sum_{k_{\rm t}^{\rm CC}} f_{k_{\rm t}^{\rm CC}} \tag{11}$$

where  $k_t^{CC}$  stands for the conformer whose C–C bond takes the trans state. Similarly,  $p_g^{CC}$ ,  $p_t^{CS}$ , and  $p_g^{CS}$  can be obtained. In Table 3, the bond conformations calculated from the free energies in Table 4 are listed.

lated from the free energies in Table 4 are listed. As seen from Table 3, the  $p_t^{CC}$  values derived from the MO data are somewhat larger than those from NMR. Because the MO calculations represent gaseous BMTE ( $\epsilon = 1$ ), the difference comes partly from solvent effect. On the other hand,  $p_t^{CS}$  and  $p_g^{CS}$  obtained from the MO energies are comparable to those from NMR.

**3.4. Statistical Weight Matrixes and Conformational Energies of BMTE.** From careful inspection of the molecular model, simple molecular mechanics calculations, and free energies in Table 4, statistical weight matrices of BMTE were formulated according to the 9  $\times$  9 matrix scheme:<sup>52,53</sup>

$$U_2 = \begin{bmatrix} 1 & \rho & \rho \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(12)

$$U_{3} = \begin{bmatrix} 1 & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \sigma & \sigma\omega & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & \sigma\omega & \sigma \end{bmatrix}$$
(13)

and

The rows and columns of matrices  $U_i$ 's (i = the bond number, see Figure 1) are indexed to the rotational states for the preceding and current bonds, respectively. The statistical weight is related to the corresponding conformational energy through the Boltzmann factor; for example,  $\rho = \exp(-E_{\rho}/RT)$ . In the (4, 3) and (7, 2) elements of  $U_4$ , the third-order interaction,  $\kappa$ , is in-

Table 5. Conformational 1	Energies <sup>a</sup> and	<b>Configuration-De</b>	pendent Properties	<sup>b</sup> of PES (BMTE),	DME, and PEO
		0			,

		BMTI	E and PES		DME	PEO		
	M	MO <sup>c</sup>		NMR		NMR and dipole moment		
	B3LYP	MP2	benzene	chloroform	MP2	nonpolar organic solvent <sup><math>d</math></sup>	Abe-Mark <sup>e</sup>	
$E_{ ho}$	-0.24	-0.41	-0.74	-0.41	1.22	1.17	0.9	
$\dot{E_{\sigma}}$	1.39	0.89	0.41	0.31	0.32	-0.25	-0.5	
$E_{\omega}$	0.40	0.45	0.40	0.53	-1.12	-0.79	0.4	
$E_{\omega'}$	$(0.00)^{f}$	$(0.00)^{f}$	$(0.00)^{f}$	$(0.00)^{f}$	$\infty$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~	
$E_{\gamma}$	0.30	0.50	0.46	0.59	-0.45	(0.00)g		
$\tilde{E_{\kappa}}$	-0.20	-0.19	-0.18	-0.22				
$\langle r^2 \rangle_0 / n l^2 h$	3.5	3.1	2.5	2.9	4.5	4.1	5.1	
$10^{3} d(\ln \langle r^{2} \rangle_{0})/dT, h K^{-1}$	-0.75	-0.89	-0.97	-0.83	-0.17	0.23	0.36	
$\langle \mu^2 \rangle / nm^{2i}$	0.13	0.22	0.38	0.44	0.34	0.41	0.49	
$10^3 d(\ln \langle \mu^2 \rangle)/dT$ , <sup>i</sup> K <sup>-1</sup>	8.7	6.4	3.8	3.3	2.2	1.9	2.9	
$S_{ m conf}$ , $^{j}$ cal mol $^{-1}$ deg $^{-1}$	5.8	6.0	6.2	6.3	5.1	5.1	5.0	

<sup>a</sup> In kcal mol<sup>-1. b</sup> Calculated for the 200 mers. <sup>c</sup> On the basis of ab initio MO calculations for BMTE or DME at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) (B3LYP) and MP2/6-311+G(3df,2p)//HF/6-31G(d) (MP2) levels. <sup>d</sup> The conformational energies were determined from NMR vicinal coupling constants of the 1,4-dioxane solution<sup>44</sup> and the dipole moment ratio of the benzene solution.<sup>77–79</sup> <sup>e</sup> Reference 15. <sup>f</sup> On the basis of the MO calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level, the  $E_{\omega'}$  value was assumed to be null.<sup>54</sup> <sup>g</sup> The  $E_{\chi}$  value was set to zero.<sup>81 h</sup> At 25 °C for PES and 40 °C for PEO. For example, the following experimental  $\langle r^2 \rangle_0 / n^2$  values have been reported, the  $\Theta$  conditions being shown in parentheses: 4.1 ± 0.4 (0.45 M K<sub>2</sub>SO<sub>4</sub> at 35 °C and 0.39 M MgSO<sub>4</sub> at 45 °C<sup>12</sup>), 4.8 (methyl isobutyl ketone at 50 °C, diethylene glycol diethyl ether at 50 °C, and 0.45 M K<sub>2</sub>SO<sub>4</sub> at 35 °C<sup>68</sup>), 7.0–9.7 (melf<sup>69</sup>), 4.2 (2.40 M NaCl at 54 °C<sup>70</sup>), 5.2 (0.45 M MgSO<sub>4</sub> at 23 °C<sup>70</sup>), 5.4 (0.30 M K<sub>2</sub>CO<sub>3</sub> at 56 °C<sup>70</sup>), 4.8 (0.30 M Ma<sub>2</sub>SO<sub>4</sub> at 25 °C<sup>70</sup>), 5.7 (0.30 M K<sub>2</sub>SO<sub>4</sub> at 52 °C<sup>70</sup>), 5.5 (0.39 M MgSO<sub>4</sub> at 43 °C<sup>70</sup>), 5.3 (0.45 M MgSO<sub>4</sub> at 23 °C<sup>70</sup>), 5.4 (0.50 M MgSO<sub>4</sub> at 26 °C<sup>70</sup>), 6.9 (melt at 80 °C<sup>71</sup>), 5.4 (1.24 M KOH at 25 °C<sup>72</sup>), 7.5–8.3 (H<sub>2</sub>O at 25 °C. <sup>j</sup> At the melting points: 216 °C for PES and 68 °C for PEO.

cluded. As discussed in section 3.3, this weight represents the extra stabilization of the  $g^{\pm}tg^{\mp}$  states.

