

# Nuclear Magnetic Resonance Studies on Poly(alkyl propenyl ether) and Model Compounds. 1. Conformational Analysis of Model Compounds

Kei Matsuzaki,\* Hisayuki Morii,<sup>†</sup> and Taiichi Kanai

Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Yuzuru Fujiwara

Institute of Electronics and Information Science, The University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan. Received October 24, 1980

**ABSTRACT:** As model compounds of poly(alkyl propenyl ether), stereoisomers of 2,4-dimethoxy-3-methylpentane and 3-methylpentane-2,4-diol were isolated and their conformations investigated by NMR spectroscopy. The conformations were also calculated based on a local interaction model. The observed coupling constants and their temperature dependence were compared with calculated results.

## Introduction

Model compounds for various types of vinyl polymers<sup>1-3</sup> have been investigated. Mainly, 2,4-disubstituted pentanes and 2,4,6-trisubstituted heptanes have been used as models for  $\alpha$ -monosubstituted vinyl polymers. Their conformational parameters and chemical shifts were determined by nuclear magnetic resonance spectroscopy. In the present study we synthesized model compounds for an  $\alpha,\beta$ -disubstituted vinyl polymer and identified the diastereomers by NMR spectroscopy.

The spin-spin coupling constant between vicinal protons gives useful information about the conformation. Moritani and Fujiwara<sup>4</sup> previously demonstrated the usefulness of the local interaction model in conformational analysis. On the basis of the measured temperature dependence of the vicinal spin-spin coupling constants, energy parameters, conformer energies, and conformational populations for pentane-2,4-diol, 2,4-dichloropentane, and 2,4-diphenylpentane could be determined. We applied this method to determine the conformational parameters of 2,4-dimethoxy-3-methylpentane and 3-methylpentane-2,4-diol as model compounds of poly(alkyl propenyl ethers).

## Experimental Section

**Synthesis of 2,4-Dimethoxy-3-methylpentane as the Model Compound.** Stereoisomers of 2,4-dimethoxy-3-methylpentane (DMMP) were prepared from fractionated 3-methylpentane-2,4-diol (MPDO). Commercial MPDO (Tokyo Kasei Co.) was separated by high-speed liquid chromatography (instrument, Toso HLC-802UR; column, LS-160H6; solvent, 97/3 mixture of *n*-hexane/ethanol). In the chromatogram three peaks were observed, but it was revealed that the first one was that of (2*R*,4*S*)- and (2*S*,4*R*)-hexane-2,4-diols and the third one includes (2*R*,4*R*)- and (2*S*,4*S*)-hexane-2,4-diols as well as MPDO. Therefore, the second and the third peaks were fractionated into three portions, designated as F-1, F-2, and F-3 (see Figure 1). The fractions and the original mixture of MPDO were converted to DMMP by Diner's method<sup>5</sup> (Scheme I).

**NMR Measurements.** <sup>1</sup>H NMR spectra were measured with a JEOL-PS-100 (100 MHz) spectrometer and <sup>13</sup>C NMR spectra with a JEOL-JNM-PS-100 (25.03 MHz) spectrometer. The samples were the F-1, F-2, and F-3 fractions and the original mixture. For MPDO, chloroform-*d*, pyridine, dimethyl-*d*<sub>6</sub> sulfide (Me<sub>2</sub>SO-*d*<sub>6</sub>), and D<sub>2</sub>O were used as solvent and for DMMP, chloroform-*d* was used. The concentration of samples was ca. 6% (v/v) for <sup>1</sup>H NMR and ca. 10% (v/v) for <sup>13</sup>C NMR. The vicinal spin-spin coupling constants between the methoxy methine proton

Scheme I

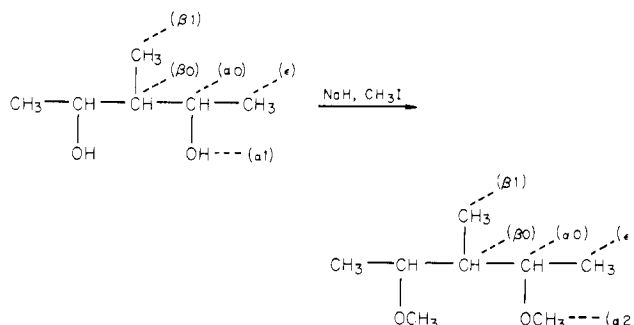
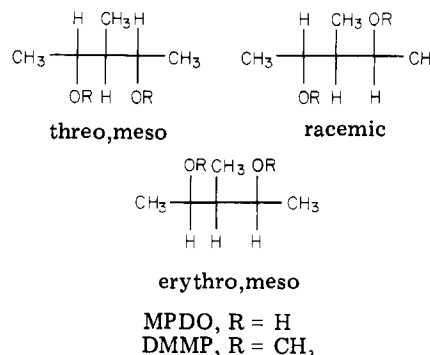


