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

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

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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 ^{13}C NMR chemical shifts of the polymer and its model compounds were interpreted by γ 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 $BF_3O(C_2H_5)_2$ is threo,meso and that from the cis monomer is threo,meso and racemic.

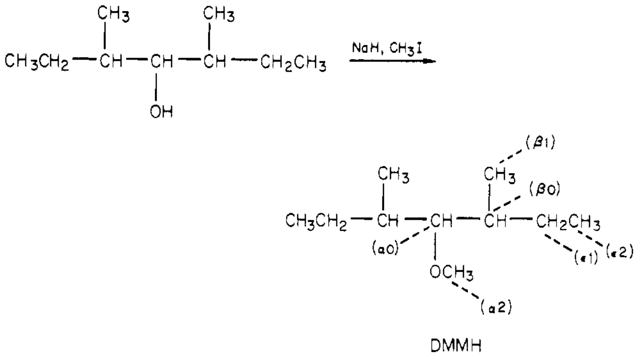
Introduction

In a previous study on the steric structure of a poly(alkyl propenyl ether), Natta et al.[1,2] showed by X-ray diffraction that crystalline poly(*trans*-isobutyl propenyl ether) prepared with $Al(C_2H_5)_2Cl$ has a threo-diisotactic structure. Ohsumi et al.[3] reported that *trans*-alkyl propenyl ethers prepared with $BF_3O(C_2H_5)_2$ 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 $BF_3O(C_2H_5)_2$-prepared poly(alkyl propenyl ethers) having a nonbranched alkoxy group have only two steric structures[4] out of the three possible unit structures (i.e., threo,meso, racemic, and erythro,meso), and poly(*cis*-ethyl propenyl ether) obtained with $Al_2(SO_4)_3$–H_2SO_4 catalyst has the third structure.[5]

In a previous report[6] 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 ^{13}C NMR chemical shifts due to configuration of the polymers is generally attributed to conformational differences in the stereosequences.[7,8] It is known that a gauche arrangement of carbon atoms separated by three bonds causes a larger upfield shift (γ effect)[9–11] than the trans conformation. Recently, ^{13}C chemical shifts of stereoisomers were calculated by using γ effects[7,12–14] and are in good agreement with the observed ones. Therefore, we applied the γ effect to calculate the ^{13}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.

Scheme I



DMMH

Experimental Section

Materials. Preparations of 3-methylpentane-2,4-diol (MPDO) and 2,4-dimethoxy-3-methylpentane (DMMP) were described in the previous paper.[6]

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

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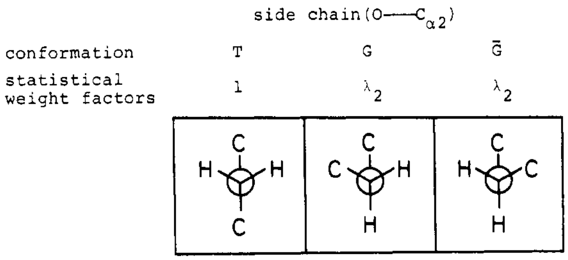


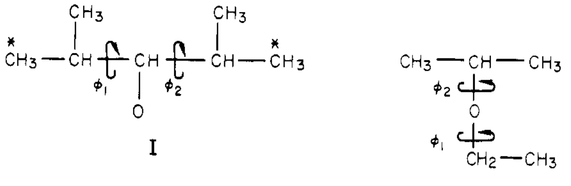
Figure 1. First-order interactions.

Table I
Second-Order Interactions[a]

interacting groups		statistical weight factors
$C_{\beta 1}$	$C_{\beta 1}$	ω_1
$C_{\alpha 0}$	$C_{\beta 1}$	ω_2
$C_{\alpha 0}$	$C_{\alpha 0}$	ω_3
$C_{\alpha 3}$	$C_{\beta 0}$	μ

[a] $C_{\alpha 3}$ is the methyl carbon of side-chain ethoxy group.

