Macromolecules **1983,** *16,* 1220–1228

Conformational Analysis of the Oligomers and Polymers of Alkyl Vinyl Ether by Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Conformational energies of the oligomers of alkyl vinyl ethers with methoxy, ethoxy, or isopropoxy side chains were calculated with semiempirical potential energy functions. Comparison of the observed vicinal coupling constants with the calculated values enabled the coupling constant parameter J^0 and gauche oxygen effect to be estimated as 12.2 Hz and 0.56 kcal·mol^{-1}, respectively. The coupling constants calculated by use of the weighting factors were in good agreement with the observed values. The correlations between statistical weight parameters and the coupling constant differences due to the variation of solvents or the side chains were calculated. From these it is concluded that the solvent effect on the conformation of the main chain of the oligomers and the polymers is related in a complicated way to several local interactions. On the other hand, it was estimated that the large side chains influence the second-order interaction parameter between the main and the side chains, resulting in the decrease of T and the increase of G and $\bar{G}$ conformations.

Introduction

The conformations of chain molecules have been successfully treated with the statistical method[1-4] including the rotational isomeric state approximation. For these conformational analyses experimental data such as characteristic ratios, optical rotation, and mean-square dipole moment are available. The NMR data and X-ray crystallographic data are obtained only for stereoregular polymers. The NMR technique has been applied mainly to model compounds such as 2,4-disubstituted pentanes[4,5] and 2,4,6-trisubstituted heptanes.

Natta et al. showed that crystalline poly(methyl vinyl ether) and poly(isobutyl vinyl ether) obtained with homogeneous catalyst at low temperature are 3/1 helices.[6] For poly(isopropyl vinyl ether) a 17/5 helix[7] was proposed. Experimental data on the solution properties of poly(alkyl vinyl ethers) were obtained by Takeda et al.,[8] Pohl and Zabusky,[9] Luisi et al.,[10] Pino et al.,[11] and Manson et al.[12] On the basis of these data, Abe carried out the calculation of the conformational energies of poly(alkyl vinyl ether) and reported on the preferred conformations.[13] He proposed that the gauche effect should be considered in the semiempirical energy calculation in a manner similar to that for polyoxide chains.[14-19]

The conformations of 2,4-dimethoxypentanes as a dimer model for poly(alkyl vinyl ether) were studied by Matsuzaki et al.[5] The solvent effect was significant, especially for the racemic isomer; the T fraction decreased and the G fraction increased in nitromethane as compared to chlorobenzene.

A number of NMR studies on the tacticity of poly(alkyl vinyl ethers) and their substituted polymers have been reported.[20-24] Recently, oligomerizations of alkyl vinyl ethers and their derivatives have been investigated, and the steric mechanisms in the propagation have been reported.[25-27] The present study was undertaken in order to determine the parameters for the calculation of their conformational characteristics. The coupling constants of oligomers were used for the conventional analysis of poly(alkyl vinyl ether). We have determined all the weight factors by the least-squares method on the basis of integrated conformer populations and have experimentally obtained coupling constants J^0 and the gauche effect energy compatible with the NMR data. The parameters were compared with the reported ones.[13] Furthermore, the solvent effect and the influence of the side chain on the conformation were investigated and attributed to the changes of the statistical weight parameters.

Experimental Section

Materials. 1,1,3-Trimethoxybutane (Ia) and *meso-* and *rac-*1,1,3,5-tetramethoxyhexane (IIa and IIIa, respectively) were prepared by the reaction of dimethyl acetal with methyl vinyl ether in toluene at 0 °C in a manner similar to that reported previously.[25,27] The produced oligomers were fractionated by distillation [Ia: bp 37–38 °C (7.5 mmHg); mixture of IIa and IIIa: bp 93–95 °C (7.5 mmHg)].

1,1,3-Triethoxybutane (Ib) and 1,1,3,5-tetraethoxyhexane (IIb and IIIb) were similarly obtained [Ib: bp 85 °C (15 mmHg); mixture of IIb and IIIb: bp 63–65 °C (0.3 mmHg)].

1,1,3-Triisopropoxybutane (Ic) and 1,1,3,5-tetraisopropoxyhexane (IIc and IIIc) were similarly obtained [Ic: bp 66–67 °C (3.5 mmHg); mixture of IIc and IIIc: bp 69–73 °C (0.34 mmHg)].

2,4-Dimethoxypentane[5] was prepared from pentane-2,4-diol and purified by distillation.

Measurement. ^{1}H NMR spectra of the oligomers were measured at 20 °C with a Nicolet NT-360 (360.06 MHz) spectrometer interfaced to a Nicolet NTCFT-1180 computer in the FT mode. Benzene-d_6 and acetone-d_6 were used as solvents for measurement. The concentration of the samples was ca. 4% (v/v). Oligomers II and III were measured as the mixture.

Calculation of Conformational Energies

The structures of vinyl ether oligomers carrying side chains such as OCH_3, OC_2H_5, and $OCH(CH_3)_2$ are shown in Figure 1. In the oligomers I–III containing chiral carbons, the 3*R* enantiomers are discussed for convenience. The bond lengths used in this calculation are 1.53 Å for the C–C bond, 1.43 Å for the C–O bond, and 1.10 Å for the C–H bond. The bond angle ∠CCC for the skeletal backbone was assumed to be 112.0°. The ∠CCO and ∠COC angles[28,29] were taken as 110.0° and 111.5°, respectively. The geometrical parameters used here are the same as those in the studies of polyoxide chains by Abe et al.[15,17] As the oligomers shown in Figure 1 have many degrees of freedom involving the internal rotation of the bonds, it is difficult to calculate the conformational energies by varying

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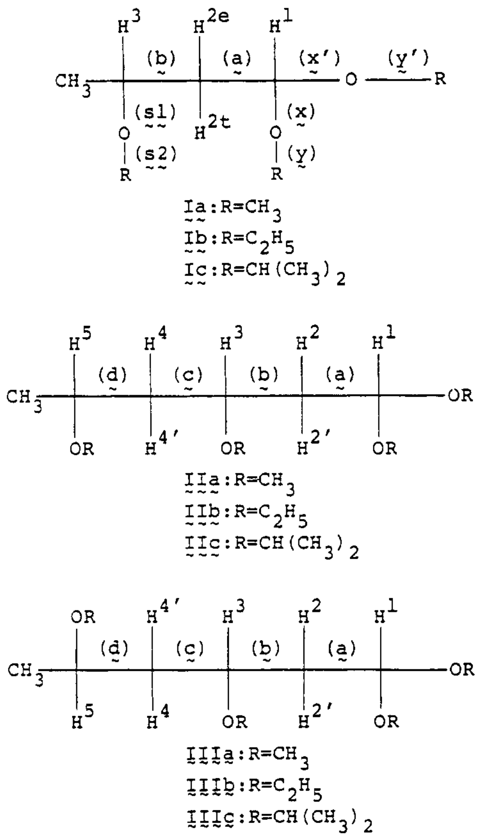

Figure 1. Structures of alkyl vinyl ether oligomers. The nomenclature of the bonds is designated in parentheses.