Chart I  
Diastereomers of Model Compounds

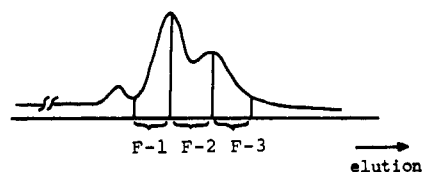


(H<sub>α0</sub>; see Scheme I) or the hydroxy methine proton (H<sub>α0</sub>) and 3-methine proton (H<sub>β0</sub>) were measured from the splitting of the methine proton (H<sub>α0</sub>) resonance.

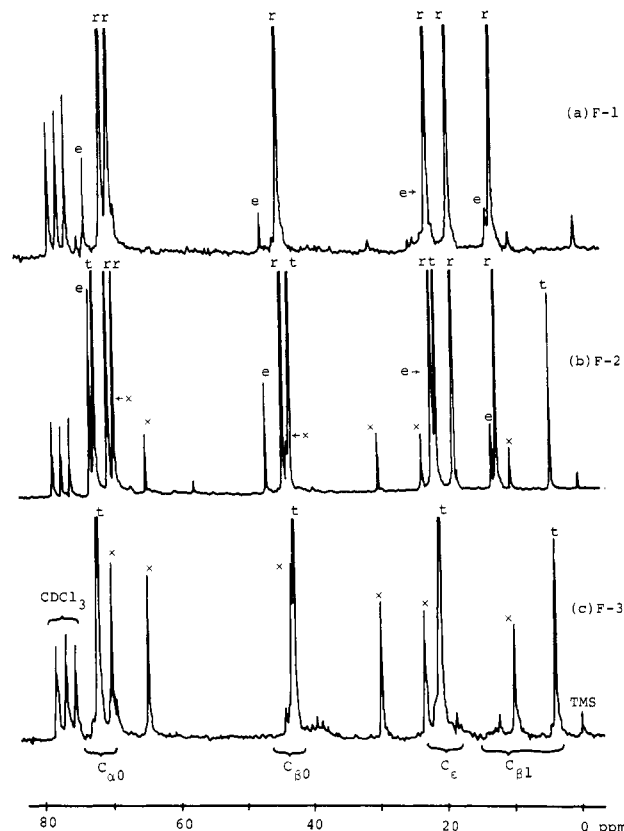
## Results and Discussion

**Identification of Diastereomers of 3-Methylpentane-2,4-diol and 2,4-Dimethoxy-3-methylpentane.** As shown in Chart I, there exist three diastereomers of MPDO as well as of DMMP. In the diastereomers of MPDO, the racemic one has six nonequivalent carbons, while the others have four nonequivalent carbons. Therefore in the <sup>13</sup>C NMR spectrum *rac*-MPDO was easily identified (Figure 2). *threo,meso*- and *erythro,meso*-MPDO are distinguished by the stable conformations in nonpolar solvents. Both diastereomers take the TT form due to intramolecular hydrogen bonds (Figure 3). In this conformation the hydroxy methine proton (H<sub>α0</sub>) and the 3-methine proton (H<sub>β0</sub>) are gauche for the *threo,meso*

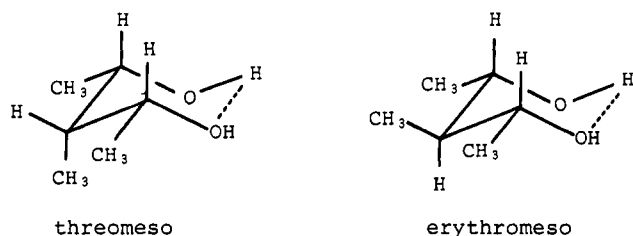
\* Present address: Research Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan.



**Figure 1.** Fractionation of 3-methylpentane-2,4-diol by high-speed liquid chromatography with refractive index.



**Figure 2.**  $^{13}\text{C}$  NMR spectra of fractions of 3-methylpentane-2,4-diol: r, racemic; e, erythro,meso; t, threo,meso; x, hexane-2,4-diol as impurity.



