an overall activation energy of about 24 kcal mol^{-1} for squalene and 6-dimethylocta-2,6-diene (diisoprene). The difference between the two values may be attributed to the dissociation activation energy of the initiator. The value of E_1 for benzoyl peroxide in the polymer matrix has been accurately determined to be 30 kcal mol^{-1}.[7] Therefore, $E_4 - E_5/2$ is 9 kcal mol^{-1}. Substituting these values, one finds $E_1 \approx 36$ kcal mol^{-1} for poly(isoprene) oxidation. This high activation energy is consonant with the dissociation of a relatively stable peroxide,[9-11] such as the one shown in Scheme I.

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Conformational Energies and the Random-Coil Configuration of Poly(oxypropylene)

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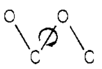
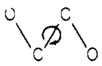
ABSTRACT: Conformational energies of the poly(oxypropylene), poly(methyloxirane), chains were calculated by using semiempirical potential energy functions. Experimental values of the same energies were also obtained from the rotational isomeric state analysis of the unperturbed dimension, dipole moment, and bond conformations observed for isotactic samples. The magnitude of stabilization energies associated with the gauche O–C–C–O arrangements was estimated from the difference between theoretical and experimental energies thus established. A value of $\Delta E_\alpha = 0.7$ kcal mol^{-1} was obtained for the gauche conformation (α) with the articulated methyl group trans to the preceding oxygen, being in fair agreement with the value (1.0 kcal mol^{-1}) reported previously for the poly(oxyethylene) chain. The gauche oxygen effect was found to be less pronounced for the conformation β in which the preceding oxygen atom is syn to both the following oxygen and the methyl group ($\Delta E_\beta = 0.2 \pm 0.1$ kcal mol^{-1}). Conformational energy parameters thus estimated were used to calculate the characteristic ratio $\langle r^2 \rangle_0/nl^2$, the dipole moment ratio $\langle \mu^2 \rangle/nm^2$, the bond conformations for the skeletal C–C bond, and their temperature coefficients for isotactic, syndiotactic, and atactic chains. The effects of atypical head-to-head and tail-to-tail placements were also examined.

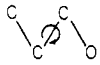
Configuration-dependent properties of polyoxide chains such as $[-(CH_2)_yO-]_x$ have been investigated in a previous paper by one of the present authors and Mark.[2] The most characteristic feature of such polymeric chains is a decisive perference for the gauche conformation over the trans around certain skeletal bonds.[2-8] In poly(oxymethylene) (POM) ($y = 1$), gauche states about an internal



bond are found to be ca. 1.5 kcal mol^{-1} lower in energy than the alternative trans state.[3-5] It has been shown[9] that such conformational characteristics possess some common aspects with the "anomeric effect"[10] known in carbohydrate chemistry. Gauche states for the



bond of poly(oxyethylene) (POE) ($y = 2$) are ca. 0.4 kcal mol^{-1} below the trans state.[3,5-7] For bonds of the type



in poly(oxytrimethylene) (POM_3) ($y = 3$) and poly(oxytetramethylene) (POM_4) ($y = 4$) chains,[3,7,8] preference for gauche states is ca. 0.2 kcal mol^{-1}. Theoretical calculations based on semiempirical conformational energy functions[2,11] failed to reproduce the aforementioned energy differences.

For the POE chain, the theoretical value[2] is 0.6 kcal mol^{-1} in favor of the trans state in opposition to that (−0.4 kcal mol^{-1})[6,7] estimated from the experimental data. Similar energy discrepancies have been observed for various halogenated hydrocarbons.[12] For example, in 1,2-difluoroethane, gauche states which involve the F···F interaction should be disfavored by Coulombic repulsions. They are found, however, to be of essentially the same energy as the alternative trans states.[13] There is no simple explanation for such unusual conformational behavior termed as the "gauche effect", the "hockey-sticks effects", the "gauche-attraction effects", and so on.[14,15]

A similar "gauche oxygen" effect may be expected in the poly(oxypropylene) (POP) chain $[-CH_2CH(CH_3)O-]_x$,

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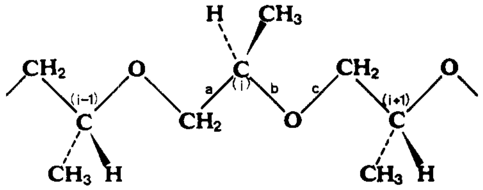


Figure 1. Schematic diagram of the isotactic poly((*R*)-oxypropylene) chain in its planar, all-trans conformation. Each skeletal bond in a repeat unit is distinguished by an alphabetical notation.

Table I
Geometrical Parameters Used for Poly(oxypropylene)

bond length, Å	bond angle, deg
C-C 1.53	∠COC 111.5
C-O 1.43	∠CCO 110
C-H 1.10	∠CCC 110
	∠CCH 110

which differs schematically from POE by the incorporation of methyl substituents. Ishikawa and Teramoto[16] have examined the unperturbed dimension and dipole moment of POP based on the rotational isomeric state approximation. In their calculations, semiempirical energy expressions involving torsional and van der Waals contributions were used to estimate conformational energy parameters of the system, Coulombic interactions occurring between partially charged atoms along the chain being entirely ignored. The agreement thus attained with experimental observations[17-19] may therefore be fortuitous for reasons stated above.

The present study was undertaken in an attempt to obtain the best set of conformational energies by the critical rotational isomeric state analysis of the experimental values of the dimension,[17] dipole moment,[20] and fractions of the conformation about the skeletal C–C bonds,[21a,22] all of which have been reported for the isotactic POP samples. Comparison of theoretical and experimental values of conformational energies thus derived should provide a quantitative estimate of the gauche oxygen effect associated with this chain molecule. The results will be specifically compared with those previously estimated for the POE chain.[2] Configuration-dependent properties of poly[oxy(1-alkylethylene)] chains ($[-CH_2CH(R)O-]_x$) carrying substituents such as R = C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$ may be treated on the same basis, steric interactions imposed by the presence of bulky side groups being properly taken into account.[23,29] This is the subject of the following paper.[24]

Structural Data and Conformational Energies

A portion of an isotactic POP chain in its planar, all-trans conformation is shown in Figure 1. As is represented here, the substituent CH_3 groups are alternatively situated above and below the plane of the backbone for an isotactic arrangement. For a syndiotactic chain, they should be located on the same side, either above or below, of the plane. Distinction between the two stereochemical arrangements, i.e., *R* and *S*, for the asymmetric tertiary carbon atoms becomes important when stereoirregular chains are examined.

