Finally, we need only to note that

$$\Lambda(\lambda) \sim [2\lambda \ln (L/b)]^{-1} \tag{A.44}$$

for $L \gg b$.

In his review of this article, Professor H. Yamakawa pointed out a potential mathematical difficulty involving the cut-off limits in eq A.10. Regarding this we comment as follows.

The results in this section depend on the evaluation of the Fourier transform of integrals such as $\int_{-\infty}^{\infty} \mathrm{d}v\, \phi(v) G(u - v)$. In u,v variables the precise cut-off for the vanishing of the kernel G becomes the requirement that $|\tanh (u/2) - \tanh (v/2)| < \epsilon$. With this restriction the Fourier transform of the above integral can be written as

$$\int_{-\infty}^{\nu} \mathrm{d}v\, e^{ikv}\phi(v) \int_{\alpha-v}^{\infty} \mathrm{d}u\, e^{iku}G(u) + \int_{-\nu}^{\infty} \mathrm{d}v\, e^{ikv}\phi(v) \int_{-\infty}^{\beta-v} \mathrm{d}u\, e^{iku}G(u)$$

where $\nu = 2 \tanh^{-1} (1 - \epsilon)$, $\alpha = 2 \tanh^{-1} (\tanh (v/2) + \epsilon)$, and $\beta = 2 \tanh^{-1} (\tanh (v/2) - \epsilon)$. Then, as $\epsilon \rightarrow 0$, $\nu \rightarrow \infty$, $\alpha - v \rightarrow 2\epsilon$, $\beta - v \rightarrow -2\epsilon$, the integral asymptotically becomes factorable, only now permitting the easy solution for $\hat{\phi}$.

The asymptotic nature of this result suggests that the term of order $[\ln (L/b)]^{-2}$ presented in section IV is still incomplete, rendering its significance even more ambiguous.

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Conformational Characteristics of Poly(alkyl vinyl ether)'s

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ABSTRACT: Conformational energies were estimated for the poly(alkyl vinyl ether) chain using semiempirical energy expressions. The results were tested for NMR data on 2,4-dimethoxypentane. The 3 × 3 statistical weight matrices derived therefrom were applied to the analysis of various configuration-dependent properties of these polymers: $\mathrm{H{+}CH_2{-}CH(OR){+}_xCH_3}$, R = methyl, ethyl, isopropyl, isobutyl, (*S*)-1-methylpropyl and (*S*)-2-methylbutyl groups. The characteristic ratio of the unperturbed dimension ($C_\infty = 6.1$–8.0) estimated from fractionated samples of poly(methyl vinyl ether) in a good solvent was reproduced in a moderately isotactic region. Experimental values of the mean-square dipole moment per repeat unit $\langle \mu^2 \rangle / x$ for isotactic samples of poly(isopropyl vinyl ether) (0.67) and poly(isobutyl vinyl ether) (0.97–1.35) were also found to be in agreement with those calculated in a reasonable range of tacticity. These properties are quite insensitive to the extra stabilization energy associated with "gauche oxygen" placements. The fraction of helical conformations was estimated for asymmetric side chains, indicating that the large enhancement in optical activity arises from the neighbor-dependent character of the polymer chain.

Configuration-dependent properties of poly-α-olefins, hydrocarbon analogues of poly(alkyl vinyl ether)'s, have been successfully treated within the framework of the rotational isomeric state approximation.[1] These include characteristic ratios C_∞,[2,3] optical anistropy,[4] interpretation of NMR spectra,[5] and optical rotation.[6,7] Recently Suter and Flory[8] carried out detailed calculations of conformational energies of polypropylene using semiempirical expressions. Large displacements of high-energy conformations from the perfectly staggered position were taken into account in their five-state matrix scheme, which thereby offers more exact representation of the energy contour map. Stereochemical equilibrium data[7] and characteristic ratios C_∞ are satisfactorily treated on this basis. They concluded on the other hand that the widely adopted three-state model is useful as well, the statistical weight ω associated with second-order interactions being treated as a somewhat arbitrarily adjustable parameter.[2,3]

Conformational energies of poly(alkyl vinyl ether)'s are more complicated, due to the presence of oxygen atoms. The semiempirical expressions customarily formulated were found to give somewhat higher estimates for conformational energies associated with "gauche oxygens" in the poly(alkylene oxide) chains.[1,9] Such gauche oxygen effects[10] will be discussed in the text. The dipole moments associated with side chains provide information which is obviously not available from the hydrocarbon polymers. The theory[11] set forth previously for the dipole moment of vinyl polmyers with flexible side chains is applicable to such properties.

Alkyl vinyl ethers $\mathrm{CH_2{=}CHOR}$ such as R = methyl, ethyl, isopropyl, or isobutyl have been known to give isotactic polymers when polymerized with homogeneous cationic catalysts.[12-14] Natta and co-workers[13,14] concluded from their

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x-ray crystallographic data that the conformations of poly(methyl vinyl ether) and poly(isobutyl vinyl ether) in the crystalline state are described by a 3/1 helix. A 17/5 helix was proposed for poly(isopropyl vinyl ether).[14] Since Bovey and Tiers[15] first applied NMR technique to the analysis of polymer tacticity, many studies of the steric structure of poly(alkyl vinyl ether)'s have been reported.[16] Isotacticities of the most stereoregular samples prepared at low temperature are usually found to be in the range 0.7–0.8 as expressed in the meso dyad content.

Experimental data on solution properties are less abundant. Manson and Arquette[17] reported viscosity and light-scattering measurements on fractionated samples of poly(methyl vinyl ether) and on unfractionated polymers having methyl, ethyl, isopropyl, and *n*-butyl groups in the side chain. The characteristic ratios C_∞ estimated from the results obtained in *n*-butanone (a good solvent) at 30 °C using the theory of Orofino and Flory[18] are 6.1–8.0 for fractionated samples, where the range indicated specifies the variation arising from the choice[19] of the hydrodynamic constant $\Phi = 2.1$ to 2.6×10^{21} dl cm^{-3} mol^{-1}. Values derived from unfractionated samples (R = methyl) tend to be somewhat higher ($C_\infty = 7.4$–9.6). Since the latter values are less reliable, we will not refer further to them. Experimental data on $\langle\mu^2\rangle/x$, the mean-square dipole moment per monomer residue, are available for poly(isopropyl vinyl ether)[20] and poly(isobutyl vinyl ether)[20–22] in the moderately isotactic to atactic region. Luisi et al.[20] reported values of 0.67 (isotactic) and 1.22 (atactic) at 25 °C for the former polymer, all moments being given in debyes. Values observed for the latter polymer are as follows: Takeda et al.[21] reported 1.35 (isotactic) and 1.14 (atactic) at 25 °C; Pohl and Zabusky[22] found 0.97 (isotactic) and 0.95 (atactic) at 30 °C; and Luisi et al.[20] reported 1.00 (isotactic) and 1.08 (atactic) at 25 °C. Various optically active poly(alkyl vinyl ether)'s have been prepared and studied extensively by Pino and co-workers.[23] Large enhancement in optical activity was observed for poly[(*S*)-1-methylpropyl vinyl ether] ($[\mathrm{M}]^{25}\mathrm{D} = +312$) over that of the model compound ($[\mathrm{M}]^{25}\mathrm{D} = +36.13$ for (*S*)-1-methylpropyl ethyl ether). Such observation parallels those found in optically active poly-α-olefins[23–25] as well as polyaldehydes.[26] Luisi et al.[20] obtained the dipole moment values ($\langle\mu^2\rangle/x$) of 0.90 (isotactic) and 0.98 (atactic) for this optically active polymer. They also reported[20] values of 1.02 (isotactic) and 1.06 (atactic) for poly[(*S*)-2-methylbutyl vinyl ether].

