Conformational Energies and the Random-Coil Dimensions and Dipole Moments of the Polyoxides $CH_3O[(CH_2)_yO]_xCH_3$

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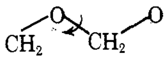
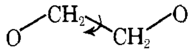
Abstract: Conformational energies of the first four members (y = 1-4) of the polyoxide series $CH_3O[(CH_2)_y\text{-}O\text{-}]_xCH_3$ were calculated using semiempirical potential energy functions in the usual manner. Experimental values of the same energies were also obtained by means of critical analysis of the unperturbed dimensions and dipole moments of these chain molecules in terms of the rotational isomeric state theory of chain configurations. The semiempirical methods do not in general successfully predict conformational energies in this class of chain molecules, as was pointed out in several earlier but more limited comparisons of this type. The present study implicates the intramolecular interactions involving oxygen atoms as the origin of this disagreement between theory and experiment and gives a quantitative estimate of the magnitude of the discrepancy for each of the interactions thus involved. The energy differences thus established should be included, as corrections, in conformational energy calculations on such molecules until more reliable potential energy functions can be derived. In any case, the energies obtained in the present investigation by direct correlation of theoretical and experimental values of the dimensions and dipole moments should be useful in the prediction of any configuration-dependent property of any member of the polyoxide series.

In recent years a variety of configuration-dependent properties of polymeric chains have been successfully treated within the framework of the rotational isomeric state approximation, provided that the neighbor-dependent character of the conformational energies is taken into account.[2] Of fundamental importance in such treatments is information by means of which one may locate suitable rotational states and establish their relative energies. The most reliable information of this type is often obtained by direct measurements, either spectroscopic or thermodynamic, on small molecules having structural features similar to those of the chain molecule under investigation.[3] In addition, semiempirical conformational energy calculations frequently provide supplementary information useful in accessing the overall conformational energy surface as a function of the skeletal rotational angles. Such calculations also provide very important information regarding the high energy conformations, which generally elude direct observation by conventional techniques. Since the potential energy functions used in such calculations are semiempirical,[2a] however, their reliability must be carefully tested against appropriate experimental data. A typical example of this approach is the calculation[4] of the conformational energies of the n-alkanes, including polymethylene (PM) $[CH_2\text{-}]_x$. The results thus obtained were found to be in satisfactory agreement with those required to reproduce the observed values of the unperturbed dimension $\langle r^2\rangle_0$ and its temperature coefficient $d \ln \langle r^2\rangle_0/dT$ for the PM chain.

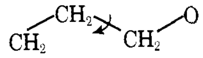
The PM chain may be converted schematically to any member of the polyoxide series $[(CH_2)_y\text{-}O\text{-}]_x$ by simply substituting oxygen atoms for methylene groups along the chain at some fixed interval. According to the rotational isomeric state interpretation of the configuration-dependent properties of such chains, their most characteristic feature is, in contrast to PM, a decisive preference for the gauche conformation over the trans around certain skeletal bonds.[5-13] Specifically, in polyoxymethylene (POM) $[CH_2\text{-}O\text{-}]_x$, gauche states about the central bond in the sequence



bring CH_2 groups and O atoms to a relatively small distance of separation; such states are found to be ca. 1.5 kcal mol^{-1} lower in energy than the alternative trans states.[2a,5,6,13] In polyoxyethylene (POE) $[CH_2\text{-}CH_2\text{-}O\text{-}]_x$, gauche states for the bonds



bring O atoms into close proximity and are ca. 0.4 kcal mol^{-1} below the trans states.[2a,7,8,11-13] For bonds of the type



in $[(CH_2)_y\text{-}O\text{-}]_x$ chains having $y > 2$, the groups brought into proximity are again CH_2 groups and O atoms, but the preference for gauche states in these cases is only ca. 0.2 kcal mol^{-1}.[2a,9-11]

Spectroscopic studies have provided additional information of relevance for some of the above types of molecules. For example, the vibrational spectra of dimethoxyethane, $CH_3OCH_2CH_2OCH_3$, a low molecular weight analogue of POE, confirm the preference for gauche states about C-C bonds.[14] NMR studies of the temperature dependence of the couplings in the ^{13}C-H proton satellite sidebands in POE and its oligomers, although difficult to interpret quantitatively,[70] also suggest that the gauche states about such bonds are of lower energy.[15,16]