In the RIS scheme, the  $\Delta G_k$  of BMTE are approximated as a function of  $E_{\xi}$ 's ( $\xi = \rho, \sigma, \omega, \chi, \text{ and } \kappa$ ). For example, the  $g^+g^+g^+$  conformation has a weight of  $\rho^2\sigma\chi$ . Thus, the  $\Delta G_k$  value may correspond to  $2E_{\rho} + E_{\sigma} + E_{\chi}$ . The  $E_{\xi}$  values were determined by minimizing the following function:

$$S(\boldsymbol{E}) = \frac{1}{K} \sum_{k} \Delta_{k}^{2}(\boldsymbol{E})$$
(15)

where

$$\Delta_k^2(\mathbf{E}) = (\sum_{\xi} L(\xi) E_{\xi} - \Delta G_k)^2 M_k \exp(-\Delta G_k/RT) \quad (16)$$

The function  $L(\xi)$  gives the number of conformational energy  $E_{\xi}$  included in the conformation. The squared difference between  $\Delta G_k$  and the sum of  $E_{\xi}$ 's was multiplied by the Boltzmann factor  $\exp(-\Delta G_k/RT)$  so as to weight low-energy conformations. The temperature T was set to 298.15 K. Conformational energies thus determined are listed in Table 5.

To evaluate experimental conformational energies of BMTE and PES in the  $\Theta$  state, the five energy parameters,  $E_{\xi}$  ( $\xi = \rho$ ,  $\sigma$ ,  $\omega$ ,  $\chi$ , and  $\kappa$ ), were adjusted so as to reproduce 20 bond conformations of BMTE in benzene or chloroform at 15, 25, 35, 45, and 55 °C. Here,  $E_{\omega'}$  of PES, reflecting CH<sub>2</sub>···CH<sub>2</sub> close contacts occurring in the g<sup>±</sup>g<sup>∓</sup> conformations for the C–S/S–C bond pairs (see Figure 2d), has been assumed to be null.<sup>54</sup> As the initial values of  $E_{\xi}$ 's, those obtained from the MP2 free energies were used. The optimization was carried out by the maximum entropy method including the RIS scheme.<sup>55</sup> Conformational energies obtained are also listed in Table 5.<sup>61</sup>

The MO calculations, representing the gaseous molecules ( $\epsilon = 1$ ), gave the  $E_{\rho}$  values of -0.24 (B3LYP) and -0.41 kcal mol<sup>-1</sup> (MP2). The <sup>13</sup>C NMR analysis yielded -0.74 and -0.41 kcal mol<sup>-1</sup> for the benzene ( $\epsilon = 2.28$ ) and chloroform ( $\epsilon = 4.81$ ) solutions, respectively. For  $E_{\rho}$ , therefore, no explicit solvent dependence can be found. On the other hand,  $E_{\sigma}$  tends to decrease with increasing  $\epsilon$ : 1.39 (gas, B3LYP), 0.89 (gas, MP2), 0.41 (benzene, NMR), and 0.31 kcal mol<sup>-1</sup> (chloroform, NMR). This may be explained as follows. Dipole moments formed along the bisector of  $\angle$ CSC are canceled out in the all-trans state. Polar solvents enhance the polarity of solute; the  $E_{\sigma}$  value is reduced in polar solvents. As mentioned in the Introduction, the following values have been reported:  $E_{\rho}$ , -0.1 kcal mol<sup>-1</sup> for PES;<sup>25–27</sup>  $E_{\sigma}$ , 1.1 kcal mol<sup>-1</sup> for gaseous BMTE,<sup>11</sup> 0.1 kcal mol<sup>-1</sup> for liquid BMTE,<sup>11</sup> and 0.4–0.7 kcal mol<sup>-1</sup> for PES.<sup>25–27</sup>

**3.5. Conformational Free Energies and Bond Conformations of DME.** Ab initio MO calculations by the CBS-Q as well as B3LYP and MP2 methods were carried out for DME. The conformer free energies are listed in Table 4. Differences in  $\Delta G_k$ 's among the three methods are slight, and the most stable conformation is indicated to be all-trans. For gaseous DME, conformer fractions were estimated by electron diffraction (ED),<sup>18</sup> and <sup>1</sup>H and <sup>13</sup>C NMR vicinal coupling constants were reported.<sup>45</sup> From the latter data, we derived the  $p_t^{CC}$ ,  $p_g^{CC}$ ,  $p_t^{CO}$ , and  $p_g^{CO}$  values of DME at 125 °C. The conformer fractions and bond conformations, calculated from  $\Delta G_k$ 's according to eqs 10 and 11, are compared with the experimental values in Tables 6 and 7, respectively.

From the tables, it can be seen that the  $\Delta G_k$  values at the MP2/6-311+G(3df,2p) level gave the best agreement with the ED and NMR experiments. From the MP2 free energies, therefore, the conformational energies were evaluated according to eqs 15 and 16. The statistical weights of the individual conformers are listed in Table 4. For DME and PEO, the energy parameter,  $E_k$ , has not been considered. In Table 5, the conformational energies determined for gaseous DME are shown. The root-mean-square errors between calculated and observed  $\Delta G_k$ 's was 0.07 kcal mol<sup>-1</sup>.

The  $E_{\rho}$  value of 1.22 kcal mol<sup>-1</sup> indicates a strong trans preference of the C–O bond. The negative  $E_{\omega}$  (–1.12 kcal mol<sup>-1</sup>) value results from the intramolecular

 
 Table 6. Calculated and Observed Conformer Fractions of Gaseous DME<sup>a</sup>

	al	o initio M	$O^b$	
	B3LYP	MP2	CBS-Q	electron diffraction <sup>c</sup>
ttt	29	20	23	$13\pm7$
ttg	10	8	9	$3\pm7$
tgt	17	13	11	$23\pm7$
tgg	41	54	50	$53\pm7$
gtg	1	1	1	5
ggg	2	4	6	3

 $^a$  In percent.  $^b$  Evaluated for the conformers at 0 °C according to the Boltzmann distribution using the free energies shown in Table 4.  $^c$  At 0 °C and 1  $\times$  10 $^{-5}$  Torr. $^{18}$ 

Table 7. Bond Conformations of Gaseous DME at 125 °C

method	$p_{ m t}^{ m CC}$	$p_{ m g}^{ m CC}$	$p_{ m t}^{ m CO}$	$p_{ m g}^{ m CO}$
	At	o Initio MO <sup>a</sup>		
B3LYP	0.35	0.65	0.64	0.36
MP2	0.28	0.72	0.58	0.42
CBS-Q	0.30	0.70	0.56	0.44
	E	Experiment		
$NMR^{b}$	0.25	0.75	0.65	0.35

 $^a$  Evaluated according to the Boltzmann distribution using the free energies shown in Table 4.  $^b$  Reference 45.

(C–H)····O attraction occurring in the tg<sup>±</sup>g<sup>∓</sup> conformations, yielding a large  $p_g^{CC}$  value of 0.72 (MP2 in Table 7), although  $E_{\sigma}$  is positive (0.32 kcal mol<sup>-1</sup>).