In this paper we treat the poly(alkyl vinyl ether)'s $\mathrm{H}{+}\mathrm{CH_2{-}CH(OR)}{+}_x\mathrm{CH_3}$ to correlate various configuration-dependent properties in terms of chain statistics. Conformational characteristics thus derived are specifically compared with those of the hydrocarbon analogues. Some of the preliminary results have been reported in a previous paper.[11]

Stereochemical Configuration and Geometrical Data

A portion of a poly(alkyl vinyl ether) chain in its planar, all-trans conformation is shown in Figure 1. As here represented, the substituent OR groups may be situated above or below the plane of the backbone depending upon the stereochemical configuration of the tertiary carbon atoms C^α.[27] We shall define this stereochemical arrangement as . . . *ddld* . . . when viewed from left to right. For a symmetric side chain such as R = $\mathrm{CH_3}$, $\mathrm{CH(CH_3)_2}$, or $\mathrm{CH_2CH(CH_3)_2}$, as pointed out by Flory and co-workers,[1,27] distinction between these two stereochemical configurations at C^α is unimportant. When R groups in the side chain involve asymmetric centers, however, the definition of *d* and *l* is no longer pseudoasymmetric. Such distinction will therefore become important in the later part of the paper in which configuration-dependent properties of poly(alkyl vinyl ether)'s having asymmetric side chains are discussed.[28]

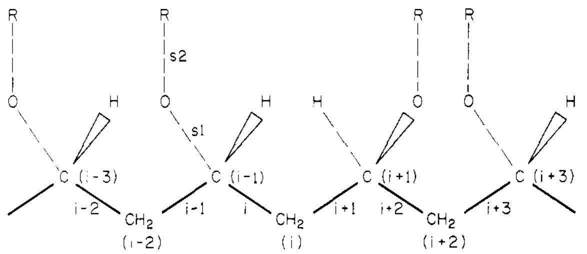


Figure 1. Schematic representation of a poly(alkyl vinyl ether) chain (. . . *ddld* . . .) in its planar trans conformation. Rotation states t, g$^+$, g$^-$ about bond s1 in the side chain are defined by the relative position of bond s2 in reference to bond *i*.

Table I
Geometrical Parameters Used for Poly(alkyl vinyl ether)'s

Bond length, Å		Bond angle, deg	
C–C	1.53	∠CCC	112
C–O	1.43	∠COC	111.5
C–H	1.10	∠CCO	110
		∠CCH	110

The bond lengths and bond angles used in this study are listed in Table I. The bond angles ∠CCC are assumed to be 112° for the skeletal backbone.[29,30] The ∠COC angle (111.5°) for the side chain was taken from the results obtained for dimethyl ether by microwave spectroscopy, as reported by Blukis, Kasai, and Myers.[31]

Conformational Energy Calculations

Dyads. Energy contours were computed for the *dd* meso and *dl* racemic dyad as a function of consecutive bond angles φ_i and φ_{i+1} using the standard expression[1]

$$E = E_\mathrm{t} + E_\mathrm{v} + E_\mathrm{c} \tag{1}$$

where

$$E_\mathrm{t} = (E_0/2)(1 - \cos 3\varphi) \tag{2}$$

$$E_\mathrm{v} = \sum_{k<l} [a_{kl} \exp(-b_{kl} r_{kl}) - c_{kl}/r_{kl}{}^6] \tag{3}$$

and

$$E_\mathrm{c} = \sum_{k<l} \delta_k \delta_l / \epsilon r_{kl} \tag{4}$$

Here φ represents the bond rotation angle measured from the trans form, and r_{kl} is the distance between the centers of atoms *k* and *l*. The threefold torsional potential intrinsic to a given bond is represented by eq 2. Barrier heights (E_0) of 2.8 and 1.8 kcal mol^{-1} were assigned to the rotations around C–C[1,32] and C–O bonds,[9] respectively. The two terms in eq 3 represent respectively the repulsive and attractive components of the van der Waals interactions between the nonbonded atoms. Values of the constants *a*, *b*, and *c* used in the present study are listed in Table II. Parameters for the atomic pairs H···H, C···H, and C···C are those used previously in the analysis of *n*-alkane chains.[32] For consistency, the other parameters were derived in a similar manner.[9] The quantity r_min given in the last column represents the distance at which the van der Waals interaction energy for the given nonbonded pair is a minimum. Coulombic contributions to the conformational energy are expressed by eq 4, where δ_k and δ_l denote partial electronic charges assigned to the nonbonded atoms *k* and *l*, respectively. Partial electronic charges were estimated[9,33] for

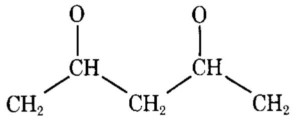
Table II
Parameters for Nonbonded van der Waals Interactions[a]

Atom pair k,l	$a_{kl} \times 10^{-3}$	b_{kl}	c_{kl}	r_{min}
H···H	9.95	4.54	45.2	2.6
C···H	86.1	4.57	127.0	3.1
C···C	908.6	4.59	363.0	3.6
O···H	41.85	4.57	96.5	2.9
O···O	223.0	4.59	245.0	3.2
C···O	438.5	4.59	294.0	3.4

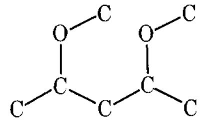
[a] Units of a, b, and c are such as to give E in kcal mol^{-1} when r is in Å.

the carbon ($\delta_C = 0.155$) and oxygen atoms ($\delta_O = -0.31$) joined by each C–O bond, using the bond moment of 1.07 D, which corresponds to the observed dipole moments 1.20 ± 0.10 D of various aliphatic ethers as summarized in McClellan's table.[34] The effective dielectric constant ϵ required in eq 4 was taken to be 3.0, the same value being used in the analysis of poly(alkylene oxide)'s in a previous paper.[9]

In practice, contributions from the torsional potentials and nonbonded van der Waals interactions were estimated for a portion of the chain such as



Omission of the flexible side chain beyond oxygen atoms can be justified provided that the steric effects imposed by the presence of R groups are separately taken into account (see below). For higher energy conformations, bond rotations about the adjacent bonds (φ_{i-1} and φ_{i+2}) were supplementarily adjusted to minimize the total energies. Coulombic contributions were calculated for the skeletal portion of the dyad



where an additional substituent (carbon) on each oxygen atom is included in the side chain to keep the electronic neutrality. The terminal O–C bonds thus introduced were placed in one of the lowest energy conformations.

Results of calculations are summarized in Table III. Well-defined energy minima were found for the conformations given in the second column, where g and $\bar{g}$ denote[27,35] the rotational state in which C$^\alpha$ is gauche relative to CH$_2$, and the one in which C$^\alpha$ is gauche relative to both CH$_2$ and O, respectively. Locations of the conformational energy minima (φ_i, φ_{i+1}) are listed in the third column. Following the definition introduced by Flory, Sundararajan, and DeBolt,[27] the rotation angles φ are measured in the opposite sense for the two bonds flanking a given C$^\alpha$. Thus, for the *dd* meso dyad, φ_i is expressed in a right-handed sense while φ_{i+1} is given in the opposite sense. Both φ_i and φ_{i+1} for the *dl* racemic dyad are expressed in the right-handed sense. Contributions to the conformational energy from eq 2 and 3 and those from eq 4 are separately given in the fourth and fifth column, where energies are expressed relative to that for the (gg)$_r$ conformation of the racemic dyad. The minimum energies associated with the conformation (φ_i, φ_{i+1}), given by the sum of the quantities listed in the preceding two columns, are shown in the last column. The $\bar{g}$ conformation inevitably imposes severe second-order steric interactions between groups bonded to the neighboring C$^\alpha$ atoms. The $\overline{gg}$ conformers are entirely dismissed. In conformations such as (gg)$_m$ for the meso and $(g\bar{g})_r$ (or $(\bar{g}g)_r$) for the racemic dyad, two methylene groups separated by four bonds are brought into close proximity. The energy minima appear in a doublet in the former, their energies being 2.62 kcal mol^{-1} above that of the stable conformer ((tg)$_m$ or (gt)$_m$). In the latter conformation, a pair of associated minima are unequally divided; the higher minimum (3.58 kcal mol^{-1}) at (+112°, −79°) (or (−79°, +112°)) is not listed in Table III. The (tt)$_m$ conformation (7°, 7°), which separates two neighboring oxygen atoms at a distance of ca. 2.75 Å, is of moderately low energy. Coulombic repulsion between these oxygen atoms (0.41 kcal mol^{-1}) is the major contribution involved in this conformation.