Some preliminary calculations[17] of conformational energies were carried out for dimethoxymethane, $CH_3OCH_2OCH_3$, and dimethoxyethane, $CH_3OCH_2CH_2OCH_3$, for trans and gauche states, located precisely at 0 and 120°, respectively, about the O-C and C-C skeletal bonds. In addition to the torsional and van der Waals contributions, it was necessary of course in these cases to include coulombic interactions[18] occurring between partially charged atoms along the chain. The results[17] thus calculated failed to reproduce the aforementioned energy differences and, in fact, in neither case was the gauche state predicted to be of lower energy, as is found experimentally. Conformational analyses using similar semiempirical energy expressions have been carried out by Allegra, Calligaris, and Randaccio[19] on POM and by Gorin and Monnerie[20] on POE. Again, the significantly large negative energies favoring the gauche conformations noted above were not explicable in either case.

Quantum mechanical (MO) studies on dimethoxymethane by Tvaroška and Bleha[21] are at least qualitatively successful

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in that they predict that the $g^{\pm}g^{\pm}$ conformation for the central bond pair is the most stable. Although these calculations, based on the CNDO/2 method, approximately reproduced the observed energy difference, the dipole moment of the molecule was overestimated by ca. 40%, as compared to the experimental value. Also of relevance are two studies in which Jeffrey, Pople, and Radom[22] investigated methanediol, $HOCH_2OH$, and methoxymethanol, CH_3OCH_2OH, as models for carbohydrates. They reported a Fourier expansion of the conformational energies obtained by ab initio molecular orbital calculations for methanediol as a function of rotational angle. According to their analysis, the leading term in the expression is due to dipole-dipole interactions, and the contribution from the twofold potential attributable to charge delocalization of 2p electrons[71] is similar in magnitude to that of the regular threefold potential arising from the repulsive interaction between the bond orbitals due to the Pauli exclusion principle. Such results are qualitatively interesting but do not yet provide the quantitative information needed with regard to the conformational energies of POM. Yet another attempt[23] at a quantum mechanical calculation of the conformational energies of small molecule analogues of POM and POE gave equally discouraging results. The calculations employed an ab initio self-consistent field, with double zeta accuracy, and were carried out for the pertinent conformations of both dimethoxymethane and dimethoxyethane. In the former case, the energy difference between gauche and trans states was found to be of the correct sign, but of twice the observed magnitude. In the latter, the energy difference was of the wrong sign. Finally, a number of semiquantitative explanations[24-26] have been advanced for such unusual "steric attractions" or "gauche effects" as have now been observed in a variety of molecules. None, unfortunately, provides the type of quantitative information required for the purposes at hand.

Although the unexpectedly strong preference for gauche states in POM and its analogues has attracted the most attention, the smaller but still pronounced corresponding preference in POE and its analogues is obviously equally puzzling. As pointed out by Abraham and Parry[27] in their semiempirical treatment of 1,2-difluoroethane, it is unlikely that the estimations of nonbonded steric or coulombic interactions are so much in error (ca. 1 kcal mol^{-1}) at these moderately large interatomic distances. It is perhaps appropriate to include here some preliminary comments on other polyoxide chains as well. Poly(trimethylene oxide) (POM_3) $[CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_x$ should also exhibit coulombic attractions between CH_2 groups and O atoms which would be expected to favor gauche conformations about the C-C skeletal bonds.[2a,9] Since three CH_2 groups separate the electronegative O atoms in the repeat unit of this polyoxide, however, the coulombic effects should be relatively small. The same argument suggests that coulombic interactions would be essentially negligible in poly(tetramethylene oxide) (POM_4) $[CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_x$.[2a,10,11] Accordingly, the situation in these latter two molecules may be quite similar to that in *n*-propyl fluoride, for which the energy difference ($E_g - E_t$) is reported[28] to be −0.5 kcal mol^{-1}. In further analogy, this difference in *n*-propyl fluoride apparently cannot be accounted for by the relatively weak C···H bond dipole moments in this molecule.[29] In brief summary of the point most relevant here, it can be stated that in molecules having O atoms or other atoms such as F which also have unshared p electrons, there are frequently preferences for gauche states that are inexplicable in terms of the semiempirical methods currently much in use for the calculation of conformational energies.