The bond lengths and bond angles used in this study are listed in Table I. The bond angles ∠CCO are assumed to be 110° for the skeletal backbone.[25] The ∠COC angle (111.5°) was taken from the value reported for dimethyl ether.[26]

Statistical weight matrices applicable to the constituent bonds of a repeating unit, designated as a, b, and c in Figure 1, are given[3] respectively by

$$\mathbf{U}_a{}^R = \begin{bmatrix} 1 & \alpha & \beta \\ 0 & \alpha & \beta\omega \\ 1 & \alpha\omega & 0 \end{bmatrix} \tag{1}$$

$$\mathbf{U}_b{}^R = \begin{bmatrix} 1 & 0 & 1 \\ 1 & 0 & \omega \\ 1 & 0 & 1 \end{bmatrix} \tag{2}$$

$$\mathbf{U}_c{}^R = \begin{bmatrix} 1 & \sigma & 0 \\ 1 & 0 & 0 \\ 1 & 0 & \sigma \end{bmatrix} \tag{3}$$

Where superscripts *R* represent the stereochemical configuration at the asymmetric center (C_i), and rows and columns of each matrix are customarily indexed to the rotational states in the order *t*, g^+, and g^- for the bond pair under consideration. Under the assumption that interactions between groups separated by more than five bonds are negligible, statistical weight matrices thus defined should be independent of the asymmetric character of the neighboring units (C_{i-1} and C_{i+1} in Figure 1). Special care should be required as usual[3,27] for the terminal bonds of the chain. Statistical weight parameters α, β, and σ, respectively, are defined for each first-order interaction (between groups separated by three bonds) and ω for the second-order interaction (between groups separated by four bonds). Each statistical weight factor is normalized to the weight of unity for the corresponding *tt* state. Following the conventional procedure,[3] statistical weight parameters are taken to be simple Boltzmann factors in the corresponding conformational energies.

Statistical weight matrices for the *S* unit incorporated in a polymer chain may be easily derived[3] from those of the *R* unit (cf. eq 1–3) by pre- and postmultiplying an operator matrix **Q**. Thus in general,

$$\mathbf{U}_a{}^S = \mathbf{Q}\mathbf{U}_a{}^R\mathbf{Q} \tag{4}$$

where

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{5}$$

performs an interchange of the second and third rows or columns. The matrices $\mathbf{U}_b{}^S$ and $\mathbf{U}_c{}^S$ may be derived similarly. It follows from the relation $\mathbf{QQ} = \mathbf{I}_3$ (the identity of order three) that

$$\mathbf{U}_a{}^S U_b{}^S U_c{}^S = \mathbf{Q}[\mathbf{U}_a{}^R U_b{}^R U_c{}^R]\mathbf{Q} \tag{6}$$

The relation specified by eq 4 (or more generally by eq 6) holds in general for enantiomorphic structures.[3]

Theoretical values of conformational energies were calculated as a function of rotation angles according to the procedure set forth in the previous paper.[2] Threefold intrinsic potentials with barriers of 2.8 and 1.8 kcal mol^{-1} were assigned to the rotation around C–C and C–O bonds,[2,28,29] respectively. Nonbonded interactions were computed by using the Buckingham 6-exp energy function for each pair of interacting atoms.[2,28,29] Parameters required in the expression were taken from Table II of the

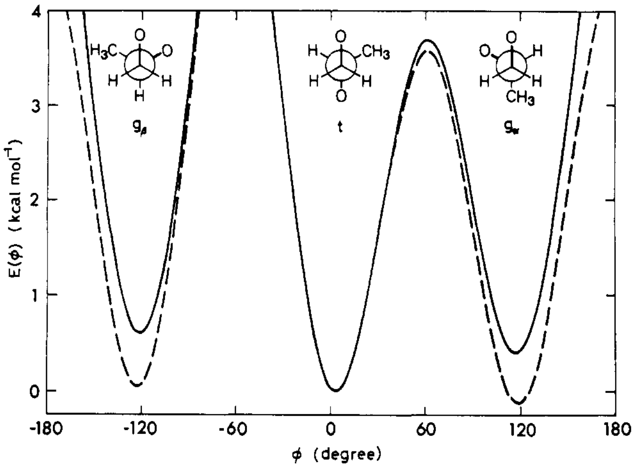


Figure 2. Conformational energies of (*R*)-1,2-dimethoxypropane calculated as a function of rotation angles about the C–C bond, the adjoining O–C and C–O bonds being kept trans. The solid and dashed curves indicate respectively energies computed with and without the Coulombic contribution. Energies are expressed relative to the *t* state. Two gauche conformations occurring about $\varphi = \pm(^2/_3)\pi$ are designated with g_α and g_β, respectively.

previous paper.[2] Electrostatic contributions to the conformational energy were assessed by assigning partial charges to the carbon ($\delta_C = 0.155$) and oxygen atoms ($\delta_O = -0.31$) joined by each C–O bond,[2,29] 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.[30] The effective dielectric constant was taken to be 3.0, the same value being used previously.[2,29]

Conformational energies associated with the rotation about C–C bonds (bond a in Figure 1) were calculated for (*R*)-1,2-dimethoxypropane, a monomer model. The results are shown in Figure 2 as a function of rotation angle φ, adjoining O–C and C–O bonds being kept trans. Energies are expressed relative to that of the trans minimum ($\varphi = 3°$). For the latter purpose, we introduce new notations g_α and g_β to distinguish two gauche states occurring about C–C bonds in the POP chain, each being associated with the statistical weight parameter given as the subscript. For a C–C bond jointed 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. The solid and dashed curves in Figure 2 indicate conformational energies calculated with and without the Coulombic interaction, respectively. The van der Waals interaction between two oxygen atoms occurring in the g_α state ($\varphi = 117°$), as shown by the dashed curve, is slightly less repulsive (ca. 0.1 kcal mol⁻¹) than those between the CH_3 group and oxygen in the alternative trans state. In the g_β state ($\varphi = -123°$), restrictions imposed by the steric interaction between O···O and O···CH_3 raise the energy by ca. 0.05 kcal mol⁻¹ relative to the trans state. Major contributions to the conformational energies associated with the g_α and g_β states are therefore Coulombic as indicated by the solid curve in Figure 2. It follows from the previous analysis on polyoxide chains[2] that extra stabilization energies ΔE associated with the "gauche oxygen" effect may be treated as correction terms to the energy expression;[9] thus we let

$$E_\alpha = 0.4 - \Delta E_\alpha \qquad (7)$$

and

$$E_\beta = 0.6 - \Delta E_\beta \qquad (8)$$

Energy parameters E_α and E_β expressed in kcal mol⁻¹ will be treated as variables in the following rotational isomeric state calculations of the dimension, dipole moment, and bond conformation of the isotactic POP chain. Comparison of these calculated results with the best currently available experimental results will then provide the experimentally most reliable values of ΔE_α and ΔE_β.

Steric interactions taking place around bond b (Figure 1) should be approximately equivalent to those encountered in isopropyl methyl ether, $CH(CH_3)_2OCH_3$. Conformational energy calculations for this model yielded two identical minima for the C_1 form with displacement $\Delta\varphi \simeq 20°$ from the regularly staggered position.[29] Similar displacement of methyl groups has been suggested from the crystallographic analysis on poly(methyl vinyl ether).[31] Due to very severe steric overlaps between methyl groups, the conformational energy calculated for the C_s form is very high (4.2 kcal mol⁻¹ relative to the other two minima).[29] Snyder and Zerbi[32] concluded from infrared studies on a series of isopropyl ethers that the C_s form is almost entirely suppressed. In the POP chain, Coulombic interactions occurring between partially charged carbon atoms may enhance the energy of the gauche states above that of the trans state for bond b. The energy contribution from this source is however estimated to be only 0.07 kcal mol⁻¹, indicating that Coulombic interactions are negligibly small. Accordingly, the statistical weight parameters are taken to be 1, 0, and 1 respectively for the rotational states t, g^+, and g^- about bond b (eq 2).

Interactions between $(CH)_i$ and $(CH)_{i+1}$ occur for rotations about bond c (Figure 1). To the extent that CH may be considered the equivalent of CH_2, a statistical weight σ is assigned to represent the contribution from such first-order interactions in the gauche conformation (eq 3), in keeping with the scheme applied previously to the POE chain.[2] Conformational energy calculations[2] gave a value (E_σ) of 1.25 kcal mol⁻¹ in reasonable agreement with experimental observations on low molecular weight analogues.[33-35] Such calculations also indicate a displacement of ca. 20° for the associated gauche minima.[2]

We consider now second-order interactions; those between groups separated by four bonds. Such interactions occurring for bond pair bc in the g^-g^+ conformation involve severe steric repulsions between CH_2 and CH groups. Conformational energy calculations carried out for the POE chain[2] suggest that energy minima associated with such conformation are very shallow and scarcely noticeable on the shoulder of the potential curves. Similar steric requirements should be involved in the second-order interactions between CH_3 and CH groups in the tg^- conformation for the same bond pair. As the inspection of a model reveals, steric repulsions involved in the g^+g^+ and g^+g^- states are more severe. Correspondingly, the statistical weight parameters for these conformations are set equal to zero (eq 3). Contributions from the g^+t and g^-g^- conformations for bond pair ca are also negligible (eq 1) for the reasons mentioned above.[2]

A statistical weight parameter ω was assigned to the second-order interactions in which O atoms are participants. Such interactions arise in the $g^\pm g^\mp$ states about bond pair ca (eq 1) as well as the g^+g^- state for bond pair ab (eq 2). The associated energies E_ω were taken to be 0.4 kcal mol⁻¹, the same value being adopted in the analysis on the POE chain.[2]

Results of these considerations are summarized in the second column of Table II. Rotational angles φ given in the table apply to the bonds associated with the *R* unit. These parameters are termed "set I" in the following treatment. In the previous analysis[2] on the POE chain, some of the parameters were modified so as to refine the

Table II
Conformational Parameter Sets Adopted for the Bonds Associated with the R-Monomeric Residue[a]

	set I	set II
E_σ	1.3	0.9
E_ω	0.4	0.4
φ(C-C) t	0	0
g^+	120	110
g^-	−120	−120
φ(C-O) t	−20	−10
g^+	120	120
g^-	−100	−110
φ(O-C) t	0	0
g^+	100	110
g^-	−100	−110

[a] Conformational energies are given in kcal mol^{-1}, and rotational angles are in degrees.

agreement with observed values of the unperturbed dimension, dipole moment, and their temperature coefficients; i.e., the first-order interaction energy E_σ was lowered to 0.9 kcal mol^{-1}, and correspondingly rotation angles $\varphi_{g\pm}$ about C–C, C–O, and O–C bonds were all adjusted to ±110°. Similar revisions adopted for the POP chain are summarized as "set II" in the last column of Table II, where φ_{g^-} for the C–C bond remains unchanged in consideration of the steric requirement. Signs of rotational angles φ given in Table II should be inverted for the bonds associated with the antipode; thus for each bond of the S unit, $\varphi_t^S = -\varphi_t^R$ and $\varphi_{g\pm}^S = -\varphi_{g\mp}^R$ (cf. eq 4 and 6).

Unperturbed Dimensions, Dipole Moments, and Bond Conformations

Experimental values reported in the literature for isotactic samples of POP and the model compound 1,2-dimethoxypropane (1,2-DMP) are summarized in Table III. The unperturbed dimension and dipole moment are expressed as the characteristic ratio $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$, respectively, where n is the number of skeletal bonds, and l^2 and m^2 are the averaged values of the square of their bond lengths and dipole moments.

Allen, Booth, and Price[17] carried out viscosity measurements on fractionated samples of crystalline POP under Θ conditions (in isooctane at 50 °C). From the well-known relation[36] between the intrinsic viscosity $[\eta]_\Theta$ and molecular weight M, a value of $\langle r^2\rangle_0/nl^2$ was estimated

$$[\eta]_\Theta = \Phi\left[\frac{\langle r^2\rangle_0}{M}\right]^{3/2} M^{1/2} \tag{9}$$

to be ca. 6.0 (the second column) by using a hydrodynamic constant[3] $\Phi = 2.6 \times 10^{21}$ dL cm^{-3} mol^{-1}. Kamata et al.[37] have reported viscometric data for atactic samples, which lead to a lower value of $\langle r^2\rangle_0/nl^2$ (ca. 4.0). Stereochemical arrangements along the polymer chain for such samples are not known, however. Dipole moment ratios $\langle\mu^2\rangle/nm^2$ derived from dielectric measurements[20] are listed in the third column. Values are somewhat higher in benzene for both 1,2-DMP and crystalline POP. To avoid some possible solvent effect,[38] lower values obtained in cyclohexane will be used for comparison with theoretical calculations in the following section. Hirano, Khanh, and Tsuruta[21a] carried out NMR analysis of vicinal coupling constants between methylene and methine protons by using poly(*trans*-3-methyloxirane-2-*d*) in various solvents. Conformer fractions were deduced from these data by adopting values[21b] of $^3J_t = 9.1$ Hz and $^3J_g = 2.6$ Hz for the trans and gauche couplings, respectively. Oguni, Maeda, and Tani[22] reported similar studies on polymers derived from *cis*- and *trans*-3-methyloxirane-2-*d*. Fractions of the conformation about the skeletal C–C bond f_t, f_α, and f_β thus estimated are approximately in the range 0.4, 0.5, and 0.1, respectively (the last column). Here fractions f_α and f_β are defined as those of gauche conformations associated with statistical weight parameters α and β, respectively (see Figure 2).

Theoretical Calculations for the Isotactic Chain and Comparison with Experimental Data. Values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ were computed for isotactic chains $CH_3O[-CH_2CH(CH_3)O-]_xCH_3$ with $x = 100$ ($n = 302$) by using the rotational isomeric state theory according to the conventional procedure;[3,27] for simplicity, bond angles are assumed to be uniformly 111.5° along the skeletal chain,[2] other structural data and bond dipole moment for the C–O bond being given in the preceding section. (The bond dipole moment for the C–C bond is assumed to be null.[2]) Results obtained using parameter sets I and II (see Table II) are plotted against E_β for a given value of E_α in Figures 3 and 4, respectively. The left and right ordinates in these figures indicate values of the characteristic ratio and dipole moment ratio, respectively. The scales on both ordinates are so adjusted that the observed values for $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ meet at the same height. In order to facilitate comparison with observations, calculations were carried out for the temperatures equivalent to those employed in the corresponding experiments.

The characteristic ratio $\langle r^2\rangle_0/nl^2$ increases rapidly with E_β while it varies less sensitively with E_α over the range investigated. The dipole moment ratio $\langle\mu^2\rangle/nm_2$ decreases with an increase in E_β, which is opposite to the tendency

Table III
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 1,2-Dimethoxypropane (DMP) and Isotactic Poly(oxypropylene) (POP)[a]

			fraction of conformers for C–C bonds			
compd	$\langle r^2\rangle_0/nl^2$	$\langle\mu^2\rangle_0/nm^2$	f_t	f_α	f_β	
1,2-DMP		0.59 (C_6H_6)[c] 0.54 (c-C_6H_{12})[c]	0.41	0.48	0.11	(c-C_6D_{12})[e]
POP	6.0 (i-C_8H_{18})[b]	0.54 (C_6H_6)[c,d] 0.49 (c-C_6H_{12})[c,d]	0.40	0.4_9	0.1_1	(C_6H_6)[f]
			0.42	0.46	0.12	(C_6D_6)[g]
			0.35	0.5_2	0.1_3	($CHCl_3$)[f]
			0.34	0.49	0.17	($CDCl_3$)[g]
			0.42	0.5_7	0.0_1	(c-C_6D_{12})[f]

[a] Solvents used are given in parentheses. [b] Observed at 50 °C, ref 17. [c] Observed at 25 °C, ref 20. [d] The values cited in this table are slightly higher than those given in ref 20. Averaged values for the dipole moment ratio determined by several independent measurements, including some unpublished data, were adopted in the present work. Values refined more recently are reported in ref 20. The difference is trivial however. [e] (R)-1,2-Di(methoxy-d_3)propane, from the ^{1}H NMR vicinal coupling constants, observed at 24 °C: T. Hirano and A. Abe, unpublished data. [f] Observed at 25 °C, ref 21. [g] Observed at 25 °C, ref 22.

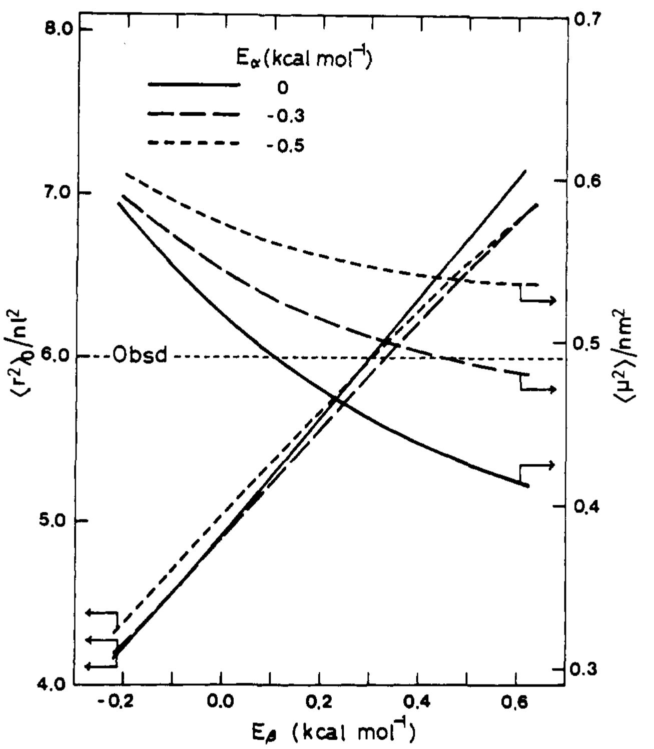


Figure 3. The characteristic ratio and dipole moment ratio for the isotactic POP chain having $x = 100$ ($n = 302$) calculated by using parameter set I, E_α and E_β being treated as variables. Values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ obtained for the temperature of 50 and 30 °C, respectively, are plotted against E_β for a given value of E_α. The horizontal dashed line indicates the appropriate observed values for both ordinates, as taken from Table III.

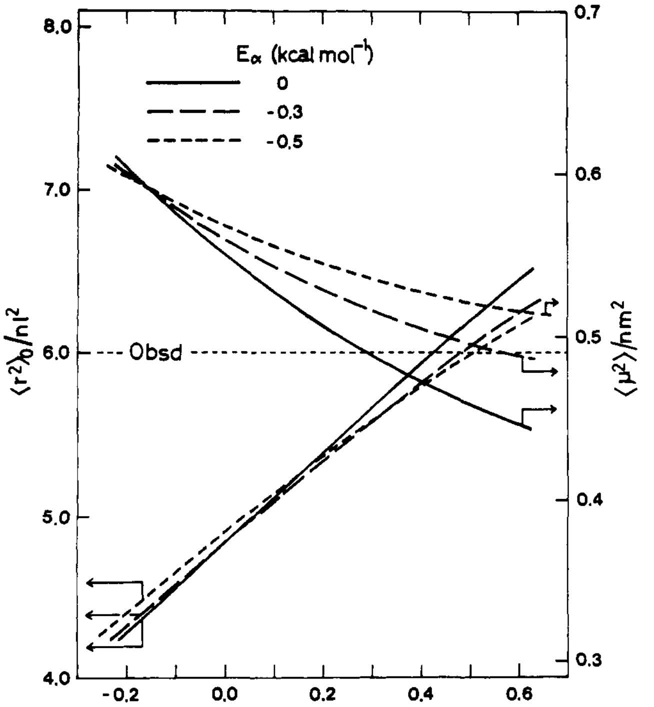


Figure 4. Values of $\langle r^2\rangle_0/nl^2$ at 50 °C and $\langle \mu^2\rangle/nm^2$ at 30 °C calculated for the isotactic POP chain by using parameter set II. See legend to Figure 3.

found for $\langle r^2\rangle_0/nl^2$. In the range $E_\beta > -0.2$ kcal mol^{-1}, the ratio $\langle \mu^2\rangle/nm^2$ tends to decrease with an increase in E_α as well. From each curve given in Figures 3 and 4, a pair of conformational energies E_α and E_β, which reproduce the observed value of $\langle r^2\rangle_0/nl^2$ (6.0) or $\langle \mu^2\rangle/nm^2$ (0.49), may be estimated. Values of E_α and E_β thus obtained are plotted against each other in Figure 5; the results pertinent to parameter set I are indicated by the heavy-solid ($\langle r^2\rangle_0/nl^2$) and heavy-dashed curves ($\langle \mu^2\rangle/nm^2$) and those to set II by the light-solid ($\langle r^2\rangle_0/nl^2$) and light-dashed curves ($\langle \mu^2\rangle/nm^2$), respectively. Within a certain range of E_α (>−0.3 kcal mol^{-1}), a pair of solid and dashed curves for each parameter set tends to be parallel with maximum separation of ca. 0.2 kcal mol^{-1} in E_β. Considering the uncertainty imposed by experimental errors, it is improbable to choose any descrete set of E_α and E_β from this figure. In this respect, the analysis of bond conformations about the skeletal C–C bonds should provide supplemental information.

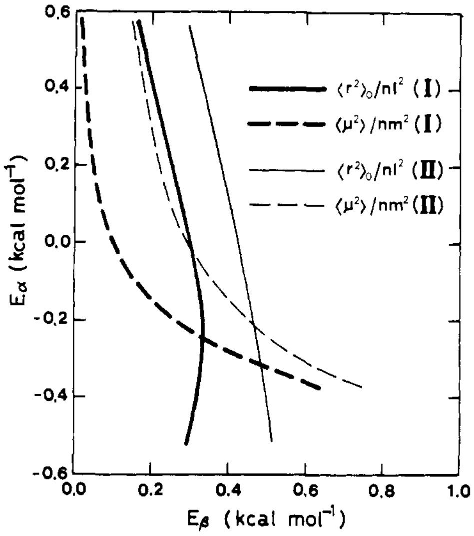


Figure 5. Pairs of conformational energies E_α and E_β chosen so as to reproduce the observed values of $\langle r^2\rangle_0/nl^2$ (6.0) and $\langle \mu^2\rangle/nm^2$ (0.49). Values of E_α and E_β were taken from the results shown in Figures 3 and 4, with supplemental calculations which are not included therein. The heavy-solid and heavy-dashed curves respectively are those derived from $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ by using parameter set I. The results obtained from parameter set II are similarly shown by the light curves.

Bond conformations f_t, f_α, and f_β ($\equiv 1 - f_t - f_\alpha$) about the skeletal C–C bonds are calculated according to the conventional expression[3]

$$f_\zeta = (1/x)\sum_\eta (\partial \ln Z/\partial \ln P_{\eta\zeta}) \qquad (10)$$

where Z is the configurational partition function defined in the usual manner, and $P_{\eta\zeta}$ denotes the statistical weight parameter assigned to the (η,ζ) element of $\mathbf{U}_a$ matrices (eq 1 and 4). Results obtained for the isotactic chain ($x = 100$), using parameter set I, are shown in Figure 6. Variation of (f_t, f_α, f_β) with E_α and E_β is indicated by solid and dashed curves, respectively. The effect arising from alteration of E_σ from 1.3 (set I) to 0.9 kcal mol^{-1} (set II) is trivial; the results of calculations for parameter set II are not illustrated. Observed values (taken from Table III) are indicated by filled circles. They are located in the range of $E_\alpha = -0.3 \pm 0.1$ kcal mol^{-1} but are scattered over a wide range of E_β (0.5 to 1.5 kcal mol^{-1}). It should be recalled here that the ranges of E_β suggested from the analysis of observed values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ (see Figure 5) may not be beyond 0.4 and 0.6 kcal mol^{-1} respectively for parameter sets I and II. Consequently, values of E_β were chosen to be 0.35 (I) and 0.5 kcal mol^{-1} (II), E_α being set equal to −0.3 kcal mol^{-1}. The unperturbed dimension, dipole moment, and bond conformations calculated by using parameter sets thus derived are as follows: (set I) $\langle r^2\rangle_0/nl^2 = 6.1$ (50 °C), $\langle \mu^2\rangle/nm^2 = 0.50$ (30 °C), $f_t{:}f_\alpha{:}f_\beta =$

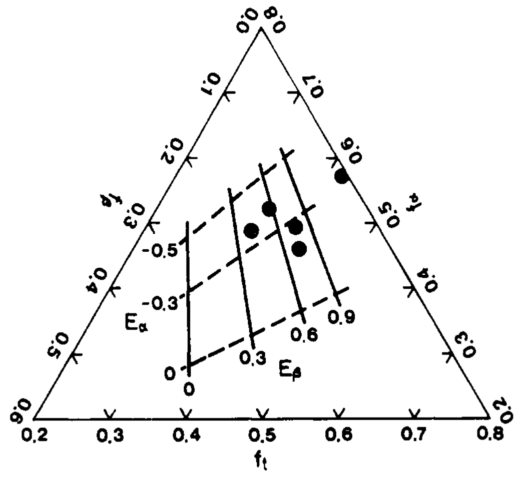


Figure 6. Conformations about the skeletal C–C bonds for the isotactic POP chain having $x = 100$ calculated by using parameter set I, E_α and E_β being treated as variables. The solid curves represent variation of fractions f_t, f_α, and f_β with E_α, values of E_β being kept constant as indicated. The dashed curves indicate variation with E_β, keeping E_α at a constant value. The relevant experimental data (Table III) are given by filled circles.

0.35:0.46:0.19 (25 °C); (set II) $\langle r^2\rangle_0/nl^2 = 6.0$ (50 °C), $\langle \mu^2\rangle/nm^2 = 0.50$ (30 °C), f_t:f_α:f_β = 0.36:0.49:0.15 (25 °C). Agreement with observed data (Table III) is reasonable with either set of parameters.

The dipole moment ratio of 1,2-DMP was examined in a similar manner. Theoretical values derived from the aforementioned parameter sets I and II were identical, $\langle \mu^2\rangle/nm^2 = 0.56$ being in fair agreement with experiment. Fractions of conformers at equilibrium were estimated to be f_t:f_α:f_β = 0.35:0.46:0.19 (set I) and 0.36:0.50:0.14 (set II) at 25 °C. In agreement with observations, these fractions differ very little from those calculated for the C–C bonds incorporated in a polymeric chain, indicating that such fractions are determined mainly by interactions of short range.

Stereoirregular Chains. Calculations of $\langle r^2\rangle_0$, $\langle \mu^2\rangle$, and bond conformations were carried out in a usual manner for Monte-Carlo chains of 100 units, each of which was generated from a series of random numbers. Characteristic ratios $\langle r^2\rangle_0/nl^2$ and dipole moment ratios $\langle \mu^2\rangle/nm^2$ obtained by using parameter set I are plotted against dyad replication probability P_r (i.e., the probability of an isotactic dyad placement) in Figure 7a; values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ are indicated respectively on the left and right ordinates. Both of these ratios decrease gradually as P_r varies from 1.0 (the isotactic) to 0.0 (the syndiotactic). In the estimation of E_α and E_β presented in the preceding section, the results of calculations carried out for perfectly isotactic POP chains ($P_r = 1.0$) were compared with experimental data[17,20–22] observed on polymers formed from the *RS*-racemic monomer. NMR spectroscopic analyses[43,44] suggest that the crystallizable part of isotactic polymer samples prepared by using coordination catalysts from (*RS*)-methyloxirane may contain a small amount (less than 5%) of syndiotactic dyad placements. Effects arising from such stereochemical irregularities are estimated to be ca. 2% in $\langle r^2\rangle_0/nl^2$ and 0.1% in $\langle \mu^2\rangle/nm^2$ over the range P_r = 1.0 to 0.95 (Figure 7a), both values being well within the experimental error. Loveluck[18] and more recently Le Fèvre and Sundaram[19] studied dipole moments of oligomers and low molecular weight samples ($x < 70$) of atactic poly(propylene glycol) in benzene at 25 °C. The dipole moment ratio $\langle \mu^2\rangle/nm^2$ derived therefrom is 0.46 for a sample having $x = 69$. Being consistent with theoretical calculations, this value is lower than those obtained for isotactic samples under similar conditions.

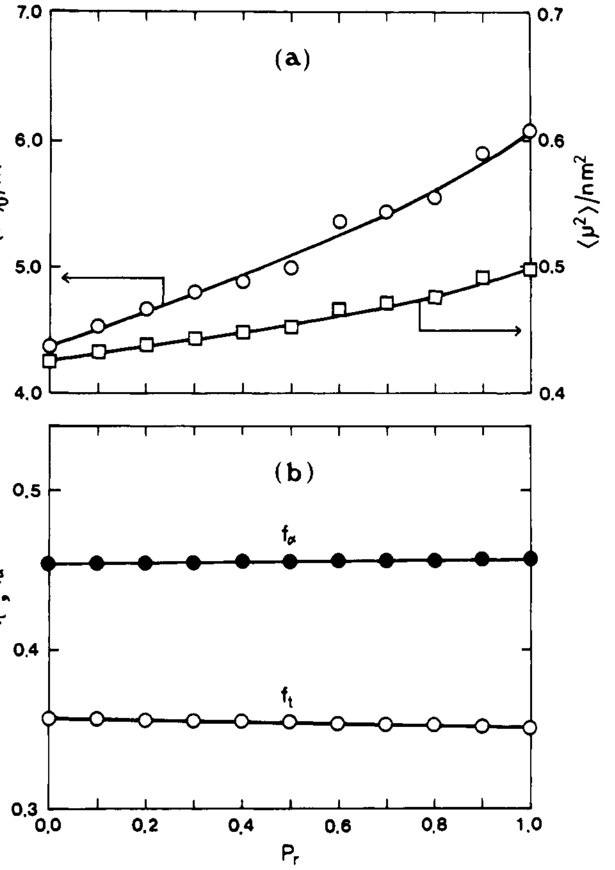


Figure 7. Statistical properties of POP chains shown as a function of replication probability P_r. (a) The characteristic ratio (50 °C) and dipole moment ratio (30 °C) calculated for Monte-Carlo chains of 100 units by using parameter set I are given by open circles and open squares, respectively. (b) Fractions of the t and g_α conformation about skeletal C–C bonds (25 °C) calculated by using the same parameter set are represented by filled (f_α) and open circles (f_t). Values of f_β ($\equiv 1 - f_t - f_\alpha$) for the g_β conformation are not illustrated explicitly.

Table IV
Temperature Coefficients d ln $\langle r^2\rangle_0/\mathrm{d}T$ and d ln $\langle \mu^2\rangle/\mathrm{d}T$ Calculated for Representative Model Chains and 1,2-DMP[a]

polymer chains (P_r)	[d ln$\langle r^2\rangle_0$/dT] × 10^3, K^{-1} (50 °C)	[d ln$\langle \mu^2\rangle$/dT] × 10^3, K^{-1} (30 °C)
isotactic (1.0)	−1.59	0.43
stereoblock (0.9)	−1.40	0.56
atactic (0.5)	−0.25	1.06
syndiotactic (0.0)	0.64	1.56
1,2-DMP		0.55

[a] Calculated by using parameter set I for Monte-Carlo chains of 100 units.

Bond conformations f_t and f_α ($\equiv 1 - f_t - f_\beta$) for the C–C bonds are quite insensitive to P_r, as is illustrated in Figure 7b. The results shown here again suggest that conformations about each C–C bond are largely determined by local effects, and they are quite independent of the stereochemical character of the neighboring units. Results of calculations using parameter set II do not differ appreciably from those illustrated in Figure 7.

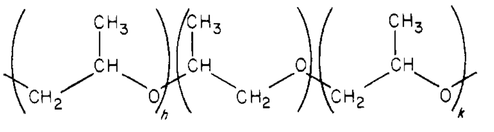
Temperature Dependence. Temperature coefficients of $\langle r^2\rangle_0$ and $\langle \mu^2\rangle$ were computed for representative model chains having isotactic ($P_r = 1.0$), stereoblock (0.9), atactic (0.5), and syndiotactic (0.0) arrangements, respectively. Results obtained by using parameter set I are listed in Table IV, where the temperature coefficient d ln $\langle \mu^2\rangle/\mathrm{d}T$

calculated for 1,2-DMP is also included. It is interesting to note that the calculated temperature coefficient d ln $\langle r^2 \rangle_0/\mathrm{d}T$ (50 °C) varies from an appreciably large negative value (-1.59×10^{-3} K^{-1}) at $P_r = 1.0$ to a small positive one (0.64×10^{-3} K^{-1}) at $P_r = 0.0$. No experimental data are available however. Values of d ln $\langle \mu^2 \rangle/\mathrm{d}T$ (30 °C) increase similarly from 0.43 to 1.56×10^{-3} K^{-1} with a decrease in P_r, as is shown in the third column of Table IV. Observed coefficients[20] derived from experimental values of $\langle \mu^2 \rangle/nm^2$ determined in cyclohexane over the temperature range 25–50 °C are 0.7 (±1.0) $\times 10^{-3}$ K^{-1} for an isotactic POP sample and 0.5 (±0.5) $\times 10^{-3}$ K^{-1} for 1,2-DMP, both values being in fair agreement with those calculated.

Variation of bond conformations with temperature was estimated by computing the coefficient $\mathrm{d}f/\mathrm{d}T$ for chains given above. Values (10^4 $\mathrm{d}f/\mathrm{d}T$, K^{-1}) obtained for the isotactic and syndiotactic chain by using parameter set I (25 °C) are given in the order t, g_α, and g_β as follows: −0.2, −3.2, 3.4 ($P_r = 1.0$) and −0.1, −3.2, 3.3 ($P_r = 0.0$), respectively. The temperature coefficients of the polymer are quite insensitive to P_r but somewhat different from those (−0.4, −2.6, and 3.0) estimated for 1,2-DMP. Values of $\mathrm{d}f_\alpha/\mathrm{d}T$ and $\mathrm{d}f_\beta/\mathrm{d}T$ are similar in magnitude but opposite in sign for all the chains examined. Correspondingly, fractions of the trans conformation f_t vary less sensitively with temperature. Use of parameter set II yielded similar results for all of the properties examined.

Discussion

Price and his co-workers[45,46] have studied the degradation of POP to dimer glycols by using ozone and n-butyllithium. Based on the chromatographic analysis of dipropylene glycols thus produced, they concluded that the principal irregularity in the structure of the amorphous POP accompanying the isotactic polymer prepared by coordination catalysts arises from abnormal head-to-head and tail-to-tail sequences and that each insertion of such a unit involves an inversion of stereochemical configuration at the asymmetric secondary carbon atom of the epoxide monomer. Consequently, such abnormal sequences incorporated in moderately isotactic samples may be predominantly of the type



It is interesting to note here that the atactic polymer prepared from racemic monomer by using KOH (or t-BuOK) catalyst was found to be nearly free from the head-to-head, tail-to-tail arrangements.[44,45,47] These observations were confirmed by NMR studies on poly(2-methyloxirane-2-d) as reported by Oguni, Tani, and their colaborators.[43] They suggested that the highly crystalline fraction of isotactic POP prepared by conventional coordination catalysts may contain a few percent of these abnormal linkages.

The effect arising from the presence of head-to-head, tail-to-tail placements was therefore examined for the characteristic ratio $\langle r^2 \rangle_0/nl^2$ and the dipole moment ratio $\langle \mu^2 \rangle/nm^2$, as is shown in Figure 8. It was assumed here that such abnormal linkages are randomly distributed along the chain which would be otherwise perfectly isotactic. Calculations were carried out for chains of 100 units by using parameter set I; statistical weight matrices required for the bonds associated with these abnormal units may be easily derived in the usual manner. The characteristic ratio $\langle r^2 \rangle_0/nl^2$ decreases almost linearly with an increase in the content of head-to-head, tail-to-tail placements within the range investigated. Inclusion of 5% of such units lowers the value of $\langle r^2 \rangle_0/nl^2$ from 6.1 (for the perfectly isotactic chain) to 5.6. The dipole moment ratio $\langle \mu^2 \rangle/nm^2$ decreases as well, but the effect is negligibly small even at 5% of such abnormal placements (Figure 8). The experimental value of $\langle r^2 \rangle_0/nl^2$ cited above (Table III) was taken from the work reported by Allen, Booth, and Price.[17] The polymer was prepared from racemic monomer in dioxane by using a diethylzinc–water catalyst and recrystallized from isooctane at 40 °C. Crystalline fractions thus obtained should be highly isotactic, the content of head-to-head, tail-to-tail placements being less than a few percent.[43]

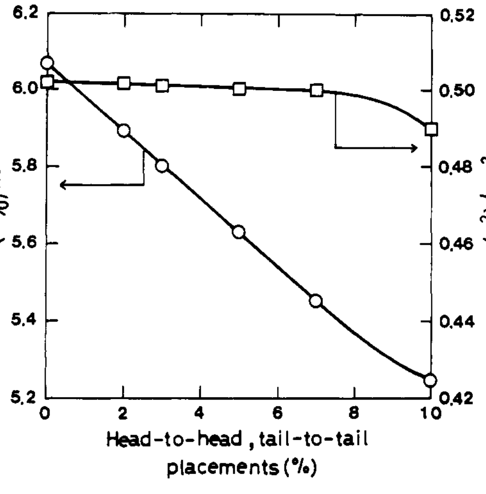


Figure 8. Effects of atypical head-to-head, tail-to-tail placements on $\langle r^2 \rangle_0/nl^2$ (50 °C) and $\langle \mu^2 \rangle/nm^2$ (30 °C). Calculations were carried out by using parameter set I. The abnormal units of the type discussed in the text were assumed to be randomly distributed along the chain (x = 100) which would be otherwise perfectly isotactic.

Table V
Gauche Oxygen Effects Associated with the Gauche Conformations for the Skeletal C-C Bond

conform	E, kcal mol^{-1} calcd[a]	E, kcal mol^{-1} exptl[b]	$\Delta E = E_{\mathrm{calcd}} - E_{\mathrm{exptl}}$
g_α	0.4	−0.3	0.7
g_β	0.6	0.35 (I) 0.5 (II)	0.2 ± 0.1

[a] Calculated by using semiempirical energy expressions.
[b] Obtained by comparison of theoretical and experimental 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 C-C bond.

Extra stabilization energies (ΔE) associated with the gauche oxygen effect have been defined[2] as the difference between the conformational energies (E_{calcd}) calculated by using semiempirical expressions and those (E_{exptl}) derived from the analysis of the experimental data such as $\langle r^2 \rangle_0/nl^2$, $\langle \mu^2 \rangle/nm^2$, and bond conformations. Values of ΔE thus estimated for the gauche conformations about C–C bonds are listed in Table V. It should be noted here that all the energies are expressed relative to that of the trans state in which the articulated methyl group is situated in a close proximity to the preceding oxygen atom (see Figure 1). The stabilization effect associated with such $CH_3 \cdots O$ arrangement may be small, but yet significant; a value of $\Delta E \simeq 0.2$ kcal mol^{-1} was found for the $CH_2 \cdots O$ gauche interaction involved in the poly(oxytetramethylene) chain.[2] A larger gauche oxygen effect is expected for the g_α conformation in which two oxygen atoms are interacting, the methyl group being apart from the preceding oxygen. The stabilization energy estimated for the C–C bond of the POE chain,[2] expressed relative to the corresponding state, is ca. 1 kcal mol^{-1}. A value of $\Delta E_\alpha = 0.7$ kcal mol^{-1} given in Table V is therefore in good agreement with that of POE. In the g_β conformation, the preceding oxygen atom is syn to both the following oxygen and the methyl group; first-order interactions O···O and O···CH$_3$ take place simultaneously. Since the van der Waals radius of the oxygen atom is relatively small, contribution from steric repulsions is insignificant. Electrostatic interaction raises the conformational energy E_β by ca. 0.5 kcal mol^{-1}. If extra stabilization effects such as those stated above were valid for the relevant gauche oxygen arrangements, a large negative contribution should be anticipated. The value of E_β was however estimated to be ca. 0.35–0.5 kcal mol^{-1} (Table V), indicating that such a stabilization effect is largely suppressed in this conformation.[48] A similar situation has been found for 5-methoxy-1,3-dioxane derivatives. Eliel et al.[52] and Hutchinson et al.[53] estimated the free-energy difference between the equatorial and axial conformer to be −0.8 to −1.0 kcal mol^{-1} in nonpolar media. In the former conformer, the O–C–C–O arrangements may be identified as "trans", and thus the stabilization effect from the gauche oxygen placement cannot be expected. This conformation is the preferred one, nonetheless.

Various "gauche oxygen" effects discussed here as well as in the previous papers[2,9] are probably related to each other. The origin of these anomalous effects is yet unknown.[14,15] Similar phenomena are also known with other electronegative atoms such as nitrogen or halogens.[14] If such an effect can be regarded as a feature of the inherent torsional potentials,[2] the energy difference estimated above should be approximately transferable to other molecules embodying the same intramolecular interactions. Various poly[oxy(1-alkylethylene)] chains, which differ only in their side groups, will be investigated in the following paper.[24]

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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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