Low-energy conformations such as (tg)$_m$, (gt)$_m$, (tt)$_r$, and (gg)$_r$ require special attention. Their energy contours are shown in the vicinity of the corresponding minima in Figure 2. Small displacements of the rotational states from the perfectly staggered position 0, ±120° may be taken into account by adopting the expression[1,2]

$$\begin{aligned} \varphi_t &= \Delta\varphi_t \\ \varphi_g &= 120° - \Delta\varphi_g \end{aligned} \tag{5}$$

Results of calculations shown in Figure 2 suggest $\Delta\varphi_t \approx 0$ and $\Delta\varphi_g \approx 5°$ for the meso and $\Delta\varphi_t \approx 3°$ and $\Delta\varphi_g \approx 5°$ for the racemic dyad. The x-ray crystallographic data[13,14] on poly(methyl vinyl ether) and poly(isobutyl vinyl ether) are best described by a 3/1 helix; hence $\Delta\varphi_t = \Delta\varphi_g \approx 0$. Natta, Bassi, and Allegra[29] suggested displacements of $\Delta\varphi_t = \Delta\varphi_g = 10°$ for poly(isopropyl vinyl ether). By gathering such information together, possible displacements for the molecule unconstrained by the crystalline lattice may be considered to be in the range $0 \leq \Delta\varphi_t < \Delta\varphi_g \leq 10°$.

Side Chain Effect. We define the rotational isomeric state t, g$^+$, and g$^-$ for the first articulated bond (s1) by relative position of the second bond (s2) in reference to the skeletal bond i (see Figure 1). In keeping with the previous definition,[27]

Table III
Results of Conformational Energy Calculations for Meso and Racemic Dyads

Dyad	Conformation	(φ_i, φ_{i+1})	$E_t + E_v$	E_c	E_{min}
Meso (*dd*)	tt	(7°, 7°)	−0.18	0.41	0.23
	tg, gt	(0°, 115°), (115°, 0°)	−0.24	−0.20	−0.44
	t$\bar{g}$, $\bar{g}$t	(23°, −118°), (−118°, 23°)	1.18	−0.27	0.91
	gg	(116°, 79°) (79°, 116°)	2.19	−0.01	2.18
	g$\bar{g}$, $\bar{g}$g	(90°, −109°), (−109°, 90°)	2.37	−0.23	2.14
Racemic (*dl*)	tt	(3°, 3°)	−0.58	−0.29	−0.87
	tg, gt	(23°, 113°), (113°, 23°)	0.74	−0.08	0.66
	t$\bar{g}$, $\bar{g}$t	(13°, −113°), (−113°, 13°)	0.92	0.27	1.19
	gg	(115°, 115°)	0.0	0.0	0.0
	g$\bar{g}$, $\bar{g}$g	(77°, −118°), (−118°, 77°)	2.52	−0.17	2.35

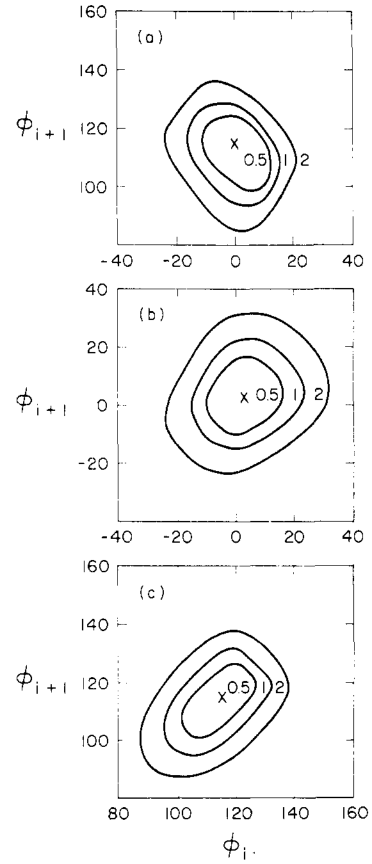


Figure 2. Energies calculated in the vicinity of low-energy conformations as a function of φ_i and φ_{i+1}: (a) $(tg)_m$, (b) $(tt)_r$, and (c) $(gg)_r$, respectively. Energy contours are labeled in kilocalories per mole relative to each minimum indicated by X. The energy map for the $(gt)_m$ conformation may be obtained from that for the $(tg)_m$ (part a) by inversion about the axis defined by $\varphi_i = \varphi_{i+1}$.

bond rotations in the side chain are measured in the right-handed sense when they are associated with the *d* configuration at C^{α}. The opposite applies to those with the *l* configuration.

In treating the dipole moment of poly(alkyl vinyl ether)'s, spatial arrangement of the s2 bond (O–C) is important. The first-order interactions taking place around bond s1 should be essentially identical with those encountered in methyl isopropyl ether. Conformational energy calculations for this model yielded two identical energy minima for the C_1 form with displacements $\Delta\varphi \approx 20°$ from the regularly staggered position. Due to very severe steric overlaps between methyl groups, the conformational energy associated with the C_s form is very high (4.2 kcal mol^{-1} relative to the other two minima). Snyder and Zerbi[36] studied a series of isopropyl ethers $(CH_3)_2CHOR$ having R = CH_3, CH_2CH_3, and $CH(CH_3)_2$ by infrared spectroscopy. In the case of R = CH_3, two weak bands, which were not found in the solid state (−196 °C), were detected in the spectrum of the liquid at 24 °C. These were assigned to the C_s form. With R = CH_2CH_3 and $CH(CH_3)_2$, however, no bands were observed which would indicate the presence of the corresponding C_s conformer at 25 °C. These results suggest that the g^- conformation is almost entirely suppressed around bond s1 in the poly(alkyl vinyl ether) chains. A displacement of $\Delta\varphi_s = 20°$ for the t and g^+ state about bond s1 has been suggested from the crystallographic analysis on poly(methyl vinyl ether)[30] and poly(isopropyl vinyl ether).[29]

The second-order interactions between the β substituent (CH, CH_2, or CH_3) in the side chain and either one of the methine groups ($(CH)_{i-3}$ or $(CH)_{i+1}$) in the main chain involve very large steric overlaps. As previously discussed in the analysis of poly(trimethylene oxide),[9] no legitimate rotational minima may be found for these interactions. Contribution from such conformation is therefore entirely neglected in the succeeding treatment. Side chain conformations dependent on the rotation about bonds beyond s2 will be discussed in the following section.

Table IV
Separate Interaction Energy Parameters

Statistical wt factor	Interacting groups	Interaction energy parameter, kcal mol^{-1}
η	$\mathrm{C^{\alpha}H\text{-}CH_2 \rightarrow C^{\alpha}H\text{-}O}$	−0.44
τ	$\mid$ $\mathrm{CH_2}$	0.5
ω''	$\mathrm{O\text{-}C^{\alpha}H \leftarrow CH_2 \rightarrow C^{\alpha}H\text{-}O}$	1.1
ω'	$\mathrm{CH_2—C^{\alpha}H \leftarrow CH_2 \rightarrow C^{\alpha}H\text{-}O}$	0.9–1.6
ω	$\mathrm{CH_2C^{\alpha}H \leftarrow CH_2 \rightarrow C^{\alpha}H—CH_2}$	1.9–2.2

Statistical Weights

Statistical weight matrices generally applicable to the meso and racemic dyad of a vinyl polymer have been given by Flory et al.[27] Adopting their notations, we have for the meso dyad,

$$\mathbf{U}_m'' = \begin{bmatrix} \eta^2\omega'' & \eta & \eta\tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\tau\omega' & \tau\omega' & 0 \end{bmatrix} \tag{6}$$

and for the racemic dyad

$$\mathbf{U}_r'' = \begin{bmatrix} \eta^2 & \eta\omega' & \eta\tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\tau\omega'' & \tau\omega & 0 \end{bmatrix} \tag{7}$$

where rows and columns are indexed to rotational states in the order t, g, and $\bar{g}$ for bonds like *i* and *i* + 1, respectively (see Figure 1). Each statistical weight factor is normalized to the weight of unity for the gg state of the racemic dyad. Since these matrices are presented in a symmetrical form, distinctions between *dd* and *ll* (meso) and between *dl* and *ld* (racemic) are not required. Each element of these statistical weight matrices may be identified with one of the conformational energies given in Table III using a Boltzmann factor. Thus, for example, the statistical weight factor η, designating the first-order interaction between oxygen and $C^{\alpha}H$, may be given for the tg or gt state of eq 6 by

$$\eta = \exp(-E_\eta/RT) \tag{8}$$

where $E_\eta = -0.44$ kcal mol^{-1}. The same factor may be estimated for the tt state of eq 7, giving $E_\eta = -0.435$ kcal mol^{-1}. The good agreement between these two values assures the applicability of these schemes (eq 6 and 7) to poly(alkyl vinyl ether) chains. The statistical weight factor τ, representing the first-order interaction associated with the $\bar{g}$ conformation, cannot be estimated explicitly by separating it from the associated second-order interaction factors. In the following treatment, therefore, the energy parameters $E_{\min}$ given in Table III will be used without further resolution. To facilitate comparison with the other related polymer systems, however, the range estimated for the individual factors using $E_\tau = 0.5$ kcal mol^{-1} is listed in Table IV.