Chart I
Model Compounds for Calculations



I

II

solution was stirred under nitrogen for 2 h. After the addition of 2-bromobutane, 25 mL of 2-methylbutanal was dropped into the flask and stirred for 4 h. The reaction mixture was poured into 500 mL of ice–water containing 1% acetic acid and then extracted by ether. Fifteen milliliters of 3,5-dimethyl-4-heptanol [bp 68 °C (7 mmHg)] was obtained by distillation. 3,5-Dimethyl-4-methoxyheptane [bp 56–58 °C (30 mmHg)] was synthesized from 3,5-dimethyl-4-heptanol by Diner's method[15] as shown in Scheme I.

Measurements. ^{13}C NMR spectra of DMMH were measured with a JEOL-JNM-PS-100 (25.03 MHz) spectrometer in pyridine at 50 °C. The concentration of the sample was about 20% (v/v).

Calculations. As described in the previous report,[6] the conformation of the polymer and its model compounds, such as DMMH, was treated by a local interaction model. Some of the necessary matrices and statistical weight factors were already indicated. Other necessary matrices and statistical weight factors are summarized in Tables I and II and Figure 1. These parameters, which are related to the first- and second-order interactions, are determined in the same way as in the previous report.[6] By calculating conformational energies of the model compounds shown in Chart I and comparing with the matrix representation of a local interaction model, we estimated the statistical weight factors listed in Table III in addition to those reported previously.[6]

The partition functions of compounds I and II and DMMH are listed in Table IV. The partition function of the polymer which has a specific configuration is expressed in eq 1. Here we

$$Z = \mathbf{I}'\mathbf{D}_n\mathbf{V}''_{n,n-1}\mathbf{U}_{n-1,n-2}\cdots\mathbf{U}_{m+1,m}\cdots\mathbf{U}_{4,3}\mathbf{D}_2\mathbf{I} \qquad (1)$$

consider a polymer structure, both ends of which are CH_3-CH(OR)- groups. The statistical weight matrix, **W**, of the whole side chain is expressed in eq 2 for poly(ethyl propenyl ether) (PEPE).

$$\mathrm{W}_{m+1,m} = \begin{bmatrix} \mathrm{Y}_{m+1,1}f(\mathrm{I}'\mathrm{B}_2\mathrm{S}_{2,1})\mathrm{B}_1\mathrm{Y}_{1,m} \\ {}^{t}[\mathrm{Y}_{m,1}f(\mathrm{I}'\mathrm{B}_2\mathrm{S}_{2,1})\mathrm{B}_1\mathrm{Y}_{1,m+1}] \end{bmatrix} \qquad (2)$$

Table II
Statistical Weight Matrices[a]

matrix	bonds corresponding to the row and column of the matrix
$\mathbf{B}_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_2 \end{bmatrix}$	$O—C_{\alpha 2}$
$\mathbf{V}_{tt}' = \begin{bmatrix} \omega_1 & 1 & \omega_2 \\ 1 & \omega_3 & \omega_2 \\ \omega_2 & \omega_2 & \omega_1\omega_3 \end{bmatrix}$	$C_{\beta 0}\overset{t}{—}C_{\alpha 0}\overset{t}{—}C_{\beta 0}$
$\mathbf{V}_{te}' = \begin{bmatrix} 1 & \omega_1 & \omega_2 \\ \omega_2 & \omega_3 & 1 \\ \omega_1 & \omega_2\omega_2 & \omega_3 \end{bmatrix}$	$C_{\beta 0}\overset{t}{—}C_{\alpha 0}\overset{e}{—}C_{\beta 0}$
$\mathbf{V}_{ee}' = \begin{bmatrix} \omega_1 & \omega_2 & 1 \\ \omega_2 & \omega_1\omega_3 & \omega_2 \\ 1 & \omega_2 & \omega_3 \end{bmatrix}$	$C_{\beta 0}\overset{e}{—}C_{\alpha 0}\overset{e}{—}C_{\beta 0}$
$\mathbf{S}_{21} = \begin{bmatrix} 1 & 1 & 1 \\ \mu & \mu & 1 \\ \mu & 1 & \mu \end{bmatrix}$	$C_{\alpha 2}—O—C_{\alpha 0}$

[a] The expression is in the same manner as that of previous papers. V_{et}' is the transposed matrix of V_{te}'.

