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(48) Infrared absorption spectra of 1,2-dichloropropane, a halogenated hydrocarbon analogue of 1,2-dimethoxypropane, have been studied by Mizushima and Shimanouchi.[49] Conformational energies of the gauche g_α and g_β isomers relative to the trans isomer were estimated to be 0.2 and 0.9 kcal mol^{-1} in the neat liquid and 1.2 and 1.9 kcal mol^{-1} for the vapor phase, respectively. Dempster[50] suggested from reexamination of the previously reported NMR data[51] that conformational energies of the two gauche isomers should be reassigned, so that the more sterically hindered isomer (g_β) in which the primary chlorine atom is syn to both the other chlorine atom and the methyl group is more stable than the gauche conformer (g_α) with the primary chlorine atom trans to the methyl group. NMR studies[21a,22] using partially deuterated POP samples eliminate such ambiguity in the present case.

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Conformational Characteristics of Poly[oxy(1-alkylethylenes)] Carrying Side Chains Such as Ethyl, Isopropyl, and *tert*-Butyl Groups

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ABSTRACT: Configuration-dependent properties of a series of poly[oxy(1-alkylethylene)] chains $CH_3O[-CH_2CH(R)O-]_xCH_3$ having various side chains differing in size and shape were examined. Conformational energy parameters established for poly(oxypropylene) in the preceding paper were adopted in common to the skeletal configuration, steric interactions imposed by larger substituents being taken into account separately. Within the reasonable range of conformational energies, observed values of the characteristic ratio $\langle r^2\rangle_0/nl^2$ (R = CH_2CH_3, $C(CH_3)_3$) and the dipole moment ratio $\langle\mu^2\rangle/nm^2$ (R = $CH(CH_3)_2$) for isotactic polymers were reproduced. Fractions of the conformation about internal C–C bonds calculated by using the same parameter set were compared favorably with those estimated from NMR data (R = $CH(CH_3)_2$, $C(CH_3)_3$). Calculations were extended to evaluate $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ for atactic to syndiotactic chains. In the case of poly[oxy(1-*tert*-butylethylene)], values of $\langle r^2\rangle_0/nl^2$ decrease drastically from 16.0 for the isotactic to 0.9 for the syndiotactic chain. The latter value is smaller than that (2.2) calculated for the freely rotating model, indicating that the polymer chain configuration is remarkably compact in the state unperturbed by any long-range interactions. Finally, the partition function z for a monomer residue were deduced from the corresponding molecular partition function Z by $Z = z^x$. The conformational flexibility of the isotactic chain thus estimated decreases in the order R = H (z = 4.35) > CH_2CH_3 (3.96) > CH_3 (3.65) ≫ $CH(CH_3)_2$ (2.15) ≫ $C(CH_3)_3$ (1.42). Characteristics associated with the cooperative nature of bond rotations along the polymer chain are discussed in comparison with those of vinyl polymers.

In this paper, we treat the configuration-dependent properties of poly[oxy(1-alkylethylenes)] carrying substituents such as ethyl, isopropyl, and *tert*-butyl groups. When the results are assembled with those reported previously for poly(oxyethylene)[2] and poly(oxypropylene),[3] conformational studies on a series of polyoxide chains expressed by a generalized formula $CH_3O[-CH_2CH(R)-O-]_xCH_3$ will be completed.

Flexibility of polymeric chains should vary implicitly with the chemical structure of side chains. The effect of side chain conformations on properties such as unperturbed dimension, dipole moment, and optical rotation has been studied for a series of poly-α-olefins[4,5] and poly(alkyl vinyl ethers).[6,7] In these vinyl polymers, the stiffness of a polymer chain, as defined by the number of conformations permitted to the system, is primarily determined by the bulkiness of the side groups and the stereochemical configuration along the main chain. Results of the rotational isomeric state analysis suggest that the skeletal chain becomes particularly stiff when side chains are branched at the α or β position. It was also found that the highest cooperativity between the neighboring bond rotations is realized in the isotactic arrangement.[4-8]

Poly[oxy(1-alkylethylenes)] differ fundamentally from vinyl polymers in their chemical structure. Each repeating unit of the former comprises three bonds: C–C, C–O, and O–C, respectively. In the polymer system with R = H or CH_3, rotations around the skeletal C–C bonds render appreciable flexibility to the chain.[2,3,9,10] Introduction of bulky side chains such as R = i-C_3H_7 or t-C_4H_9 should enhance conformational rigidity of the chain by largely restricting the rotation around these bonds.

Conformational energies estimated for the poly(oxypropylene) chains, as presented in the preceding paper[3] (hereafter referred to as paper 1), should be applicable to the skeletal configuration of poly[oxy(1-alkylethylene)] chains carrying side chains other than methyl, provided that the effects of steric interactions imposed by the bulky side chains are taken into account separately in the manner described elsewhere.[4-7] Theoretical values of the unper-

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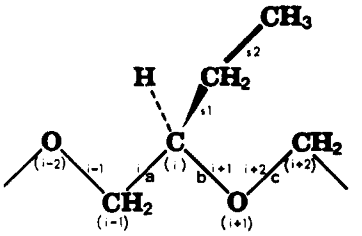


Figure 1. A portion of a poly[(*R*)-oxy(1-alkylethylene)] chain (R = CH_2CH_3) in its planar conformation. Bond s2 is placed trans to the skeletal bond *i*.

turbed dimension, dipole moment, and bond conformations thus obtained will be compared with those estimated from the existing experimental data. Conformational analyses carried out in this way should provide further information for the gauche oxygen effect[2,3,11,12] characteristic to the poly[oxy(1-alkylethylene)] system.

Conformational Energies and Statistical Weight Matrices

A portion of a poly[(*R*)-oxy(1-alkylethylene)] chain (R = CH_2CH_3) in its planar conformation is shown in Figure 1, where the second bond (s2) of the side chain is placed trans to the preceding skeletal bond *i* (i.e., bond type a). For simplicity, bond lengths and bond angles along the skeletal chain are taken to be identical with those previously adopted to poly(oxypropylene):[3] l_{CC} = 1.53 Å, l_{CO} = 1.43 Å, and ∠CCO = ∠OCO = 111.5°. Bond dipole moments are assumed to be m_{CO} = 1.07 D and m_{CC} = 0 as usual.[2,3]