For the above reason, the present study was undertaken in an attempt to obtain and compare the best experimental and theoretical values of the interaction energies in various conformations of the first four members (y = 1-4) in the polyoxide series $[(CH_2)_y\text{-}O\text{-}]_x$, namely POM, POE, POM_3, and POM_4, respectively. Theoretical values of the energies are to be obtained using the most reliable semiempirical potential energy functions currently available; possible effects of displacements $\Delta\varphi$ of any rotational states from their perfectly symmetrical locations at 0, 120, and −120° will be taken into account. Experimental values of these same energies are to be obtained by critical rotational isomeric state analysis of the best values of the dimensions and dipole moments and their temperature coefficients, which have been reported for these chain molecules. Comparison of theoretical and experimental values of conformational energies in this way will provide quantitative values of the extra stabilization energy exhibited in gauche states in these polyoxide chains. If, at least tentatively, this energy difference can be regarded as a feature of the inherent torsional potentials,[17] it should be approximately transferable, as a correction, to conformational energy calculations on other molecules embodying the same intermolecular interactions. Such a suggestion is, of course, highly conjectural and requires extensive testing before its validity can be accepted. A very direct test of this type is the subject of the following paper.[30] It deals with the conformational energies of 2-methoxytetrahydropyran, a cyclic compound which has been extensively studied because of its importance with regard to structural features of carbohydrate molecules.

Table I. Geometric Parameters Used for POM, POE, POM_3, and POM_4

Parameter	POM	POE, POM_3, POM_4
l(C–H), Å	1.10	1.10
l(C–O), Å	1.42	1.43
l(C–C), Å		1.53
∠COC, deg	112.0	111.5
∠OCO, deg	112.0	
∠CCO, deg		111.5
∠CCC, deg		111.5

Theoretical Values of the Conformational Energies

Structural Features of the Chains. Bond lengths and bond angles used in the present study are listed in Table I. Astrup[31] suggested from the results of an electron diffraction study of dimethoxymethane that the central C–O bonds in this molecule are shorter (1.382 ± 0.004 Å) than the terminal ones (1.432 ± 0.004 Å). The C–O bond length of *s*-trioxane determined by Clark and Hewitt[32] in the gaseous state by electron diffraction is 1.411 ± 0.002 Å, while the corresponding value in *p*-dioxane reported by Davis and Hassel[33] is 1.423 ± 0.003 Å. Kimura and Kubo[34] found a value of 1.416 ± 0.003 Å for the length of this bond in dimethyl ether, also by electron diffraction. This value was confirmed by Blukis, Kasai, and Myers[35] who obtained a value of 1.410 ± 0.003 Å from the microwave spectrum of the same molecule. Following the suggestion made by Astrup[31] and by Pople,[36] we chose a slightly smaller value (1.42 Å) for the C–O bond length in POM than that (1.43 Å) widely adopted[2a] for ether linkages in general.

Results of electron diffraction on dimethoxymethane[31,37] suggest that the bond angles (∠COC = 112-115°, and ∠OCO ≈ 114°) are widened as compared to that observed for dimethyl ether (∠COC = 111.5 ± 0.5°) by microwave spectroscopy.[35] A value of 112.0° was therefore assigned to the bond angle ∠COC in POM and 111.5° to that for the other chains. For simplicity, bond angles are assumed to be uniform throughout each polymeric chain.

Parameters for the Conformational Energy Calculations. Conformational energies were estimated using the standard equation[2a]

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

Atom pair	$a \times 10^{-3}$	b	c	$r_{\min}$
H···H	9.95	4.54	45.2	2.6
C···H	86.1	4.57	127.0	3.1
C···C	908.6	4.59	363.0	3.6
O···H	41.85	4.57	96.5	2.9
O···O	223.0	4.59	245.0	3.2
C···O	438.5	4.59	294.0	3.4