**3.6.**  $\mathbf{C}$ – $\mathbf{S}$  and  $\mathbf{C}$ – $\mathbf{O}$  Bond Dipole Moments. Bond dipole moments  $m_{C-X}$  were attempted to be determined from the MO calculations for BMTE and DME; the  $m_{C-X}$  value was optimized so as to minimize the  $f(m_{C-X})$  function

$$f(m_{\rm C-X}) = \sum_{k} (\mu_{k}^{\rm MO} - \mu_{k}^{\rm BOND})^{2} M_{k} \exp(-\Delta G_{k}/RT)$$
(17)

where  $\mu_k^{\rm MO}$  is the dipole moment of conformer k, obtained from MO calculations, and  $\mu_k^{\rm BOND}$  is calculated from

$$\mu_k^{\text{BOND}} = m_{\text{C-X}} \sum_i \mathbf{b}_i^k \tag{18}$$

with  $\mathbf{b}_{i}^{k}$  being the unit vector along the *i*th C–X bond of the conformer *k*. The  $m_{C-C}$  value has been assumed to be null. In the optimization for  $m_{C-X}$ , free energies, dipole moments, and geometrical parameters obtained by each MO method were used. As for free energies of DME, however, only those at the MP2 level, being the most reliable, were adopted. The results are listed in Table 8.

From the table, it can be seen that  $\mu_k^{\text{BOND}}$ 's agree fairly well with  $\mu_k^{\text{MO}}$ 's in all cases. The  $m_{\text{C}-\text{S}}$  value was optimized as  $1.22 \pm 0.02$  (B3LYP) or  $1.35 \pm 0.01$  D (MP2) and the  $m_{\text{C}-\text{O}}$  value, as  $1.18 \pm 0.04$  (B3LYP),  $1.29 \pm 0.04$  (MP2), or  $1.46 \pm 0.07$  D (CBS-Q). The B3LYP parameters gave the  $m_{\text{C}-\text{S}}$  value close to that (1.21 D) so far used for polysulfides  $^{25-27,62}$  and the  $m_{\text{C}-\text{O}}$  value in agreement with that (1.17-1.19 D) optimized for PPO and poly(tetramethylene oxide).<sup>21</sup> In a previous study,<sup>51</sup> we evaluated  $m_{\text{C}-\text{S}}$  for poly(methylene sulfide) as  $1.23 \pm 0.08$  D from the parameters at the B3LYP/6-311+G-(2d, p)//B3LYP/6-31G(d) level. The MP2 and CBS-Q calculations may overestimate the bond dipole moments. Therefore, we have employed  $m_{\text{C}-\text{S}}$  of 1.22 D for PES and  $m_{\text{C}-\text{O}}$  of 1.18 D for PEO. **3.7. Characteristic Ratio, Dipole Moment Ratio, and Configuration Entropy of PES.** Statistical weight matrices for bonds A, B, and C (see Figure 1) in the repeating unit of PES may be expressed as

and

$$U_{\rm C} = U_4 \tag{21}$$

As described above, <sup>54</sup>  $\omega'$  has been assumed to be unity for PES (i.e.,  $E_{\omega'} = 0$ ). Because these statistical weight matrices will be adapted later for PEO, however,  $\omega'$  is included in  $U_A$ . The  $\langle r^2 \rangle_0 / nl^2$  and  $\langle \mu^2 \rangle / nm^2$  values of unperturbed PES were calculated by the RIS scheme<sup>14</sup> using the statistical weight matrices defined as above. Although the  $\Theta$  state of PES is imaginary, it should be meaningful to investigate the configuration-dependent properties of PES and compare them with those of other polymers. Geometrical parameters at the B3LYP/6-31G-(d) level were used in the calculations:<sup>63</sup> bond lengths,  $l_{C-S} = 1.839$  Å and  $l_{C-C} = 1.528$  Å; bond angles,  $\angle CSC$ = 99.45° and  $\angle CCS = 109.39°$ ; dihedral angles,  $\angle CS = 99.45°$  and  $\angle CCS = 109.39°$ ; dihedral angles,  $\phi_{trans}^{C-S} = \phi_{trans}^{C-C} = 0.00°$ ,  $\phi_{gauche\pm}^{C-S} = \pm 104.24°$ , and  $\phi_{gauche\pm}^{C-C} = \pm 115.04°$ . In Table 5, the  $\langle r^2 \rangle_0 / nl^2$  and  $\langle \mu^2 \rangle / nm^2$  values and their temperature coefficients of PES (degree of polymerization, x = 200) at 25 °C are listed for each energy set.

The configurational entropy  $S_{\text{conf}}$  of PES of x = 200at the melting point of 216 °C was calculated according to the conventional method  $^{25,51,64-67}$  The results are also shown in Table 5. Enthalpy ( $\Delta H_{\text{u}}$ ) and entropy ( $\Delta S_{\text{u}}$ ) of fusion of PES were experimentally estimated as 3.4 kcal mol<sup>-1</sup> and 6.9 cal mol<sup>-1</sup> deg<sup>-1</sup>, respectively.<sup>2,25</sup> The entropy can be broken down into two terms,  $S_{\text{conf}}$  and  $\Delta S_{\nu}$ , where  $\Delta S_{\nu} = (\alpha/\beta)\Delta V_{\text{u}}$ , with  $\alpha$ ,  $\beta$ , and  $\Delta V_{\text{u}}$  being thermal expansion coefficient, compressibility, and volume change on melting, respectively. Because the contribution of  $S_{\text{conf}}$  to  $\Delta S_{\text{u}}$  amounts to at least 70% in most polymers, our  $S_{\text{conf}}$  values of 5.8–6.3 cal mol<sup>-1</sup> deg<sup>-1</sup> are reasonable. Abe estimated the  $S_{\text{conf}}$  value of PES (x = 200) to be 6.1 cal mol<sup>-1</sup> deg<sup>-1</sup>.<sup>25</sup>

**3.8. Unperturbed Dimensions of PEO.** For PEO, a wide range of  $\langle r^2 \rangle_0 / nl^2$  values (4.1–9.7) and a variety of  $\Theta$  conditions have been determined experimentally (see footnote *h* of Table 5).<sup>12,68–75</sup> The temperature