Table III
Statistical Weight Factors

$\omega_1 = 0.003$
$\omega_2 = 0.004$
$\omega_3 = 0.006$
$\mu = 0.15$
$\lambda_2 = 0.03$

Table IV
Partition Functions[a]

compound	partition function Z
I (racemic)	$I'D_eV_{et}'D_tI$
II	$I'B_2S_{21}B_1I$
threo,meso-DMMH	$I'D_0{}^tV_{t0}''D_t$- $[(Y_{t1}B_1Y_{1t})*V_{tt}']D_tV_{t0}''D_0I$
rac-DMMH	$I'D_0{}^tV_{e0}''D_e$- $[(Y_{e1}B_1Y_{1t})*V_{et}']D_tV_{t0}''D_0I$
erythro,meso-DMMH	$I'D_0{}^tV_{e0}''D_e$- $[(Y_{e1}B_1Y_{1e})*V_{ee}']D_eV_{e0}''D_0I$

[a] The matrices D_0, V_{t0}'', and V_{e0}'', which are necessary only for model compounds, are assumed as

$$D_0 = \begin{bmatrix} \eta_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad V_{t0}'' = \begin{bmatrix} \psi_2 & 1 & 1 \\ 1 & \psi_3 & 1 \\ \psi_3 & \psi_2 & 1 \end{bmatrix}$$

$$V_{e0}'' = \begin{bmatrix} 1 & \psi_2 & 1 \\ \psi_3 & 1 & 1 \\ \psi_2 & \psi_3 & 1 \end{bmatrix}$$

When a side-chain bond $C_{\alpha 0}$–O takes the Ḡ conformation and its neighboring main-chain bond m is trans to the side-chain bond O–$C_{\alpha 2}$, the first expression is adopted and when it is gauche, the second expression is adopted. The function f is defined as the following:

$$f\colon \begin{bmatrix} a \\ b \\ c \end{bmatrix} \rightarrow \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \qquad (3)$$

I and I′ are vectors whose components are all ones.

$$\mathrm{I} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \qquad \mathrm{I}' = (1 \quad 1 \quad 1) \qquad (4)$$

U is the statistical weight matrix per monomer unit

$$\mathbf{U}_{m+1,m} = \mathbf{D}_{m+1}(\mathbf{V}'_{m+1,m}{}^{*}\mathbf{W}_{m+1,m})\mathbf{D}_m\mathbf{V}''_{m,m-1} \qquad (5)$$

where the operator * is defined as

$$(a_{i,j})^{*}(b_{i,j}) = (c_{i,j}) \qquad c_{i,j} = a_{i,j}\cdot b_{i,j} \qquad (6)$$

The fraction of neighboring bonds m and $m - 1$ in the conformations i and j (representing any of T, G, and $\bar{\mathrm{G}}$) is $P_{(i,j)}$ represented by

$$P_{(i,j)} = Z'_{(i,j)}/Z \qquad (7)$$

In this expression $Z'_{(i,j)}$ is defined as

$$Z'_{(i,j)} = \mathbf{I}'\mathbf{D}_n\mathbf{V}''_{n,n-1}\mathbf{U}_{n-1,n-2}\ldots\mathbf{D}_{m+1}(\mathbf{V}'_{m+1,m}{}^{*}\mathbf{W}_{m+1,m})\cdot\mathbf{D}_m\bar{\mathbf{V}}''_{m,m-1(i,j)}\ldots\mathbf{U}_{4,3}\mathbf{D}_2\mathbf{I} \qquad (8)$$

where $\bar{\mathbf{V}}''_{m,m-1(i,j)}$ expresses the matrix the (i,j)th element of which is equal to that of $\mathbf{V}''_{m,m-1}$ and the other elements are zero.