The statistical weight matrix U′ generally applicable to any vinyl chains such as $H(CH_2CHX)_xCH_3$ in conjunction with U″'s given in eq 6 and 7 takes the form[27]

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & \omega & 1 \\ 1 & 1 & 0 \end{bmatrix} \tag{9}$$

where the conformational energy associated with the factor ω should be approximately equivalent to that estimated for the $(gg)_m$ conformation. Statistical weights attributable to side chain conformations may be evaluated according to the procedure described elsewhere.[6,11] Thus,

$$\beta(\xi,\zeta) = \mathbf{S}_1{}^{(p)} \tag{10}$$

where ξ and ζ denote each of the rotational states about skeletal bonds ($i - 1$ and i in Figure 1) on both sides of C^α. Each $\mathbf{S}_h$ in eq 10 represents the statistical weight matrix for bond h in the side chain; it is formulated in a manner similar to the procedure employed for statistical weight matrices of the skeletal bonds of a chain molecule.[1,37] Each element (ξ,ζ) of the $\mathbf{U}'$ matrix given in eq 9 is multiplied by the corresponding statistical weight factor $\beta(\xi,\zeta)$ to complete the expressions required for the vinyl polymer system with flexible side chains.[6,11] Thus

$$\mathbf{U}' = [u_{\xi\zeta}'\beta(\xi,\zeta)] \tag{11}$$

As is easily shown by inspection of a model, statistical weight matrices $\mathbf{U}''$ should not be affected by the side chain conformations under the assumption that interactions of higher orders are negligible.

As a consequence of conformational energy considerations presented in the preceding section, the state g^- is suppressed for bond s1. With a symmetrical side chain OR, various conformations realizable through rotations about the second or a higher bond dictate equal statistical weights for the rotational states (t and g^+) permitted for bond s1. Side chain contributions, as assembled in a matrix scheme, are given by

$$\beta = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 2 & 2 \\ 1 & 2 & 2 \end{bmatrix} \tag{12}$$

This simple expression should be generally applicable to poly(alkyl vinyl ether) chains having a symmetrical side chain such as R = CH_3, CH_2CH_3, $CH(CH_3)_2$, or $CH_2CH(CH_3)_2$.[38]

When the R group involves an asymmetric center, however, statistical weights associated with the t and g^+ states for bond s1 are no longer equivalent. Thus, any simple cancellation of statistical weights between these two states cannot be expected in principle. In general, the β matrix should assume the form either

$$\beta_d = \begin{bmatrix} 0 & b & b \\ a & a+b & a+b \\ a & a+b & a+b \end{bmatrix} \tag{13}$$

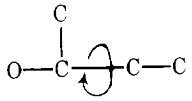
or

$$\beta_l = \begin{bmatrix} 0 & a & a \\ b & a+b & a+b \\ b & a+b & a+b \end{bmatrix} \tag{14}$$

depending upon the stereochemical configuration (d or l) at C^α. With R = $C^*H(CH_3)CH_2CH_3(S)$, a and b may be identified as

$$\begin{aligned} a &= \eta + 1 + \tau \\ b &= 1 + \tau \end{aligned} \tag{15}$$

where both η and τ are statistical weight factors assigned to the first-order interactions dependent on the rotation about bond s3, i.e.,



(the terminal CH_3 group is gauche relative to the oxygen (η) and gauche relative to both oxygen and CH_3 (τ)). Since these interactions resemble those encountered previously in the analysis of the dyads, the same notations are applied. Essentially identical situations may be found in the poly(butene-1 oxide) chain; those occur through rotations about the first articulated bond in the side chain. Analysis of the characteristic ratio C_∞ of this polymer, supplemented by conformational energy calculations on a relevant model, suggests $E_\eta \approx -0.5$ and $E_\tau \approx 0.5$ kcal mol^{-1}.[39]

For R = $CH_2C^*H(CH_3)CH_2CH_3(S)$, a and b are given by

$$\begin{aligned} a &= 3 + 2\sigma + 2\tau' + 2\tau'' + \sigma\tau'' + \omega' \\ b &= 3 + \sigma + 2\tau' + 2\tau'' + \sigma\tau'' + \omega' + \sigma\omega' \end{aligned} \tag{16}$$

where conformational energies estimated for the individual interactions (shown in parentheses) are as follows: E_σ(C—O$\curvearrowright$C—C)[9] = 0.9, $E_{\tau'}$(O—C$\curvearrowright$C(C)—C) = 0.5, $E_{\tau''}$(C—C(C)$\curvearrowright$C—C)[3] = 1.5, and $E_{\omega'}$(O$\curvearrowleft$C$\curvearrowright$C—C—C)[9] = 0.7 kcal mol^{-1}. Since no relevant experimental data are available for $E_{\tau'}$, the value adopted above is somewhat uncertain. As will be noted later, however, only the ratio such as $(a - b)/b$ is important for the present purpose. Some ambiguity associated with $E_{\tau'}$ is therefore inconsequential.

Multiplications of eq 9 by eq 13 and 14 in the manner specified by eq 10 yield a pair of $\mathbf{U}'$ matrices, i.e., $\mathbf{U}_d'$ and $\mathbf{U}_l'$, for an asymmetric side chain. With a symmetric side chain $a = b$, and naturally eq 13 and 14 reduce to eq 12.

Special care must be taken for the terminal bonds of the chain. Lack of the preceding or the following bond affects side chain conformations as well. For a symmetric side chain, we define for the second bond (or the initial bond of the first dyad),

$$\mathbf{U}_1' = \begin{bmatrix} 1 & 2 & 2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{17}$$

and for the last bond,

$$\mathbf{U}_x = \begin{bmatrix} 1 \\ 2 \\ 2 \end{bmatrix} \tag{18}$$

Combined use of $\mathbf{U}_0 = [1 \quad 0 \quad 0]$ for the first bond of the chain leads to the standard expression[27] for the configurational partition function

$$Z = \mathbf{U}_0 \left(\prod_{k=1}^{x-1} \mathbf{U}_k'\mathbf{U}_k'' \right) \mathbf{U}_x \tag{19}$$

where $\mathbf{U}_k''$'s must be properly chosen depending upon the stereochemical character of the kth dyad.

For a polymer carrying asymmetric side chains such as those discussed above, expressions to be used for eq 17 and 18 are given by

Table V
Fraction of Conformers for Meso and Racemic 2,4-Dimethoxypentane

		Obsd[a]			
Isomer	Conformation (C–C bond)	Chlorobenzene	Chlorobenzene–methylene chloride	Nitro-methane	Calcd[b]
Meso	t	0.50	0.54	0.50	0.52
	g	0.45	0.43	0.46	0.43
	$\bar{\mathrm{g}}$	0.05	0.03	0.04	0.05
Racemic	t	0.64	0.46	0.47	0.52
	g	0.24	0.40	0.47	0.45
	$\bar{\mathrm{g}}$	0.12	0.14	0.06	0.03

[a] Estimated from the observed vicinal coupling constants: K. Matsuzaki, K. Sakota, and M. Okada, *J. Polym. Sci., Part A-2,* **7,** 1444 (1969). [b] Calculated for a temperature of 20 °C.

$$\mathbf{U}_{d;1}' = \begin{bmatrix} a & a+b & a+b \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_{l;1}' = \begin{bmatrix} b & a+b & a+b \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{20}$$

and by symmetry,

$$\mathbf{U}_{d;x} = \begin{bmatrix} b \\ a+b \\ a+b \end{bmatrix}$$

$$\mathbf{U}_{l;x} = \begin{bmatrix} a \\ a+b \\ a+b \end{bmatrix} \tag{21}$$

where subscripts d and l specify the stereochemical configuration of C^{α} at the terminals. Parameters a and b are given in eq 15 and 16 for the individual polymer systems. For an asymmetric vinyl chain, $\mathbf{U}_k'$ as well as $\mathbf{U}_k''$ in eq 19 vary with the sterechemical character of the corresponding dyad.