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

$$E(\varphi_i) = (E_0/2)\,(1 - \cos 3\varphi_i) + \sum_{k<l} [a_{kl} \exp(-b_{kl} r_{kl}) - c_{kl}/r_{kl}^6 + \delta_k \delta_l / \epsilon r_{kl}] \quad (1)$$

where φ_i represents the bond rotation angle measured from the trans form and r_{kl} is the distance between the centers of atoms k and l. The intrinsic torsional potential, of threefold symmetry, is represented by the term $(E_0/2)(1 - \cos 3\varphi_i)$, in which the barrier height E_0 was assigned the value 2.8 and 1.8 kcal mol^{-1} for rotations about the C-C[4] and C-O bonds, respectively. The latter value was chosen so as to reproduce the observed rotational barrier height (2.72 kcal mol^{-1}) of dimethyl ether[35] when used[4] in combination with the nonbonded interaction parameters as given below. The first two terms in the summation in eq 1 represent respectively the repulsive and attractive components of the van der Waals interactions between the two nonbonded atoms. Values of the interatomic interaction parameters a, b, and c used in the present study are listed in Table II. Parameters for the atomic pairs H···H, C···H, and C···C are those used previously in the analysis of n-alkane chains.[4] For consistency, the other parameters were derived in a similar manner.[4] The quantity $r_{\min}$ given in the last column represents the distance at which the interaction energy for the given nonbonded pair is a minimum. The values shown correspond to slightly larger values than the sum of the van der Waals radii deduced from crystallographic data,[38] for reasons given elsewhere.[4,18] Following Brant et al.,[18] coulombic contributions to the conformational energy were estimated using the last term of eq 1 by assigning partial electronic charges to the carbon (δ_C) and oxygen atoms (δ_O) joined by each C-O bond. For POM, a value of $\delta_C = -\delta_O = 0.31$ was used; it was obtained from a value of the bond dipole moment of 1.07 D, which was estimated from the observed dipole moment (2.07 D) of s-trioxane,[39] using the structural information provided by electron diffraction measurements.[32] Observed dipole moments of various aliphatic ethers, as summarized in McClellan's tables,[40] fall in the range of 1.20 ± 0.10 D, which leads again to a bond dipole moment of 1.07 ± 0.09 D for a C-O bond. Accordingly, partial electronic charges of $\delta_C = 0.155$ and $\delta_O = -0.31$ were used for the other polyoxide chains, in which more than one CH_2 group separates the O atoms. The effective dielectric constant ϵ required in eq 1 was set equal to 3.0, a value similar to that used for this purpose in other calculations of coulombic energies of chain molecules.[2a,18,41]

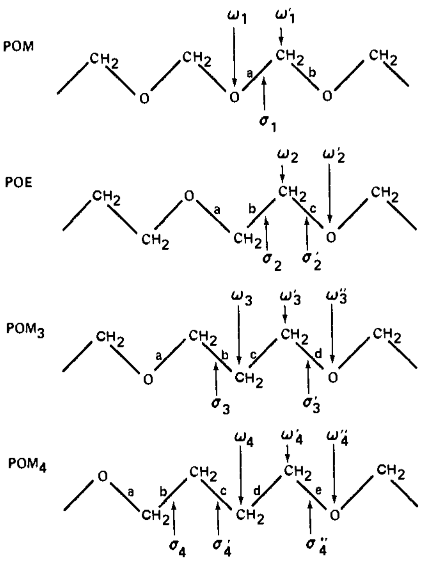


Figure 1. Schematic diagram of the polyoxides investigated. Each skeletal bond in a repeat unit is distinguished by an alphabetical notation. Statistical weight factors for the first and second-order interactions are defined[2a] using arrows at the central bonds for the former and at the central atoms for the latter.

Theoretical Values of the Conformational Energies. A portion of the skeletal backbone for each polymeric chain investigated is shown in Figure 1. In all cases depicted, every bond in a repeating unit possesses different conformational characteristics, and they are therefore distinguished from one another by each being assigned an alphabetical notation. Following the scheme previously introduced,[2a] statistical weight parameters σ and ω respectively are defined for each "first-order interaction" (between groups separated by three bonds) and each "second-order interaction" (between groups separated by four bonds). Numerical subscripts y are affixed to each statistical weight parameter to specify the polymeric chain with which they are associated.