Results and Discussion

Conformation of DMMH and Poly(ethyl propenyl ether). The weight factors ω_1, ω_2, and ω_3, which represent the second-order interactions among the methyl groups and the main chain, were slightly smaller than the second-order weight factor ω (=0.08–0.13) of polymethylene,[16] while the weight factor μ was nearly the same as ω. This nature of ω_1, ω_2, and ω_3 can be explained by the difficulty of torsional deformation which relieves steric interactions. The conformer fractions of DMMH and poly(ethyl propenyl ether) were calculated by using the parameters in Table III and those in Table IV of the previous report.[6] The results are listed in Table V. The conformations of DMMH and DMMP are a little different from those of PEPE, depending on the configuration, because the model compounds are too simple. It is pointed out that the preferred conformation of threo-diisotactic PEPE is TG (=GT) and that of the disyndiotactic polymer is TT. Overwhelmingly preferred conformations of erythro-diisotactic sequences do not exist. This characteristic of an erythro-diisotactic polymer chain is due to the fact that erythro,meso sequences cannot avoid second-order interactions, differing from threo,meso and racemic sequences.

Table V
Conformer Fractions of DMMH and PEPE at 50 °C[a]

	threo,meso	racemic (threo–erythro)	erythro,meso
DMMH	TG + GT = 0.84	TT = 0.38	$\mathrm{T\bar{G}} + \mathrm{\bar{G}T} = 0.63$
	$\mathrm{T\bar{G}} + \mathrm{\bar{G}T} = 0.13$	$\mathrm{G\bar{G}} = 0.33$ TG = 0.15	$\mathrm{G\bar{G}} + \mathrm{\bar{G}G} = 0.28$
PEPE (β centered)	TG + GT = 0.94	TT = 0.83 $\mathrm{T\bar{G}} = 0.07$	TG + GT = 0.38 $\mathrm{T\bar{G}} + \mathrm{\bar{G}T} = 0.36$ $\mathrm{G\bar{G}} + \mathrm{\bar{G}G} = 0.20$
PEPE (α centered)	TG + GT = 0.96	TT = 0.85 $\mathrm{G\bar{G}} = 0.07$	$\mathrm{T\bar{G}} + \mathrm{\bar{G}T} = 0.44$ TG + GT = 0.41 $\mathrm{G\bar{G}} + \mathrm{\bar{G}G} = 0.13$

[a] The conformation of PEPE was calculated for the center unit of 200-mer.

Calculation of Chemical Shifts. The observed chemical shifts of the β-methyl carbon ($C_{\beta 1}$) of MPDO diastereomers indicate remarkable differences depending on steric structures as shown in Figure 2, which can be interpreted by a γ effect with the expression written in eq 9. A(C) and A(O) are the populations of carbon and

$$-\delta = \gamma_C A(\mathrm{C}) + \gamma_O A(\mathrm{O}) - \delta' \qquad (9)$$

oxygen atoms at the γ position, respectively, which are in a gauche conformation relative to the carbon atom which is being observed, and γ_C and γ_O are the coefficients of the γ effect indicating the upfield shift per atom. $-\delta'$ is a parameter to obtain the chemical shift from Me_4Si. For $C_{\beta 1}$ of MPDO the following coefficients of the γ effect yielded good agreement of the calculated chemical shifts with those observed: $\gamma_C = -5.6$ ppm and $\gamma_O = -7.5$ ppm. $\gamma = -5.3$ ppm has been given for the γ effect by methylene or methyl carbons for a polypropylene model compound[7] and an ethylene–propylene copolymer,[8] and $\gamma = -5.0$ ppm for poly(vinyl chloride).[13] The γ_C value obtained here is nearly the same in magnitude. These γ values were applied to calculate the chemical shifts of β-methyl carbons of DMMP, DMMH, and PEPE. The order of the calculated chemical shifts (erythro,meso, threo,meso, and racemic, from low magnetic field) of DMMP does not agree with the order of the observed chemical shifts (threo,meso, erythro,meso, and racemic), but the difference in the chemical shifts is not so large (Table VIB). As for DMMH, the $C_{\beta 1}$ absorption of the erythro part is observed at lower field than the threo part. This fact is in good agreement with calculated results. The observed chemical shifts of the β-methyl carbons ($C_{\beta 1}$) of PEPE depended on the tacticity, as shown in Table VID. Comparing the observed shifts with the calculated shifts, it is reasonable to assign the principal observed peaks of PEPE, 10.00, 10.92, and 14.53 ppm,[5] to threo,meso, racemic, and erythro,meso structures, respectively (Table VID).