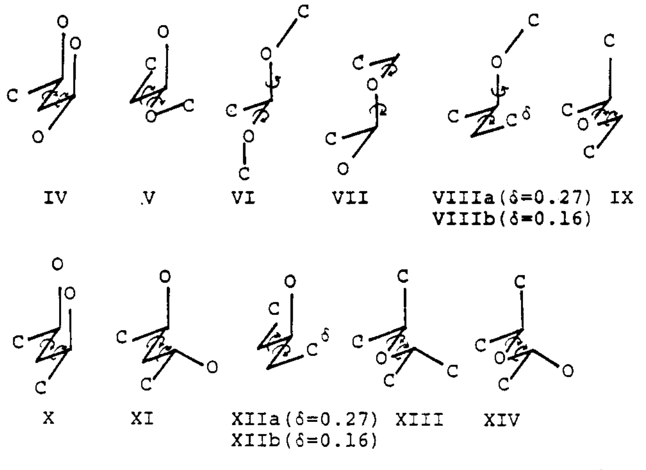

Figure 2. Structures for the calculation of conformational energies $E(\phi_1,\phi_2)$. The rotational angles ϕ_1 and ϕ_2 are expressed with the curved arrows. The partial electronic charges of the atoms are expressed with δ.

the rotational angles of all the bonds. Therefore, the energy calculation was carried out for the compounds shown in Figure 2, which have structures corresponding to parts of the oligomers. Some of them are imaginary compounds without electronic neutrality. These compounds have two degrees of freedom for internal rotation, which are expressed by ϕ_1 and ϕ_2. Conformational energies were calculated for every 5° of ϕ_1 and ϕ_2, based on the semiempirical potential energy functions, which consist of threefold rotational potentials with barrier heights[15] of 2.8 and 1.8 kcal·mol^{-1} for the C–C and C–O bonds, respectively, the Buckingham 6-exp type function of the van der Waals interaction, and electrostatic potentials.[13] Most of the parameters for the calculation are the same as those used by Abe.[13] The partial charges of atoms were assumed to be 0.16, 0.13, 0.27, and −0.23 for tertiary and secondary carbons bonded to oxygen, acetal methine carbon, and oxygen, respectively, which are the same as previously reported values.[30] The charges of hydrogens and carbons not bonded to oxygens were small and they were neglected. The effective dielectric constant was taken to be 3.0 as used for poly(ethylene oxide) by Abe and Mark.[15]

The calculated conformational energies were converted to conformer populations in order to determine the statistical weight factors as described in the following section (eq 1). The computed results are shown in Figure 3 as

$$P_i = \sum_i \exp(-E/RT)/\sum \exp(-E/RT) \qquad (1)$$

energy contour maps. The deviation angles of the energy minima from the staggered form are dependent on the rotational states of the neighboring bonds. The unstable conformers generally seem to have large deviation angles. The GG form of the meso dyad has two energy minima (Figure 3a). Energy minima were not found for $\bar{G}\bar{G}$ forms of the main-chain dyads. The side-chain C–O bond is almost restricted to unfolded conformations and the locations of the energy minima are substantially (ca. 25°) displaced from the staggered forms (Figure 3d–f).

It seems necessary to consider the potential energy curve as a function of one degree of freedom integrated for other degrees of freedom involving the neighboring bonds in the discussion of the characteristics depending on locations of the energy minima. Therefore, the rotational angle dependence of the conformational energy was calculated according to eq 2. The calculated potential curves $E(\phi)$

$$E(\phi_1) = -RT \ln \left(\sum_{\phi_2} \exp(-E(\phi_1,\phi_2)/RT)\right) \qquad (2)$$

for main-chain bonds in several model compounds are shown in Figure 4. Although the energies of the potential minima are different from each other, the potential angles of the energy minima and the shapes of the potential energy curves are almost the same irrespective of the structure of the model compounds. The displacements from the perfectly staggered positions are 11° for the G form, 3° for the T form, and 6° for the $\bar{G}$ form. The potential energy curves for bond rotation shown in Figure 4 reflect the averaged behavior of neighboring bonds and they have similar displacements of rotational angles. Accordingly, the displacements of the energy minima for a long sequence such as a polymer are assumed to be similar to those of the model compounds. The large displacement of the G form is probably to be attributed to the steric repulsion between two main-chain carbons. For the same reason, the $\bar{G}$ form is displaced in the direction of the T form. The T form has only a little repulsion between oxygen and main-chain carbon, and the displacement is small. For the skeletal bond a of the acetal end, the displacements of both the G and $\bar{G}$ forms are about 3°, similar to the T form described above. The deviation angles seem to be dependent on the species of the two atoms which are neighbors in the gauche conformation and are little influenced by more remote atoms.

Local Interaction Model

Following the method of Flory,[1] we base the conformational analysis on the matrix representation considering the first- and second-order interactions (between groups separated by three and four bonds, respectively). The statistical weight matrices are composed of the first-order interaction parameters designated as shown in Figure 5. The skeletal bonds are named a, b, c, and d in series from the acetal end, and the side-chain bonds are designated s1 and s2 from skeletal backbone. the alkoxy groups of

Table I
Statistical Weight Matrices[a]

$$\mathbf{V}_m = \begin{bmatrix} \psi_1 & 1 & \psi_2 \\ 1 & \psi_3 & \psi_2 \\ \psi_2 & \psi_2 & \psi_1\psi_3 \end{bmatrix} \qquad \mathbf{V}_r = \begin{bmatrix} 1 & \psi_2 & \psi_1 \\ \psi_2 & 1 & \psi_3 \\ \psi_1 & \psi_3 & \psi_2\psi_2 \end{bmatrix}$$

$$\mathbf{V}_0 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & \omega & 1 \\ 1 & 1 & \omega \end{bmatrix} \qquad \mathbf{V}_{ba} = \begin{bmatrix} \psi_4 & 1 & \psi_4 \\ \psi_5 & \psi_5 & 1 \\ \psi_4\psi_5 & \psi_4 & \psi_5 \end{bmatrix}$$

$$\mathbf{Y}_{b1} = \begin{bmatrix} 1 & 1 & \kappa_4 \\ 1 & 1 & 1 \\ \kappa_4 & 1 & 1 \end{bmatrix} \qquad \mathbf{Y}_{c1} = \begin{bmatrix} 1 & \kappa_1 & 1 \\ 1 & 1 & 1 \\ \kappa_1 & 1 & 1 \end{bmatrix}$$

$$\mathbf{Y}_{ax} = \begin{bmatrix} \kappa_2 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & \kappa_2 & 1 \end{bmatrix} \qquad \mathbf{Y}_{ax'} = \begin{bmatrix} \kappa_2 & 1 & 1 \\ 1 & 1 & \kappa_2 \\ 1 & 1 & 1 \end{bmatrix}$$

$$\mathbf{Y}_{xx'} = \begin{bmatrix} \kappa_3 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & \kappa_3 & 1 \end{bmatrix} \qquad \mathbf{S}_{21} = \begin{bmatrix} 1 & 1 & 1 \\ \mu_1 & \mu_1 & 1 \\ \mu_1 & 1 & \mu_1 \end{bmatrix}$$

$$\mathbf{S}_{xy} = \begin{bmatrix} 1 & \mu_3 & \mu_2 \\ 1 & \mu_2 & 1 \\ 1 & 1 & \mu_3 \end{bmatrix} \qquad \mathbf{S}_{x'y'} = \begin{bmatrix} 1 & \mu_2 & \mu_3 \\ 1 & \mu_3 & 1 \\ 1 & 1 & \mu_2 \end{bmatrix}$$

$$\mathbf{S}_{21}^{(p)} = \begin{bmatrix} \mu_6\mu_6 & \mu_6 & \mu_6 \\ \mu_6 & 1 & \mu_6 \\ \mu_6 & \mu_6 & 1 \end{bmatrix} \qquad \mathbf{S}_{xy}^{(p)} = \begin{bmatrix} \mu_4\mu_5 & \mu_4 & \mu_5 \\ \mu_4 & 1 & \mu_4 \\ \mu_5 & \mu_5 & 1 \end{bmatrix}$$

$$\mathbf{S}_{x'y'}^{(p)} = \begin{bmatrix} \mu_4\mu_5 & \mu_5 & \mu_4 \\ \mu_5 & 1 & \mu_5 \\ \mu_4 & \mu_4 & 1 \end{bmatrix}$$