Table 8. Dipole Moments of Conformers of BMTE and D	<b>)ME</b> <sup>a</sup>
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			BMTE				DME				
		B3LYP		MP2		B3LYP		MP2		CBS-Q	
k	conformation	$\mu_k^{\text{MO}}$	$\mu_k^{\text{BOND}}$	$\mu_k^{\mathrm{MO}}$	$\mu_k^{\text{BOND}}$	$\mu_k^{\mathrm{MO}}$	$\mu_k^{\text{BOND}}$	$\mu_k^{\mathrm{MO}}$	$\mu_k^{\text{BOND}}$	$\mu_k^{\mathrm{MO}}$	$\mu_k^{\text{BOND}}$
1	ttt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	ttg±	1.96	1.94	2.19	2.15	1.66	1.67	1.67	1.68	1.94	1.90
3	tg≟t	2.36	2.54	2.56	2.72	1.43	1.63	1.49	1.69	1.66	1.91
4	$t g^{\pm} g^{\pm}$	2.92	3.12	3.28	3.43	2.41	2.58	2.58	2.74	2.85	3.10
5	t g <sup>±</sup> g <sup>∓</sup>	1.73	1.72	1.86	1.84	1.59	1.46	1.62	1.50	1.88	1.70
6	$g^{\pm} t g^{\pm}$	2.38	2.35	2.64	2.60	2.21	2.20	2.37	2.35	2.53	2.66
7	$g^{\pm} t g^{\mp}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	$\tilde{\mathbf{g}}^{\pm}  \mathbf{g}^{\pm}  \mathbf{g}^{\pm}$	2.40	2.59	2.74	2.89	1.29	1.51	1.41	1.60	1.45	1.81
9	$\mathbf{g}^{\pm} \mathbf{g}^{\pm} \mathbf{g}^{\mp}$	2.37	2.39	2.63	2.64	1.91	1.91	2.08	2.06	2.21	2.34
10	$g^{\pm} g^{\mp} g^{\pm}$	0.13	0.21	0.13	0.22	0.06	0.15	0.12	0.21	0.15	0.24
	$m_{\mathrm{C}-\mathrm{X}}$ , <sup>b</sup> D	1.22	$2\pm0.02$	1.35	$\pm 0.01$	1.18	$\pm 0.04$	1.29	$\pm 0.04$	1.46	$\pm 0.07$

<sup>*a*</sup> In debye.  $\mu_k^{MO}$ 's were evaluated from ab initio MO calculations at the individual levels, and  $\mu_k^{BOND}$ 's were obtained from eq 21. <sup>*b*</sup> The bond dipole moments  $m_{C-X}$ 's (X = S and O) were determined by the least-squares fittings according to eq 17. The  $m_{C-C}$  value was assumed to be null.

 Table 9. Free Energy Differences between Trans and Gauche States in the Central C-C Bonds of PEO Oligomers,

 Evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) Level

	tr	ans	gau	uche±		
	SCF (au)	thermal correction <sup>a</sup> (au)	SCF (au)	thermal correction <sup>a</sup> (au)	$\Delta \operatorname{SCF}^{b}$ (kcal mol <sup>-1</sup> )	$\Delta G^c$ (kcal mol <sup>-1</sup> )
monomer <sup>d</sup> trimer <sup>e</sup> pentamer <sup>f</sup>	-308.976493 -616.752066 -924.527630	0.107135 0.214387 0.321611	-308.976066 -616.751941 -924.527499	0.107919 0.214501 0.321767	0.27 0.08 0.08	0.76 0.15 0.18

<sup>*a*</sup> At the B3LYP/6-31G(d) level. <sup>*b*</sup>  $\Delta$  SCF = SCF<sub>gauche</sub> – SCF<sub>trans</sub>. <sup>*c*</sup>  $\Delta$ *G* = *G*<sub>gauche</sub> – *G*<sub>trans</sub>, where *G* = SCF + thermal correction (including the entropy term). <sup>*d*</sup> DME, CH<sub>3</sub>OCH<sub>2</sub>-CH<sub>2</sub>OCH<sub>3</sub>. <sup>*e*</sup> CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>-CH<sub>2</sub>OCH<sub>2</sub>-CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>. <sup>*f*</sup> CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O]<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>O[CH<sub>2</sub>CH<sub>2</sub>O]<sub>2</sub>CH<sub>3</sub>.

coefficient, 10<sup>3</sup> d(ln  $\langle r^2 \rangle_0 \rangle/dT$ , ranges from positive and negative values: 0.23  $\pm$  0.2 (amorphous network at 60 °C), <sup>12</sup> 0.2  $\pm$  0.2 K<sup>-1</sup> (extrapolated from benzene solution at 35 °C), <sup>76</sup> -1.5  $\pm$  0.5 (1.24 M KOH at 25 °C), <sup>72</sup> and -0.3 K<sup>-1</sup> (melt at 130 °C). <sup>74</sup> On the other hand, experimental dipole moment ratios ( $\langle \mu^2 \rangle / nm^2$ ) obtained from the benzene solutions at ambient temperature are found within a narrow range of 0.40–0.42. <sup>77–79</sup> Here, the  $\langle \mu^2 \rangle / nm^2$  values are calibrated with the  $m_{C-O}$  value (1.18 D) determined as above. The temperature coefficient, 10<sup>3</sup> d(ln  $\langle \mu^2 \rangle / dT$ , was estimated as 2.6 K<sup>-1</sup>. <sup>78</sup>

Statistical weight matrices of DME and PEO may be obtained by minor modifications of those of BMTE and PES. The  $U_2$  and  $U_3$  matrices of DME and PEO are assumed to have the same formats as those of BMTE, but  $U_4$  and  $U_C$  of DME and PEO do not include the statistical weight  $\kappa$ . The short C–O bond does not allow  $g^{\pm}g^{\mp}g^{\pm}$  conformational sequences to exist; therefore, the (6,8) and (8,6) elements of  $U_A$ ,  $U_B$ , and  $U_C$  (eqs 19–21) of PES must be replaced by zero.<sup>80</sup>