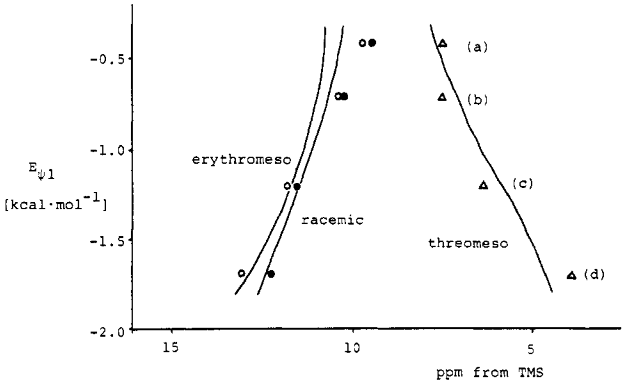


Figure 2. Observed and calculated β-methyl carbon chemical shifts of MPDO in various solvents. Solid lines indicate the calculated chemical shifts with a common $-\delta'$ value. $E_{\psi 1}$ is the second-order interaction energy between side-chain hydroxyl groups. Solvent: (a) H_2O; (b) Me_2SO; (c) pyridine; (d) chloroform-d. Observed shift: (○) erythro,meso; (●) racemic; (△) threo,meso.

Chemical shifts of the end methyl carbon (C_ϵ) of MPDO can also be interpreted with a γ effect. A γ value (γ_C') of the main-chain carbon bonded to oxygen ($C_{\alpha 0}$), of which the electronic charge is +0.16 from a CNDO/2 calculation, of −2.8 ppm was obtained in order to get good agreement with the observed chemical shifts. This γ_C' value is smaller in absolute value than the previous γ_C value, which is −5.6 ppm. This tendency that the γ effect of carbon bonded to an electronegative atom is smaller than that of other carbons is also observed for poly(vinyl chloride), as reported by Tonelli.[13] We consider that there exists a linear relation between the electronic charge of the atom causing the γ effect and its γ value. Then the γ_C'' value of the methoxy carbon ($C_{\alpha 2}$), of which the electronic charge is +0.10, was estimated to be −3.9 ppm.

The β-methine carbon ($C_{\beta 0}$) of MPDO has no large nucleus in its γ position. Nevertheless its chemical shift changes with configuration. Perhaps this is due to the anisotropic effect of the carbon–oxygen bond. There exists

Table VI
Observed and Calculated Chemical Shifts of MPDO, DMMP, DMMH, and PEPE[a]

A. 3-Methylpentane-2,4-diol (MPDO)

		$C_{\beta 1}$		$C_{\beta 0}$		$C_{\alpha 0}$		C_{ϵ}	
solvent	structure	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
H_2O	t	7.41	6.91	45.16	45.37	70.18	69.59	20.63	20.52
	r r_t	9.46	9.59	45.55	45.15	69.49	69.29	20.00	20.33
	r_e					68.42	69.25	19.65	19.51
	e	9.66	10.04	46.28	46.48	(70.18)	70.14	18.92	18.83
Me_2SO	t	7.56	6.97	45.45	45.63	68.71	68.31	21.70	21.64
	r r_t	10.34	10.56	45.84	45.39	68.32	67.68	21.17	21.29
	r_e					66.81	67.67	20.82	20.95
	e	(10.48)	10.84	46.82	47.08	(68.71)	68.87	20.24	20.05
pyridine	t	6.49	6.24	45.45	45.88	70.76	70.48	(21.99)	21.97
	r r_t	11.66	11.84	46.04	45.62	68.37	69.10	20.43	21.29
	r_e					69.84	69.17	(22.09)	21.98
	e	11.85	11.93	47.94	47.93	(70.76)	70.99	21.36	20.62
$CDCl_3$	t	3.95	4.79	43.40	44.24	72.52	72.33	21.31	21.35
	r r_t	12.34	12.14	44.38	44.04	69.69	70.39	18.78	20.40
	r_e					70.67	70.48	22.04	21.93
	e	13.12	12.48	47.06	46.56	73.11	72.78	21.85	20.28