$$\mathbf{D}_0 = [\eta_1 \quad 1 \quad \tau_1] \qquad \mathbf{D}_a = [\eta_3 \quad 1 \quad 1]$$

$$\mathbf{D}_b = [\eta_2 \quad 1 \quad \tau_2] \qquad \mathbf{B}_0 = [\lambda_1 \quad 1 \quad 1]$$

$$\mathbf{B}_1 = [\lambda_1 \quad \epsilon \quad 1] \qquad \mathbf{B}_x = [\lambda_3 \quad \lambda_4 \quad 1]$$

$$\mathbf{B}_{x'} = [\lambda_3 \quad 1 \quad \lambda_4] \qquad \mathbf{B}_2 = [1 \quad \lambda_2 \quad \lambda_2]$$

$$\mathbf{B}_y = [1 \quad \lambda_5 \quad \lambda_5] \qquad \mathbf{B}_2^{(p)} = [\lambda_6 \quad 1 \quad 1]$$

$$\mathbf{B}_y^{(p)} = [\lambda_7 \quad 1 \quad 1]$$

[a] The first-order interactions are expressed in vector form.

Table II
Statistical Weight Factors for Second-Order Interactions[a]

weight factor	interacting groups		weight factor	interacting groups	
ψ_1	O	O	κ_3	C_{A2}	C_{A2}
ψ_2	O	$C_{\beta 0}$	κ_4	$C_{\alpha 2}$	C_{A0}
ψ_3	$C_{\beta 0}$	$C_{\beta 0}$	μ_1	$C_{\alpha 3}$	$C_{\beta 0}$
ψ_4	O	O_A	μ_2	C_{A3}	$C_{\beta 0}$
ψ_5	O_A	$C_{\beta 0}$	μ_3	O_A	C_{A3}
ω	$C_{\alpha 0}$	$C_{\alpha 0}$	μ_4	$C_{\beta 0}$	$C_{A3}^{(p)}$
κ_1	$C_{\alpha 0}$	$C_{\alpha 2}$	μ_5	O_A	$C_{A3}^{(p)}$
κ_2	$C_{\alpha 0}$	C_{A2}	μ_6	$C_{\beta 0}$	$C_{\alpha 3}^{(p)}$

[a] The subscripts $\alpha 0$ and $\beta 0$ are used to designate methine and methylene carbons in the main chain, respectively. The numeric subscripts 2 and 3 designate the number of bonds between the subscripted atoms in the side chain and the main-chain carbon. The subscript A expresses the atom included in the acetal end group.

the acetal end are distinguished by prochirality, and the bonds of the pro-*R* alkoxy group are named x and y in order from the acetal methine carbon, whereas the bonds of the pro-*S* alkoxy group are designated x′ and y′.

The statistical weight matrices for the second-order interactions correspond to the set of neighboring bonds as shown in Figure 6. The conformations T, G, and $\bar{G}$ were defined as shown in Figure 7. For bonds a, s1, x, and x′, the T form is the folded conformation. The statistical weight matrices are represented with the statistical weight parameters listed in Table I. The weight parameters are related to the second-order interactions between the pairs of groups listed in Table II. Each weight parameter is taken to be a simple Boltzmann factor for the interaction energy. The second-order interaction parameters are normalized to the weight of unity for the interaction between the atom pair containing the hydrogen. The first-order parameters are normalized to a weight of unity for one conformation for convenience. The matrices $\mathbf{V}_{ba}$, $\mathbf{Y}_{b1}$, and $\mathbf{Y}_{c1}$ are defined for the structure with *R* chirality on the 3-position carbon. When C-3 has *S* chirality, it is necessary to exchange the second and third columns, and the converted matrices are designated $\mathbf{V'}_{ba}$, $\mathbf{V'}_{b1}$, and $\mathbf{Y'}_{c1}$. In the case that the chirality of the 5-position is *S*, the second and the third diagonal elements of matrix $\mathbf{B}_1$ are exchanged and the new matrix is designated $\mathbf{B'}_1$.

The partition functions of oligomers I–III are represented as listed in Table III. For the compounds shown in Figure 2, the partition functions are listed in Table IV. The asterisk operator indicates multiplication of the elements in the same row and column. The function *f* serves to convert the vector to the diagonal matrix. On the basis of the conformer populations obtained from the energy calculation for compounds IV–XIV and the partition functions composed of the statistical weight parameters, the weight factors at 20 °C and the corresponding interaction energies were obtained by the least-squares method as listed in Table V. The calculation with the electric charges[30] $\delta = +0.16$ for the isopropoxy methine carbon instead of $\delta = +0.13$ for the ethoxy methine carbon in compounds VIIIa, VIIIb, and VI produced almost the same weight parameters in the range of errors by the least-squares method. The second-order interaction energies between oxygens represented by ψ_1 and ψ_4 are about 0.8–1.0 kcal·mol^{-1}, and those between oxygen and carbon represented by ψ_2, ψ_5, μ_3, and μ_5 are smaller than the former and are about 0.4–0.9 kcal·mol^{-1}. This tendency is similar to that of poly(oxyethylene), poly(oxytrimethylene), and poly(oxytetramethylene),[1,32-35] of which the second-order interactions are 0.25 kcal·mol^{-1} between two oxygens and about 0.35 kcal·mol^{-1} between the oxygen and the carbon. For the sterically hindered system, the second-order interaction energy seems to be higher than that for the less hindered system. The interaction energies between two