**Figure 3.** Preferred conformations of 3-methylpentane-2,4-diol. The dotted lines indicate hydrogen bonding.

compound and trans for the erythro,meso compound. As the vicinal spin-spin coupling constants observed in chloroform-*d* are 2.0 and 8.2 Hz for the two meso diastereomers, it is deduced from the Karplus equation that the former is threo,meso and the latter is erythro,meso. The identification agrees with the observation that the coupling constant ( $J_{\alpha\beta}$ ) of the erythro,meso compound decreases and that of the threo,meso compound increases as the solvent polarity increases (Figure 4). As DMMP was prepared by the reaction shown in Scheme I, the configurations of MPDO are retained in DMMP. The content of diastereomers in the fractions was determined from the NMR spectra shown in Figure 2. Therefore, F-1 is the racemic compound, with a small amount of the erythro,

**Table I**  
Second-Order Interactions (Four-Bond Interactions)<sup>a</sup>

interacting groups		statistical weight factors
OR	OR	$\psi_1$
$\text{C}_{\beta_0}^b$	OR	$\psi_2$
$\text{C}_{\beta_0}^b$	$\text{C}_{\beta_0}^b$	$\psi_3$
$\text{C}_{\alpha_2}$	$\text{C}_{\beta_1}$	$\kappa_1$
$\text{C}_{\alpha_2}$	$\text{C}_{\alpha_0}$	$\kappa_2$

<sup>a</sup> The names of the groups are shown in Scheme I.

<sup>b</sup> For MPDO and DMMP,  $\text{C}_e$  is adopted as the interacting group instead of  $\text{C}_{\beta_0}$ .

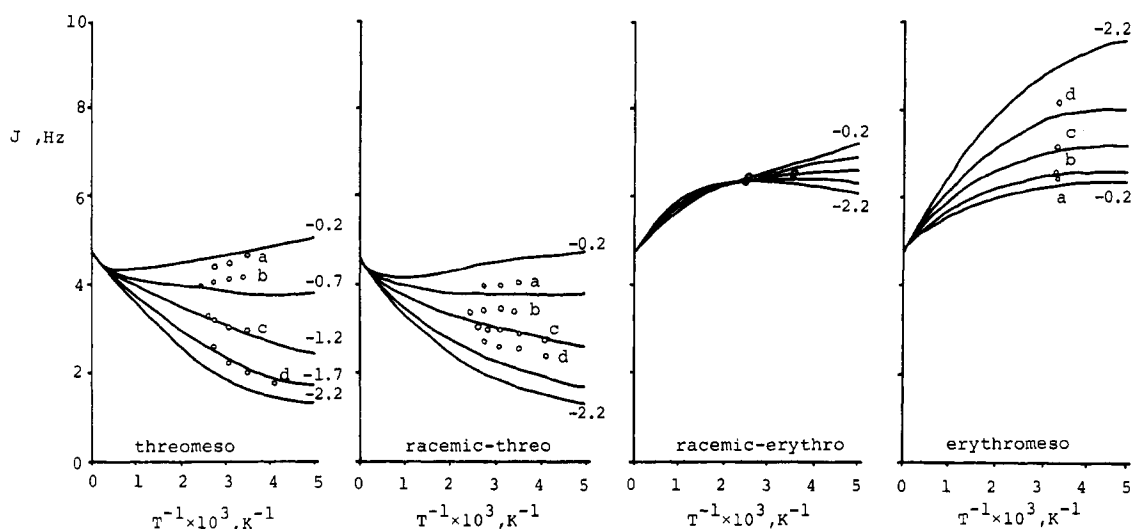
**Table II**  
Statistical Weight Matrices<sup>a</sup>