Conformational Analysis on 2,4-Dimethoxypentane

Matsuzaki, Sakota, and Okada[40] studied meso and racemic isomers of 2,4-dimethoxypentane, the dimer model, by NMR spectroscopy. Vicinal coupling constants between methine and methylene protons were measured in various solvents. Reevaluation of their data gave the fraction of various conformers as listed in the third through fifth columns of Table V, where values of $J_{\mathrm{T}} = 10.7$ and $J_{\mathrm{G}} = 2.7$ Hz were adopted for all trans and gauche couplings,[40,41] respectively. These results differ from those given by the original authors[40] for inclusion of $\bar{\mathrm{g}}$ states. Calculations carried out using conformational energy parameters given in Table III yielded the results shown in the last column. The agreement is satisfactory within experimental uncertainties.

In order to examine some possible anomeric effect associated with gauche interactions involving oxygen atoms,[9] calculations were carried out for another (modified) set of conformational energy parameters. From the previous studies on poly(alkylene oxide)'s,[9] the extra stabilization energy of the order of 0.2–0.3 kcal mol^{-1} may be expected for each of the first-order interactions represented by η and possibly a smaller amount[39] for those designated with τ in eq 6 and 7. Fractions estimated for the extra stabilization energy $\Delta E_{\eta} = 0.2$ kcal mol^{-1} are 0.53 (t), 0.42 (g), and 0.05 ($\bar{\mathrm{g}}$) for the meso and 0.65 (t), 0.32 (g), and 0.03 ($\bar{\mathrm{g}}$) for the racemic isomer, respectively. The major effect arising from such revisions is to stabilize the tt conformation of the racemic isomer. The value obtained above is close to that observed in chlorobenzene, being higher than those estimated using the other solvents (see Table V). These results suggest that the "gauche oxygen effect", if any exists, should be in the range 0–0.2 kcal mol^{-1} in these systems.

Characteristic Ratios C_{∞} and Mean-Square Dipole Moments $\langle\mu^2\rangle/x$

Corresponding to the expression given for the configurational partition function Z in eq 19, the mean square of the second moment M^2 for a vinyl chain is expressed by[27]

$$\langle M^2\rangle = Z^{-1}\mathcal{G}_0\left(\prod_{k=1}^{x-1}\mathcal{G}_k'\mathcal{G}_k''\right)\mathcal{G}_x \tag{22}$$

where $\mathcal{G}_k'$ and $\mathcal{G}_k''$ are the generator matrices defined for the first and the second bond of the kth dyad, respectively. When the bond moment $\mathbf{m}$ is defined for a single bond of the skeletal chain, pseudoelements of matrix $\mathcal{G}_k'$ (similarly $\mathcal{G}_k''$) may be expressed as

$$\mathcal{G}_k' = [u_{\xi\zeta}'\mathbf{G}_{\zeta}']_k \tag{23}$$

where

$$\mathbf{G}_{\zeta}' = \begin{bmatrix} 1 & 2\mathbf{m}^{\mathrm{T}}\mathbf{T} & \mathrm{m}^2 \\ \mathbf{0} & \mathbf{T} & \mathbf{m} \\ 0 & \mathbf{0} & 1 \end{bmatrix} \tag{24}$$

$\mathbf{m}^{\mathrm{T}}$ being the transpose of $\mathbf{m}$. Here $\mathbf{T}$ is the transformation[27] relating the Cartesian coordinate system affixed to bond $i + 1$ to that affixed to bond i, thus being defined as a function of the bond angle $(\pi - \theta)$ between these two bonds and the rotational states φ_{ζ} of bond i. For the terminal bonds, $\mathbf{G}_0$ and $\mathbf{G}_x$ may be identified as the first row and the final column of eq 24, respectively. Identification of $\mathbf{m}$ with the bond vector

$$\mathbf{l} = \begin{bmatrix} l \\ 0 \\ 0 \end{bmatrix} \tag{25}$$

gives the mean square of the chain vector $\langle r^2\rangle_0$ according to eq 22.

In the poly(alkyl vinyl ether) system, bond dipoles

$$\mathbf{m}_1 = -\mathbf{m}_2 = \begin{bmatrix} m \\ 0 \\ 0 \end{bmatrix} \tag{26}$$

may be assigned to the first (s1) and the second bond (s2) of side chains (see Figure 1), respectively, corresponding to the group dipole moment of the ether linkage. The orientation of bond dipole $\mathbf{m}_1$, being invariably defined in the coordinate system affixed to bond i, depends only on the skeletal conformation of the chain. Spatial arrangement of $\mathbf{m}_2$ requires specification of rotational states (t, g$^+$, g$^-$) about bond s1 in addition to those of the backbone chain.

The theory set forth previously,[11] which is generally applicable to dipole moments of vinyl polymers with flexible side chains, may be adopted with minor modifications. The bond moment $\mathbf{m}$ appearing in eq 24 should be replaced by the averaged quantity $\hat{\mathbf{m}}$ over all side chain conformations in the coordinate system fixed to bond i. Thus, for a given skeletal conformation (ξ,ζ) about bonds $i-1$ and i, we have

$$\hat{\mathbf{m}} = \begin{bmatrix} \hat{\mathrm{m}}_x \\ \hat{\mathrm{m}}_y \\ \hat{\mathrm{m}}_z \end{bmatrix} = \mathbf{T}_0\mathbf{m}_1 + \beta^{-1}\mathbf{T}_0(\mathbf{S}_1 \otimes \mathbf{E}_3)\|\mathbf{T}\|\,(\mathbf{E}_2 \otimes \mathbf{m}_2)\mathbf{S}_2{}^{p-1} \tag{27}$$

where ⊗ denotes the direct product. The factor β represents the sum of statistical weights as defined by eq 10, $\mathbf{E}_2$ and $\mathbf{E}_3$ being the identity matrices of the order specified by the subscripts. The matrix $\mathbf{S}_1$ is expressed in a 1 × 2 row form by eliminating the g$^-$ conformation for bond s1,[37] and consequently

$$\|\mathbf{T}\| = \begin{bmatrix} \mathbf{T}_\mathrm{t} & \\ & \mathbf{T}_{\mathrm{g}^+} \end{bmatrix} \tag{28}$$

where each transformation matrix is defined in the usual manner[1] for the given rotational state about bond s1. The matrix $\mathbf{T}_0$ performs the transformation from the coordinate system of the first bond s1 in the side chain to that of skeletal bond i:

$$\mathbf{T}_0 = \begin{bmatrix} \cos\theta_0 & -\sin\theta_0 & 0 \\ \sin\theta_0\cos\varphi_0 & \cos\theta_0\cos\varphi_0 & -\sin\varphi_0 \\ \sin\theta_0\sin\varphi_0 & \cos\theta_0\sin\varphi_0 & \cos\varphi_0 \end{bmatrix} \tag{29}$$

where $\theta_0 = \angle C_iC_{i-1}O = 110°$, and $\varphi_0 = -60°$ is the dihedral angle between planes defined by bonds $i-1$ and i and by bonds s1 and i, respectively. (A choice of $\theta_0 = -\angle C_iC_{i-1}O$ and $\varphi_0 = 120°$ reduces eq 29 to the conventional expression.[1]) The expression 24 now requires specification of two consecutive rotational states (ξ,ζ) about bonds $i-1$ and i. Thus the generator matrix $\mathcal{G}_k{}'$ may be read as

$$\mathcal{G}_k{}' = [u_{\xi\zeta}{}'\mathbf{G}_{\xi\zeta}{}']_k \tag{30}$$

The mean square of dipole moment $\langle\mu^2\rangle$ can be calculated by eq 22 provided that proper account[11] is taken of the terminal bonds.

Symmetric Side Chains. Characteristic ratios $C_\infty = \langle r^2\rangle_0/nl^2$, $n = 2x$ being the number of bonds, calculated for Monte Carlo chains with $x = 200$ units ($n = 400$ bonds) using the conformational energy parameters given in Table III, are plotted in Figure 3a as a function of the dyad replication probability Pr, i.e., the probability of a meso placement. To facilitate comparison with experimental observations, computations were carried out for a temperature of 30 °C. The solid curve indicates results obtained assuming the perfectly staggered isomeric states ($\Delta\varphi_\mathrm{t} = \Delta\varphi_\mathrm{g} = 0$). Values of C_∞ vary from 15.9 for the isotactic (Pr = 1.0) to 9.9 for the syndiotactic chain (Pr = 0.0) through minimum values of ca. 4 in the range Pr = 0.3 to 0.5. As shown by the dashed curve, adoption of displacement $\Delta\varphi_\mathrm{g} = 10°$, $\Delta\varphi_\mathrm{t}$ being unchanged, enhances C_∞ of the syndiotactic (racemic) chain to 12.7. The effect diminishes gradually with increase in meso dyad placements; $C_\infty = 16.1$ at Pr = 1.0.

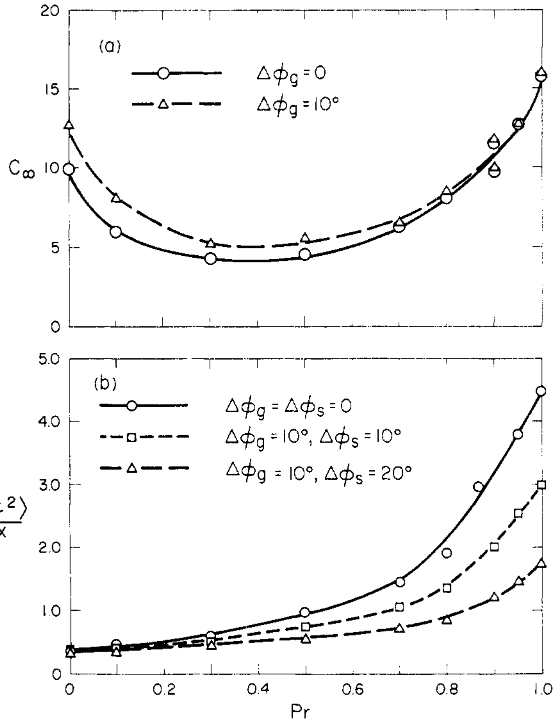


Figure 3. (a) Characteristic ratios C_∞ calculated for poly(alkyl vinyl ether)'s having a symmetric side chain. Computations were carried out using Monte Carlo Chains of 200 units for given values of $\Delta\varphi_\mathrm{g}$, $\Delta\varphi_\mathrm{t}$ being kept at 0; $T = 30$ °C. (b) Mean-square dipole moments per repeat unit $\langle\mu^2\rangle/x$ calculated for Monte Carlo chains of 100 units. Displacements of rotational states are indicated in the figure for the main chain ($\Delta\varphi_\mathrm{g}$) and side chain (about s1) conformations ($\Delta\varphi_\mathrm{s}$), respectively, $\Delta\varphi_\mathrm{t}$ being kept at 0; $T = 25$ °C.

The mean-square dipole moment $\langle\mu^2\rangle/x$ (25 °C) calculated for chains with $x = 100$ units is shown in Figure 3b, the moment μ being given in debyes. Variation of $\langle\mu^2\rangle/x$ with $\Delta\varphi$'s is most distinct for the isotactic chain (Pr = 1.0); the value of $\langle\mu^2\rangle/x = 4.5$ calculated for the perfect staggering ($\Delta\varphi_\mathrm{t} = \Delta\varphi_\mathrm{g} = \Delta\varphi_\mathrm{s} = 0$) decreases to 3.0 with displacements of $\Delta\varphi_\mathrm{g} = \Delta\varphi_\mathrm{s} = 10°$ and further to 1.7 for $\Delta\varphi_\mathrm{s} = 20°$. In contrast to the results shown for C_∞ in Figure 3a, values of $\langle\mu^2\rangle/x$ decrease monotonically from Pr = 1.0 to 0.0. The ratio calculated for the syndiotactic chain varies little with alterations in rotational minima; $\langle\mu^2\rangle/x = 0.36$, 0.37, and 0.38 respectively for the three sets of $\Delta\varphi$'s given above.

The characteristic ratios C_∞ estimated from experimental data[17] are in the range 6 to 8 for moderately isotactic poly(methyl vinyl ether). The results obtained for polymers with R = C_2H_5, i-C_3H_7, or n-C_4H_9 on unfractionated samples, although less reliable, possibly suggest that these ratios C_∞ are in a similar range.[17] As indicated by NMR studies,[16] tacticities of these "moderately" isotactic samples may be in a range of Pr = 0.7 to 0.8. Experimental observations are satisfactorily reproduced in Figure 3a by either set of parameters chosen for $\Delta\varphi$'s.

The mean-square dipole moment $\langle\mu^2\rangle/x$ observed[20] for moderately isotactic poly(isopropyl vinyl ether) (0.67) corresponds to that calculated for the set $\Delta\varphi_\mathrm{g} = 10°$ and $\Delta\varphi_\mathrm{s} = 20°$ at Pr ≈ 0.7. The value $\langle\mu^2\rangle/x$ should decrease further if larger displacements in $\Delta\varphi_\mathrm{t}$ or $\Delta\varphi_\mathrm{s}$ are assumed for the bulky substituent such as R = $CH(CH_3)_2$; e.g., a choice of $\Delta\varphi_\mathrm{t} = 10°$ gives agreement with the observed value at Pr ≈ 0.8. The higher value (1.22) observed[20] for the atactic sample is how-

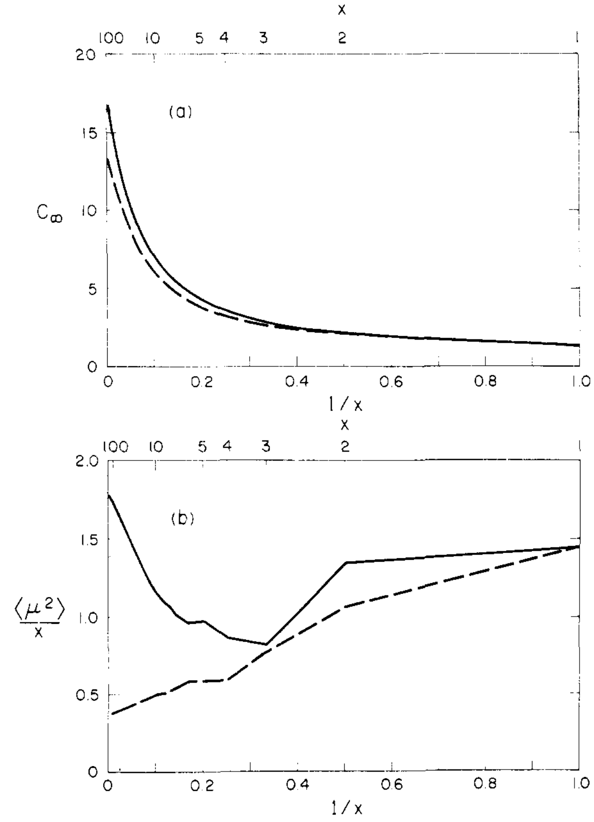


Figure 4. Dependence of C_∞ and $\langle\mu^2\rangle/x$ on $1/x$. The solid curves indicate results for the isotactic (Pr = 1.0) and the dashed curves for the syndiotactic chain (Pr = 0.0), both having a symmetric side chain. Calculations were carried out for (a) $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$ and (b) $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$, $\Delta\varphi_s = 20°$.

ever at variance with the results presented in Figure 3b. Observed dipole moments for poly(isobutyl vinyl ether)[20-22] vary little with the tacticity in the moderately isotactic to atactic region. Experimental values $\langle\mu^2\rangle/x = 0.95$ to 1.35 are reasonably approximated by the curves calculated for $\Delta\varphi_g = 10°$ and $\Delta\varphi_s = 10°$ to 20° in the range Pr = 0.7 to 0.8.

Possible effects arising from the extra stabilization energy associated with "gauche oxygen" placements were examined using the set ($\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$, $\Delta\varphi_s = 20°$). Inclusion of $\Delta E_\eta = 0.3$ kcal mol^{-1} raises C_∞ from 10.5 to 12.7 for Pr = 0.0, but the value decreases slightly (ca. 3%) at Pr = 1.0. Consequently the ratios C_∞ are insensitive to such modifications in the moderately isotactic region. The effect on $\langle\mu^2\rangle/x$ was estimated to be trivial (<3%) over the entire range of Pr. Based on these results, conformational energy parameters given in Table III were adopted without any revision in the following calculations.

In Figures 4a and 4b, values of C_∞ and $\langle\mu^2\rangle/x$ calculated for the isotactic and syndiotactic chains are plotted as a function of $1/x$. While the ratios C_∞ decrease monotonically with $1/x$, values of $\langle\mu^2\rangle/x$ vary somewhat periodically. These may be understood from the fact that the backbone chain prefers helical conformations. The dipole moment of the isotactic chain reaches a minimum value at $x = 3$ (and also a little minimum at $x = 6$) corresponding to the 3/1 helix observed for high polymers in the crystalline state.[13,14]

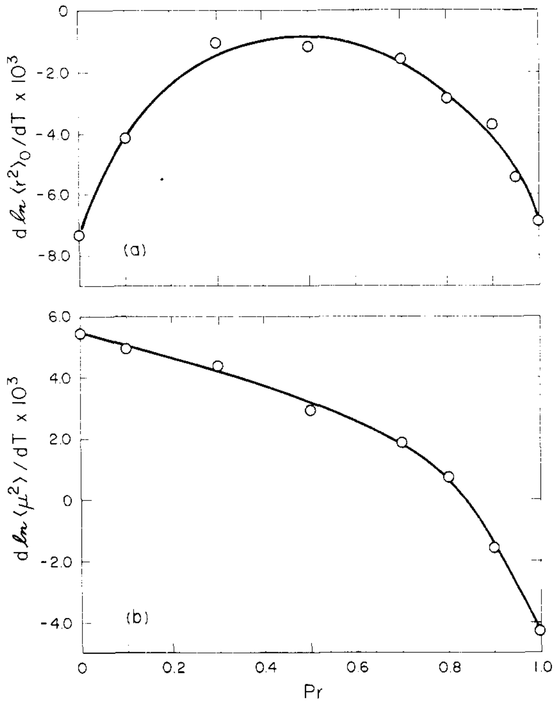


Figure 5. Variation of temperature coefficients d ln $\langle r^2\rangle_0/dT$ and d ln $\langle\mu^2\rangle/dT$ as a function of Pr; see legend for Figure 3. Calculations were carried out for (a) $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$ over the temperature range 30–80 °C and (b) $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$, $\Delta\varphi_s = 20°$ over the range 25–75 °C.

The temperature coefficients d ln $\langle r^2\rangle_0/dT$ and d ln $\langle\mu^2\rangle/dT$ calculated over the temperature range 30–80 °C and 25–75 °C for the set ($\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$, $\Delta\varphi_s = 20°$) are plotted in Figures 5a and 5b, respectively, as a function of Pr. Due to the considerable spatial extension of the backbone chain, large negative values of d ln $\langle r^2\rangle_0/dT$ are expected for the stereoregular polymers, either isotactic or syndiotactic. Values of ca. -2.0×10^{-3} K^{-1} are estimated for moderately isotactic polymers (Pr = 0.7 to 0.8). The temperature coefficient of the dipole moment varies from large positive to large negative values with Pr; for the range Pr = 0.8 to 0.5, d ln $\langle\mu^2\rangle/dT$ = 1.0 to 3.0×10^{-3} K^{-1}. Experimental data (Takeda et al.[21]) observed between 25° and 50 °C for poly(isobutyl vinyl ether) lead to d ln $\langle\mu^2\rangle/dT$ = ca. 3.0×10^{-3} K^{-1} in the corresponding range of tacticity.

Asymmetric Side Chains. Calculations were carried out for poly[(*S*)-1-methylpropyl vinyl ether] and poly[(*S*)-2-methylbutyl vinyl ether] using conformational energy parameters set forth previously. The characteristic ratios C_∞ computed for chains with $x = 200$ units ($n = 400$ bonds) for a temperature of 30 °C are shown in Figure 6a. Results indicated by the dashed curve for R = $CH_2C^*H(CH_3)C_2H_5$(S) are entirely indistinguishable from those calculated for the symmetric side chain (the dashed curve in Figure 3a). The effect of asymmetric side chains becomes distinguishable only for polymers having R = $C^*H(CH_3)C_2H_5$(S) either in the isotactic (Pr > 0.8) or in the syndiotactic region (Pr < 0.2). Large enhancement in C_∞ may be expected for the stereoregular chains at Pr = 1.0 and 0.0. Such effect may be best described by a parameter such as $q = (a - b)/b$, a and b being given in eq 15 or 16; $q = 0.003$ for the former and 1.63 for the latter polymer. The effect of asymmetric side chains should be suppressed for $q = 0$ (i.e., $a = b$). Thus q provides a measure of the "asymmetric effect".[42]

Variation of the mean-square dipole moment $\langle\mu^2\rangle/x$ with Pr is shown in Figure 6b, where computations were carried out for $x = 100$ units for a temperature of 25 °C. These results are to be compared with those given in Figure 3b (the dashed curve) calculated for the symmetric side chain. On the contrary to what is observed for C_∞ (Figure 6a), no enhancement in $\langle\mu^2\rangle/x$ may be expected for the syndiotactic chain; in fact $\langle\mu^2\rangle/x$ decreases slightly with increase in the q value. In the

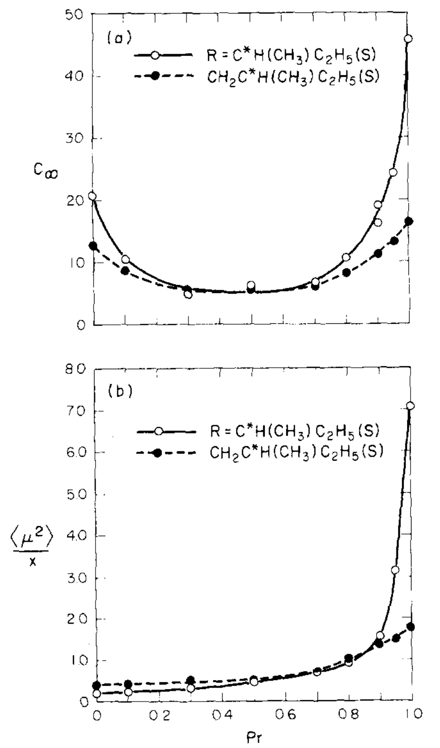


Figure 6. Characteristic ratios and mean-square dipole moments calculated for poly(alkyl vinyl ether)'s carrying asymmetric side chains ($R = C^*H(CH_3)C_2H_5(S)$ and $CH_2C^*H(CH_3)C_2H_5(S)$). (a) C_∞: Monte Carlo chains of $x = 200$ units; $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$; $T = 30$ °C. (b) $\langle\mu^2\rangle/x$: $x = 100$ units; $\Delta\varphi_t = 0$, $\Delta\varphi_g = 10°$, $\Delta\varphi_s = 20°$; $T = 25$ °C.

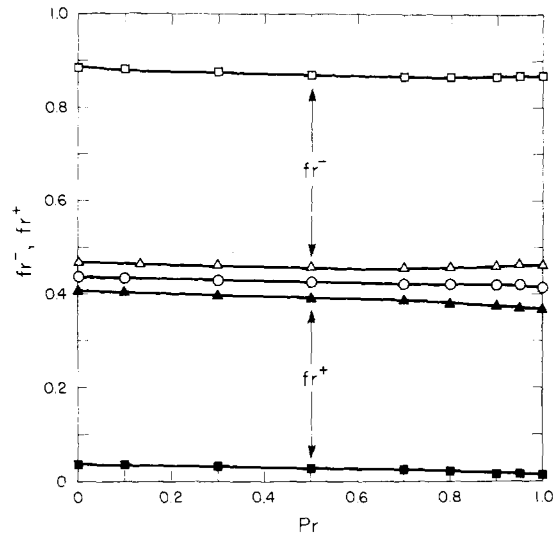


Figure 7. Fractions of the left-handed (fr^-) and right-handed helical conformations (fr^+). The open (□) and filled squares (■) indicate the results obtained for $R = C^*H(CH_3)C_2H_5(S)$, and the open (△) and filled triangles (▲) for $R = CH_2C^*H(CH_3)C_2H_5(S)$. For a symmetric side chain, $fr^- = fr^+$, the results are shown by the open circles (○). All calculations were carried out for Monte Carlo chains of 200 units for a temperature of 25 °C.

highly isotactic region ($Pr > 0.9$), values of $\langle\mu^2\rangle/x$ increase very rapidly with Pr for $R = C^*H(CH_3)C_2H_5(S)$.

Experimental data on $\langle\mu^2\rangle/x$ are available for these polymers in the moderately isotactic to atactic region;[20] 0.90 (isotactic), 0.98 (atactic) for $R = C^*H(CH_3)C_2H_5(S)$ and 1.02 (isotactic), 1.06 (atactic) for $R = CH_2C^*H(CH_3)C_2H_5(S)$, respectively, in benzene at 25 °C. Values obtained for isotactic polymers (fractions insoluble in diethyl ether) are in agreement with those calculated for $Pr \approx 0.8$. Slightly higher values derived from atactic (acetone insoluble) fractions are however somewhat at variance with the present analysis (see Figure 6b). As pointed out by Luisi et al.,[20] the dipole moment of poly(alkyl vinyl ether) is quite insensitive to the chemical structure of side chains, whether symmetric or asymmetric, in the moderately isotactic region. Distinct effects should be expected only for the "highly" isotactic polymers having high q values.

Temperature coefficients $d \ln \langle r^2\rangle_0/dT$ and $d \ln \langle\mu^2\rangle/dT$ calculated as a function of Pr resemble those shown in Figures 5a and 5b, respectively, for the symmetric side chains. Absolute values are somewhat larger for $R = C^*H(CH_3)C_2H_5(S)$ in the highly isotactic and syndiotactic regions.

Conformational Asymmetry in Relation to Optical Rotatory Properties

In the present notation, preferred helical (main chain) conformations of the left-handed sense may be identified for a bond pair like $i - 1$ and i as $(gt)_d$ and $(tg)_l$ and those associated with the opposite sense as $(tg)_d$ and $(gt)_l$, respectively, where the subscripts d and l denote the stereochemical character of the C_{i-1}^{α} atom (cf. eq 6, 7, and 9). The other high-energy conformations occur only occasionally. Fractions of left- and right-handed conformations thus defined should be equivalent to each other for a symmetric side chain. With an asymmetric side chain, as is apparent from the inspection of eq 13 and 14, a left-handed conformation, either $(gt)_d$ or $(tg)_l$, is necessarily associated with the statistical weight a and a right-handed one with b. To facilitate further discussion, let us define the side chain conformations mentioned above as conformations "a" and "b", respectively. As demonstrated in the analysis of optically active poly-α-olefins[6] using the Whiffen–Brewster empirical rule,[43] the optical rotatory power associated with conformations "a" and "b" is different from each other. When they are incorporated in a vinyl polymer system, disproportion between the fractions of "a" and "b" become magnified as a consequence of the neighbor-dependent character of the chain. This is the main feature involved in the enhancement of optical rotation observed in vinyl polymer systems.

Fractions of the left-handed (designated with fr^-) and right-handed conformation (fr^+) were calculated for Monte Carlo chains with $x = 100$ units in the usual manner[1,6] (Figure 7). The open circles indicate the results obtained for a symmetric side chain, for which $q = 0$ and thus $fr^- = fr^+$. Results for polymers having $R = C^*H(CH_3)C_2H_5(S)$ ($q = 1.63$) and $CH_2C^*H(CH_3)C_2H_5(S)$ ($q = 0.033$) are shown by the squares (□, ■) and triangles (△, ▲), respectively. Disparity between fr^- and fr^+ is markedly high for the former polymer (0.013 to 0.868 at $Pr = 1.0$), indicating that conformational rigidity imposed by branching at the β position in the side chain is very high. Such effect becomes smaller for the latter polymer. Values of fr are amazingly invariant in each case over the entire range of Pr.

With these results, one would immediately expect that the optical activity enhancement is very high for poly[(*S*)-1-methylpropyl vinyl ether]. It is interesting to note that such enhancement should not much depend on the stereoregularity of the chain. The effect for poly[(*S*)-2-methylbutyl vinyl ether] should be essentially the same but smaller in magnitude. Experimental observations reported by Pino and co-workers[23] are $[M]^{25}D = +312$ for the former and $+5.6$ for the latter polymer. These values are to be compared with those observed for the corresponding model compounds;[23] $[M]^{25}D = +36.13$ for (*S*)-1-methylpropyl ethyl ether and $+1.18$ for (*S*)-2-methylbutyl ethyl ether, respectively. In accordance with the preceding analysis on C_∞ and $\langle\mu^2\rangle/x$, tacticities of these moderately isotactic polymers may be in the range Pr = 0.7 to 0.8.

Discussion

Poly(alkyl vinyl ether)'s resemble poly-α-olefins in their molecular structures. Methylene groups at the α position of the side chain in the latter are replaced by oxygen atoms in the former. Major differences to be noted are as follows: (1) steric interactions involving oxygen atoms are less repulsive due to their smaller van der Waals radii compared to those of CH_2 groups; (2) Coulombic interactions between partial charges become important in certain conformations; (3) a shorter bond length of C–O (1.43 Å) compared to C–C (1.53 Å) considerably enhances steric interactions of groups in the side chain with those of the skeletal backbone.

Statistical weight matrices $\mathbf{U}_m$ and $\mathbf{U}_r$ given in eq 6 and 7 may be reduced formally to those adopted some time ago for the treatment of C_∞ of polypropylene[2] by setting $\eta = 1$ and representing all the second-order interactions by a single factor ω. Recently Suter and Flory[8] estimated

$$\eta = 1.05 \exp(-0.070/RT) \qquad (30)$$

for this polymer based on more elaborate conformational energy calculations supplemented by the analysis on stereochemical equilibrium data. The corresponding energy parameter E_η is estimated to be -0.44 kcal mol^{-1} for the poly(alkyl vinyl ether) (see eq 8); inclusion of a possible "gauche oxygen effect" may lower the value to ca. -0.6 kcal mol^{-1}. Accordingly conformations such as $(tg)_m$ (or $(gt)_m$) and $(tt)_r$ are more stabilized for a bond pair like i and $i-1$ (see Figure 1) in the latter polymer. The effect of the smaller size of the oxygen atoms is most clearly reflected in the higher statistical weight of the $(tt)_m$ conformation. Another characteristic feature of these polymers is the entire suppression of the tt conformation for bonds $i-1$ and i; $\mathbf{U}'(t,t) = 0$ even with R = CH_3. A similar effect has been discussed for poly-α-olefins having larger substituents.[3,6] With side chains such as C_2H_5 or n-C_3H_7, substantial statistical weight was assigned to this conformation,

$$\mathbf{U}'(t,t) = \exp(-1.5/RT) \qquad (31)$$

in recognition of the fact that the g^- conformation about bond s1 of the side chain is sterically less hindered. The entire suppression of this conformation is required only with side chains branched at the α or β position.[3] In this respect, configuration-dependent properties should be more susceptible to the chemical structure of side chains for hydrocarbon analogues.

In spite of these differences, the results obtained for C_∞ (Figure 3a) and conformational analysis (Figure 7) presented in relation to the optical rotation are quite similar in these two types of vinyl polymers.

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