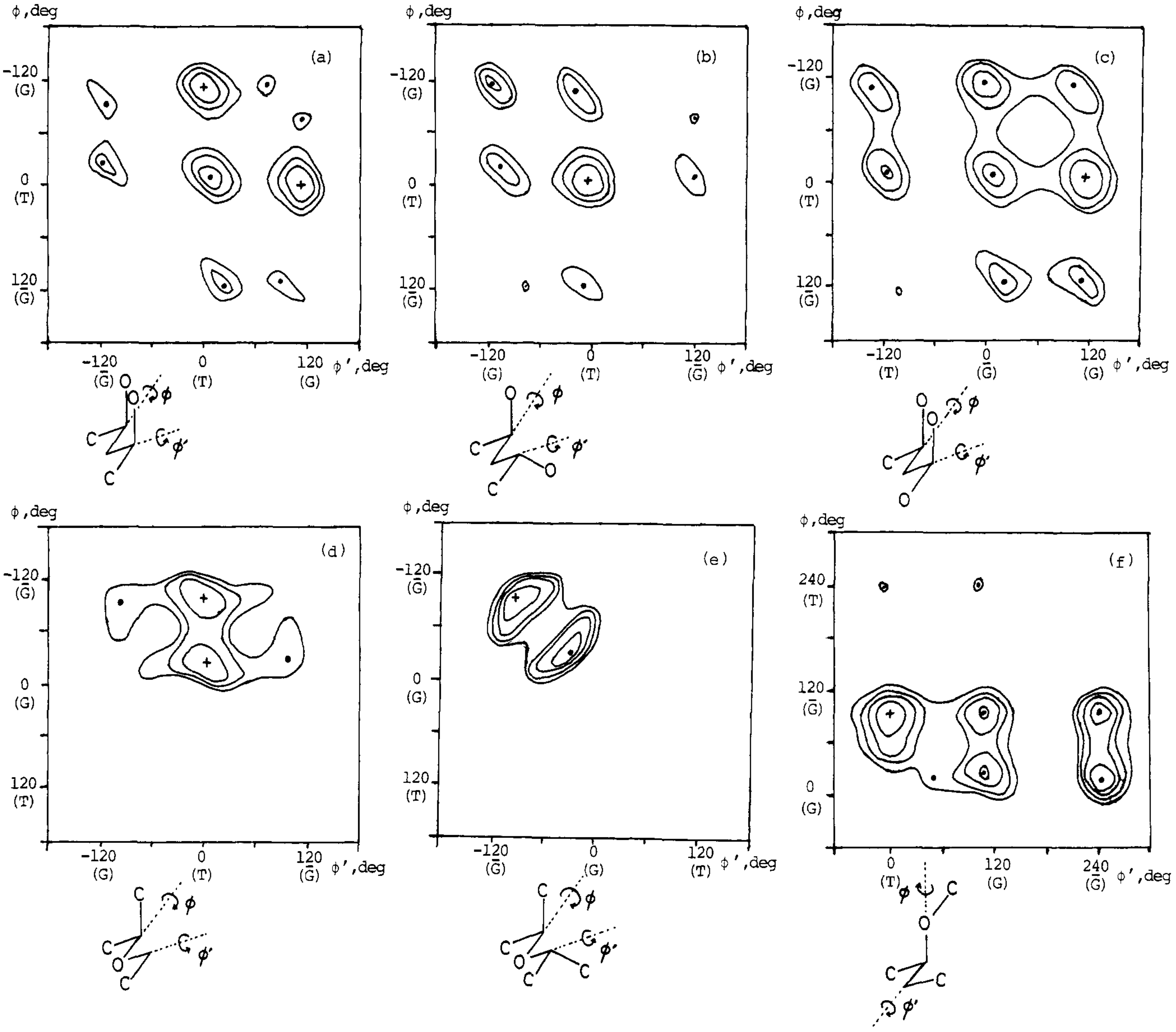

Figure 3. Calculated energy maps as a function of the rotational angles ϕ and ϕ' of the neighboring bonds. The energy contours were drawn for every 1 kcal·mol^{-1} relative to the minimum point indicated by the cross. The solid circles denote local minima.

Table III
Partition Functions of Oligomers I–III[a,b]

compound	partition function
Ia	$B_1{}^tY_{b1}D_bV_{ba}D_aW_1B_x$
IIa	$B_1{}^tY_{c1}'D_0V_mD_0W_2D_0V_{ba}D_aW_1B_x$
IIIa	$B_1{}'{}^tY_{c1}D_0V_rD_0W_2D_bV_{ba}D_aW_1B_x$
Ib	$B_2S_{21}B_1{}^tY_{b1}D_bV_{ba}D_aW_3B_xS_{xy}B_y$
IIb	$B_2S_{21}B_1{}^tY_{c1}'D_0V_mD_0W_4D_bV_{ba}D_aW_3B_xS_{xy}B_y$
IIIb	$B_2S_{21}B_1{}'{}^tY_{c1}D_0V_rD_0W_4D_bV_{ba}D_aW_3B_xS_{xy}B_y$
Ic	$B_2{}^{(p)}S_{21}{}^{(p)}B_1{}^tY_{b1}D_bV_{ba}D_aW_5B_xS_{xy}{}^{(p)}B_y{}^{(p)}$
IIc	$B_2{}^{(p)}S_{21}{}^{(p)}B_1{}^tY_{c1}'D_0V_mD_0W_6D_bV_{ba}D_aW_5B_xS_{xy}{}^{(p)}B_y{}^{(p)}$
IIIc	$B_2{}^{(p)}S_{21}{}^{(p)}B_1{}'{}^tY_{c1}D_0V_rD_0W_6D_bV_{ba}D_aW_5B_xS_{xy}{}^{(p)}B_y{}^{(p)}$

[a] The W matrices are expressed as follows. $W_1 = Y_{ax}*(Y_{ax'}B_{x'}{}^tY_{xx'})$; $W_2 = V_0*(Y_{c1}B_0{}^tY_{c1}')$; $W_3 = Y_{ax}*(Y_{ax'}f(I'B_y{}^tS_{x'y'})B_{x'}{}^tY_{xx'})$; $W_4 = V_0*(Y_{c1}f(I'B_2S_{21})B_0{}^tY_{c1})$; $W_5 = Y_{ax'}f(I'B_y{}^{(p)t}S_{x'y'}{}^{(p)})B_{x'}{}^tY_{xx'})$; $W_6 = V_0*(Y_{c1}f(I'B_2{}^{(p)}S_{21}{}^{(p)})B_0{}^tY_{c1}'$. [b] The vectors are converted to diagonal matrices and then multiplied by the matrices.

carbons expressed by ψ_3, ω, κ_1, κ_3, and κ_4 are about 1.7–2.1 kcal·mol^{-1}. On the other hand, those represented by μ_1, μ_2, μ_4, and μ_6, which are the second-order interactions between two carbons involving the third atoms in the side chains, are about 0.7–1.2 kcal·mol^{-1}.

The first-order interaction parameters are important because they strongly influence the conformation of the corresponding bonds. By the least-squares method the interaction parameters η_1 and τ_1 were obtained as −0.56 and −0.03 kcal·mol^{-1}, respectively. Abe[13] proposed −0.44 and 0.5 kcal·mol^{-1} for them. The weight parameter representing the interaction associated with the $\bar{G}$ conformation is a little different from the authors'. For the gauche conformation about the C–C bond of poly(oxy-

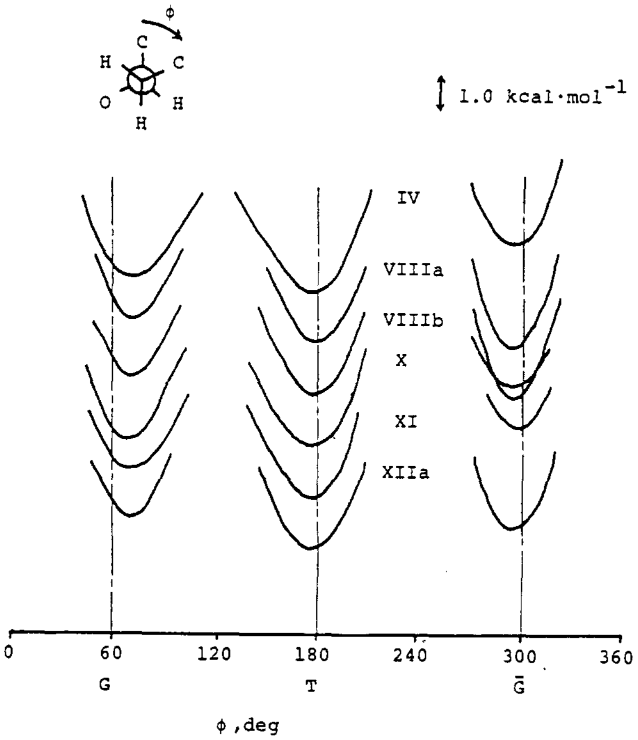

Figure 4. Dihedral angle dependence of the relative energies of the model compounds.

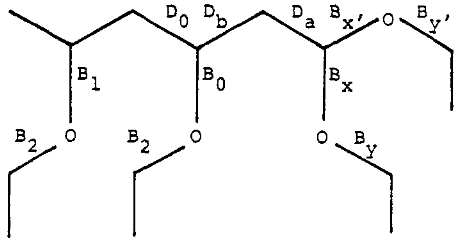

Figure 5. Matrices for the first-order interactions.

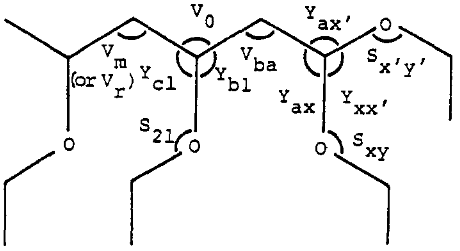

Figure 6. Matrices for the second-order interactions.