matrix		bonds corresponding to the row and column of the matrix
$\mathbf{D}_t = \begin{bmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{bmatrix}$		$\text{C}_{\alpha_0}^t\text{C}_{\beta_0}$
$\mathbf{D}_e = \begin{bmatrix} \tau_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \tau_2 \end{bmatrix}$		$\text{C}_{\alpha_0}^e\text{C}_{\beta_0}$
$\mathbf{B}_1 = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$		$\text{C}_{\alpha_0}\text{O}$
$\mathbf{V}_{tt}'' = \begin{bmatrix} \psi_1 & 1 & \psi_2 \\ 1 & \psi_3 & \psi_2 \\ \psi_2 & \psi_2 & \psi_1\psi_3 \end{bmatrix}$		$\text{C}_{\alpha_0}^t\text{C}_{\beta_0}^t\text{C}_{\alpha_0}$
$\mathbf{V}_{te}'' = \begin{bmatrix} 1 & \psi_2 & \psi_1 \\ \psi_2 & 1 & \psi_3 \\ \psi_1 & \psi_3 & \psi_2\psi_2 \end{bmatrix}$		$\text{C}_{\alpha_0}^t\text{C}_{\beta_0}^e\text{C}_{\alpha_0}$
$\mathbf{V}_{ee}'' = \begin{bmatrix} \psi_1 & 1 & \psi_2 \\ 1 & \psi_3 & \psi_2 \\ \psi_2 & \psi_2 & \psi_1\psi_3 \end{bmatrix}$		$\text{C}_{\alpha_0}^e\text{C}_{\beta_0}^e\text{C}_{\alpha_0}$
$\mathbf{Y}_{1t} = \begin{bmatrix} \kappa_1 & 1 & \kappa_2 \\ \kappa_2 & \kappa_1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$		$\text{O}-\text{C}_{\alpha_0}^t\text{C}_{\beta_0}$
$\mathbf{Y}_{1e} = \begin{bmatrix} 1 & \kappa_1 & \kappa_2 \\ \kappa_2 & 1 & \kappa_1 \\ 1 & 1 & 1 \end{bmatrix}$		$\text{O}-\text{C}_{\alpha_0}^e\text{C}_{\beta_0}$
$\mathbf{Y}_{t1} = \begin{bmatrix} \kappa_1 & 1 & \kappa_2 \\ 1 & 1 & \kappa_1 \\ \kappa_2 & 1 & 1 \end{bmatrix}$		$\text{C}_{\beta_0}^t\text{C}_{\alpha_0}\text{O}$
$\mathbf{Y}_{e1} = \begin{bmatrix} 1 & 1 & \kappa_2 \\ \kappa_1 & 1 & 1 \\ \kappa_2 & 1 & \kappa_1 \end{bmatrix}$		$\text{C}_{\beta_0}^e\text{C}_{\alpha_0}\text{O}$

<sup>a</sup> In the expression  $\text{A}-\text{A}'-\text{A}''$  (e.g.,  $\text{C}_{\alpha_0}-\text{C}_{\beta_0}-\text{C}_{\alpha_0}$ ), bond  $\text{A}-\text{A}'$  corresponds to the row and bond  $\text{A}'-\text{A}''$  to the column ( $t$  = threo;  $e$  = erythro). In the matrix  $\mathbf{Y}_{1m}$  ( $m$  =  $t$  or  $e$ ), the bond  $m$  of the main chain and the side chain  $\text{O}-\text{C}_{\alpha_2}$  bond are trans when the  $\text{C}_{\alpha_0}-\text{O}$  bond is in the  $\bar{G}$  conformation, and in  $\mathbf{Y}_{m1}$ , they are gauche. Matrix  $\mathbf{V}_{ee}''$  is the transpose of matrix  $\mathbf{V}_{te}''$ .

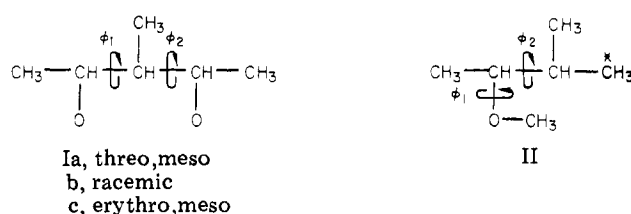
meso compound, F-3 is mainly (62%) the threo,meso compound, but F-2 includes 45% racemic compound, 36% threo,meso compound, and 12% erythro,meso compound with other impurities.

**Local Interaction Model.** In this paper the conformation of the model compounds is treated by means of a matrix method representation.<sup>6</sup> For the calculation of  $\alpha,\beta$ -disubstituted vinyl polymers and their models, we need more matrices than for  $\alpha$ -monosubstituted vinyl polymers because of the configurational complexity. Moreover, some matrices are necessary for calculation of side-chain conformation. The intramolecular interactions taken into consideration are summarized in Figure 5 and Table I. Statistical weight matrices are listed in Table II. The partition functions of some model compounds shown in



**Figure 4.** Temperature dependence of  $H_{\alpha\alpha}-H_{\beta\beta}$  vicinal coupling constant  $J$  for diastereomers of 3-methylpentane-2,4-diol. The solid lines indicate curves calculated for the values of  $E_{\psi_1(\text{MPDO})} - E_{\psi_1(\text{DMMP})}$  (i.e.,  $-0.2, -0.7, -1.2, -1.7, -2.2$  kcal $\cdot$ mol $^{-1}$ ). Open circles indicate the observed coupling constants in various solvents: a,  $\text{D}_2\text{O}$ ; b,  $\text{Me}_2\text{SO}-d_6$ ; c, pyridine; d, chloroform- $d$ .