Conformational energies of PEO were attempted to be determined by a simulation<sup>55</sup> for C-C and C-O bond conformations obtained from <sup>1</sup>H and <sup>13</sup>C NMR vicinal coupling constants of PEO in 1,4-dioxane ( $\epsilon = 2.10$ ) at 40 °C<sup>44</sup> and the dipole moment ratio (0.41) of PEO in benzene<sup>77–79</sup> ( $\epsilon = 2.28$ ). This is partly because the NMR coupling constants and dipole moment ratio are free from the excluded volume effect in contrast with the characteristic ratio, partly because the  $\epsilon$  values of the two solvents are close to each other (the results may be little subjected to the solvent effect). Then, as the initial values, the conformational energies obtained from the MP2 calculations were used, except for  $E_{\gamma}$  which was set to zero.<sup>81</sup> For comparison with previous studies, geometrical parameters offered by Abe and Mark (set II)<sup>15</sup> were used: bond lengths,  $I_{C-O} = 1.43$  Å and  $I_{C-C} =$ 1.53 Å; bond angles,  $\angle COC = \angle CCO = 111.5^{\circ}$ ; dihedral angles,  $\phi_{\text{trans}}^{\text{C}-\text{O}} = \phi_{\text{trans}}^{\text{C}-\text{C}} = 0.0^{\circ}$  and  $\phi_{\text{gauche}\pm}^{\text{C}-\text{O}} = \pm 110^{\circ}$ . The conformational energies thus optimized, designated as "nonpolar organic solvent", are shown in Table 5. The  $p_{\text{t}}^{\text{CC}}$ ,  $p_{\text{g}}^{\text{CO}}$ ,  $p_{\text{t}}^{\text{CO}}$ , and  $p_{\text{g}}^{\text{CO}}$  values were obtained as 0.19, 0.81, 0.71, and 0.29, respectively, being in complete agreement with the experimental values. The  $\langle r^2 \rangle_0 / n_{\text{f}}^P$ ,  $10^3$  d(ln  $\langle r^2 \rangle_0 / dT$ , and  $10^3$  d(ln  $\langle \mu^2 \rangle$ )/d*T* values (Table 5) were also calculated from the energy parameters. The  $\langle r^2 \rangle_0 / n_{\text{f}}^P$  (4.1) and  $10^3$  d(ln  $\langle \mu^2 \rangle_0 / dT$  (0.23 K<sup>-1</sup>) values agree with those (4.1 and 0.2–0.23 K<sup>-1</sup>) estimated experimentally,<sup>12,76</sup> and the  $10^3$  d(ln  $\langle \mu^2 \rangle$ )/d*T* value (1.9 K<sup>-1</sup>) is comparable to the experiment (2.6 K<sup>-1</sup>).<sup>78</sup> The configuration-dependent properties calculated from the energy set of Abe and Mark<sup>15</sup> and the 9 × 9 statistical weight matrices defined here are also listed in Table 5. The calculated characteristic ratio (5.1) agrees well with that (5.2 ± 0.1) determined by light scattering for a 0.45 M K\_2SO\_4 aqueous solution at 34.5 °C.<sup>75</sup>

To investigate the chain length dependence of  $E_{\sigma}$  of PEO, free energy differences between trans and gauche states of the central C–C bonds of its monomer (DME), trimer, and pentamer were evaluated from MO calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. Since the MP2 calculation is time-consuming, the B3LYP method was used. The frequency calculations, required for the thermal corrections, were also carried out at the B3LYP/6-31G(d) level. As shown in Table 9, the free energies of the monomer, trimer, and pentamer were obtained as 0.76, 0.15, and 0.18 kcal mol<sup>-1</sup>, respectively. The terminal bonds seem to have a larger  $E_{\sigma}$  than the inner bonds. This property was also found for poly(methylene oxide).<sup>51</sup>

From Table 5, it can be seen that  $E_{\sigma}$  decreases and  $E_{\omega}$  increases in the order "MP2"  $\rightarrow$  "nonpolar organic solvent"  $\rightarrow$  "Abe–Mark". By the MO calculations, the

isolated (gaseous) PEO chain was suggested to have an  $E_{\sigma}$  value smaller than 0.2 kcal mol<sup>-1</sup>. Polar solvents such as water must further enhance the gauche stability of the C-C bond, because of the resultant dipole moment in the gauche form and the attractive polymersolvent interaction. When the C-C and C-O bonds are in the gauche and trans conformations respectively, the O-C-C-O portion acts as an efficient electron donor, as found for crown ethers. If the Abe-Mark parameters approximately represent PEO in the  $\Theta$  solvent, 0.45 M  $\tilde{K}_2$ SO<sub>4</sub> at 34.5 °C, the ions are suggested to reduce the gauche stability of the C-C bond. From NMR coupling constants of PEO in pure water, the  $E_{\sigma}$  value was estimated as -1.2 kcal mol<sup>-1</sup>,<sup>44</sup> being much smaller than -0.5 kcal mol<sup>-1</sup> (Abe–Mark). This is probably because the ions compete for the oxygen atom of PEO with water.<sup>82</sup> In the gas phase, the intramolecular (C-H)...O attraction is not disturbed by solvent, and hence the  $E_{\omega}$  values is as small as -1.12 kcal mol<sup>-1</sup> (for DME by MP2). Polar solvents (and ions), being stronger electron acceptors than the methylene protons of PEO, can capture the oxygen atom of PEO, the  $E_{\omega}$  value appears to increase from negative to positive in the order "MP2" (gas phase)  $\rightarrow$  "nonpolar organic solvent"  $\rightarrow$  "Abe-Mark" (0.45 M K<sub>2</sub>SO<sub>4</sub>). Recent molecular dynamics simulations on PEO and water systems have suggested that  $E_{\sigma}$  decreases and  $E_{\omega}$  increases with increasing water concentration; in a fully dilute solution, the gauche state of the C-C bond is so stabilized that the  $E_{\sigma}$  value reaches -1.49 kcal mol<sup>-1</sup>.<sup>83</sup> This value is comparable to that  $(-1.2 \text{ kcal mol}^{-1})$  determined by NMR for PEO in water.<sup>44</sup> The interdependent behavior of  $E_{\sigma}$  and  $E_{\omega}$  in RIS simulations for experimental configuration-dependent properties of PEO has been discussed in a previous study.<sup>84</sup> Molecular mechanics calculations<sup>85</sup> on a trimeric model compound of PEO have indicated that  $E_{\sigma}$  decreases and  $E_{\omega}$  increases with increasing dielectric constant of solvent; the ttt conformer is the most stable in the gas phase, whereas tgt is favored in polar solvents. The  $E_{\sigma}$  value was suggested to change the sign from positive to negative at  $\epsilon = 1.5$ .

**3.9. NBO Analysis.** The NBO analysis enables us to interpret the MO calculations in terms of the Lewis structure, i.e., hybridization, covalence, bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) orbitals, lone pair (n), etc.<sup>30–34</sup> Bond–bond ( $\sigma \rightarrow \sigma$ ) interactions are repulsive, whereas bond–antibond ( $\sigma \rightarrow \sigma^*$ ) and lone pair and antibond ( $n \rightarrow \sigma^*$ ) interactions are attractive. In the NBO analysis, the stabilization energy  $\Delta E_{da}^{(2)}$  associated with electron delocalization from donor (d) to acceptor (a) orbitals is estimated from<sup>34,86</sup>

$$\Delta E_{\rm da}^{(2)} = \rho_{\rm d} \frac{F({\rm d},{\rm a})^2}{E_{\rm d} - E_{\rm a}}$$
(22)

where  $\rho_d$  is the donor orbital occupancy,  $E_d$  and  $E_a$  are energy levels of the donor and acceptor orbitals respectively, and F(d,a) is the off-diagonal NBO Fock matrix element. Although the NBO analysis itself was carried out at the MP2/6-311+G(3df,2p) level, the  $\Delta E_{da}^{(2)}$  energy, estimated at the HF level, should be considered a semiquantitative measure. For ttt, tg<sup>+</sup>t, and ttg<sup>+</sup> conformations of DME and BMTE, the stabilization energies due to vicinal bond-antibond and lone pairantibond interactions around the C-C and C-O bonds are summarized in Tables 10 and 11. The  $n2_{X5} \rightarrow \sigma_{X2-C3}^*$  interaction, whose donor and acceptor are sepa-