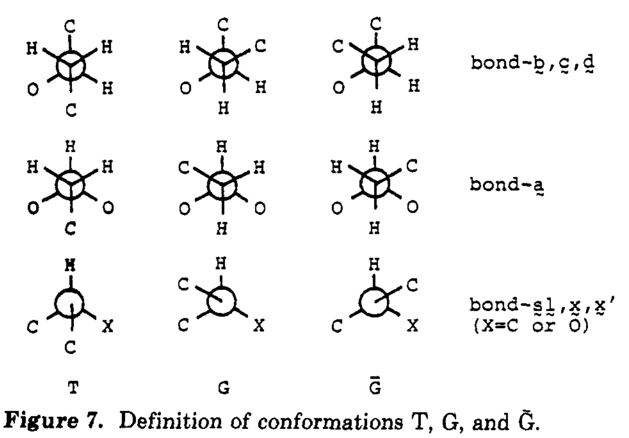

Figure 7. Definition of conformations T, G, and Ḡ.

trimethylene),[34,35] the first-order interaction energy was reported as −0.2 ± 0.2 kcal·mol⁻¹. This means that the gauche arrangement of a carbon and an oxygen is not a destabilizing factor but a factor contributing a little to stabilization. Therefore, it does not seem improper that the first-order interaction energy for the Ḡ form is almost the same as that for the G form in the present study. For the same reason, the energy of the weight factor η_3 is almost zero. In other words, the first-order interactions of bond a are almost equal in the T, G, and Ḡ forms. Also, the values of E_{η_1} and E_{η_2} are close to the energy difference $-E_\sigma$ between the trans and gauche forms of the polymethylene chain, that is, about −0.5 kcal·mol⁻¹. However, as described later, these values need to be modified by considering the gauche effect. The first-order interactions corresponding to the s1 and s2 bonds of the isopropyl side chain are about 4.3–5.0 kcal·mol⁻¹ in the folded conformation represented here with T. The unfolded conformation of the bond s1, in which the side-chain s2 is situated in a gauche arrangement about the end methyl group of the main chain, is unstable by 0.3 kcal·mol⁻¹ as compared with another unfolded conformation. This end-group ef-

Table IV
Partition Functions for Compounds IV–XIV (Figure 2)

compound	partition function	compound	partition function
IV	$D_bV_{ba}D_a$	X	$D_0V_mD_0$
V	$D_aY_{ax'}B_{x'}$	XI	$D_0V_rD_0$
VI	$B_xY_{xx'}B_{x'}$	XIIa	$D_0V_0D_b$
VII	$B_xS_{xy}B_y$	XIIb	$D_0V_0D_0$
VIIIa	$D_bY_{b1}B_1$	XIII	$B_2^{(p)}S_{21}^{(p)}B_0$
VIIIb	$D_0Y_{c1}B_1$	XIV	$B_{x'}S_{x'y'}^{(p)}B_y^{(p)}$
IX	$B_2S_{21}B_0$		

Table V
Statistical Weight Parameters Calculated by the Least-Squares Method[a]

weight factor	value at 20 °C	interaction energy, kcal·mol⁻¹
η_1	2.6	−0.56 ± 0.08
η_2	2.8	−0.60 ± 0.12
η_3	1.05	−0.03 ± 0.11
τ_1	1.05	−0.03 ± 0.12
τ_2	1.06	−0.03 ± 0.17
ϵ	0.62	0.28 ± 0.12
λ_1	0.0006	4.3[b]
λ_2	0.075	1.51 ± 0.61
λ_3	0.014	2.49 ± 0.54
λ_4	0.19	0.97 ± 0.12
λ_5	0.18	1.00 ± 0.13
λ_6	0.0002	5.0[c]
λ_7	0.0002	5.0[c]
ψ_1	0.17	1.03 ± 0.17
ψ_2	0.23	0.86 ± 0.24
ψ_3	0.048	1.8[b]
ψ_4	0.25	0.81 ± 0.21
ψ_5	0.37	0.58 ± 0.33
ω	0.029	2.1[b]
κ_1	0.055	1.69 ± 0.89
κ_2	0.11	1.3[b]
κ_3	0.025	2.15 ± 0.43
κ_4	0.047	1.78 ± 0.97
μ_1	0.20	0.9[b]
μ_2	0.30	0.7[b]
μ_3	0.42	0.51 ± 0.47
μ_4	0.14	1.15[c]
μ_5	0.47	0.44[c]
μ_6	0.13	1.19[c]

[a] Some weight parameters are modified by the differences of solvents and side chains as described in the text. Also, the parameters η_1 and η_2 are modified by the gauche effect. [b] The calculation errors were larger than 2.0 kcal·mol⁻¹. [c] As there were insufficient data, these values were obtained by simultaneous equations.

Table VI
Vicinal Coupling Constants of Compounds I-III with Various Side Chains[a]

compound	bond	proton	coupling constants, Hz						
			R = CH_3		R = C_2H_5		R = $CH(CH_3)_2$		R = CH_3 calcd
			Bz	Ac	Bz	Ac	Bz	Ac	
I	a	H^1, H^{2e}	4.28	4.38	4.05	4.22	3.60	3.85	4.9
	a	H^1, H^{2t}	7.31	7.08	7.42	7.36	7.35	7.23	6.9
	b	H^{2e}, H^3	8.22	7.90	8.38	8.21	8.49	8.18	8.1
	b	H^{2t}, H^3	4.58	4.87	4.47	4.65	4.04	4.42	4.5
II	a	H^1, H^2	4.91	4.35	(5.13)	4.39	4.73	3.94	5.0
	a	H^1, $H^{2'}$	6.58	7.17	(6.39)	7.10	6.08	6.91	6.8
	b	H^2, H^3	7.65	8.09	7.39	7.95	7.30	7.84	7.7
	b	$H^{2'}$, H^3	4.82	4.55	5.16	4.39	4.68	4.19	4.6
	c	H^3, H^4	5.71	5.79	5.17	5.56	4.28	4.82	6.0
	c	H^3, $H^{4'}$	6.90	6.62	6.93	6.87	7.69	7.47	6.2
	d	H^4, H^5	7.43	7.23	7.71	7.34	8.03	7.85	7.6
	d	$H^{4'}$, H^5	5.01	5.45	4.99	5.19	4.36	4.57	5.0
III	a	H^1, H^2	4.87	5.31	(4.84)	(5.4)	5.30	(5.56)	5.6
	a	H^1, $H^{2'}$	6.53	6.39	(6.46)	(6.2)	5.79	(5.57)	6.2
	b	H^2, H^3	7.14				6.34		6.1
	b	$H^{2'}$, H^3	5.26				5.65		5.9
	c	H^3, H^4	4.05	4.50	4.16	4.41	4.51	4.56	3.9
	c	H^3, $H^{4'}$	8.66	8.16	8.65	8.31	7.60	7.56	9.0
	d	H^4, H^5	8.98	8.16	8.96	8.56	8.12	7.83	9.5
	d	$H^{4'}$, H^5	3.69	4.03	3.72	4.21	3.96	4.10	3.6

[a] The coupling constants were observed in benzene-d_6 (Bz) and acetone-d_6 (Ac) at 20 °C. The values in parentheses are not exact due to the overlapping of resonances.

fect is expressed by the weight parameter ϵ, which was adopted previously for the model compounds of poly(alkyl propenyl ether).[30]