**Chart II**  
Model Compounds for Calculation<sup>a</sup>



<sup>a</sup> The carbon atom with an asterisk is regarded to have the same charge as the carbons bonded to oxygen.

**Table III**  
Partition Functions

compound	partition function $Z$
Ia or threo,meso-MPDO	$I'D_t V_{tt}'' D_t I$
Ib or rac-MPDO	$I'D_e V_{et}'' D_t I$
Ic or erythro,meso-MPDO	$I'D_e V_{ee}'' D_e I$
II	$I'B_1' Y_{ie} D_e I$
threo,meso-DMMP	$I'B_1' Y_{it} D_t V_{tt}'' D_t Y_{ti} B_1'' I$
rac-DMMP	$I'B_1' Y_{ei} D_e V_{et}'' D_t Y_{ti} B_1'' I$
erythro,meso-DMMP	$I'B_1' Y_{ei} D_e V_{ee}'' D_e Y_{ie} B_1' I$

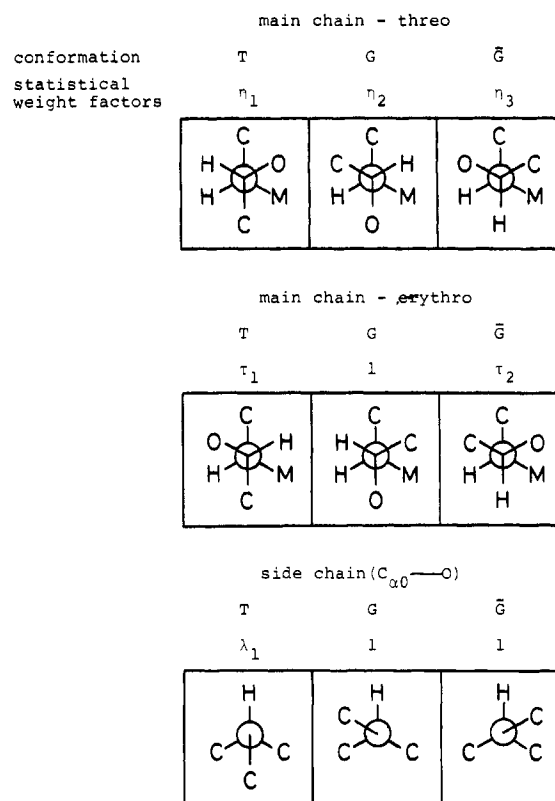
<sup>a</sup>  $B_1'$  and  $B_1''$  are defined as

$$B_1' = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \epsilon \end{bmatrix} \quad B_1'' = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

where  $\epsilon$  is introduced to calibrate the difference between the two gauche conformations of the  $\text{C}_{\alpha 0}-\text{O}$  bond; that is,  $\text{C}_{\alpha 2}$  and  $\text{C}_e$  are gauche and/or  $\text{C}_{\alpha 2}$  and  $\text{C}_{\beta 0}$  are gauche.

Chart II are expressed in Table III.

**Calculation of Conformational Energies.** The conformational energies of the model compounds were calculated with consideration of torsional energy and interatomic force, that is, van der Waals interaction and Coulombic force. The equations and parameters for the calculation are the same as those used by Abe in the study of poly(vinyl ethers)<sup>7</sup> except the electric charges of the atoms. The partial electric charges were computed by CNDO/2 for three predominant conformers of DMMP and their average values were  $\delta = -0.23$  for oxygen atoms,  $\delta = +0.16$  for tertiary carbon atoms bonded to oxygen, and  $\delta = +0.10$  for the methyl carbon of the methoxy group. As the charges of hydrogens and carbons not bonded to ox-



**Figure 5.** First-order interactions (three-bond interactions). M indicates  $\beta$ -methyl carbon ( $\text{C}_{\beta 1}$ ).