Table 10. Stabilization Energies ( $\Delta E_{da}^{(2)}$ 's) Due to Vicinal	
Bond-Antibond and Lone Pair-Antibond Interactions	of
ttt, tg <sup>+</sup> t, and ttg <sup>+</sup> Conformers of DME	

		$\Delta E$	$\Delta E_{ m da}^{(2)}$ , a kcal mol <sup>-1</sup>		
donor (d)	acceptor (a)	ttt	tg+t	ttg <sup>+</sup>	
$\sigma_{\rm C3-HA}$	$\sigma^*_{C4-HB'}$	2.9			
	$\sigma^*_{C4-HB}$	0.6	2.9		
	$\sigma^{*}_{C4-O5}$	0.8	1.9		
$\sigma_{\mathrm{C3-HA'}}$	$\sigma^*_{C4-HB'}$	0.6	0.5		
	$\sigma^*_{C4-HB}$	2.9			
	$\sigma^*_{C4-O5}$	0.8	4.3		
$\sigma_{ m O2-C3}$	$\sigma^*_{C4-HB'}$		1.1		
	$\sigma^*_{C4-HB}$				
	$\sigma^*_{C4-O5}$	1.6			
sum <sup>b</sup>		20.4	21.4		
n2 <sub>05</sub>	$\sigma^*_{C4-HB'}$	9.2		3.6	
	$\sigma^*_{C4-HB}$	9.2		2.2	
	$\sigma^*_{C3-C4}$			9.0	
	$\sigma^{*}_{\Omega^{2}-\Omega^{3}}$			1.4	
$\sigma_{\rm O5-C6}$	$\sigma^*_{CA-\mu P'}$			0.8	
	$\sigma_{C4-\mu}^*$			0.9	
	$\sigma_{C2-C4}^{*}$	1.6		-	
$\mathbf{sum}^b$	- 03-04	21.6		19.6	

<sup>*a*</sup> Values smaller than the threshold of 0.5 kcal mol<sup>-1</sup> are not counted. <sup>*b*</sup> The  $\sigma_A - \sigma_B^*$  interaction yields the same amount of stabilization as  $\sigma_B - \sigma_A^*$ . Therefore, the  $\sigma_A - \sigma_B^*$  interactions are counted doubly.

Table 11. Stabilization Energies ( $\Delta E_{da}^{(2)}$ s) Due to Vicinal Bond-Antibond and Lone Pair-Antibond Interactions of ttt, tg<sup>+</sup>t, and ttg<sup>+</sup> Conformers of BMTE

		$\Delta E_{ m da}^{(2)}$ , $^a$ kcal mol $^{-1}$		
donor (d)	acceptor (a)	ttt	tg+t	ttg <sup>+</sup>
$\sigma_{\rm C3-HA}$	$\sigma^*_{C4-HB'}$ $\sigma^*_{C4-HB}$	3.3	3.4	
$\sigma_{\rm C3-HA'}$	$\sigma_{C4-S5}^{C4-S5}$ $\sigma_{C4-HB'}^{*}$ $\sigma_{C4-HB}^{*}$	3.3	0.7	
$\sigma_{\rm S2-C3}$	$\sigma_{C4-S5}$ $\sigma_{C4-HB'}^{*}$ $\sigma_{C4-HB}^{*}$		5.2 2.8	
$\operatorname{sum}^b$	$\sigma^*_{C4-S5}$	4.4 22.0	24.2	
n2 <sub>S5</sub>	$\sigma^*_{C4-HB'}$ $\sigma^*_{C4-HB}$	6.1 6.1		4.0
085-CR	$\sigma_{C3-C4}^{*}$ $\sigma_{S2-C3}^{*}$			5.6 1.8
535-00	$\sigma_{C4-HB'}^{*}$ $\sigma_{C4-HB}^{*}$			1.6
$\mathbf{sum}^b$	~ U3-U4	12.2		14.6

<sup>*a*</sup> Values smaller than the threshold of 0.5 kcal mol<sup>-1</sup> are not counted. <sup>*b*</sup> The  $\sigma_A - \sigma_B^*$  interaction yields the same amount of stabilization as  $\sigma_B - \sigma_A^*$ . Therefore, the  $\sigma_A - \sigma_B^*$  interactions are counted doubly.

rated by two bonds, has a significant magnitude of  $\Delta E_{da}^{(2)}$ , thus being included in the tables. Each X atom has two lone pair orbitals,  $n_{X5}$  and  $n_{2X5}$  (see Figure 8). The latter is the highest occupied orbital and hence an efficient electron donor.

From Tables 10 and 11, we can find a rule: When the acceptor is antiperiplanar to the donor, stabilization due to the electron delocalization is maximized. This has been accepted as a general principle in the NBO analysis.<sup>87</sup> For both DME and BMTE, the tg<sup>+</sup>t conformer is shown to be more stable than ttt by compari-



**Figure 8.** Lone pair orbitals, n1 and n2, in (a) ttt, (b)  $tg^+t$ , and (3)  $ttg^+$  conformations of BMTE and DME. The n1 orbital, being represented as  $sp^{0.49}$  (BMTE) or  $sp^{1.56}$  (DME) hybrid, is almost parallel to bisector of  $\angle$ CXC. The n2 orbital, being substantially a pure p orbital and the highest occupied orbital, is almost perpendicular to the CXC plane.

son of sums of the stabilization energies. The gauche stabilization of the C–C bond, coming mainly from the  $\sigma_{C3-HA'} \rightarrow \sigma^*_{C4-X5}$  interaction, is larger in BMTE than in DME. However, both NMR experiments and MO calculations for BMTE showed the strong trans preference of the C–C bond. To settle this contradiction, repulsive interactions must also be considered. The S···S steric repulsion may be a predominant factor; the S···S distance in the ttt conformer is 4.43 Å at the B3LYP/ 6-31G(d) level, whereas that (3.44 Å) of tg<sup>+</sup>t is smaller than double (3.6 Å) van der Waals radius of sulfur.<sup>88</sup> In addition, the favorable (antiparallel) dipole–dipole interaction formed in the ttt conformer enhances the trans stability.

For DME, the sum of  $\Delta E_{da}^{(2)}$ 's of the ttt conformation was estimated to be larger than that of ttg<sup>+</sup> by 2.0 kcal mol<sup>-1</sup>. For BMTE, however, the sum of ttt is smaller than that of ttg<sup>+</sup> by 2.4 kcal mol<sup>-1</sup>. Therefore, the conformational preference of the C–X bond, found experimentally and theoretically, is consistent with that suggested only from the vicinal  $n_X \rightarrow \sigma^*$  and  $\sigma \rightarrow \sigma^*$ delocalizations. The C–S bond is so long as not to disturb the intrinsic gauche stability, although steric repulsions (bond–bond interactions) in the gauche state may be more severe than those in the trans state.