The first- and second-order interactions dependent upon the rotation around the articulated bond s1 may be evaluated for each of the fixed rotational states about skeletal bonds (*i* and *i* + 1 in Figure 1) on both side of the atom (C_i) flanking the side chain.[5-7] The results derived for the polymer with R = CH_2CH_3 (Figure 1) are summarized in a matrix form

$$\begin{array}{cc} & \begin{array}{ccc} & i+1 & \\ (t) & (g^+) & (g^-) \end{array} \\ i & \\ \begin{array}{c} (t) \\ \mathbf{V}^R = (g^+) \\ (g^-) \end{array} & \begin{bmatrix} \gamma\omega' + \delta & 1 + \gamma\omega' & 1 + \gamma\omega' + \delta \\ \gamma + \delta & 1 + \gamma & 1 + \gamma + \delta \\ \gamma & 1 + \gamma & 1 + \gamma \end{bmatrix} \end{array} \qquad (1)$$

where superscript *R* represents the stereochemical character of the asymmetric center (C_i), rows and columns of the matrix being indexed to rotational states t, g^+, and g^- for the bond pair *i* and *i* + 1. Here γ and δ denote respectively the statistical weight parameters assigned to the first-order interactions encountered in the g^+ and g^- states defined for bond s1; see Figure 2a. These statistical weight parameters are taken to be simple Boltzmann factors in the corresponding conformational energies by following conventional procedure.[9] Preliminary calculations using the semiempirical energy expression[2,3] gave $E_\gamma \simeq 0.5$ and $E_\delta \simeq 1$ kcal mol^{-1}. These values are however somewhat ambiguous due to the possible gauche oxygen effect[2] ($CH_3 \cdots O_{i+1}$), of the order of 0.2 kcal mol^{-1}. The statistical weight parameter ω' represents second-order interactions occurring between the terminal CH_3 group in the side chain and the O_{i-2} atom in the skeletal chain when bonds *i* and s1 are in the rotational states t and g^+, respectively. A similar $CH_2 \cdots O$ arrangement has been previously encountered in the poly(oxytetramethylene) chain $[-(CH_2)_4O-]_x$. The conformational energy $E_{\omega'}$ estimated therefrom is ca. 0.7 kcal mol^{-1} after being corrected for the Coulombic contribution.[2] The other second-order interactions involve much higher steric repulsions and are excluded in the present treatment.

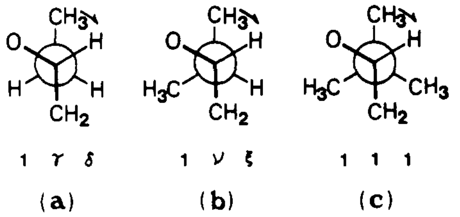


Figure 2. First-order interactions defined for the first articulated bond of side chains. Statistical weight parameters are given from left to right to the conformations generated by rotations indicated by the arrows: (a) R = CH_2CH_3, (b) R = $CH(CH_3)_2$, (c) R = $C(CH_3)_3$. (For convenience, let us define the conformations depicted above as trans.)

For polymers with R = $CH(CH_3)_2$ or $C(CH_3)_3$, steric interactions involving the terminal methyl groups of these side chains become more proliferated. Statistical weight matrices $\mathbf{V}^R$ for these side chains may be given as follows: For R = $CH(CH_3)_2$

$$\mathbf{V}^R = \begin{bmatrix} \xi\omega' & \nu\omega' & 1 + \nu\omega' + \xi\omega' \\ \xi & \nu & 1 + \nu + \xi \\ 0 & \nu & \nu \end{bmatrix} \qquad (2)$$

where ν and ξ are statistical weight parameters assigned to the side-chain conformations, as is defined in Figure 2b. Inspection of a model suggests that (1) the conformational energy E_γ is small, either positive or negative, and (2) E_ξ is of the order of 1 to 2 kcal mol^{-1}.[2-5] Takahashi, Tadokoro, Tsuruta, and their co-workers[13] reported the results of X-ray crystallographic analysis on optically active poly[oxy(1-isopropylethylene)]. In the solid state, the side chain prefers the conformation in which both of the terminal methyl groups are situated syn to the O_{i+1} atom of the skeletal chain (cf. Figures 1 and 2b). In the following calculations, the statistical weight factors ν and ξ will be treated as somewhat adjustable parameters. The second-order interaction designated with ω' (eq 2) is sterically more hindered than that (eq 1) encountered in the poly[oxy(1-ethylethylene)] chain; displacement of the rotational angle about bond s1 to alleviate the steric conflict ($CH_3 \cdots O_{i-2}$) should be largely suppressed in the polymer system with branched side chains (cf. Figures 1 and 2).[2] Accordingly, the conformational energy $E_{\omega'}$ may be taken to be slightly higher than the one (0.7 kcal mol^{-1}) previously estimated.

For R = $C(CH_3)_3$, we have

$$\mathbf{V}^R = \begin{bmatrix} 0 & 0 & \omega' \\ 0 & 0 & 1 \\ 0 & 0 & \omega'' \end{bmatrix} \qquad (3)$$

Since this side group possesses threefold symmetry about bond s1, the first-order interaction dependent upon the rotation about this bond should be equally weighted, and therefore no distinction is required among the rotational states (Figure 2c). Due to very severe steric conflicts, the t and g^+ conformations are entirely suppressed for bonds like *i* + 1 (or bond b) (cf. Figures 1 and 2c). Among the remaining states, the second-order interaction $CH_3 \cdots O_{i-2}$ arises in the tg^- and g^-g^- conformation for bond pairs like *i*, *i* + 1. The former is equivalent to that previously encountered in the poly[oxy(1-isopropylethylene)] chain, being given the weight of ω'. The latter designated with

ω'' should occur very rarely. In the polymer system with R = CH_2CH_3 or $CH(CH_3)_2$, contributions from such conformations are negligibly small since lower energy states are alternatively allowed for bond s1 (cf. eq 1 and 2). Ignoring the effect of ω'' for the polymer carrying side chains such as R = $C(CH_3)_3$ cannot be justified. Here we assume $E_{\omega''} \gg E_{\omega'}$. From the X-ray crystallographic analysis on isotactic samples obtained from racemic monomer, Sakakihara et al.[14] reported that the conformation of isotactic poly[oxy(1-*tert*-butylethylene)] may be described by a 9/4 helix, mainly consisting of g^+g^-t (for bonds abc) sequences.

Each element (η,ζ) of statistical weight matrices $\mathbf{V}^R$ derived as above represents the effect attributable to the side chain when skeletal bonds i and $i + 1$ are in the rotational states η and ζ, respectively. The expression generally applicable to the skeletal portion of the poly[(*R*)-oxy(1-alkylethylene)] chain has been given by eq 1–3 of paper 1. When the procedure described in ref 5 and 7 is followed, each element $u_{\eta\zeta}$ of the $\mathbf{U}_b{}^R$ matrix given in eq 2 of paper 1 is multiplied by the corresponding statistical weight factor $\mathbf{V}^R(\eta,\zeta)$ to complete a revised expression for the polymer system under consideration. Thus

$$\mathbf{U}_b{}^R = [u_{\eta\zeta}\mathbf{V}^R(\eta,\zeta)] \qquad (4)$$

As is easily shown by inspection of a model, statistical weight matrices $\mathbf{U}_a{}^R$ and $\mathbf{U}_c{}^R$, given respectively in eq 1 and 3 of paper 1, should not be affected by the side-chain conformation under the assumption that interactions of higher orders are negligible.[9] The expression $\mathbf{U}^R$ for a repeating unit associated with the *R* center is thereby completed:

$$\mathbf{U}^R = \mathbf{U}_a{}^R\mathbf{U}_b{}^R\mathbf{U}_c{}^R \qquad (5)$$

Statistical weight matrices for the *S* unit can be derived easily from those of the *R* unit in the manner specified by eq 4–6 of paper 1. Thus, the configurational partition function may be evaluated for any given polymer chain by properly choosing **U** matrices depending upon the stereochemical character of the chain sequence. Special care is required as usual for the terminals of the chain.[2,3]

Unperturbed Dimension, Dipole Moment, and Bond Conformations

Listed in Table I are the experimental values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ reported in the literature for isotactic poly[oxy(1-alkylethylenes)]. Fractions of conformers $(f_t{:}f_\alpha{:}f_\beta)$ for the skeletal C–C bond estimated from NMR data are also included in the last three columns. Here, following the definition introduced in paper 1, notations f_t, f_α, and f_β represent the fraction of conformers in trans, gauche α, and gauche β states, respectively. For a C–C bond associated with the *R* center, the g_α conformation is identified with g^+ and g_β with g^-. The opposite applies to the bond associated with the *S* center.

Matsushima, Fukatsu, and Kurata[15] reported the results of viscometric studies on fractionated samples of poly[oxy(1-ethylethylene)] prepared with a diethylzinc–butylene glycol catalyst. Similar studies were carried out later by Booth and Orme,[16] who employed the polymer derived from a diethylzinc–water catalyst system. The characteristic ratio $\langle r^2\rangle_0/nl^2$ was estimated from the data obtained under the Θ condition (in 2-propanol at 30 °C) by using a hydrodynamic constant $\phi = 2.6 \times 10^{21}$ dL cm^{-3} mol^{-1}. The results thus obtained are somewhat divergent between these two observations. An approximate value of $\langle r^2\rangle_0/nl^2$ for the isotactic poly[oxy(1-*tert*-butylethylene)] was estimated by extrapolation from viscometric data obtained in a thermodynamically good solvent (xylene at 80 °C) as reported by Doddi, Forsman, and Price.[17]

Table I
Observed Values of the Characteristic Ratio $\langle r^2\rangle_0/nl^2$, Dipole Moment Ratio $\langle\mu^2\rangle/nm^2$, and Bond Conformations about the Skeletal C–C Bonds for Poly[oxy(1-alkylethylenes)] $[-CH_2CH(R)O-]_x$

polymer (R)	$\langle r^2\rangle_0/nl^2$	$\langle\mu^2\rangle/nm^{2a}$	fraction of conform. about the skeletal C–C bond f_t	f_α	f_β	
CH_2CH_3	5.4^b 6.3^c					
$CH(CH_3)_2$		0.83^e	0.29	0.50	0.21	$(c\text{-}C_6D_{12})^f$
			0.25	0.53	0.22	$(C_6D_6)^f$
			0.30	0.50	0.20	$(CDCl_3)^f$
$C(CH_3)_3$	16^d		0	1.0	0	$(CCl_4)^{g,h}$

[a] Calculated for bond dipole moments m_{C-O} = 1.07 D and m_{C-C} = O. [b] A value obtained from viscosity measurements in a Θ solvent (2-propanol at 29.8 °C), ref 15. [c] From viscosity measurements in 2-propanol at 30 °C, ref 16. [d] An extraporated value from viscosity measurements in a good solvent (xylene at 80 °C), ref 17. [e] In benzene at 25 °C, ref 18. [f] Estimated from vicinal proton coupling constants in NMR observed at 25 °C. Solvents used are given in parentheses, ref 19. [g] From vicinal proton coupling constants in NMR. Observed in CCl_4 at 50 °C, ref 20. [h] From vicinal proton coupling constants in NMR. Observed in CCl_4 at 81 °C, ref 21.

Experimental values of the dipole moment are available only for poly[(*S*)-oxy(1-isopropylethylenes)]. The dipole moment ratios $\langle\mu^2\rangle/nm^2$ were found to be 0.89 and 0.83 for polymer samples prepared from a dimethoxyzinc and a diethylzinc–water catalyst, respectively.[18] The value derived from the higher molecular weight sample is adopted in Table I.

Tsuji, Hirano, and Tsuruta[19] observed NMR vicinal coupling constants between methine and methylene protons for isotactic poly[(*S*)-oxy(1-isopropylethylene)] in solvents such as those indicated in the table. Fractions were estimated therefrom, using values of ^3J_t = 10.0 and ^3J_g = 2.0 Hz for trans and gauche couplings, respectively. Observed values of coupling constants involving the side-chain methine proton were found to be consistent with the results cited in Table I.[19] Price and Fukutani[20] and Tani and Oguni[21] independently reported NMR data on poly[oxy(1-*tert*-butylethylene)]. They concluded that the main-chain C–C bonds in the isotactic chain exist in solution preferentially in the g_α conformation.

Calculations for Isotactic Chains

Poly[oxy(1-ethylethylene)]. Values of $\langle r^2\rangle_0/nl^2$ were calculated for the temperature of 30 °C with isotactic chains of 200 units (n = 602) in the usual manner.[9,22] Variations of the characteristic ratio with E_γ and E_δ are shown in Figure 3, $E_{\omega'}$ being set equal to 0.7 kcal mol^{-1}. Conformational energies associated with the skeletal portion of the chain were taken from paper 1: (set I) $E_\alpha = -0.3$, $E_\beta = 0.35$, $E_\sigma = 1.3$, $E_\omega = 0.4$, in kcal mol^{-1}; (set II) $E_\alpha = -0.3$, $E_\beta = 0.5$, $E_\sigma = 0.9$, $E_\omega = 0.4$, in kcal mol^{-1}. Rotational angles for the individual parameter set have been given in Table II of paper 1. As is illustrated in Figure 3, use of parameter set II for the skeletal chain (dashed curves) leads to somewhat lower values of $\langle r^2\rangle_0/nl^2$ as compared to those (solid curves) of set I. Since experimental values reported by two groups[15,16] are quite divergent from each other (5.4 and 6.3, respectively), the choice of a single set of parameters from this figure is improbable; ranges estimated are $E_\gamma = 0.5 \pm 0.25$ and E_δ

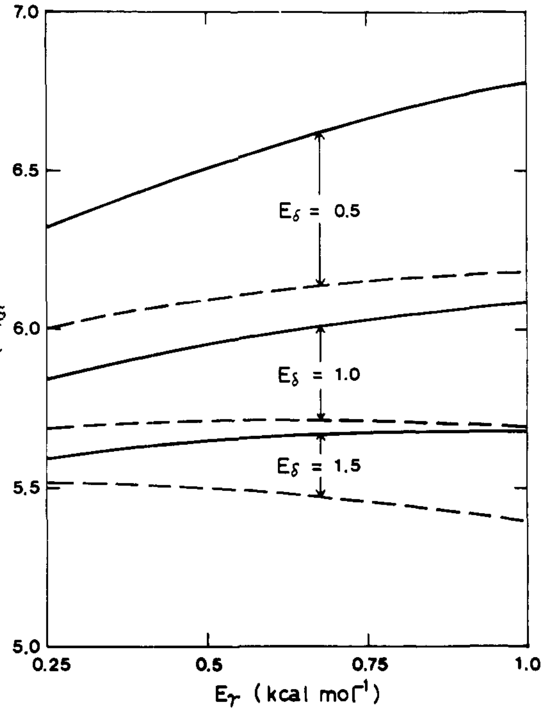


Figure 3. The characteristic ratio for isotactic poly[oxy(1-ethylethylene)] chains having $x = 200$ ($n = 602$) calculated as a function of E_γ for the temperature of 30 °C. Values of E_δ are illustrated with each curve, $E_{\omega'}$ being set equal to 0.7 kcal mol^{-1}. Solid and dashed curves were obtained by using parameter sets I and II, respectively.

Table II
Properties of the Isotactic Poly[oxy(1-ethylethylene)] Chain (x = 200), Estimated by Using the Parameter Set as Indicated[a]

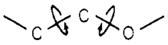
parameter set	$\langle r^2\rangle_0/nl^2$	$\langle\mu^2\rangle/nm^2$	fractions of conform. about the skeletal C-C bond f_t	f_α	f_β
I	6.0	0.77	0.33	0.50	0.19
II	5.7	0.72	0.35	0.50	0.15

[a] Calculated employing $E_\gamma = 0.5$, $E_\delta = 1.0$, and $E_{\omega'}$ = 0.7 kcal mol^{-1} for the temperature of 30 °C.

= 1.0 ± 0.5 kcal mol^{-1}. As is evident from inspection of eq 2, contribution from the high-energy conformation associated with ω' is relatively unimportant. For a range of $E_{\omega'}$ = 0.7 ± 0.1 kcal mol^{-1}, values of $\langle r^2\rangle_0/nl^2$ vary by less than 0.5%.

Theoretical values of $\langle r^2\rangle_0/nl^2$, $\langle\mu^2\rangle/nm^2$, and bond conformations, obtained by using $E_\gamma = 0.5$ and $E_\delta = 1.0$ kcal mol^{-1}, are summarized in Table II. Results are rather insensitive to the choice of parameter set for all the properties investigated herein. Temperature coefficients of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle$ calculated for the temperature of 30 °C are appreciably large and negative: 10^3 d ln $\langle r^2\rangle_0$/dT = -1.4 (set I) and -2.0 K^{-1} (set II); 10^3 d ln $\langle\mu^2\rangle$/dT = -1.0 (set I) and -1.1 K^{-1} (set II).

Poly[oxy(1-isopropylethylene)]. For polymer chains having bulky side chains such as R = $CH(CH_3)_2$ or $C(CH_3)_3$, rotations about the bonds on both sides of the articulated carbon atom should be largely suppressed. The most stable conformation for the C–C bond is g_α, as is estimated from NMR data (Table I).[19-21] Inspection of eq 2 as well as eq 1–3 of paper 1 suggests that the following C–O bond is overwhelmingly in a single skew conformation. Consequently, the most probable arrangement for bond pair ab (cf. Figure 1) is g^+g^- for the R unit (g^-g^+ for the S unit). In such a high-energy conformation, large displacements of the rotational states from the regular position should be required. Conformational energy calculations carried out previously for a portion



of the POE chain[2] gave energy minima for the $g^\pm g^\mp$ states at φ(C–C) = ±110° and φ(C–O) = ∓85°. We adopt a set of revised values of rotational angles for bond pair ab based on these considerations; φ_{g^+}(C–C) = 110° and φ_{g^-}(C–O) = -85° are commonly used in parameter sets I and II (cf. Table II of paper 1), the other parameters being unaltered.

Results of calculations for the dipole moment ratio $\langle\mu^2\rangle/nm^2$ pertaining to a high molecular weight poly[(R)-oxy(1-isopropylethylene)] are shown in Figure 4 as a function of E_ν. The solid and dashed curves were obtained using parameter sets I and II, respectively, for the skeletal chain. Curves designated with 1, 2, and 3 represent respectively the results obtained by setting (1) $E_\xi = 1.0$, $E_{\omega'} = 1.0$, (2) $E_\xi = 2.0$, $E_{\omega'} = 1.0$, and (3) $E_\xi = 2.0$, $E_{\omega'} = 0.7$, units being in kcal mol^{-1}. Calculated values of $\langle\mu^2\rangle/nm^2$ increase quite sensitively with E_ν, and with $E_{\omega'}$ as well (compare curves 2 and 3), in the region investigated. They are however relatively insensitive to E_ξ over the range 1.0 to 2.0 kcal mol^{-1} (compare curves 1 and 2). Values of E_ν chosen so as to reproduce the observed dipole moment ratio $\langle\mu^2\rangle/nm^2 \simeq 0.83$ are given as follows: from the solid curves (1) 0.2 ± 0.05, (2) 0.3 ± 0.05, (3) 0.65 ± 0.05 kcal mol^{-1}; from the dashed curves (1) 0.8 ± 0.05, (2) 0.65 ± 0.05, (3) 1.3 ± 0.1 kcal mol^{-1}, respectively. The difference between the values taken from curves 1 and 2 is trivial within each group. For a given pair of E_ξ and $E_{\omega'}$, use of parameter set II (dashed curves) requires higher values of E_ν (by 0.3 to 0.6 kcal mol^{-1}) than set I (solid curves).

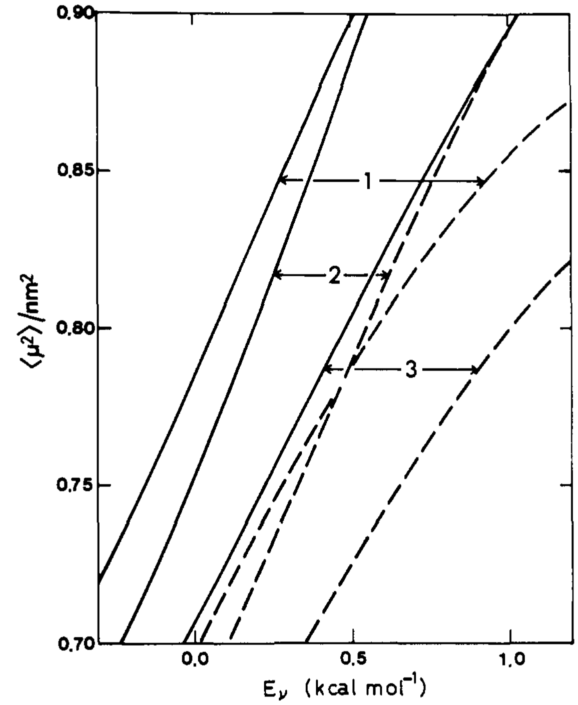


Figure 4. The dipole moment ratio for isotactic poly[oxy(1-isopropylethylene)] chains having $x = 200$ ($n = 602$) calculated as a function of E_ν for the temperature of 25 °C. The other parameters associated with side-chain conformations are given as follows: curves (1) $E_\xi = E_{\omega'}$ = 1.0 kcal mol^{-1}; (2) E_ξ = 2.0 kcal mol^{-1}, $E_{\omega'}$ = 1.0 kcal mol^{-1}; (3) E_ξ = 2.0 kcal mol^{-1}, $E_{\omega'}$ = 0.7 kcal mol^{-1}. Results obtained by using parameter set I are represented by the solid curves, and those from parameter set II are represented by the dashed curves.

Table III
Properties of the Isotactic Poly[oxy(1-isopropylethylene)] Chain (x = 200), Calculated for Some Representative Parameter Sets[a]

parameter set				fractions of conform. about the skeletal C–C bond		
skeletal chain	side chain	$\langle r^2\rangle_0/nl^2$	$\langle \mu^2\rangle/nm^2$	f_t	f_α	f_β
I	$E_\nu = 0.3$; $E_\xi = 2.0$; $E_{\omega}{}' = 1.0$	7.4	0.83	0.30	0.51	0.19
	$E_\nu = 0.6$; $E_\xi = 2.0$; $E_{\omega}{}' = 0.7$	6.9	0.82	0.29	0.50	0.21
II	$E_\nu = 0.6$; $E_\xi = 2.0$; $E_{\omega}{}' = 1.0$	6.8	0.81	0.27	0.56	0.17
	$E_\nu = 1.2$; $E_\xi = 2.0$; $E_{\omega}{}' = 0.7$	6.3	0.82	0.26	0.54	0.20

[a] Computed for the temperature of 25 °C.

The characteristic ratio $\langle r^2\rangle_0/nl^2$, dipole moment ratio $\langle \mu^2\rangle/nm^2$, and fraction of conformers about the main chain C–C bonds calculated for some representative sets of parameters are shown in Table III. Observed values of the fractions (see Table I) are satisfactorily reproduced with any set of parameters. The unperturbed dimension $\langle r^2\rangle_0/nl^2$ of the isotactic poly[oxy(1-isopropylethylene)] chain is estimated to be ca 7.0, being slightly higher than those of poly(oxypropylene)[3] and of poly[oxy(1-ethylethylene)]. As has been pointed out previously, the magnitude of E_ν should be small, possibly of the order of a few hundred calories per mole. We shall tentatively adopt the first set of parameters of Table III in the following calculations.[23] Temperature coefficients of $\langle r^2\rangle_0$ and $\langle \mu^2\rangle$ calculated with these parameters are 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = -0.78$ K^{-1} and 10^3 d ln $\langle \mu^2\rangle/\mathrm{d}T = -1.61$ K^{-1} (at 25 °C).

The dipole moment ratio of 1,2-dimethoxy-3-methylbutane, a monomer model, was found to be 0.45 ± 0.03 D (benzene, 25 °C),[18] being appreciably lower than that of the polymer (Table I). Theoretical calculations of $(\langle \mu^2\rangle/nm^2)_{x=1}$ with parameter set I gave a value of 0.56.

Poly[oxy(1-*tert*-butylethylene)]. With side chains R = $C(CH_3)_3$, the lowest-energy conformation of the *R* polymer chain involves g^+g^- states for bond pair ab (see eq 3). Revised values were adopted for the corresponding rotational angles by following the justification presented in the preceding section; φ_{g^+}(C–C) = 110° and φ_{g^-}(C–O) = −85° in both parameter sets I and II. Characteristic ratios $\langle r^2\rangle_0/nl^2$ were calculated for an isotactic chain of 200 units for the temperature of 80 °C. Results are shown in Figure 5 as a function of $E_{\omega'}$, values of $E_{\omega''}$ used being indicated on the curves. The steric requirement involved in the second-order interaction designated with ω' is similar to that encountered in the poly[oxy(1-isopropylethylene)] chain. The value of $E_{\omega'}$ was estimated to be ca. 1.0 kcal mol^{-1}. The solid curves were obtained by using parameter set I for the skeletal portion of the chain. The agreement with the observed value[17] $\langle r^2\rangle_0/nl^2 \simeq 16$ is satisfactory in the range $E_{\omega''}$ = 2.0 to 3.0 kcal mol^{-1}. Alternative calculations using parameter set II gave the results shown by the dashed curves. Values of $\langle r^2\rangle_0/nl^2$ thus obtained are somewhat lower; e.g., at $E_{\omega'}$ = 1.0 and $E_{\omega''}$ = 3.0 kcal mol^{-1}, $\langle r^2\rangle_0/nl^2 = 11$. Agreement with the observed value can be barely improved by adopting a similar alteration in E_α as is done in the case of poly[oxy(1-isopropylethylene)] (cf. ref 23).

For purposes of illustration, the characteristic ratio, dipole moment ratio, and bond conformations calculated with $E_{\omega'}$ = 1.0 and $E_{\omega''}$ = 3.0 kcal mol^{-1} are summarized in Table IV. Similar to the tendency found in $\langle r^2\rangle_0/nl^2$, values of $\langle \mu^2\rangle/nm^2$ calculated by using parameter set II are appreciably lower (by ca. 40%) than those obtained with set I. The fraction of conformers given in the last three columns is however little affected by the choice of the parameter set. As is shown by inspection of eq 3 and eq 1–3 of paper 1, values of the fraction are largely determined by the magnitude of $E_{\omega'}$ and $E_{\omega''}$; e.g., with $E_{\omega'}$, = 1.0 and $E_{\omega''}$ = 3.0 kcal mol^{-1}, $f_t \simeq \omega'/(1 + \omega' + \omega'') = 0.19$, $f_\alpha \simeq 1/(1 + \omega' + \omega'') = 0.80$, and $f_\beta \simeq \omega''/(1 + \omega' + \omega'') = 0.01$. The experimental value[20,21] of $f_\alpha \simeq 1$ reported for isotactic samples should require $E_{\omega'} \gg 1.0$ kcal mol^{-1}. In this respect, the results of calculations are somewhat at variance with those observed. Temperature coefficients calculated at $E_{\omega'}$ = 1.0 and $E_{\omega''}$ = 3.0 kcal mol^{-1} by using parameter set I are 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T = -4.1$ K^{-1} and 10^3 d ln $\langle \mu^2\rangle/\mathrm{d}T = -5.6$ K^{-1} (at 80 °C). A large negative value of 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T \simeq -10$ K^{-1} is suggested[17] from light-scattering measurements in a good solvent (*o*-dichlorobenzene, 80–100 °C).

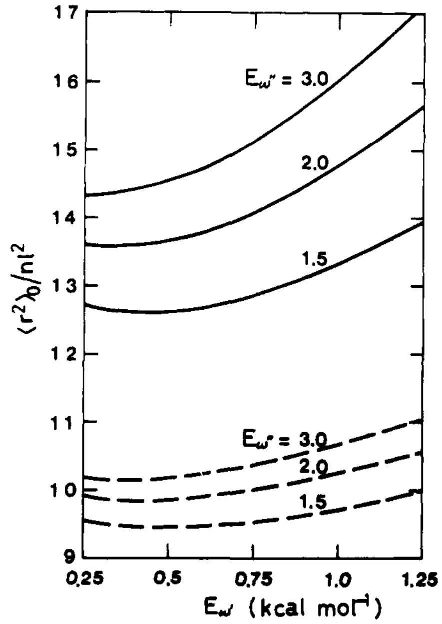


Figure 5. Values of $\langle r^2\rangle_0/nl^2$ at 80 °C for isotactic poly[oxy(1-*tert*-butylethylene)] chains having x = 200 (n = 602). Results are shown as a function of $E_{\omega'}$, values of $E_{\omega''}$ being indicated on each curve. The solid curves correspond to parameter set I and the dashed curves to parameter set II.

Table IV
Properties of the Isotactic Poly[oxy(1-*tert*-butylethylene)] Chain (x = 200), Calculated by Using the Parameter Set as Indicated[a]

param-eter set	$\langle r^2\rangle_0/nl^2$	$\langle \mu^2\rangle/nm^2$	fractions of conform. about the skeletal C–C bond		
			f_t	f_α	f_β
I	16.0	1.57	0.22	0.77	0.01
II	10.7	0.99	0.23	0.76	0.01

[a] Calculated with $E_{\omega}{}' = 1.0$ and $E_{\omega}{}'' = 3.0$ kcal mol^{-1} for the temperature of 80 °C.

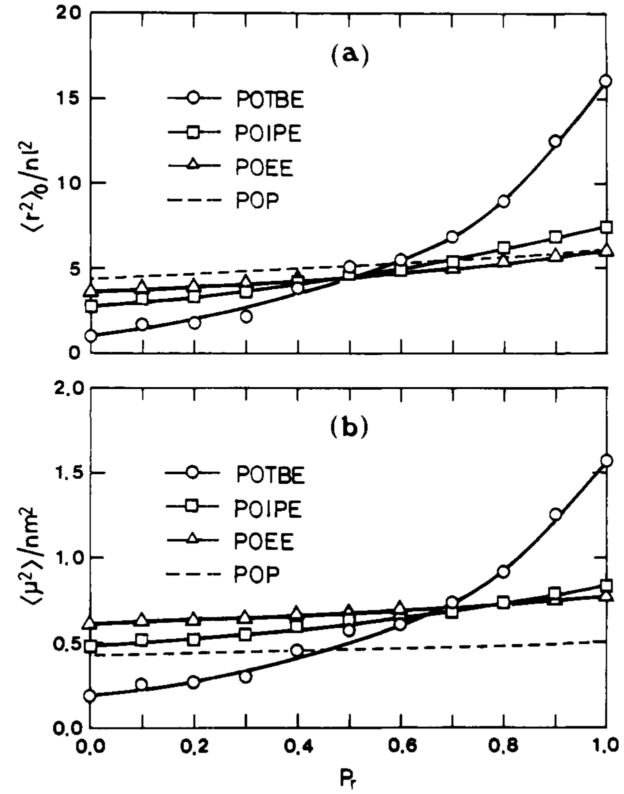


Figure 6. Characteristic ratios (a) and dipole moment ratios (b) calculated by using parameter set I for Monte-Carlo chains of 200 units (n = 602) each. Curves shown are for poly[oxy(1-*tert*-butylethylene)] (POTBE, circles, T = 80 °C), poly[oxy(1-isopropylethylene)] (POIPE, squares, T = 25 °C), and poly[oxy(1-ethylethylene)] (POEE, triangles, T = 30 °C). The results obtained previously for poly(oxypropylene) (POP) are taken from Figure 7 of paper 1 and given by the dotted curves.

Atactic and Syndiotactic Chains

The mean-square length $\langle r^2\rangle_0$ and dipole moment $\langle \mu^2\rangle$ for chains which are subject to statistical variations in tacticity were calculated in a conventional manner.[9,22] Results obtained by using parameter set I (cf. Tables II, III, and IV) for Monte-Carlo chains of 200 units are shown in Figure 6, where computations were carried out for the same temperatures as those employed in the preceding section. For comparison, results of calculations reported in paper 1 for the poly(oxypropylene) chain[3] are also indicated by the dotted curves (cf. Figure 7 of paper 1). In the case of poly[oxy(1-*tert*-butylethylene)], the characteristic ratio $\langle r^2\rangle_0/nl^2$ decreases drastically from the isotactic (replication probability P_r = 1.0) to the syndiotactic (P_r = 0.0) (Figure 6a). As the side chain becomes less bulky, variation of $\langle r^2\rangle_0/nl^2$ with P_r tends to be moderate. Values of $\langle r^2\rangle_0/nl^2$ calculated for P_r = 0.0 are as follows: R = CH_3 (4.4) (50 °C), CH_2CH_3 (3.5) (30 °C), $CH(CH_3)_2$ (2.7) (25 °C), and $C(CH_3)_3$ (0.9) (80 °C).

The dipole moment ratios $\langle \mu^2\rangle/nm^2$ are plotted against P_r in Figure 6b. It is interesting to note here that the curves drawn in the upper and lower figures bear a strong resemblance to each other, although the scales on both ordinates are quite difference. While values of $\langle \mu^2\rangle/nm^2$ decrease very rapidly with P_r in the polymer system carrying R = $C(CH_3)_3$, those calculated for R = CH_3 vary very little over the entire range of P_r. Values of $\langle \mu^2\rangle/nm^2$ obtained for P_r = 0.0 are R = CH_3 (0.42) (30 °C), CH_2CH_3 (0.60) (30 °C), $CH(CH_3)_2$ (0.48) (25 °C), and $C(CH_3)_3$ (0.18) (80 °C). In the atactic region (P_r = 0.4 to 0.6) where curves calculated for various polymer systems fall in the same range, values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ are most insensitive to the variation of side groups.

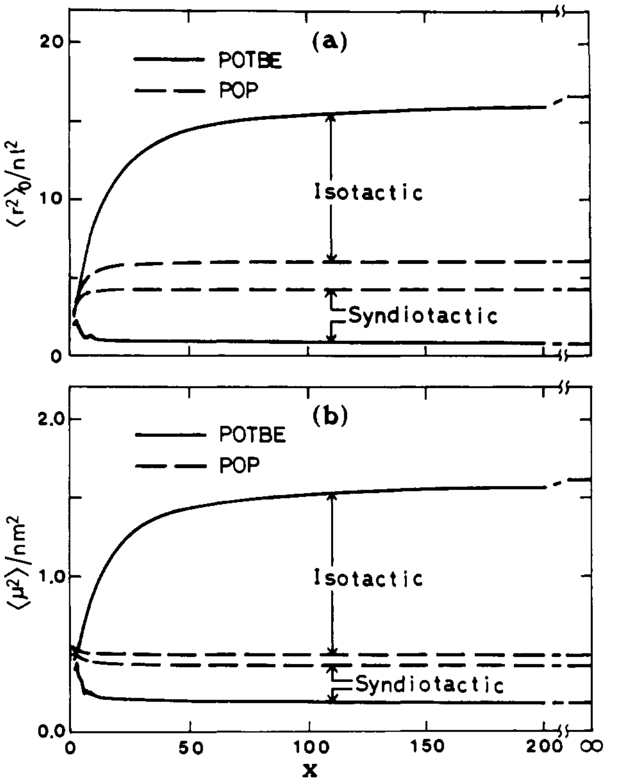


Figure 7. Dependence of the characteristic ratio (a) and dipole moment ratio (b) on the degree of polymerization x for stereoregular isotactic and syndiotactic chains of poly[oxy(1-alkylethylenes)]. Solid curves represent the results obtained for polymers having R = $C(CH_3)_3$ by using parameter set I (T = 80 °C). Dashed curves are those for polymers with R = CH_3 ((a) T = 50 °C, (b) T = 30 °C)[3]. The asymptotes of the curves are indicated on the right-hand ordinate.

The characteristic ratio $\langle r^2\rangle_0/nl^2$ and dipole moment ratio $\langle \mu^2\rangle/nm^2$ were calculated as a function of the number of monomeric units x. Asymptotic curves obtained for the isotactic and syndiotactic chains of poly[oxy(1-*tert*-butylethylene)] are shown in Figure 7, where those obtained for poly(oxypropylene) are also included for comparison. The asymptotic values for $x \to \infty$ are given on the right-hand ordinates. Curves calculated for chains with intermediate tacticities fall between those of the isotactic and syndiotactic polymers. For ordinary flexible polymers, values of $\langle r^2\rangle_0/nl^2$ increase asymptotically with the chain length.[9] The result obtained for the syndiotactic poly[oxy(1-*tert*-butylethylene)] is in this respect somewhat unusual (the lower solid curve in Figure 7a); values of $\langle r^2\rangle_0/nl^2$ decrease monotonically with x except in the region (x < 10) where some small bumps and troughs are noticed. The value of $(\langle r^2\rangle_0/nl^2)_{x\to\infty}$ = 0.9 is smaller than that (2.2) calculated for the *freely rotating model*, indicating that the polymer chain configuration is remarkably compact in the state unperturbed by any long-range interactions. In the poly[oxy(1-*tert*-butylethylene)] system, bulky side groups render appreciably high rigidity to the polymer chain. With side chains such as R = CH_2CH_3 and $CH(CH_3)_2$, values of $\langle r^2\rangle_0/nl^2$ tend to increase with x even for the syndiotactic configuration.

Variation of $\langle \mu^2\rangle/nm^2$ with x is shown by the solid and dashed curves in Figure 7b for polymers with R = $C(CH_3)_3$ and CH_3, respectively. Among the polymer systems investigated, poly[oxy(1-*tert*-butylethylene)] again yields the largest and smallest values of $\langle \mu^2\rangle/nm^2$ for the isotactic and syndiotactic configuration, respectively. Polymers carrying less bulky substituents such as R = CH_2CH_3 or

Table V
Conformational Partition Function for a Monomer Residue[a] Estimated by Assigning a Weight of Unity to the Lowest-Energy Conformation

polymer (R)	lowest-energy conform. for the *R* residue[b] bond a	bond b	bond c	z_{iso}	z_{syn}	z_{syn}/z_{iso}
H[c]	$g^{\pm}$	t	t	4.35		
CH_3[d]	g^+	t	t	3.65	3.65	1.00
CH_2CH_3[d]	g^+	g^-	t	3.96	3.96	1.00
$CH(CH_3)_2$[e]	g^+	g^-	t	2.15	2.16	1.01
$C(CH_3)_3$[f]	g^+	g^-	t	1.42	1.45	1.02

[a] Calculated for chains with $x = 200$, using parameter set I. [b] Those for the *S* residue may be obtained by changing signs of rotation for every gauche state. [c] Estimated by using the eigenvalue method for the limit $x \rightarrow \infty$, $T = 30$ °C. For parameters, see ref 2. [d] $T = 30$ °C. [e] $T = 25$ °C. [f] $T = 80$ °C.

$CH(CH_3)_2$ exhibit intermediate behaviors.

As was shown in Figure 7b of paper 1, fractions of conformers about the skeletal C–C bonds are little affected by P_r in the polymer system with R = CH_3. As the side group becomes bulkier, the effect of stereoregularity should increase. With R = $C(CH_3)_3$, calculated values of f_t, f_α, and f_β for the syndiotactic configuration ($P_r = 0.0$) are 0.19:0.80:0.01 (parameter set I). These results are to be compared with those (0.22:0.77:0.01) of the isotactic chain given in the second row of Table IV. Variation is smaller in the intermediate region of P_r.

Discussion

In each of the poly[oxy(1-alkylethylene)] chains considered, the same set of parameters for the skeletal chain gave a satisfactory account of most of the experimental information available on the chain dimensions, dipole moments, and bond conformations. Parameter set I affords slightly better agreement with observations than does the second set (II); the difference is however trivial in view of the uncertainties involved in experiments as well as in the rotational isomeric state approximation. The results presented in this paper indicate that extra stabilization energies (the gauche oxygen effect) associated with the gauche arrangements about the skeletal C–C bond are ΔE_α = ca. 0.7 and ΔE_β = ca. 0.2 kcal mol^{-1} throughout the series of poly[oxy(1-alkylethylene)] chains examined. The former value is comparable to that (ca. 1 kcal mol^{-1}) found in the poly(oxyethylene) chain,[2] while the latter is characteristic to the hindered conformation designated as g_β. Conformational energies associated with the side-chain conformation were established within reasonable ranges. For further refinement of these energy parameters, complemental experimental data regarding the configuration-dependent properties and especially their temperature coefficients will be indispensable.

The stiffness of a polymer chain, as is defined by the number of conformations permitted to the system, is primarily determined by the bulkiness of the side groups. Let Z and z denote the conformational partition function for a polymer chain and that for an internal monomer residue, respectively. Then for a large x

$$Z = z^x \tag{6}$$

Here Z may be evaluated by successive multiplications of the statistical weight matrices defined for each bond of the chain.[9,22] A value of z estimated therefrom represents the relative number of conformations allowed to a monomer residue. If the chain comprises regular succession of identical structural units, z may be replaced by the largest eigenvalue of the statistical weight matrix of the unit.[9] Listed in the second through fourth columns of Table V are the lowest-energy conformations permitted to the internal *R* monomer residue. The corresponding conformations for the *S* residue can be easily deduced by changing signs of every gauche rotation. In the following calculations, each element of the statistical weight matrices is taken relative to the preferred state mentioned above. Values of z evaluated on this basis for the isotactic and syndiotactic chains are given in the fifth and sixth columns, respectively, where computations were carried out for chains of $x = 200$ by using parameters established above. For the purpose of comparison, a value of z calculated for the poly(oxyethylene) chain (R = H) at the limit $x \rightarrow \infty$ is included in the second row. The flexibility of a polymer chain defined in this way decreases in the order R = H > CH_2CH_3 > CH_3 ≫ $CH(CH_3)_2$ ≫ $C(CH_3)_3$. It is interesting to note here that polymers with R = CH_2CH_3 are slightly more flexible than those with CH_3. In the former, the alternative conformation (i.e., tg^-t for *R* residue) differs from the lowest-energy arrangement by only ca. 0.02 kcal mol^{-1} in the free energy, while in the latter, the all-trans conformation which is of secondary importance is less stable by ca. 0.3 kcal mol^{-1} than the most populated species (cf. Table V). Steric interactions proliferated by the presence of longer side chains (R = CH_2CH_3) make the skeletal chain statistically more flexible. Among the polymer chains examined, poly[oxy(1-*tert*-butylethylene)] exhibits the highest rigidity.

Values of z, evaluated according to eq 6, tend to increase slightly from the isotactic to the syndiotactic chain, as is indicated by the ratio z_{syn}/z_{iso} in the last column of Table V. The ratios z_{syn}/z_{iso} derived for individual polymers vary very little with the stiffness of the chain in constrast to the tendency found in vinyl polymers[4,22] $[-CH_2CH(R)-]_n$. The ratio calculated for poly(oxypropylene) is nearly unity (Table V) while that estimated for polypropylene[24] is 1.4 for a monomer residue. Under the assumption that spacial interactions of longer range beyond the second order are negligible, correlations between the neighboring substituents (R) are dismissed very rapidly as the number of intervening bonds exceeds two. With bulky side chains such as R = $CH_2CH(CH_3)_2$ (in poly(4-methyl-1-pentene)), steric requirements on skeletal bond rotations become very severe irrespective of the tacticity, and consequently the ratio z_{syn}/z_{iso} approaches unity in vinyl polymers as well.[4,22]

Finally, it should be pointed out that the contracted dimension ($\langle r^2 \rangle_0/nl^2 = 0.9$) assigned to the syndiotactic poly[oxy(1-*tert*-butylethylene)] chain is closely related to the rigidity of its chain skeleton. As inspection of a model reveals, cyclic conformations,[25] which bring groups separated by ca. 6 monomer residues (ca. 18 bonds) within a distance of strong steric repulsion, take place statistically quite often. Such interactions of longer range are usually treated as excluded volume effects separately from the short-range interactions here considered. Since the aforementioned cyclic conformation is associated with the lowest-energy arrangement (see Table V) around each constituent bond, it may not be appropriate to simply exclude these long-range interactions from the present treatment. More detailed conformational analyses will be required on this account. The very small characteristic ratios arising from the same physical origin have been predicted for a few biopolymers.[9,26,27]

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A Case Study of the Conformation of Poly(α-aminoisobutyric acid): α- or 3_{10}-Helix

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ABSTRACT: The relative stabilities of α- and 3_{10}-helical structures for polymers of α-aminoisobutyric acid (Aib) have been worked out, using the classical potential energy functions. To make a comparative study, we have used Buckingham "6-exp" and Kitaigorodsky's potential functions. Conformational analysis of the dipeptide segment with Aib residue indicates the necessity for nonplanar distortion of the peptide unit, which is a common feature in the observed crystal structures with Aib residues. In the range of $\Delta\omega$ −10 to +10° studied, α-helical conformations are preferred in the region $-3° < \Delta\omega < +10°$, and 3_{10}-helical conformations are preferred in the region $-3° > \Delta\omega > -10°$. Minimum energy conformations for right-handed structures are found in the +*ve* region of $\Delta\omega$ and correspondingly for left-handed structures in the −*ve* region of $\Delta\omega$. For $\Delta\omega \sim 6°$, α-helical structures have four- or near fourfold symmetry with $h \sim 1.5$ Å. Such a helix with $n = 4$ and $h = 1.5$ Å is termed an α′-helix. This structure is found to be consistent with the electron diffraction data of Malcolm[3] and energetically more favorable than the standard 3_{10}-helix.

α-Aminoisobutyric acid (Aib) differs from the usual amino acids in that it has two methyl groups attached (corresponding to LD positions) to the C^α atom. The simultaneous presence of two methyl groups reduces the allowed region in the conformational space quite considerably as has been reported earlier.[1,2] Burgess and Leach[2] have suggested an obligatory α-helix for the polymer of Aib. Malcolm,[3] on the basis of electron diffraction and infrared studies, has indicated a 3_{10}-helical structure for poly(Aib). This prompted us to investigate in detail the relative stabilities of α- and 3_{10}-helices for poly(Aib), taking into account the available structural informations about the Aib residue. Crystal-structure analyses of oligopeptides containing Aib residues indicate nonplanar distortion of the peptide unit.[4-10] Nonplanar distortion of the peptide unit has been taken into account in our conformational energy calculations on the dipeptide segment of Aib and poly(Aib), and the results of such calculations are presented in this paper. The most important result is that a modified α-helix of pitch nearly 6 Å is found to be energetically more stable than a 3_{10}-helical structure.

Results and Discussion

The dipeptide fragment of the Aib residue is shown in Figure 1. The conformational angles φ, ψ, and ω are defined according to the IUPAC-IUB Commission.[11] Standard Pauling-Corey geometry for the trans-peptide unit was assumed throughout the calculations. While in-

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