**Table IV**  
Statistical Weight Factors for DMMP at 50 °C

$\psi_1 = 0.45$	$\psi_1 = 0.15$	$\lambda_1 = 0.001$
$\eta_2 = 0.15$	$\psi_2 = 0.06$	$\epsilon = 0.8$
$\eta_3 = 0.65$	$\psi_3 = 0.002$	
$\tau_1 = 0.15$	$\kappa_1 = 0.07$	
$\tau_2 = 0.60$	$\kappa_2 = 0.05$	

gen are less than 0.03 in absolute value, they are neglected. The conformational energy  $E(\phi_1, \phi_2)$  calculated for the rotational angles  $\phi_1$  and  $\phi_2$  was converted to conformer fraction  $P_{(i,j)}$  as represented in eq 1 and 2. In

$$P(\phi_1, \phi_2) = \exp(-E(\phi_1, \phi_2)/RT) \quad (1)$$

$$P_{(i,j)} = \frac{\sum_{\text{in}(i,j)} P(\phi_1, \phi_2)}{\sum_{\text{whole}} P(\phi_1, \phi_2)} \quad (2)$$

( $i, j = T, G$ , and  $\bar{G}$ )

practice, conformer fraction matrix  $\mathbf{P}$  is expressed by the statistical weight factors with the partition function listed in Table III. Comparing the calculated  $\mathbf{P}$  from eq 2 with the theoretical  $\mathbf{P}$  obtained with the use of the local interaction model, we estimated the statistical weight factors by least squares. They were modified slightly in the range of error by the experimental data described in the next section, as shown in Table IV. Weight factors such as  $\psi_3$ , which have small values, showed large standard errors. Previously, Abe<sup>7</sup> proposed second-order interaction weight factors in kcal-mol<sup>-1</sup> for poly(alkyl vinyl ether), which correspond to  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  in our representation. They were 0.18, 0.25–0.08, and 0.05–0.03, respectively, when converted to weight factors at 50 °C. Our estimated values are almost consistent with them.

**Experimental Verification of Statistical Weight Factors.** In order to verify the statistical weight factors shown in Table IV experimentally, the observed coupling constant between the  $\alpha$ -methine proton ( $H_{\alpha 0}$ ) and the  $\beta$ -methine proton ( $H_{\beta 0}$ ) of DMMP and MPDO were compared with the calculated values. The calculated spin-spin coupling constants were obtained by eq 3, where,  $\mathbf{P}_{mn}$  is

$$\mathbf{J} = \mathbf{J}_0 \mathbf{P}_{mn} \mathbf{I} \quad (3)$$

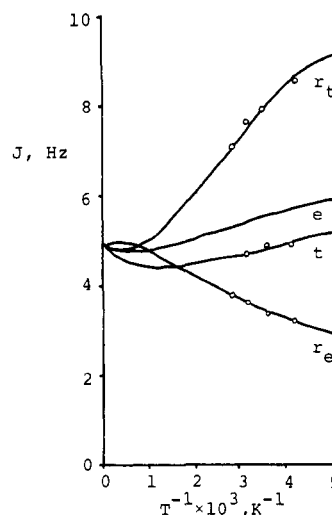
the conformer fraction matrix expressed by statistical weight factors. When the bond  $m$  is for the threo configuration, the vector  $\mathbf{J}_0$  is ( $J_t J_g J_g$ ) and for erythro, ( $J_g J_g J_g$ ).  $J_t$  and  $J_g$  are the trans and gauche coupling constants, respectively. Since every statistical weight factor  $\sigma$  is a function of temperature, as indicated in eq 4, coupling

$$\sigma = \exp(-E_\sigma/RT) \quad (4)$$

constants vary with temperature. This temperature dependence indicates whether the statistical weight factors are proper or not. For DMMP the dependence of calculated coupling constants on temperature is shown in Figure 6. In order to get good agreement between observed and calculated coupling constants over the temperature range from -30 to +90 °C,  $J_t = 11.5$  Hz and  $J_g = 1.5$  Hz were adopted. The concentration of *erythro,meso*-DMMP in the F-1 fraction was so low that the coupling constants could not be measured.

For MPDO the temperature dependence of the coupling constants is calculated and the results are shown in Figure 4. In this calculation, the statistical weight factor  $\psi_1$ , which corresponds to the second-order interaction between two oxygens, is taken as a variable because MPDO forms intramolecular hydrogen bonds, the energy of which changes remarkably with the solvent polarity. For MPDO, too, the observed and calculated temperature dependence of the coupling constants showed good agreement for  $J_t = 11.5$  Hz and  $J_g = 1.5$  Hz, which were the same values as for DMMP. The error of  $J_t$  and  $J_g$  values was estimated to be  $\pm 1.0$  Hz. For MPDO the first-order interaction parameters were modified slightly to be  $\eta_1 = 0.65$ ,  $\eta_2 = 0.2$ ,  $\eta_3 = 0.9$ ,  $\tau_1 = 0.4$ , and  $\tau_2 = 0.6$  in order to get better agreement between observed and calculated coupling constants.