In Table 12, antibond occupancies  $\rho^*$ 's and lengths of bonds 2, 3, and 4 of BMTE and DME are listed. When the C-X bond is in the gauche conformation, the  $\rho^*$ values in bond 3 of BMTE and DME are seen to be enhanced. Then, stabilization energies due to the  $n_{X5}$  $\rightarrow \sigma^*_{C_3-C_4}$  delocalizations amount to 5.6 and 9.0 kcal mol<sup>-1</sup> for BMTE and DME, respectively. The maximum  $\rho^*$  values of bonds 2 and 4 are found in  $g^\pm tg^\mp$  for BMTE  $(\rho^* = 0.0214)$  and in tg<sup>±</sup>t for DME ( $\rho^* = 0.0157$ ). These conformations are formed in the individual crystals.<sup>4,7</sup> Of all conformers of BMTE, the  $g^{\pm}tg^{\mp}$  states, being the most stable, have the maximum  $\rho^*$  values in bonds 2–4. Thus, their stabilities come partly from the electron delocalization. It is known that bond length tends to increase with decreasing bond order, which may be simply calculated from  $(\rho - \rho^*)/2$ , with  $\rho$  being bond occupancy. This rule approximately holds for the data

Table 12. Antibond Occupancies<sup>a</sup> (p\*'s) and Lengths<sup>b</sup> (r's) of Skeletal Bonds of Representative Conformations of BMTE and DME

	bond 2 (	X <sub>2</sub> -C <sub>3</sub> )	bond 3 (	C <sub>3</sub> -C <sub>4</sub> )	bond 4 (	$C_4 - X_5$ )
conformation	$\rho^*$	ρ	$\rho^*$	ρ	$\rho^*$	ρ
-		BMTE	E(X = S)			
ttt	0.0154	1.818	0.0073	1.526	0.0154	1.818
$ttg^{\pm}$	0.0193	1.820	0.0159	1.526	0.0172	1.816
tg≚t	0.0170	1.819	0.0087	1.527	0.0170	1.819
$g^{\pm}tg^{\pm}$	0.0213	1.818	0.0249	1.527	0.0213	1.818
$\mathbf{g}^{\pm}\mathbf{t}\mathbf{g}^{\mp}$	0.0214	1.818	0.0251	1.527	0.0214	1.818
		DM	E(X = O)	)		
ttt	0.0094	1.394	0.0133	1.514	0.0094	1.394
$ttg^{\pm}$	0.0106	1.394	0.0202	1.520	0.0096	1.398
tg≚t	0.0157	1.393	0.0142	1.511	0.0157	1.393
$g^{\pm}tg^{\pm}$	0.0111	1.399	0.0270	1.525	0.0111	1.399
g±tg∓	0.0111	1.399	0.0270	1.525	0.0111	1.399

<sup>a</sup> At the MP2/6-311+G(3df,2p) level. <sup>b</sup> At the HF/6-31G(d) level.



**Figure 9.** Atomic (group) charges of (a) ttt, (b) ttg<sup>+</sup>, (c) tg<sup>+</sup>t, (d) g<sup>+</sup>tg<sup>+</sup>, and (e) g<sup>+</sup>tg<sup>-</sup> conformations of BMTE and DME. Atomic charges of hydrogens are summed into the bonded carbons.

shown in Table 12; the bond length, in principle, increases with  $\rho^*$ .

Figure 9 shows atomic (or group) charges of component atoms of five representative conformers of BMTE and DME. The oxygen atom of DME is seen to be more negative than sulfur in the corresponding conformer of BMTE. This is because the electronegativity (2.5) of sulfur is almost equal to that of carbon and smaller than that (3.5) of oxygen.<sup>89</sup> If bond 4 takes the gauche conformation, the  $\rho^*$  values of bonds 2 and 3 become large (Table 12), and the negative charge of the X<sub>2</sub> atom increases correspondingly. When bond 3 is in the gauche state, charges of the  $X_2$  and  $X_5$  atoms are small in magnitude. In the  $g^\pm tg^\mp$  conformations, two large dipole moments are formed along bisectors of  $\angle C_1 X_2 C_3$  and  $\angle C_4 X_5 C_6$  and canceled out, as shown by the arrows in Figure 9e. The  $g^{\pm}tg^{\mp}$  conformers of BMTE show slightly larger electron delocalization than  $g^{\pm}tg^{\pm}$  and are further stabilized by the antiparallel dipole-dipole interaction. The conformational energy  $E_{\kappa}$  of ca. -0.2 kcal mol<sup>-1</sup>, found for BMTE, probably reflects these extra stabilizations.

**Table 13. SCF Energies of All-Trans and Crystal** Conformations of PES Oligomers, Evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) Level

	SCF en	SCF energy, au	
	all-trans	crystal	$\Delta$ SCF, <sup>b</sup> kcal mol <sup>-1</sup>
monomer	-954.949353	-954.950704	-0.85
dimer	-1431.819686	-1431.822374	-1.69
trimer	-1908.690047	-1908.694082	-2.53

<sup>a</sup> Crystal conformations of the monomer, dimer, and trimer are g<sup>+</sup>tg<sup>-</sup>, g<sup>+</sup>tg<sup>-</sup>g<sup>-</sup>tg<sup>+</sup>, and g<sup>+</sup>tg<sup>-</sup>g<sup>-</sup>tg<sup>+</sup>g<sup>+</sup>tg<sup>-</sup>. Both terminals are methyl groups.  ${}^{b}\Delta SCF = SCF_{crystal} - SCF_{all-trans}$ .

The highest antibond occupancies of bonds 2, 3, and 4 of BMTE were found in the  $g^{\pm}tg^{\mp}$  conformations, which are formed in the crystal and here referred to as "crystal conformation" . We calculated the SCF energy difference ( $\triangle$ SCF's) between the crystal and all-trans conformations of the monomer, dimer, and trimer of BMTE at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G-(d) level, in expectation that the electron delocalization might be extended over the crystallized PES chain. The results are shown in Table 13. The  $\triangle$ SCF values of the monomer, dimer, and trimer were obtained as -0.85, -1.69, and -2.53 kcal mol<sup>-1</sup>, respectively; therefore, the ratio is exactly 1:2:3. Contrary to our expectation, no additional stabilization dependent on the chain length was found. The energy levels of antibond orbitals 2, 3, and 4 of the  $g^{\pm}tg^{\mp}$  conformations of BMTE, calculated at the MP2/6-311+G(3df,2p) level, are 0.40836, 0.63734, and 0.40836 au, respectively. The high C-C antibond energy interrupts the long-range electron delocalization.

## 4. Concluding Remarks

The intramolecular (C-H)...O interaction of polyethers has been a subject of controversy.<sup>90</sup> As has been shown above, the PEO chain adjusts itself to the environment by varying the conformational energies. In particular,  $E_{\sigma}$  and  $E_{\omega}$  are sensitive to solvent. Consequently, PEO is soluble in a variety of solvents including water. On the other hand, the skeletal C-C bond of PPO has a moderate trans preference; the first-order interaction energies,  $E_{\alpha}$  and  $E_{\beta}$ , for the g<sup>+</sup> and g<sup>-</sup> states of isotactic  $(\tilde{R})$ -PPO in benzene are 0.3 and 0.8 kcal mol<sup>-1</sup>, respectively.<sup>20,21</sup> In addition, the methyl side chain prevents solvent molecules from approaching the lone pair of PPO. Therefore, PPO is insoluble in water. Conformational energies,  $E_{\omega 1}$  and  $E_{\omega 2}$ , of PPO, representing the intramolecular (C-H)...O interactions are kept negative even in comparatively polar solvents such as dimethyl sulfoxide.<sup>20,21</sup> The methyl group differentiates PPO from PEO in physicochemical properties.

In the  $tg^{\pm}g^{\mp}$  conformations of BMTE, no particular close contact between the methyl hydrogen and sulfur atoms was found. The distance between sulfur and the nearest methyl hydrogen was evaluated as 2.96 Å from the MO calculations at the HF/6-31G(d) level, being almost equal to the sum (3.0 Å) of the van der Waals radii of hydrogen and sulfur.88 The conformational energy  $E_{\omega}$  was determined by the MO calculations and NMR experiments to be 0.40-0.53 kcal mol<sup>-1</sup>, and hence the (C–H)····S interaction is somewhat repulsive.

The  $\langle r^2 \rangle_0 / nl^2$  value of PES was calculated to be 2.5-2.9 from the experimental energy parameters, indicating the flexibility of PES (Table 5). The flexibility can also be confirmed from the calculated  $S_{\text{conf}}$  value of 6.2–6.3 cal mol<sup>-1</sup> K<sup>-1</sup> (cf. for PEO,  $\langle r^2 \rangle_0 / nl^2 = 4.1-5.1$  and  $S_{\text{conf}} = 5.0-5.1$  cal mol<sup>-1</sup> K<sup>-1</sup>).<sup>91</sup> Nevertheless, PES has a much higher melting point (216 °C) than PEO (68 °C) and dissolves in a few solvents at high temperatures. These properties must come from  $\Delta H_{\rm u}$  (PES) >  $\Delta H_{\rm u}$ (PEO). The experimental  $\Delta H_{\rm u}$  values have been reported as follows: PES, 3.37 kcal mol<sup>-1</sup>;<sup>2,25</sup> PEO, 1.75-2.79 kcal mol<sup>-1</sup>.<sup>1,25</sup> Bhaumik and Mark<sup>92</sup> calculated the intermolecular energies between a pair of PES or PEO chains in the crystalline-state conformation by semiempirical potential energy functions, and suggested that the interaction energy of PES is about twice as much as that of PEO. The energy difference between PES and PEO is primary due to van der Waals interactions, rather than to dipolar effects. On the other hand, Takahashi et al.<sup>3</sup> pointed out that the strong dipoledipole interactions of the C-S-C group play an important role in forming the crystal structure. In the future, sophisticated treatment for intermolecular interactions, based on ab initio MO theory, is expected to be developed and settle these problems.

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the  $E_0$  value was obtained as shown in Table 5. Ab initio MO calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G-(d) level gave the  $\Delta G_k$  value of ttg<sup>+</sup>g<sup>-</sup>tt as -0.43 kcal mol<sup>-1</sup>, and hence  $E_{\omega}$  was estimated from  $-0.43 - (-0.24) \times 2$  to be  $0.05 \text{ kcal mol}^{-1}$  The long C–S bond may permit such bent conformations to exist without additional energy. In this study, the  $E_{\omega'}$  value of PES has been assumed to be null.

(55) In the simulation, the experimental bond conformations must be satisfactorily reproduced. Agreement between theory and experiment may be monitored by

$$\delta^{2} = \sum_{T} \sum_{A} \sum_{\eta} \left[ p_{\eta,\text{calcd}}^{A}(T) - p_{\eta,\text{obsd}}^{A}(T) \right]^{2} / \epsilon_{\text{exp}}^{2}$$

where *T*,  $\eta$ , and A, respectively, stand for temperature, conformation (t or g), and bond (CC or CS), and  $\epsilon_{exp}$  is the average experimental error. Entropy regarding the conformer fractions is defined as

$$S = \sum_{T} \sum_{k}^{K} \{f_{k}(T) - m_{k}(T) - f_{k}(T) \ln[f_{k}(T)/m_{k}(T)]\}$$

where  $m_k(T)$  is an initial model of  $f_k(T)$ . The most probable solution of  $f_k(T)$ 's may maximize *S*. Accordingly, the solution can be found at maximum

$$Q = \alpha S - \delta^2/2$$

where  $\alpha$  is the regularization constant. The entropy *S* is convex, and  $\delta^2$  is concave. Thus, Q always reaches a unique maximum.<sup>56,57</sup> The  $f_k(T)$  values are calculated according to the RIS scheme.<sup>14</sup> If  $\delta^2$  is modified so as to be suitable for the experiment, this methodology is applicable to a variety of conformational analyses.58-60

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- (81) This approximation gives hardly any significant effect on the results, because the  $\chi$  interaction occurs only in the  $g^{\pm}g^{\pm}g^{\pm}$  conformations. Dependence of the simulated data on each conformational energy  $E_{\xi} (\xi = \sigma, \rho, \omega, \text{ or } \chi)$  may be estimated from the first derivative at the optimized energies; e.g.,  $\partial \langle r^2 \rangle_0 / nP^2 / \partial E_{\xi}$ 's ( $\partial \langle \langle \mu^2 \rangle / nm^2 \rangle / \partial E_{\xi}$ 's), which were obtained as 1.4 (-0.09) mol kcal<sup>-1</sup> for  $E_{\sigma}$ , 1.0 (-0.26) mol kcal<sup>-1</sup> for  $E_{\sigma}$ , 1.5 (-0.01) mol kcal<sup>-1</sup> for  $E_{\omega}$ , and -0.02 (-1.0 × 10<sup>-3</sup>) mol kcal<sup>-1</sup> for  $E_{\chi}$ . Here, the values in the parentheses represent those for the dipole moment ratio. In the simulation, the effect of  $E_{\chi}$  is negligibly small.
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