Coupling Constants

The spin-spin coupling constants of the oligomers I were obtained from the splitting of the methylene protons (H^{2e} and H^{2t}; see Figure 1) and the acetal methine proton (H^1). The vicinal coupling constants of H^{2e} and H^{2t} were distinguished by comparing their coupling constants with those calculated with consideration of the gauche effect, for which the value was roughly estimated as 0.2 kcal·mol^{-1}.[13] In this calculation the trans and gauche coupling constants were estimated as 11.5 and 1.5 Hz,[30] respectively. The coupling constants of oligomers II and III were obtained from the splitting of the methylene protons (H^2, $H^{2'}$, H^4, and $H^{4'}$), the acetal methine proton (H^1), and the alkoxy methine protons (H^3 and H^5). The NMR spectra are shown in Figure 8. As the meso diastereomer was dominant[25] irrespective of the kind of side chain, the proton resonances could be easily assigned to those of the meso and racemic diastereomers. The methylene protons H^2 and $H^{2'}$ could be distinguished from H^4 and $H^{4'}$ by decoupling the methine protons H^3 and H^5. In addition, the methylene protons H^4 and $H^{4'}$ were assigned by the NMR spectra of the oligomers of deuterated ethyl vinyl ether.[36] The coupling constants between the methine proton H^3 and the methylene proton H^2 or $H^{2'}$ of the racemic diastereomer were difficult to determine because of overlapping. As these spin systems are ABXY type with large $\Delta\nu/J$ ratios between methylene (A and B) and methine (X and Y), the patterns of the spectra could be easily recognized, and the coupling constants were obtained with a manual calculation. The errors in the observed values were about ±0.05 Hz. The coupling constants observed in acetone-d_6 and benzene-d_6 are listed in Table VI.

The calculation of the coupling constants by use of J_t = 11.5 Hz and J_g = 1.5 Hz did not agree well with the observed values without considering the gauche effect. Therefore, the gauche effect was taken into consideration as the value of ΔE_η, which is the energy difference between the observed and the calculated energies E_{η_1} and E_{η_2}. The coupling constants of the gauche and trans arrangements were estimated from the Karplus equation (eq 3), where

$$J_k = J^0 \cos^2 \theta_k - 0.3 \qquad (3)$$

only the value J^0 was determined experimentally. Instead of $\cos^2 \theta$, the integrated value $\int p(\theta) \cos^2 \theta \, d\theta / \int p(\theta) \, d\theta$

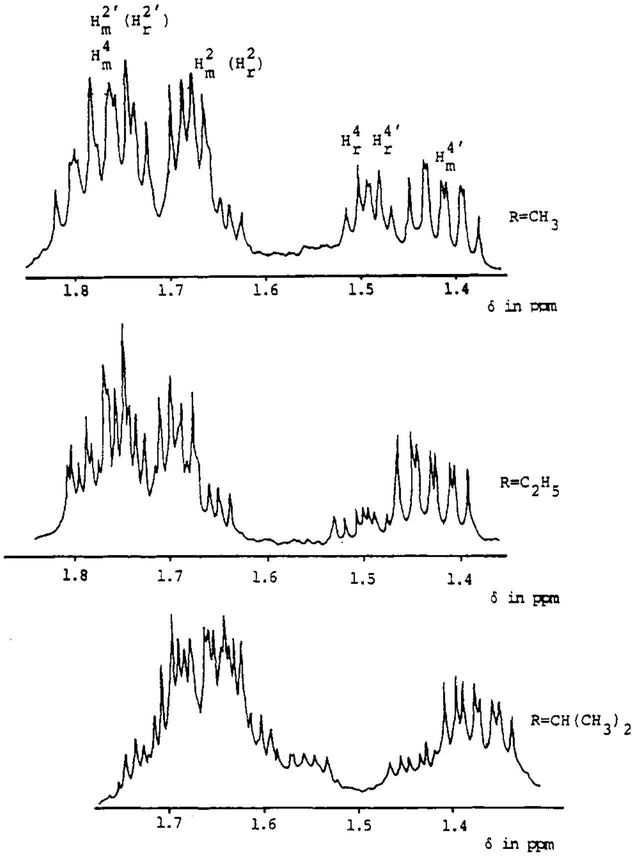

Figure 8. ^1H NMR spectra of 1,1,3,5-tetraalkoxyhexane in acetone-d_6.

Table VII
Dihedral Angles of Vicinal Protons at the Potential Minima and the Coupling Constants Calculated with the Karplus Equation

bond	config of methylene proton	dihedral angles, deg			coupling constants, Hz		
		T	G	$\bar{G}$	T	G	$\bar{G}$
a	erythro	58	65	179	3.13	1.88	11.90
a	threo	58	179	65	3.13	11.90	1.88
b, c, d	erythro	177	71	66	11.87	0.99	1.72
b, c, d	threo	66	172	51	1.72	11.66	4.53

Table VIII
Correlation Coefficients between the Coupling Constant Differences among Solvents or Side Chains and the Differential Coefficients of Coupling Constants by the Interaction Energy of Statistical Weight Factors[a]

differential coefficient	$\Delta J_{\mathrm{Ac\text{-}Bz}}{}^{\mathrm{Me}}$	$\Delta J_{\mathrm{Ac\text{-}Bz}}{}^{\mathrm{Et}}$	$\Delta J_{\mathrm{Ac\text{-}Bz}}{}^{i\mathrm{Pr}}$	$\Delta J_{\mathrm{Bz}}{}^{\mathrm{Et\text{-}Me}}$	$\Delta J_{\mathrm{Bz}}{}^{i\mathrm{Pr\text{-}Me}}$
$\partial J/\partial E_{\eta_1} + \partial J/\partial E_{\eta_2}$	0.45	0.16	0.10	0.01	0.06
$\partial J/\partial E_{\epsilon}$	0.53	0.32	0.34	−0.33	−0.37
$\partial J/\partial E_{\tau_1} + \partial J/\partial E_{\tau_2}$	−0.28	−0.04	−0.06	−0.00	0.17
$\partial J/\partial E_{\psi_1} + \partial J/\partial E_{\psi_4}$	0.17	0.17	0.26	−0.11	−0.08
$\partial J/\partial E_{\psi_2} + \partial J/\partial E_{\psi_5}$	−0.06	0.14	−0.02	0.03	0.24
$\partial J/\partial E_{\kappa_1}$	0.10	−0.10	−0.33	0.63	0.77

[a] The vectors ΔJ and $\partial J/\partial E$ consist of the 20 elements corresponding to the different sets of protons listed in column 3 of Table VI. The coupling constant differences $\Delta J_{\mathrm{Ac\text{-}Bz}}{}^{\mathrm{R}}$ and $\Delta J_{\mathrm{Bz}}{}^{\mathrm{R'\text{-}R}}$ express $J_{\mathrm{Ac}}{}^{\mathrm{R}} - J_{\mathrm{Bz}}{}^{\mathrm{R}}$ and $J_{\mathrm{Bz}}{}^{\mathrm{R'}} - J_{\mathrm{Bz}}{}^{\mathrm{R}}$, respectively. The subscripts Ac and Bz designate the solvents acetone-d_6 and benzene-d_6. The side chains are expressed with subscripts Me, Et, and *i*Pr.

should be adopted in the strict calculation. However, it is difficult to estimate the dihedral angle dependence of the population $p(\theta)$ precisely for compounds with many degrees of freedom. As described in the previous section, the displacement of the dihedral angles from energy minima can be estimated from Figure 4. For a pair of protons designated with the subscript *i*, the coupling constant is expressed as shown in eq 4, where p_{ik} is the

$$J_i = \sum_k p_{ik} J_k \qquad (k = \mathrm{T, G, and\ }\bar{\mathrm{G}}) \tag{4}$$

population of each conformation *k* and J_k is the corresponding coupling constant. The populations p_{ik} are functions of ΔE_η, and J_k is a function of J^0. The J_i is expressed by Maclaurin's expansion with the residue *R* as follows.

$$J_i^{\mathrm{obsd}} = J_i^{\mathrm{calcd}} + \left(\frac{\partial J_i}{\partial E_{\eta_1}} + \frac{\partial J_i}{\partial E_{\eta_2}}\right)\cdot\delta(\Delta E_\eta) + \left(\sum_k P_k \cos^2 \theta_k\right)\cdot\delta J^0 + R$$

The sum of the square of the errors, $\sum_i (J_i^{\mathrm{obsd}} - J_i^{\mathrm{calcd}})^2$, was minimized by converging $\delta(\Delta E_\eta)$ and δJ^0 to zero asymptotically. As the approximately converged values, the gauche effect ΔE_η was obtained as −0.56 ± 0.08 kcal·mol^{-1} and the coupling constant J^0 was calculated to be 12.2 ± 0.3 Hz for the observed coupling constants of oligomers Ia, IIa, and IIIa in benzene-d_6. Consequently, the coupling constants for the conformations T, G, and $\bar{\mathrm{G}}$ were estimated as listed in Table VII. The gauche coupling constants are not equal to each other.

Solvent Effect

The influence of each weight parameter on the coupling constants was estimated by calculating differential coefficients $\partial J_i/\partial E_\sigma$. The sums of the absolute values $\sum_i |\partial J_i/\partial E_\sigma|$ or $\sum_i |\partial J_i/\partial E_\sigma + \partial J_i/\partial E_{\sigma'}|$ were calculated to be about 40 Hz·kcal^{-1} for η_1 and η_2, 21 Hz·kcal^{-1} for ϵ, 20 Hz·kcal^{-1} for ψ_2 and ψ_5, 18 Hz·kcal^{-1} for ψ_1 and ψ_4, 14 Hz·kcal^{-1} for κ_1', 9 Hz·kcal^{-1} for η_3, 8 Hz·kcal^{-1} for τ_1 and τ_2, 4 Hz·kcal^{-1} for μ_1, and less than 2 Hz·kcal^{-1} for the other parameters. For the coefficients $\partial J_i/\partial E_\sigma$ of the weight parameters bearing a large influence on J_i, their correlation factors with the coupling constant differences ΔJ_i, which are the differences due to solvents or side chains, were calculated (see Table VIII). For the compounds with methoxy side chains, the differences ΔJ_i due to solvents showed high correlations with $\partial J_i/\partial E_\epsilon$ and $\partial J_i/\partial E_{\eta_1} + \partial J_i/\partial E_{\eta_2}$. As the correlation factor between $\partial J_i/\partial E_\epsilon$ and $\partial J_i/\partial E_{\eta_1} + \partial J_i/\partial E_{\eta_2}$ is near 1.0, it was difficult to determine both coefficients at the same time. It is concluded that both E_{η_1} and E_{η_2} increase by 0.08 ± 0.06 kcal·mol^{-1} or E_ϵ increases by 0.17 ± 0.12 kcal·mol^{-1} in acetone as compared to benzene.

For the compounds with ethoxy side chains, the solvent effect appears in the factor ϵ, and its energy seems to increase by 0.11 ± 0.14 kcal·mol^{-1} in acetone. With regard to isopropoxy side chains, the solvents seem to influence the factors ϵ and κ_1. The energy of ϵ increases by 0.11 ± 0.12 kcal·mol^{-1} and that of κ_1 decreases by 0.20 ± 0.22 kcal·mol^{-1} in acetone as compared to benzene. Common to methoxy, ethoxy, and isopropoxy side chains, there exists a small positive correlation between ΔJ_i and $\partial J_i/\partial E_{\psi_1} + \partial J_i/\partial E_{\psi_4}$. The correlation between ΔJ_i and $\partial J_i/\partial E_{\eta_1} + \partial J_i/\partial E_{\eta_2}$ is lower for the compounds with ethoxy or isopropoxy side chains than for those with methoxy side chains. This is explained by the large side chains sterically preventing the interference of the solvent with the first-order interaction designated by η_1 and η_2. The increase of E_{η_1} and E_{η_2} for the compounds with methoxy side chains in acetone as compared to benzene seems to correspond to weakened Coulombic forces between the oxygen and the alkoxy methine carbon in polar solvents. The correlation between ΔJ_i and $\partial J_i/\partial E_\epsilon$ suggests that the side chain of the initial residue is surrounded by the solvent. The conformation in which bond s2 is situated in a trans arrangement about the end methyl group may be stabilized by the hydrophobic interaction in acetone. The correlation of ΔJ_i with $\partial J_i/\partial E_{\kappa_1}$ for isopropoxy side chains is higher than that for methoxy or ethoxy side chains. It seems that the hydrophobic interaction among the main chain and the large side chains such as the isopropoxy group lowers the interaction energy E_{κ_1} in acetone. The variations of the conformation due to solvents were calculated by using the values ΔE_ϵ = 0.17 kcal·mol^{-1} for methoxy side chains, ΔE_ϵ = 0.11 kcal·mol^{-1} and ΔE_{κ_1} = −0.20 kcal·mol^{-1} for iso-

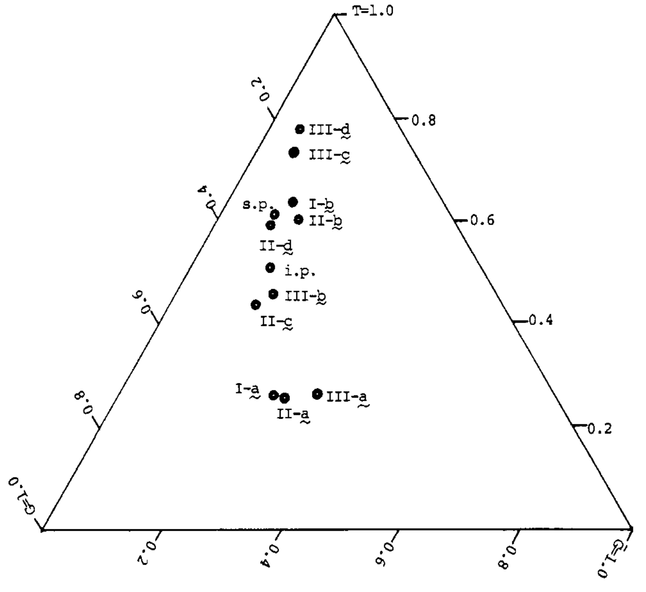

Figure 9. Conformer fractions of oligomers and polymers with methoxy side chains in benzene (e.g., the expression III-a designates bond a of compound III). The isotactic and syndiotactic polymers are denoted i.p. and s.p. for short, respectively.

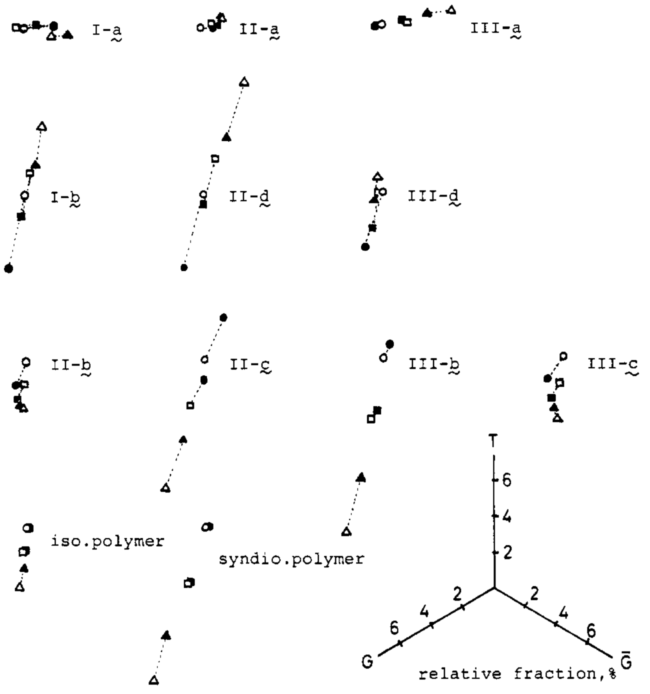

Figure 10. Changes of conformer fractions due to solvents and various side chains: (○,●) OCH_3; (□,■) OC_2H_5; (△,▲) $OCH(CH_3)_2$. The open and filled marks correspond to the conformer fractions in benzenes and acetone, respectively. Symbolism (e.g., I-a) is the same as that in Figure 9.

propoxy side chains. The results are summarized in Figures 9 and 10.

For bond b of I and bond d of II and III the changes of E_ϵ with solvents result in a decrease of the T form and an increase of the G form by about 1–4% in acetone (Figure 10). The conformation populations of the polymers with methoxy or ethoxy side chains do not vary with the change of E_ϵ arising from the change of solvents. On the other hand, the polymer with isopropoxy groups showed an increase of the T form in a polar solvent. Although these calculations showed that the conformations of poly(methyl vinyl ether) and poly(ethyl vinyl ether) are not changed by the change of E_ϵ, small changes of κ_1, η_1, η_2, ψ_1, and ψ_4 with solvents, however, may lead to a change of the polymer conformation. The differences between the conformer populations in acetone and benzene are small as compared with that caused by side-chain variation, which will be described in the following section.

Table IX
Observed and Calculated Coupling Constants of 2,4-Dimethoxypentane in Benzene-d_6 at 20 °C

diastereomer	config of vicinal protons	coupling constants, Hz obsd	calcd
meso	erythro	6.78	6.1
	threo	6.03	6.0
racemic	erythro	6.78	6.8
	threo	5.72	5.7

Effect of Variation of Side Chains

The coupling constant difference ΔJ_i resulting from the change of side chain (e.g., $\Delta J_{Bz}{}^{Et-Me}$) showed high correlations with $\partial J_i/\partial E_\epsilon$ and $\partial J_i/\partial E_{\kappa_1}$, as listed in the fifth and sixth columns of Table VIII. Variation of the side chains in the order methoxy, ethoxy, and isopropoxy increased the stabilization of E_ϵ and the destabilization of E_{κ_1}. As compared with the compound with methoxy side chains, the energy E_ϵ decreased by 0.06 ± 0.05 kcal·mol^{-1} for ethoxy compounds and by 0.20 ± 0.12 kcal·mol^{-1} for isopropoxy compounds. Simultaneously, the energy E_{κ_1} increased by 0.17 ± 0.09 kcal·mol^{-1} for ethoxy compounds and by 0.56 ± 0.16 kcal·mol^{-1} for isopropoxy compounds. It is believed that the decrease of E_ϵ is due to steric hindrance between the large alkoxy group and the main chain. The correlation between ΔJ_i and $\partial J_i/\partial E_{\kappa_1}$ is remarkably high. The large side chain was considered to cause significant steric hindrance with the main chain. Consequently, the conformations with κ_1 interactions seem to be destabilized. It seems noteworthy that three- or four-bond interaction factors such as κ_1 and ϵ are influenced significantly by the neighboring surroundings.

The calculated variations of the conformer populations with side chains are shown in Figures 9 and 10. For bonds b and c of compounds II and III with ethoxy side chains, a decrease of the T form and an increase of the G form by about 1–3% were estimated as compared with the methoxy compounds. For the isopropoxy compounds the decrease of the T form and the increase of the G form are significant (2–10%). Poly(ethyl vinyl ether) has a smaller fraction of the T form and a larger fraction of the G form by about 1–3% than poly(methyl vinyl ether). Similarly, the conformation of poly(isopropyl vinyl ether) varies by 3–8% as compared with that of poly(methyl vinyl ether). The syndiotactic polymer shows especially large conformational changes due to side-chain variation. If the same parameters are used in the calculation, the conformer populations of the polymers are almost the same irrespective of the kind of the side chain. Therefore, the conformational changes with the change of side chains are not caused by differences in partition functions but in weight parameters.

2,4-Dimethoxypentane

For the oligomers with methoxy side chains the weight parameters η_1 and η_2 were obtained as $E_{\eta_1} = -1.12$ kcal·mol^{-1} and $E_{\eta_2} = -1.16$ kcal·mol^{-1} and the others are listed in Table V. From these values the conformation of 2,4-dimethoxypentane was also calculated. The vicinal coupling constants were estimated by using the value $J^0 = 12.2$ Hz but they did not agree with the observed values. Good agreement was obtained, as listed in Table IX, when the value E_{η_1} was taken as −0.51 kcal·mol^{-1}. This energy value of η_1 is almost the same as that proposed by Abe, which is −0.64 kcal·mol^{-1}. The difference between E_{η_1} for the oligomers and that for 2,4-dimethoxypentane suggests that interaction farther than three bonds influences the first-order interaction η_1.

Gauche Effect

For molecules containing electronegative atoms the semiempirical energy calculation does not agree with experimental data. However, by taking into consideration the gauche effect, the estimated conformational characters become consistent with those observed. The gauche effect has been noted for the atom pairs in gauche situations such as O···O, O···C, and F···F.[31] The energies of the gauche effects are in the range of ca. 0–1 kcal·mol^{-1} but they cannot be determined only by the species of the atoms in the gauche arrangement. Abe[13] proposed the gauche effect for E_η to be −0.2 kcal·mol^{-1} from experimental data, that is, coupling constants of 2,4-dimethoxypentane, the dipole moment, and the characteristic ratio of polymers. Our investigation results in a value of −0.56 kcal·mol^{-1} for the gauche effect, which is a little larger than the value proposed by Abe. One of the causes of this difference seems to be that the energy E_{τ_1} for the $\bar{\mathrm{G}}$ form estimated by Abe is higher than our results. The gauche effect, which is derived from the incompleteness of the functions for the conformational energy calculation, is not the extra stabilization effect of the gauche arrangement. Therefore, the energy functions as used here should be modified by the experimental results, as described in this paper.

Registry No. Ia, 10138-89-3; Ib, 5870-82-6; Ic, 85883-21-2; (±)-(*R**,*R**)-IIa, 85883-17-6; (±)-(*R**,*R**)-IIb, 85883-19-8; (±)-(*R**,*R**)-IIc, 85883-22-3; (±)-(*R**,*S**)-IIIa, 85883-18-7; (±)-(*R**,*S**)-IIIb, 85883-20-1; (±)-(*R**,*S**)-IIIc, 85883-23-4; 2,4-dimethoxypentane, 41021-50-5.

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Excluded Volume in Star Polymers: Chain Conformation Space Renormalization Group

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ABSTRACT: The chain conformational renormalization group method is applied to the calculation of the distribution functions for intersegment distance vectors, the mean square intersegment distances, the mean square radius of gyration, the osmotic second virial coefficient, and the interpenetration function for *f*-branched star polymers. The calculations provide the full crossover dependence of all quantities on the strength of the excluded volume interaction and the chain length. The results provide a picture of excluded volume effects on the conformations of star polymers which is rather different from that assumed in recent scaling models. Some of the important information concerning the structure of the star polymers emerges from the prefactors since many power law exponents are independent of the number of branches, thereby emphasizing the importance of evaluating these prefactors.

I. Introduction

Star polymers have been attracting a considerable amount of experimental and theoretical interest. Experimental work in dilute solutions has been performed by light scattering[1-3] and by the measurement of hydrodynamic and rheological properties.[4-6] In addition, a number of experiments have focused on star polymers in concen-

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0024-9297/83/2216-1228$01.50/0