**Solvent Effect and Conformational Character.** The conformation of MPDO dramatically changes with solvents, mainly due to change in intramolecular hydrogen bonding. The effect of solvents on the interaction of the hydroxyl groups in MPDO is expressed by  $E_{\psi_1}$ .  $E_{\psi_1}$ 's are determined experimentally to give good agreement between the observed and calculated coupling constants. The



**Figure 6.** Temperature dependence of  $H_{\alpha 0}$ - $H_{\beta 0}$  coupling constant  $J$  for diastereomers of 2,4-dimethoxy-3-methylpentane in chloroform- $d$ . The solid lines indicate the calculated curves:  $t$ , threo,meso;  $r_t$ , threo part of racemic;  $r_e$ , erythro part of racemic;  $e$ , erythro,meso.

**Table V**  
Conformer Fractions of MPDO and DMMP at 50 °C

	threo,meso	racemic (threo- erythro)	erythro, meso
MPDO in $\text{CDCl}_3$	TT = 0.71 TG + GT = 0.21	TG = 0.39 GT = 0.36 TT = 0.12	TG + GT = 0.64 TT = 0.27
MPDO in $\text{D}_2\text{O}$	TG + GT = 0.54 TT = 0.26 TG + GT = 0.15	TT = 0.35 GG = 0.27 TG = 0.16 GT = 0.15	TG + GT = 0.84
DMMP in $\text{CDCl}_3$	TG + GT = 0.51 TG + GT = 0.28 TT = 0.11	GG = 0.61 TT = 0.13 TG = 0.11 TG = 0.08	TG + GT = 0.78 GG + GG = 0.19

$E_{\psi_1(\text{MPDO})} - E_{\psi_1(\text{DMMP})}$  values, which indicate the energy difference of  $\psi_1$  between MPDO and DMMP bearing no hydrogen bonds, were obtained as -0.4 kcal-mol<sup>-1</sup> in  $\text{D}_2\text{O}$ , -0.7 kcal-mol<sup>-1</sup> in  $\text{Me}_2\text{SO}-d_6$ , -1.2 kcal-mol<sup>-1</sup> in pyridine, and -1.7 kcal-mol<sup>-1</sup> in chloroform- $d$ . These values are closely related to intramolecular hydrogen bond energy. Because of the contribution of the solvent and intermolecular hydrogen bonds, these are smaller than the values usually observed for hydrogen bond energy.

It is interesting that the values of  $\eta_2$  and  $\tau_1$  are smaller than other first-order interaction parameters for both DMMP and MPDO. The conformations corresponding to  $\eta_2$  and  $\tau_1$  have the same character, that is, two hydrogens trans to each other, as shown in Figure 5. Moreover, the conformations of threo-G and erythro-G resemble each other and have larger statistical weight factors than the others. Lipnick et al.<sup>8</sup> investigated the conformation of 2-methylbutane and estimated that 2,3-dimethylbutane is stable in the conformation in which two methine hydrogens are trans. It seems reasonable that the existence of oxygen in our model compounds leads to different results from those of 2,3-dimethylbutane.

The conformer fractions of MPDO and DMMP at 50 °C are summarized in Table V. However, the confor-

mational character of poly(alkyl propenyl ether) will be different from that of DMMP. This problem will be discussed in a subsequent report.

## References and Notes

- (1) Matsuzaki, K.; Sakota, K.; Okada, M. *J. Polym. Sci., Part A-2* **1967**, *7*, 1444.
- (2) Moritani, T.; Kuruma, I.; Shibata, K.; Fujiwara, Y. *Macromolecules* **1972**, *5*, 577.
- (3) Doskocilova, D.; Stokr, J.; Schneider, B.; Pivcova, H.; Kolinsky, M.; Petranek, J.; Lim, D. *J. Polym. Sci., Part C* **1967**, *16*, 215.
- (4) Moritani, T.; Fujiwara, Y. *J. Chem. Phys.* **1973**, *59*, 1175.
- (5) Diner, U. E.; Sweet, F.; Brown, K. *Can. J. Chem.* **1966**, *44*, 1591.
- (6) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
- (7) Abe, A. *Macromolecules* **1977**, *10*, 34.
- (8) Lipnick, R. L.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6375.