B. 2,4-Dimethoxy-3-methylpentane (DMMP)

		$C_{\beta 1}$		$C_{\beta 0}$		$C_{\alpha 0}$		C_{ϵ}	
solvent	structure	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$CDCl_3$	t	10.05	9.34	44.33	44.15	77.93	76.67	16.39	16.31
	r r_t	9.02	9.00	44.72	43.20	78.23	78.05	16.63	17.30
	r_e					76.32	77.89	16.14	15.21
	e	9.56	10.29	41.94	43.55	77.64	77.51	15.12	15.46

C. 3,5-Dimethyl-4-methoxyheptane (DMMH)

		$C_{\beta 1}$		$C_{\beta 0}$		$C_{\alpha 0}$		$C_{\epsilon 1}$		$C_{\epsilon 2}$	
solvent	structure	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
pyridine	t	14.92	14.85	37.99	38.31	88.86	89.16	27.55	27.81	(12.24)	12.54
	r r_t	14.09	14.74	37.89	37.84	89.49	89.75	28.24	27.71	12.58	12.60
	r_e	16.33	16.36	38.19	38.08			25.60	25.51	12.24	12.28
	e	16.92	16.33	(37.89)	37.73	91.30	90.73	24.82	25.17	(12.43)	12.15

D. Poly(ethyl propenyl ether) (PEPE)

		$C_{\beta 1}$		$C_{\beta 0}$		$C_{\alpha 0}$	
solvent	structure	obsd	calcd	obsd	calcd	obsd	calcd
o-dichlorobenzene	t	10.00	9.92	41.99	42.12	83.35	84.78
	r	10.92	11.62	39.65	39.41	81.79	82.96
	e	14.53	13.91	39.26	39.37	83.59	81.01

[a] The structures threo,meso, racemic, erythro,meso, threo part of racemic, and erythro part of racemic are indicated with t, r, e, r_t, and r_e. Observed principal shifts of PEPE are reproduced from the literature.[5] Observed chemical shifts are expressed in ppm downfield from Me_4Si. Chemical shifts were converted to Me_4Si reference with δ(acetone) 30.57 in water and δ(HMDS) 2.00 in Me_2SO, pyridine, and chloroform. Observed chemical shifts of r_t and r_e are not assigned definitely. Parenthesized values are uncertain because of overlapping. Chemical shifts of alkoxy carbons are not listed in this table.

a correlation between the fraction of the conformation which has two parallel C–O bonds and the chemical shifts. Therefore, we assume that this effect (β_{CO} effect) is described by the following expression:

$$-\delta = \beta_{CO}A(CO) - \delta' \qquad (10)$$

$A(CO)$ is the population of two parallel C–O bonds and β_{CO} is the coefficient of the β_{CO} effect. For MPDO, $\beta_{CO} = -5.2$ ppm was obtained to get agreement with the observed shifts.

The γ value (−2.8 ppm) of the α-methine carbon ($C_{\alpha 0}$), the γ value (−5.6 ppm) of the β-methyl carbon ($C_{\beta 1}$), and the β_{CO} value (−5.2 ppm) were applied to calculate the chemical shift of $C_{\beta 0}$ of PEPE. As listed in Table VID, the calculated chemical shifts agreed well with the observed shifts. Therefore the principal peaks at 39.26, 39.65, and 41.99 ppm can be assigned to erythro,meso, racemic, and threo,meso structures, respectively. This assignment of the tacticity is consistent with that of the β-methyl carbon ($C_{\beta 1}$).

For all the carbons except alkoxy carbons, the chemical shifts were calculated with γ_C, γ_C', γ_C'', γ_O, and β_{CO}. For some atoms good agreement was obtained, but for a few atoms the difference between the observed and the calculated shifts are large.

As described above, we achieve the assignment of the β-centered triad tacticity for PEPE. The assignment of the threo,meso structure is consistent with that of Natta et al.[1,2] and those for the racemic and erythro,meso structures are consistent with the supposition made in our previous studies.[4,5] In order to increase the certainty, we calculated the chemical shifts with the same statistical weight factors as used above except one factor each time was taken to be twice as large as the original value. The conformation of the polymers mainly depends on the second-order interaction and was not so sensitive to the changes of statistical weight factors. Therefore, the assignment of the chemical shifts in this study was not affected by these changes.

The calculation of conformer population was carried out for poly(methyl propenyl ether) (PMPE) and poly(isopropyl propenyl ether) (PIPPE) by the same method as for PEPE. There was little difference in the main-chain conformation among PMPE, PIPPE, and PEPE. Therefore, the calculated chemical shifts of $C_{\beta 1}$ and $C_{\beta 0}$ showed almost the same tendency. The assignments for the $C_{\beta 1}$ carbons of PIPPE and PMPE are similar to that of PEPE; that is, absorptions due to erythro,meso, racemic, and threo,meso structures appear in this order from low field.

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Proton Nuclear Magnetic Resonance Investigations on Trioxane–Dioxolane Copolymerization Initiated by 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts

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ABSTRACT: Trioxane–dioxolane copolymerization initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts was directly observed by NMR spectroscopy. Formation of byproducts, i.e., trioxepane and tetroxocane, was confirmed. Intensities of signals were measured in order to obtain the basic kinetic characterization of the processes investigated. The copolymerization mechanism is discussed on the basis of the results obtained.

In our previous papers[1,2] the salts of trisubstituted dioxolane were shown to initiate the homopolymerization of trioxane. Conversion–time curves obtained differed, depending on the stereochemical structure of the initiator cation. Addition of the dioxolane comonomer (D) to trioxane (TOX) was found to influence considerably the rate of polymerization. This paper presents recent results of trioxane–dioxolane copolymerizations initiated by a series of 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts, ^{1}H NMR spectroscopy being used as a convenient analytical technique.

Experimental Section

A. Initiators. The cis and trans isomers of 2-isopropyl-, 2-phenyl-, and 2-styryl-4,5-dimethyl-1,3-dioxolan-2-ylium hexachloroantimonates (**1a–c**, respectively) as well as the respective hexafluoroantimonates (**2**) and hexafluoroarsenates (**3**) (see Figure 1) were synthesized from the appropriate isomers of acetals and trityl salts by the method described previously.[2,3]

B. Monomers. Industrial trioxane (TOX) was refluxed and distilled over KOH and then over Na. Dioxolane (D) (Fluka AG, Buchs SG) was refluxed and distilled over Na–K alloy. All these operations were performed in a dry nitrogen atmosphere.

C. Solvent. Methylene chloride was treated with H_2SO_4, neutralized, washed with water, dried with anhydrous Na_2SO_4, rectified over P_2O_5 on a Vigreux column, and finally dried with P_2O_5.

D. Polymerization. Initiator and the solution of comonomers were incorporated into a NMR probe under dry nitrogen. Reagents and the solvent were added to the probe, keeping the following initiator, trioxane, and dioxolane concentrations: $[I]_0 = 10^{-2}$, $[TOX]_0 = 2$, and $[D]_0 = 2$ mol/L. The spectra were recorded during the polymerization utilizing a JNM-C-6OH (JEOL) spectrometer. Chemical shifts were measured with respect to CH_2Cl_2 and then related to Me_4Si, taking $\delta_{CH_2Cl_2} = 5.33$. Intensities of the signals were determined by means of a built-in electronic integrator.

E. Trioxepane Synthesis. Trioxepane (TOXEP) was obtained by heating paraformaldehyde with dioxolane in the presence of catalytic amounts of H_2SO_4.[4]

Results and Discussion

1. Interpretation of the Spectra. For an equimolar ratio of comonomers the reaction mixture was found to remain homogeneous until full conversion had been reached, which allowed direct NMR observations. Moreover, the precipitation of a solid trioxane–dioxolane copolymer, which occurred in the case of some slower runs for high conversions was found to begin close to the probe walls so that, fortunately, resolution of the spectra was not affected.

Figure 2c presents the spectrum of the copolymerization system investigated. Using both literature data and comparison with the spectrum of the mixture consisting of both the comonomers (Figure 2a) and the spectrum of the dioxolane homopolymerization system (Figure 2b), we assigned the signals of the NMR spectrum of the copolymerization system (Figure 2c). Thus, according to the literature data,[5–7] the three signals in the oxymethylene region were assigned to the three copolymeric triads: M*M*M, (E*M*M, M*M*E); and E*M*E (see Table I). Since no splitting of the oxyethylene signal was reported[5–7] for the trioxane–dioxolane copolymers, one would expect that

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