The statistical weight matrix for any bond in any of the polyoxide chains may be expressed in a generalized way by

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\chi & \sigma\omega \\ 1 & \sigma\omega & \sigma\chi \end{bmatrix} \quad (2)$$

the rows and columns being indexed in the order t, g$^+$, and g$^-$. Following conventional procedure,[2a] statistical weight parameters σ, χ, and ω are taken to be simple Boltzmann factors in the corresponding conformational energies. The conformational energies E_σ, E_χ, and E_ω thus required are associated with respective rotational minima defined by two consecutive bond rotations, taken relative to the tt state.[2a]

Energy calculations were carried out in most cases for the central bond pair buried in a 6-bond unit,[72] the rotational states for the adjoining bonds to the pair being kept trans. Well-defined energy minima were found for the conformations tt, tg$^\pm$, g$^\pm$t, and g$^\pm$g$^\pm$ in all cases. The energy minima of the tt state were always found at (0°, 0°). Locations of the minima $(\varphi_{i-1}, \varphi_i)$ and the associated energies $E_{\min}$ (expressed relative to the tt state) are listed in Table III for the tg$^+$ and g$^+$g$^-$ conformations. Those for the tg$^-$ and g$^-$g$^+$ conformations can be deduced from the table by symmetry. The minimum energies $E_{g^\pm g^\pm}$ for the g$^\pm$g$^\pm$ state were found to be approximately equal to the sum of the two appropriate values of $E_{tg^\pm}$ for the two consecutive bonds. Consequently, the locations of the gauche minima in g$^\pm$g$^\pm$ states are almost unaltered, and these results are therefore not included in Table III. They suggest that the second-order interactions in such states are relatively unimportant; the parameter χ was therefore set equal to unity. Values given in parentheses for g$^+$g$^-$ conformations of POM were those estimated from a g$^+$(g$^+$g$^-$)g$^-$ arrangement instead of a t(g$^+$g$^-$)t. The former may be more frequently encountered at junctions of sequences of the most stable conformations[2a,6] -(g$^+$)$_n$- and -(g$^-$)$_n$- of the POM chain.

In discussing the values of the energy presented in Table III, it is advantageous to consider first those interactions involving pairs of CH_2 groups, which are presumably less troublesome than those in which O atoms are participants. Such CH_2···CH_2 interactions occur for rotations about C-O bonds in POE, POM_3, and POM_4 and also for C-C bonds in POM_4. We cite

Table III. Low-Energy Conformations, Their Statistical Weight Factors, Locations, and Energies, and the Separate Interaction Energies Derived Therefrom

Polymer	Bond pair[a]	Conformation	Statistical wt factors	φ_{i-1}, deg	φ_i, deg	$E_{\min}$, kcal mol^{-1}	E_σ, E_ω,[b] kcal mol^{-1}
POM	ba	tg$^+$	σ_1	0.0	115.5	−0.31	
		g$^+$g$^-$	$\sigma_1{}^2\omega_1$	110.0	−110.0	0.24	
				$\begin{pmatrix}86.0\\114.0\end{pmatrix}^c$	$\begin{pmatrix}-114.0\\-86.0\end{pmatrix}^c$	$\begin{pmatrix}1.04\\1.04\end{pmatrix}^c$	$E_{\sigma_1} = -0.31$
	ab	tg$^+$	σ_1	0.0	115.5	−0.31	$E_{\omega_1} = 0.86(1.66)^c$
		g$^+$g$^-$	$\sigma_1{}^2\omega_1{}'$				
POE	ca	tg$^+$	$\sigma_2{}'$	0.0	97.5	1.25	
		g$^+$g$^-$	$\sigma_2{}'^2\omega_2{}'$	63.0	−105.0	3.39	
				105.0	−63.0	3.39	
	ab	tg$^+$	σ_2	0.0	117.5	0.55	$E_{\sigma_2} = 0.55$
		g$^+$g$^-$	$\sigma_2{}'\sigma_2\omega_2$	86.0	−110.0	2.20	$E_{\sigma_2{}'} = 1.25$
	bc	tg$^+$	$\sigma_2{}'$	0.0	97.5	1.25	$E_{\omega_2} = 0.40$
		g$^+$g$^-$	$\sigma_2\sigma_2{}'\omega_2$	110.0	−86.0	2.20	
POM$_3$	da	tg$^+$	$\sigma_3{}'$	0.0	98.0	1.18	
		g$^+$g$^-$	$\sigma_3{}'^2\omega_3{}''$	63.0	−105.0	3.21	
				105.0	−63.0	3.21	
	ab	tg$^+$	σ_3	0.0	117.5	−0.14	$E_{\sigma_3} = -0.14$
		g$^+$g$^-$	$\sigma_3{}'\sigma_3\omega_3{}'$	67.0	−117.0	2.08	$E_{\sigma_3{}'} = 1.18$
	bc	tg$^+$	σ_3	0.0	117.5	−0.14	$E_{\omega_3} = 0.90$
		g$^+$g$^-$	$\sigma_3{}^2\omega_3$	113.5	−113.5	0.62	
	cd	tg$^+$	$\sigma_3{}'$	0.0	98.0	1.18	
		g$^+$g$^-$	$\sigma_3\sigma_3{}'\omega_3{}'$	117.0	−67.0	2.08	
POM$_4$	ea	tg$^+$	$\sigma_4{}''$	0.0	98.0	1.18	
		g$^+$g$^-$	$\sigma_4{}''^2\omega_4{}''$	63.0	−105.0	3.21	
				105.0	−63.0	3.21	
	ab	tg$^+$	σ_4	0.0	116.5	0.05	$E_{\sigma_4} = 0.05$
		g$^+$g$^-$	$\sigma_4{}''\sigma_4\omega_4{}'$	67.0	−117.0	2.20	$E_{\sigma_4{}'} = 0.53$
	bc	tg$^+$	$\sigma_4{}'$	0.0	111.0	0.53	$E_{\sigma_4{}''} = 1.18$
		g$^+$g$^-$	$\sigma_4\sigma_4{}'\omega_4$	100.0	−113.0	1.14	$E_{\omega_4} = 0.56$
	cd	tg$^+$	σ_4	0.0	116.5	0.05	
		g$^+$g$^-$	$\sigma_4{}'\sigma_4\omega_4$	113.0	−100.0	1.14	
	de	tg$^+$	$\sigma_4{}''$	0.0	98.0	1.18	
		g$^+$g$^-$	$\sigma_4\sigma_4{}''\omega_4{}'$	117.0	−67.0	2.20	