## Nuclear Magnetic Resonance Studies on Poly(alkyl propenyl ether) and Model Compounds. 2. Calculation of Carbon-13 Nuclear Magnetic Resonance

Kei Matsuzaki,\* Hisayuki Morii,<sup>†</sup> Naoki Inoue, and Taiichi Kanai

Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Yuzuru Fujiwara

Institute of Electronics and Information Science, The University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan

Toshinobu Higashimura

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan. Received October 24, 1980

**ABSTRACT:** In order to elucidate the steric structure of poly(alkyl propenyl ethers), poly(ethyl propenyl ether), 3,5-dimethyl-4-methoxyheptane, and several other model compounds were synthesized and their conformations analyzed by a local interaction model. The <sup>13</sup>C NMR chemical shifts of the polymer and its model compounds were interpreted by  $\gamma$  effects, whose coefficients were determined to give good agreement of the observed chemical shifts of 3-methylpentane-2,4-diol in various solvents with the calculated shifts. It was established that the structure of poly(ethyl propenyl ether) obtained from the trans monomer with BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> is threo,meso and that from the cis monomer is threo,meso and racemic.

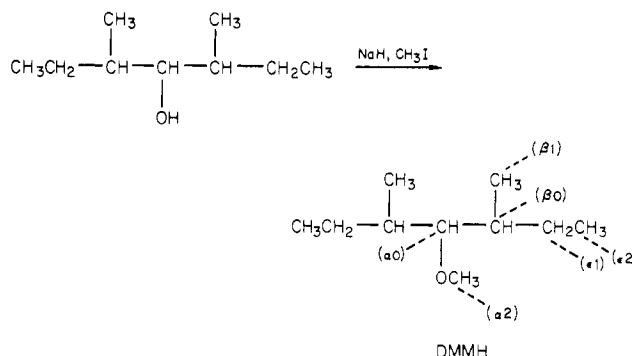
## Introduction

In a previous study on the steric structure of a poly(alkyl propenyl ether), Natta et al.<sup>1,2</sup> showed by X-ray diffraction that crystalline poly(*trans*-isobutyl propenyl ether) prepared with Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl has a threo-diisotactic structure. Ohsumi et al.<sup>3</sup> reported that *trans*-alkyl propenyl ethers prepared with BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> produce crystalline polymers. On the other hand, no crystalline polymers have been obtained from *cis*-alkyl propenyl ethers. In previous papers we showed by NMR spectroscopy that BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-prepared poly(alkyl propenyl ethers) having a nonbranched alkoxy group have only two steric structures<sup>4</sup> out of the three possible unit structures (i.e., threo,meso, racemic, and erythro,meso), and poly(*cis*-ethyl propenyl ether) obtained with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> catalyst has the third structure.<sup>5</sup>

In a previous report<sup>6</sup> we analyzed the conformation of 2,4-dimethoxy-3-methylpentane (DMMP) and 3-methylpentane-2,4-diol (MPDO) as model compounds for poly(alkyl propenyl ether) and obtained conformational parameters. In this study we synthesized and analyzed 3,5-dimethyl-4-methoxyheptane as the model compound together with DMMP and MPDO.

The difference in the <sup>13</sup>C NMR chemical shifts due to configuration of the polymers is generally attributed to conformational differences in the stereosequences.<sup>7,8</sup> It is known that a gauche arrangement of carbon atoms sepa-

Scheme I



rated by three bonds causes a larger upfield shift ( $\gamma$  effect)<sup>9-11</sup> than the *trans* conformation. Recently, <sup>13</sup>C chemical shifts of stereoisomers were calculated by using  $\gamma$  effects<sup>7,12-14</sup> and are in good agreement with the observed ones. Therefore, we applied the  $\gamma$  effect to calculate the <sup>13</sup>C NMR chemical shifts of poly(alkyl propenyl ether), the steric structure of which had not been assigned definitely, as well as its model compounds.

## Experimental Section

**Materials.** Preparations of 3-methylpentane-2,4-diol (MPDO) and 2,4-dimethoxy-3-methylpentane (DMMP) were described in the previous paper.<sup>6</sup>

**3,5-Dimethyl-4-methoxyheptane (DMMH).** Twenty-five milliliters of 2-bromobutane was dropped in a flask containing 200 mL of dried ether and 6 g of magnesium metal, and the

\* Present address: Research Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan.