Carbon-13 NMR Chemical Shifts of Dimeric Model Compounds of Poly(propylene Oxide): A Proof of Existence of the (C−H)···O Attraction

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Conformational energies of poly(propylene oxide) (PPO) have been determined from ^{13}C NMR chemical shifts of its six dimeric model compounds. The model compounds were prepared and fractionated by supercritical fluid chromatography into three components: $CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OCH_3$ (head-to-tail); $CH_3OCH_2CH(CH_3)OCH(CH_3)CH_2OCH_3$ (head-to-head); $CH_3OCH(CH_3)CH_2OCH_2CH(CH_3)OCH_3$ (tail-to-tail). Carbon-13 NMR measurements using ^{1}H broad-band decoupling and DEPT techniques were carried out for the benzene solutions at 25 °C, and all observed NMR peaks were assigned to the methine, methylene, pendant methyl, and terminal methoxy carbons. By the simulation based on the rotational isomeric state (RIS) scheme and γ- and δ-substituent effects for the ^{13}C NMR chemical shifts, the γ- and δ-effect parameters and the conformational energies were optimized; the root-mean-square error between the calculated and observed chemical shifts was minimized to 0.12 ppm. Values of the γ-anti effect (−2.6 ppm) of oxygen, the γ-gauche effects of carbon (−4.9 ppm) and oxygen (−7.9 ppm), and the δ-effect (2.1 ppm) of oxygen for the g^+g^- conformations were obtained to fall within the allowable ranges, as shown in the parentheses. The conformational energies evaluated here are comparable to those determined for isotactic PPO in our previous studies. These results confirm our interpretation of the gauche oxygen effect: The gauche stability of the C−C bond in the main chain of PPO is due to the intramolecular (C−H)···O hydrogen bonding.

1. Introduction

Poly(propylene oxide) (PPO) is prepared by the ring-opening polymerization of propylene oxide. If both C−O bonds of the monomer are cleaved, three kinds of linkages, head-to-tail (H−T), head-to-head (H−H), and tail-to-tail (T−T), are formed between the monomeric units, where H is the methine end and T is the methylene end of the monomer unit. Propylene oxide, having a chiral methine carbon, exists in either of two optical forms, *R* and *S*. Therefore, the ^{13}C NMR spectra observed from atactic PPO are too complicated to be easily analyzed.[1−3]

The γ-substituent effects have often been utilized to predict ^{13}C chemical shifts of polymers;[4,5] the γ substituent, which is separated from the observed carbon atom by three bonds, tends to shield the carbon nucleus; the magnitude of the shielding effect depends on the distance between the two atoms, thus being sensitive to the conformation of the intervening bond. By this method, the ^{13}C NMR chemical shifts of a variety of polymers have been successfully related to their microstructures.[4,5] For atactic PPO, the assignment of the chemical shifts has also been attempted.[1,4,5]

Recently, we have carried out the conformational analysis of isotactic PPO and its monomeric model compound, 1,2-dimethoxypropane (1,2-DMP), by ab initio molecular orbital (MO) calculations and ^{1}H and ^{13}C NMR vicinal coupling constants of 1,2-DMP and the RIS analysis of the characteristic ratio and dipole moment ratio of isotactic PPO.[6−9] Consequently, we have found that the gauche stability of the CH_2−CH bond (the gauche oxygen effect)[10] is due to the (C−H)···O hydrogen bonding formed in the $g^{\pm}g^{\mp}$ conformation for the C−O/C−C bond pairs, and presented the conformational energies of isotactic PPO. The (C−H)···O close contacts in, e.g., (*R*)-1,2-DMP are illustrated in Figure 1, parts d, e, and f. The ω_1 interaction is assigned to a second-order (C−H)···O attraction, with the C−C bond being in the g^+ state and the ω_2 interaction to that with the bond in the g^- state. Only the $g^+g^+g^+$ conformer is presumed to have an extra stabilization (χ). The energy parameters thus obtained successfully reproduced all of the experimental observations from both isotactic PPO and 1,2-DMP. The interpretation for the gauche oxygen effect of PPO has been supported from MO calculations using large basis sets,[11,12] and similar phenomena have been reported for poly(ethylene oxide) and its model compounds.[13,14] Such weak hydrogen bonds have been found in crystals.[15,16] However, PPO

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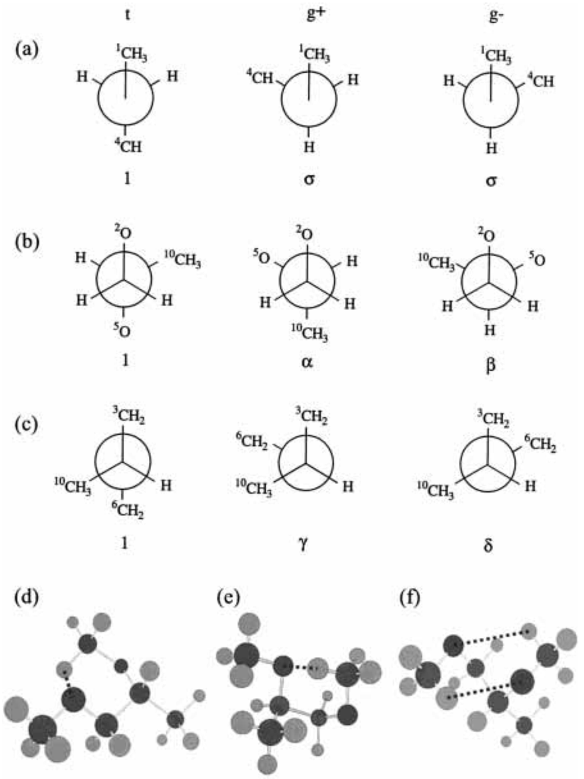


Figure 1. Intramolecular interactions of isotactic poly(propylene oxide) (PPO) and its model compounds:[6,7,9] the first-order interactions for (a) bond 2, (b) bond 3, and (c) bond 4 (the illustration is based on H−T (*RR*), see Figure 2a); the second-order interactions, (d) the ω_1 interaction found in the tg^+g^- conformation of the monomeric model, (*R*)-1,2-dimethoxypropane ((*R*)-1,2-DMP), and (e) the ω_2 interaction in the g^+g^-t conformation of (*R*)-1,2-DMP; (f) the third-order χ interaction in the $g^+g^+g^+$ conformation of (*R*)-1,2-DMP. The dotted lines represent the (C−H)···O close contacts. In the present study, the intramolecular interactions and the statistical weights of six dimeric model compounds (see Figure 2) are represented by the corresponding capital letters: A, B, Γ, Δ, Σ, Ω$_1$, Ω$_2$, and X.

and its oligomeric model compounds of interest here exist in gas or liquid phase. It must be noted that the nonbonded (C−H)···O attractions influence the conformational preferences, even when the molecules are in rapid motions.

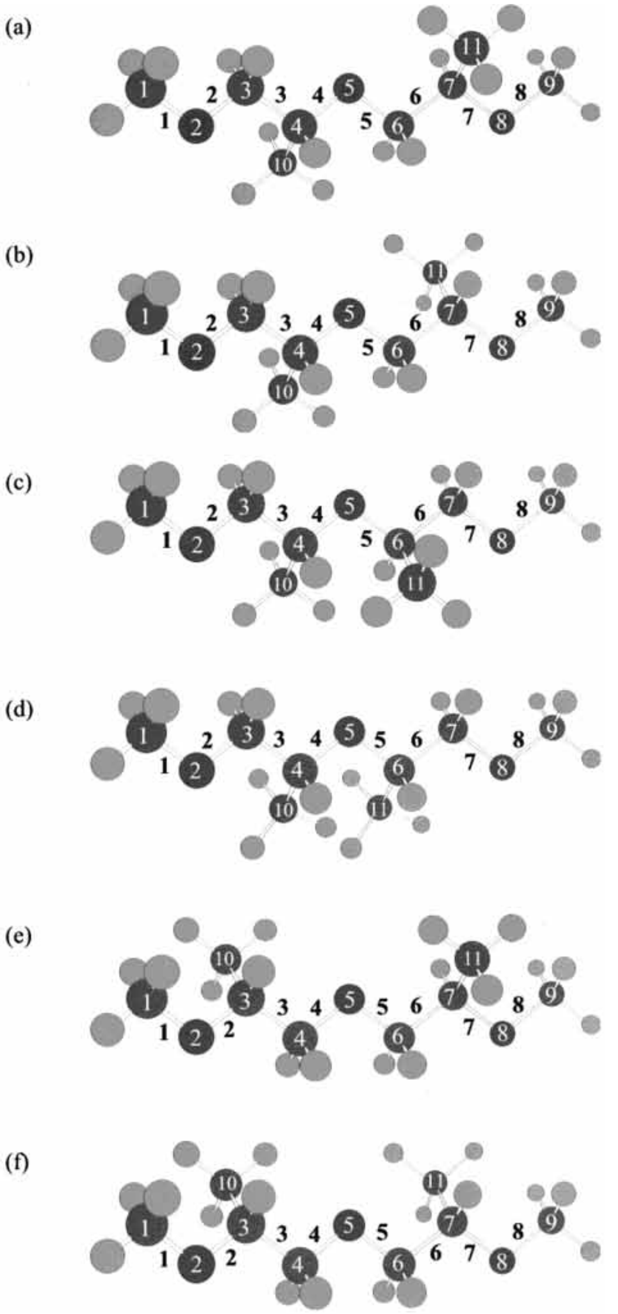


Figure 2. Schematic representation of the dimeric model compounds of PPO: (a) H−T (*RR*), (b) H−T (*RS*), (c) H−H (*RR*), (d) H−H (*RS*), (e) T−T (*RR*), and (f) T−T (*RS*) in their all-trans conformations. As indicated, the atoms and bonds are numbered.

In this study we have attempted to determine conformational energies of six dimeric model compounds (Figure 2) of PPO from their ^{13}C NMR chemical shifts by a combined use of the rotational isomeric state (RIS) scheme[17] and the substituent effects. The dimers may be the simplest compounds having different regiosequences (H−T, H−H, and T−T) and stereosequences (*RR*, *RS*, *SR*, and *SS*). Hereafter the compounds (and molecules) with the H−T, H−H, and T−T linkages are, respectively, referred to as H−T, H−H, and T−T. For each linkage, four optical isomers *RR*, *RS*, *SR*, and *SS*, exist. However, the *RR* and *SS* isomers and the *RS* and *SR* isomers are indistinguishable by NMR. In this paper, therefore, the four isomers are represented by *RR* and *RS*.

The model compounds were prepared and separated for each regiosequence by supercritical fluid chromatography (SFC). The ^{13}C NMR spectra were measured for the benzene-d_6 solution. The chemical shifts were assigned to the methine, methylene, pendant methyl, and terminal methoxy carbons and compared with the theoretical calculations based on the γ- and δ-substituent effects and the RIS scheme, including the first-order (between atoms or groups separated by three bonds), second-order (by four bonds), and third-order (by five bonds) intramolecular interactions.[18] By the analysis, we have determined the conformational energies of the dimers and confirmed the existence of the (C−H)···O attractions.

2. Theoretical Section

According to the empirical additivity relationship,[19,20] the chemical shift of a carbon atom i is given by

$$\delta_i = \sum_j^{n_{j,\alpha}} \Delta\delta_{\alpha,j} + \sum_j^{n_{j,\beta}} \Delta\delta_{\beta,j} + \sum_\eta \sum_j^{n_{j,\gamma}} p_\eta \Delta\delta^{\eta}_{\gamma,j} + \sum_{\eta\xi} \sum_j^{n_{j,\delta}} p_{\eta\xi} \Delta\delta^{\eta\xi}_{\delta,j} + S \quad (1)$$

where $n_{j,\alpha}$, $n_{j,\beta}$, $n_{j,\gamma}$, and $n_{j,\delta}$ are the numbers of nonhydrogen atoms j at the α, β, γ, and δ positions (separated by one, two, three, and four bonds from the carbon i, respectively), $\Delta\delta_{\alpha,j}$ and $\Delta\delta_{\beta,j}$ are the chemical shift increments due to the atoms at the α and β positions, and $\Delta\delta^{\eta}_{\gamma,j}$ and $\Delta\delta^{\eta\xi}_{\delta,j}$ are those due to the γ and δ atoms, with the intervening bond(s) being in the η (= t, g$^+$, or g$^-$) and $\eta\xi$ (= tt, tg$^+$... or g$^-$g$^-$) conformations, respectively. Thus, the terms representing the γ- and δ-effects include the conformational probabilities, p_η and $p_{\eta\xi}$, respectively. The α- and β-substituents induce the downfield shifts (i.e., $\Delta\delta_{\alpha,j} > 0$ and $\Delta\delta_{\beta,j} > 0$), while the γ-substituent gives the upfield shift ($\Delta\delta^{\eta}_{\gamma,j} < 0$). The sign of $\Delta\delta^{\eta\xi}_{\delta,j}$ is changeable with the structure and conformation. The steric factor S is determined by the extent of branching at the carbon i and its adjacent carbons.

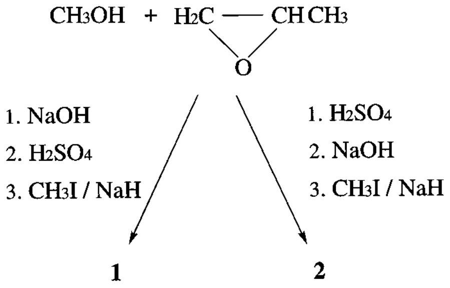
The above equation may be rewritten as

$$\delta_i = \Delta\delta_{0,i} + \sum_{\eta}\sum_{j}^{n_{j,\gamma}} p_\eta \Delta\delta_{\gamma,j}^{\ \eta} + \sum_{\eta\xi}\sum_{j}^{n_{j,\delta}} p_{\eta\xi}\Delta\delta_{\delta,j}^{\ \eta\xi} \qquad (2)$$

where $\Delta\delta_{0,i}$ is the summation of the first, second, and fifth terms of eq 1 with respect to the observed carbon atom i. The $\Delta\delta_{0,i}$ term, being independent of the conformation, may be given from the molecule that has the same atoms at the α and β positions as the compound of interest and only hydrogen atoms at the γ positions. Such a molecule is designated the *parent* compound. The parent compounds for the methine, methylene, pendant methyl, and terminal methoxy carbons of the six model compounds are 2-methoxy-1-propanol ($CH_3O\mathit{C}H(CH_3)CH_2OH$), 1-methoxy-2-propanol ($CH_3O\mathit{C}H_2CH(CH_3)OH$), 2-propanol ($\mathit{C}H_3CH(CH_3)OH$), and dimethyl ether ($\mathit{C}H_3OCH_3$), respectively. The individual carbon atoms have the same numbers and kinds of α and β atoms (CH, 2 α-C, 1 α-O, 1 β-C, and 1 β-O; CH_2, 1 α-C, 1 α-O, 2 β-C, and 1 β-O; CH_3, 1 α-C, 1 β-C, and 1 β-O; CH_3O, 1 α-O and 1 β-C), irrespective of the linkage and optical isomer. However, the β substituent *groups* are not always common; e.g., for the methine carbons, ^{4}CH of H−T, 1 β-CH_2 and 1 β-O; ^{7}CH of H−T, 1 β-CH_3 and 1 β-O; ^{4}CH and ^{6}CH of H−H, 1 β-CH and 1 β-O, ^{3}CH and ^{7}CH of T−T, 1 β-CH_3 and 1 β-O. Here the superscripts correspond to the carbon numbers in Figure 2. On this basis, it is preferable that the $\Delta\delta_{0,\zeta}$ (ζ = CH, CH_2, CH_3, or CH_3O) value should be defined according to the β-substituent group.

The γ-effect of carbon in the trans (antiperiplanar) position is negligibly small, whereas the γ-anti effect ($\Delta\delta^{t}_{\gamma,O}$) of oxygen is comparatively large (−2 to −3 ppm).[19,20] In ^{13}C NMR studies on alkanes and their oxygenated derivatives, the γ-gauche effects of carbon and oxygen, $\Delta\delta^{g\pm}_{\gamma,C}$ and $\Delta\delta^{g\pm}_{\gamma,O}$, have been found within the ranges of −4 to −6 ppm and −6 to −8 ppm, respectively.[1,4,5] The δ-effects, which are typically smaller in magnitude (≤ 0.5 ppm) than those of the α-, β-, and γ-effects, have not been taken into account, except for the $g^{\pm}g^{\mp}$ conformations of the intervening bonds. In hydrocarbon polymers, the $g^{\pm}g^{\mp}$ conformations lead to a severe steric interaction called the "pentane" effect,[17] which results in these rarely occurring. Thus, the δ-effect contribution ($\Delta\delta^{g\pm g\mp}_{\delta,C}$) to the chemical shift may be negligible in these cases. As stated in the Introduction, however, the $g^{\pm}g^{\mp}$ conformations for the C−O/C−C bond pairs of PPO and its model compounds are stabilized by the (C−H)···O hydrogen bonds. The $\Delta\delta^{g\pm g\mp}_{\delta,O}$ values of 2 to 3 ppm have been estimated,[19,20] whereas the $\Delta\delta^{g\pm g\mp}_{\delta,O}$ effect may be negligible on the above basis. Here, the δ-effects related to the other conformations have been assumed to be null: $\Delta\delta^{tt}_{\delta,C} = \Delta\delta^{tg\mp}_{\delta,C} = \Delta\delta^{g\pm t}_{\delta,C} = \Delta\delta^{g\pm g\pm}_{\delta,C} = \Delta\delta^{tt}_{\delta,O} = \Delta\delta^{tg\mp}_{\delta,O} = \Delta\delta^{g\pm t}_{\delta,O} = \Delta\delta^{g\pm g\pm}_{\delta,O} = 0$ ppm.

SCHEME 1



According to the RIS scheme,[17] for example, the fractional population $f_{g^+tg^-}$ ... of the conformation g^+tg^- ... can be calculated from statistical weight matrices U_n's (see Supporting Information) according to

$$f_{g^+tg^-} \ldots = \frac{\mathbf{J}^*[U_2'(g^+)U_3'(g^+t)U_4'(g^+\mathrm{tg}^-)\ \ldots]\mathbf{J}}{\mathbf{J}^*[\prod_{n=2}^{N-1} U_n]\mathbf{J}} \qquad (3)$$

where $\mathbf{J}^* = [100]$, $\mathbf{J}$ is the 9 × 1 column matrix of which elements are unity, and N is the number of skeletal bonds. The $U_2'(g^+)$ matrix can be obtained by filling the columns of the U_2 matrix other than that corresponding to the g^+ state with zero, and the $U_3'(g^+t)$ matrix by filling the elements of the U_3 matrix other than that corresponding to the g^+t conformation with zero, etc. Strictly, the conformational energies may be defined for each dimer. However, an outstanding advantage of the RIS scheme is to allow us to calculate the conformation-dependent and configuration-dependent properties using small number of energy parameters. In this study, the same conformational energies have been assumed to hold for the six dimers. To distinguish the energy parameters from those established for isotactic PPO,[6,7,9] the interactions and statistical weights for the dimers are represented by the corresponding capital letters: A, B, Γ, Δ, Σ, Ω_1, Ω_2, and X.

The conformational probability p_η of the nth bond is given as the sum of the fractional populations of conformers having the η state in the nth bond, and $p_{\eta\xi}$ for the nth and (n + 1)th bond pair as the sum of the populations of conformers having the $\eta\xi$ conformation in the two bonds. The chemical shift δ_i can be calculated from $\Delta\delta_{0,\zeta}$'s, $\Delta\delta^{t}_{\gamma,O}$, $\Delta\delta^{g\pm}_{\gamma,C}$, $\Delta\delta^{g\pm}_{\gamma,O}$, $\Delta\delta^{g\pm g\mp}_{\delta,O}$, p_η's, and $p_{\eta\xi}$'s.

3. Experimental Section

3.1. Sample Preparation. In the alcoholysis of propylene oxide (PO), an acid catalyst yields a mixture of 2-alkoxy-1-propanol and 1-alkoxy-2-propanol in approximately equal amounts, while a base catalyst preferentially gives the latter compound.[21] The reactions provided all the six dimeric model compounds, which were prepared as shown in Scheme 1. Propylene oxide was initially reacted with methanol to yield a mixture of 2-methoxy-1-propanol and 1-methoxy-2-propanol, and these products were then further reacted with PO to produce the dimerized alcohols. Then, two combinations of the catalysts were used in the first and second steps: **1**, NaOH and H_2SO_4; **2**, H_2SO_4 and NaOH. The concentrations of the NaOH and H_2SO_4 catalysts were 0.3 and 1.3 mol%, respectively. The individual products were treated with sodium hydride and

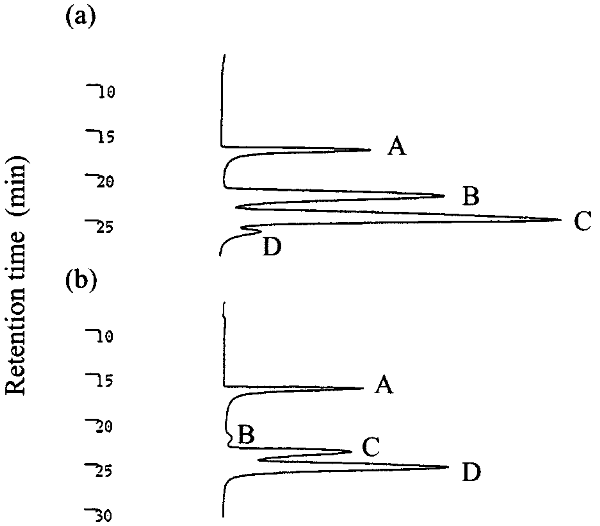


Figure 3. Supercritical fluid chromatograms of samples (a) **1** and (b) **2**. The fractions A, B, C, and D were identified by GC/MS as 1,2-DMP, H−H, H−T, and T−T, respectively.

iodomethane to yield mixtures of the model compound (referred hereafter to as samples **1** and **2** in the order mentioned). All of the chemicals were purchased from Wako Pure Chemical Ltd.

3.2. Supercritical Fluid Chromatography.[22] The mobile phase was carbon dioxide. A Shimadzu LC-6A pump was used to deliver carbon dioxide. The pump head was cooled so as to maintain a stable flow. A Shimadzu SLC-6A controller was connected to the pump to regulate the mobile phase pressure. The separation column of ODS-silica gel (250 mm × 4.6 mm) was kept at a given temperature in a column oven of a Shimadzu GC-7A system. A Rheodyne model 7125 sample injector with a 20-μL sample loop, the FID detector attached to the Shimadzu GC-7A system, and a Shimadzu C-R4A integrator were used. The flow-rate of the mobile phase was controlled by a restrictor of a capillary tube (400 mm × 50 μm i.d.).

3.3. ^{13}C NMR Measurements. Carbon-13 NMR spectra were measured at 150.80 MHz on a JEOL JMS-GSX600 spectrometer equipped with a variable-temperature controller. During the measurement, the probe temperature was maintained at 25 °C within a ±0.1 °C fluctuation. The free induction decay signals were accumulated ca. 128−1024 times by using the ^{1}H broad-band decoupling or the DEPT technique. In the former measurement, the $\pi/2$ pulse width, the data acquisition time, and the recycle delay were 6.2 μs, 0.8 s, and 2.2 s, respectively. Thus, the recycle time was ca. 3 s, being 3−6 times the spin−lattice relaxation times of PPO carbons.[1] The digital resolution of the spectra was 0.62 Hz. Benzene-d_6 was used as the solvent, and tetramethylsilane as the internal standard. The solute concentration was ca. 1 wt%.

1-Methoxy-2-propanol and 2-propanol were also examined by the NMR measurements, as purchased from Wako Pure Chemical Ltd. without further purification. The chemical shifts of 2-methoxy-1-propanol were determined by comparison between the spectrum observed from 1-methoxy-2-propanol and that from the mixture (prepared as above) of 1-methoxy-2-propanol and 2-methoxy-1-propanol.

4. Results and Discussion

4.1. Preparation, Characterization, and Purification of Samples. Figure 3 shows the supercritical fluid chromatograms of the samples **1** and **2**. By GC/MS, the fractions A, B, C, and D were identified as 1,2-DMP, H−H, H−T, and T−T, respectively. Because PO was the racemic mixture, each fraction includes *RR* and *RS*. As expected, sample **1** contains a large amount of both H−T and H−H with a small amount of T−T, whereas sample **2** includes a large amount of both T−T and H−T and a small amount of H−H. Therefore, both samples were mixed in equal quantities, dissolved in dichloromethane at 10 wt%, and the retention behavior was investigated. Consequently, the optimal conditions for the fractionation were found as follows: the carbon dioxide pressure of 90 kg cm^{-2}, the column temperature of 60 °C, and the injection of 8 μL. Under these conditions, the fractionations were repeated ca. 250 times to acquire sufficient amounts of the three components for the NMR measurements.

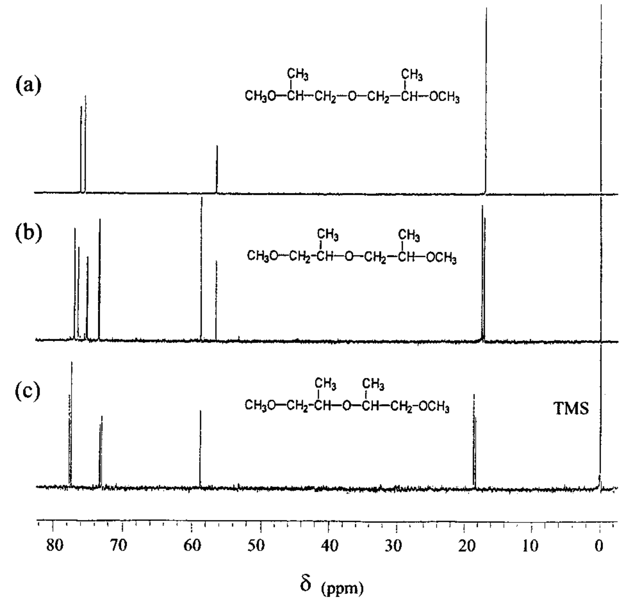


Figure 4. ^{13}C NMR spectra observed from the benzene solutions at 25 °C by using ^{1}H broad-band decoupling: (a) T−T, (b) H−T, and (c) H−H. The internal standard was tetramethylsilane.

4.2. ^{13}C NMR Spectra and Assignment. Figure 4 shows ^{13}C NMR ^{1}H broad-band decoupling spectra from benzene solutions of T−T, H−T, and H−H at 25 °C. The peaks at 17−18 ppm can be assigned to the pendant methyl carbons, and those around 56−59 ppm to terminal methoxy carbons. The signals around 74−78 ppm may be assigned to either methine or methylene carbons by reference to the DEPT spectra. In Figure 5, the methine and methylene parts of the DEPT(90) and DEPT (135) spectra of H−T in benzene at 25 °C are compared with the ^{1}H broad-band decoupling spectrum. The methylene signals are not observed by the DEPT(90) method and are inverted in the DEPT(135) spectrum. In H−T, only two methine and two methylene groups exist. However, four doublets are observed; one of the doublets arises from *RR* and the other from *RS*. The doublet spacing, corresponding to the chemical shift difference between *RR* and *RS*, was found to range from 0.00 to 0.14 ppm for H−T. The number of peaks from H−H and T−T are smaller than that from H−T because of the structural symmetry. The doublets from the H−H mixture show comparatively large spacings; for CH and CH_2, 0.27 ppm; for CH_3, 0.29 ppm; for CH_3O, 0.02 ppm. For T−T, the doublet was observed only from the methylene carbons at 75.61 and 75.66 ppm, probably owing to the influence of both nearby chiral centers. The structural similarity between H−T and H−H in atoms 1 to 5 and that between H−T and T−T in atoms 5 to 9 allow us to assign the peaks of H−T by reference to the spectra of T−T and H−H.

TABLE 1: Conformational Energies:[a] Comparison of the Present with Previous Studies

isotactic PPO[b] (previous studies)		six dimeric models (present study)		
	conformational energy kcal mol^{-1}		conformational energy kcal mol^{-1}	$\lvert\Delta(\mathrm{SD})/\Delta E\rvert$[c] ppm^2 mol kcal^{-1}
first-order interaction				
E_α	0.54 ± 0.03	E_A	0.36	15.6
E_β	0.83 ± 0.04	E_B	1.00	8.6
E_γ	2.967	E_Γ	2.86	0.1
E_δ	0.223	E_Δ	0.44	24.6
E_σ	1.406	E_Σ	1.40	8.0
second-order interaction				
E_{ω_1}	−1.040	E_{Ω_1}	−0.88	26.9
E_{ω_2}	−1.753	E_{Ω_2}	−1.53	2.7
third-order interaction				
E_χ	−0.908	E_X	−0.93	9×10^{-4}

[a] For the definition of the interactions, see Figure 1. [b] Determined from ab initio molecular orbital calculations for 1,2-DMP, ^{1}H and ^{13}C NMR vicinal coupling constants of 1,2-DMP, and the RIS analysis of the experimental observations of the characteristic ratio and dipole moment ratio of isotactic PPO. References 6, 7, and 9. [c] A measure of sensitivity of the calculated chemical shifts to each conformational energy. For the details, see text.

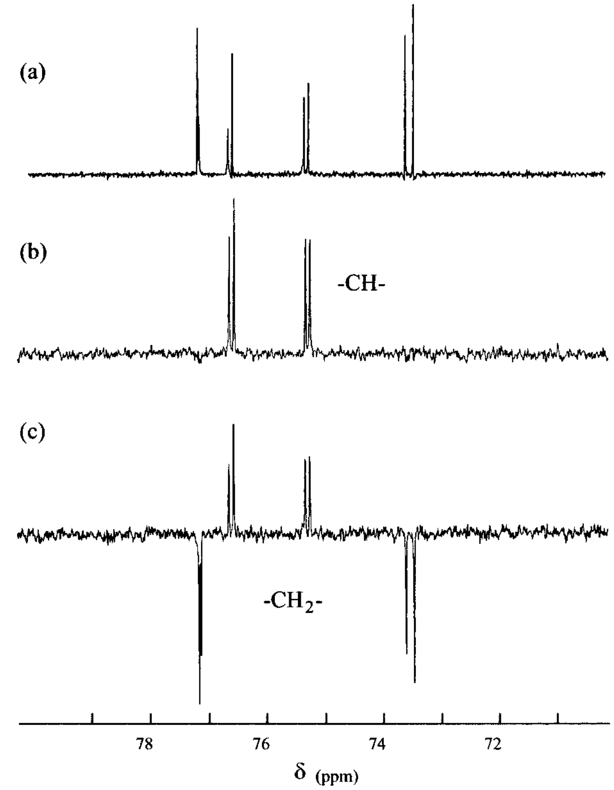


Figure 5. Methine and methylene parts of ^{13}C NMR spectra of H−T in benzene at 25 °C: (a) ^{1}H broad-band decoupling, (b) DEPT(90), and (c) DEPT(135) spectra. The internal standard was tetramethylsilane.

The ^{13}C NMR chemical shifts of the parent compounds in benzene at 25 °C, were determined from the ^{1}H broad-band decoupling and DEPT spectra.[23−26]

4.3. Calculations of Chemical Shifts by the RIS Scheme. The statistical weight matrices for the six dimeric models are shown in the Supporting Information.[28] The simulation based on eq 2 was carried out by the simplex method[29] to achieve the best agreement between the calculated and observed δ_i values. Because of the uncertainty in the assignments to *RR* and *RS* doublets, the simulation was performed using the average δ_i value. The variables were as follows: eight conformational energies, one γ-anti effect ($\Delta\delta^{t}_{\gamma,\mathrm{O}}$), two γ- gauche effect ($\Delta\delta^{g\pm}_{\gamma,\mathrm{C}}$ and $\Delta\delta^{g\pm}_{\gamma,\mathrm{O}}$) and one δ-effect ($\Delta\delta^{g\pm g\mp}_{\delta,\mathrm{O}}$) parameters, and three $\Delta\delta_{0,\mathrm{CH}}$'s ($\Delta\delta_{0,\mathrm{CH}}$(1) including the effects of substituents, α-CH$_2$, α-CH$_3$, α-O, β-O, and β-CH$_2$; $\Delta\delta_{0,\mathrm{CH}}$(2), α-CH$_2$, α-CH$_3$, α-O, β-O, and β-CH$_3$O; $\Delta\delta_{0,\mathrm{CH}}$(3), α-CH$_2$, α-CH$_3$, α-O, β-O, and β-CH), three $\Delta\delta_{0,\mathrm{CH_2}}$'s ($\Delta\delta_{0,\mathrm{CH_2}}$(1), α-O, α-CH, β-O, β-CH$_3$, β-CH$_3$O; $\Delta\delta_{0,\mathrm{CH_2}}$(2), α-O, α-CH, β-O, β-CH$_3$, β-CH; $\Delta\delta_{0,\mathrm{CH_2}}$(3), α-O, α-CH, β-O, β-CH$_3$, β-CH$_2$), one $\Delta\delta_{0,\mathrm{CH_3}}$ ($\Delta\delta_{0,\mathrm{CH_3}}$(1), α-CH, β-CH$_2$, and β-O), and two $\Delta\delta_{0,\mathrm{CH_3O}}$'s ($\Delta\delta_{0,\mathrm{CH_3O}}$(1), α-O and β-CH$_2$; $\Delta\delta_{0,\mathrm{CH_3O}}$(2), α-O and β-CH). As the initial values, the conformational energies $E_\alpha - E_\chi$ shown in Table 1,[30] the recommended values of $\Delta\delta^{t}_{\gamma,\mathrm{O}}$ (−3.0 ppm),[19] $\Delta\delta^{g\pm}_{\gamma,\mathrm{C}}$ (−5.0 ppm),[4,5] $\Delta\delta^{g\pm}_{\gamma,\mathrm{O}}$ (−7.0 ppm),[4,5] and $\Delta\delta^{g\pm g\mp}_{\delta,\mathrm{O}}$ (2.0 ppm),[19,20] and the chemical shifts of the parent compounds[31] were employed.

In Table 2, the calculated δ_i values are compared with the corresponding experimental data. The overall root-mean-square error (RMSE$_\mathrm{all}$) was minimized to 0.12 ppm, being comparable with or less than the magnitudes of the δ-effects for conformations other than $g^\pm g^\mp$.[19] These δ-effects have not been included in the present calculations. The conformational energies, $E_\mathrm{A} - E_\mathrm{X}$, determined here, differ slightly from those established for isotactic PPO, $E_\alpha - E_\chi$. As a measure of sensitivity of the calculated chemical shifts to each conformational energy E, the $\lvert\Delta(\mathrm{SD})/\Delta E\rvert$ ratio was estimated. Here the square deviation SD is defined as SD (ppm^2) $= \sum_{i=1}^{I} (\delta^{\mathrm{av}}_{i,\mathrm{calc}} - \delta^{\mathrm{av}}_{i,\mathrm{obsd}})^2$, where $\delta^{\mathrm{av}}_{i,\mathrm{calc}}$ and $\delta^{\mathrm{av}}_{i,\mathrm{obsd}}$ are, respectively, the calculated and observed values of the average chemical shift, I is the number of data. ΔE stands for a small displacement in E from the optimum value. Therefore, $\lvert\Delta(\mathrm{SD})\rvert$ corresponds to the increase in SD induced by ΔE. In the calculations, the other variables were set to the optimum values. The $\lvert\Delta(\mathrm{SD})/\Delta E\rvert$ ratios thus estimated are also listed in Table 1. Of the energy parameters, E_{Ω_1} is shown to be most effective on the calculated δ_i values. The E_Δ and E_A parameters gave comparatively large $\lvert\Delta(\mathrm{SD})/\Delta E\rvert$ values, whereas the largest E_Γ showed a small value of 0.1. This may be explained as follows. The conformer populations are calculated from the statistical weight matrices, of which elements are the Boltzmann factors of the energy parameters; a large conformational energy gives a small statistical weight, thus being less effective on conformer populations. The third-order interaction X might be negligible in the chemical-shift calculation, because $\lvert\Delta(\mathrm{SD})/\Delta E_\mathrm{X}\rvert$ is as small as 9×10^{-4}.

From the conformational energies, $E_\mathrm{A} - E_\mathrm{X}$, the t, g^+, and g^- fractions of the central C−C bond of 1,2-DMP can be evaluated as 0.37 (0.34 ± 0.01), 0.47 (0.44 ± 0.01), and 0.16 (0.22 ± 0.01), respectively, where the values in the parentheses were determined from NMR ^{1}H−^{1}H vicinal coupling constants for the benzene solution at 26 °C.[6] On the other hand, the energy parameters, $E_\alpha - E_\chi$, optimized for isotactic PPO gave better

TABLE 2: Observed and Calculated Chemical Shifts of the Dimeric Model Compounds of PPO in Benzene at 25 °C

		δ_i,[a] ppm				
		obsd		calcd [c]		
	carbon no.[b] i	$RR + RS$	avg	RR	RS	avg
H−T	1	58.82	58.82	58.90	58.89	58.90
	3	77.11, 77.13	77.12	77.54	77.42	77.48
	4	75.27, 75.34	75.31	75.28	75.33	75.31
	6	73.50, 73.64	73.57	73.54	73.62	73.58
	7	76.55, 76.62	76.59	76.59	76.65	76.62
	9	56.65, 56.66	56.66	56.83	56.81	56.82
	10, 11[d]	17.17, 17.25	17.38	17.40	17.53	17.53
		17.52, 17.56		17.58	17.59	
$RMSE_{H-T}$[e]	0.16					
H−H	1	58.82, 58.84	58.83	58.83	58.74	58.79
	3	77.48, 77.75	77.62	77.55	77.29	77.42
	4	73.06, 73.33	73.20	73.21	73.13	73.17
	6	73.06, 73.33	73.20	73.21	73.13	73.17
	7	77.48, 77.75	77.62	77.55	77.29	77.42
	9	58.82, 58.84	58.83	58.83	58.74	58.79
	10	18.35, 18.64	18.50	18.24	18.50	18.37
	11	18.35, 18.64	18.50	18.24	18.50	18.37
$RMSE_{H-H}$[e]	0.12					
T−T	1	56.64	56.64	56.57	56.57	56.57
	3	76.27	76.27	76.24	76.27	76.26
	4	75.61, 75.66	75.64	75.61	75.64	75.63
	6	75.61, 75.66	75.64	75.61	75.64	75.63
	7	76.27	76.27	76.24	76.27	76.26
	9	56.64	56.64	56.57	56.57	56.57
	10	17.07	17.07	17.03	17.08	17.06
	11	17.07	17.07	17.03	17.08	17.06
$RMSE_{T-T}$[e]	0.04					
$RMSE_{all}$[f]	0.12					

[a] Relative to the chemical shift of tetramethylsilane. [b] See Figure 2. [c] The optimized parameters are as follows: $\Delta\delta^{t}_{\gamma,O} = -2.6$ ppm, $\Delta\delta^{g\pm}_{\gamma,C} = -4.9$ ppm, $\Delta\delta^{g\pm}_{\gamma,O} = -7.9$ ppm, $\Delta\delta^{g\pm g\mp}_{\delta,O} = 2.1$ ppm, $\Delta\delta_{0,CH}(1) = 76.12$ ppm, $\Delta\delta_{0,CH}(2) = 77.33$ ppm, $\Delta\delta_{0,CH}(3) = 77.87$ ppm, $\Delta\delta_{0,CH2}(1) = 79.87$ ppm, $\Delta\delta_{0,CH2}(2) = 79.60$ ppm, $\Delta\delta_{0,CH2}(3) = 77.73$ ppm, $\Delta\delta_{0,CH3}(1) = 25.35$ ppm, $\Delta\delta_{0,CH3O}(1) = 59.17$ ppm, and $\Delta\delta_{0,CH3O}(2) = 61.09$ ppm. For the definition of these parameters, see text. The conformational energies obtained are listed in Table 1. [d] The signals from carbons 10 and 11 of H−T were not distinguishable. [e] The root-mean-square error (RMSE) is defined as RMSE (ppm) = $[\sum_{i=1}^{I}(\delta^{av}_{i,calc} - \delta^{av}_{i,obsd})^2/I]^{1/2}$, where I is the number of data. [f] The RMSE for all the data.

agreement with experiment; the t, g^+, and g^- fractions were 0.34, 0.43, and 0.23, respectively.[7,9] The γ- and δ-effect parameters were evaluated as follows: $\Delta\delta^{t}_{\gamma,O} = -2.6$ ppm (−2 to −3 ppm),[19,20] $\Delta\delta^{g\pm}_{\gamma,C} = -4.9$ ppm (−4 to −6 ppm),[1,4,5] $\Delta\delta^{g\pm}_{\gamma,O} = -7.9$ ppm (−6 to −8 ppm),[1,4,5] and $\Delta\delta^{g\pm g\mp}_{\delta,O} = 2.1$ ppm (2 to 3 ppm).[19,20] All of these parameters fall within the allowable ranges shown in the parentheses. The optimized values of the other parameters are given in the footnote c of Table 2.

5. Concluding Remarks

In the previous studies,[7−9] the gauche oxygen effect of PPO has been interpreted as follows: the gauche stability of the C−C bond in the main chain is due to the (C−H)···O hydrogen bonding formed in the $g^{\pm}g^{\mp}$ conformations for the C−O/C−C bond pairs. We determined the conformational energies of isotactic PPO from ab initio molecular orbital calculations at the MP2/6-31+G*//HF/6-31G* level and ^{1}H and ^{13}C NMR vicinal coupling constants of 1,2-DMP and the RIS analysis of the characteristic ratio and dipole moment ratio of isotactic PPO.[7,9] Each of the six dimeric model compounds treated here differs in regiosequence and stereosequence. Nevertheless, the minor modification of the above energy parameters gave the reasonable agreement between calculated and observed chemical shifts of all the dimers. These facts indicate the existence of the intramolecular (C−H)···O attractions in the molecules having the C−O−CH_2 CH(CH_3)O−C bond sequence and the validity of the RIS scheme for the chemical-shift calculations.

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Supporting Information Available: The statistical weight matrices of the six dimeric model compounds H−T (*RR*), H−T (*RS*), H−H (*RR*), H−H (*RS*), T−T (*RR*), and T−T (*RS*) dimers. This information is available free of charge via the Internet at http://pubs.acs.org.

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(23) ^{13}C NMR of 2-methoxy-1-propanol $^{1}CH_3O^{2}CH(^{3}CH_3)^{4}CH_2OH$ (C_6D_6, 25 °C, δ): 56.19 (C-1), 78.04 (C-2), 15.60 (C-3), 66.16 (C-4). The superscripts in the chemical formula represent the carbon numbers. The internal standard was tetramethylsilane.
(24) ^{13}C NMR of 1-methoxy-2-propanol $^{1}CH_3O^{2}CH_2{}^{3}CH(^{4}CH_3)OH$ (C_6D_6, 25 °C, δ): 58.64 (C-1), 78.86 (C-2), 66.32 (C-3), 19.26 (C-4).
(25) ^{13}C NMR of 2-propanol $^{1}CH_3{}^{2}CH(CH_3)OH$(C_6D_6, 25 °C, δ): 25.43 (C-1), 63.87 (C-2).
(26) The boiling point (−24.8 °C) of dimethyether $^{1}CH_3OCH_3$ is lower than the freezing point (−11 °C) of benzene-d_6. The chemical shift (59.4 in δ) of C-1 was taken from ref 27.
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N is the number of bonds ($= 8$), and $p_{n,\eta}$ ($\eta = t$, g^+, or g^-) is the bond conformation of the η state of the bond n.

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(30) The conformational energies of isotactic PPO and 1,2-DMP were shown to exhibit large solvent dependence.[6,7] The energy parameters $E_\alpha - E_\chi$ shown in Table 1, determined from NMR ^{1}H-^{1}H vicinal coupling constants of 1,2-DMP in benzene,[6] dipole moment ratios of isotactic PPO in benzene,[9] and ab initio MO calculations including the self-consistent reaction field effect for 1,2-DMP in benzene,[7] were used here as the initial values.

(31) 78.04 ppm for the methine, 78.86 ppm for the methylene, 25.43 ppm for the pendant methyl, and 59.4 ppm for the terminal methoxy carbons.