[a] See Figure 1. [b] The energies E_ω were calculated as $E_{\min}$ minus the energies of the two appropriate tg$^+$ states; see Figure 1. [c] For POM, the characteristics of the g$^+$g$^-$ states were alternatively estimated using a g$^+$(g$^+$g$^-$)g$^-$ sequence; in this case, the value of $E_{\min}$ was taken to be $E_{g^+g^+g^-g^-} - 2E_{tg^+} - E_{tttt}$. These results are given within the parentheses.

first some experimental data on small molecules pertinent to such interactions as engendered by rotations about C–O bonds. Wieser et al.[42] studied diethyl ether over the temperature range −40 to 40 °C by infrared spectroscopy and reported a value of 1.1 kcal mol^{-1} for the energy of a gauche state relative to a trans. A somewhat higher value (1.5 ± 0.2 kcal mol^{-1}) was found by Kitagawa and Miyazawa[43] from infrared studies on methyl ethyl ether over the range 30–150 °C. Calculated values of this energy difference in POE, POM$_3$, and POM$_4$ are found to be 1.25–1.18 kcal mol^{-1}, in reasonable agreement with these observations. Conformational energy calculations also indicate a displacement of ca. 20° for the associated gauche minima (see Table III). Displacements of similar magnitude in the rotational states have been suggested in crystallographic studies on poly(alkyl vinyl ether)'s [CH_2–$CH(OR)$–]$_x$. Corradini and Bassi[44] interpreted x-ray data on isotactic poly(methyl vinyl ether) by assuming the displacement $\Delta\varphi_s = 20°$ for the C–O bond in the side chain. (In such conformations, the interaction of the CH_3 group in the side chain with one of the CH_2 groups in the backbone *is* essentially the same as the first-order interaction in tg$^+$ states about the polyoxide C–O bonds under consideration.) Similarly, Natta, Bassi, and Allegra[45] adopted the same value of $\Delta\varphi_s$ in the analysis of x-ray data on isotactic poly(isopropyl vinyl ether).

The $CH_2 \cdots CH_2$ interactions arising from rotations about C–C bonds in POM$_4$ should be essentially the same as those occurring in simple *n*-alkane chains. The value obtained here, 0.53 kcal mol^{-1}, for the tg$^+$ state is in good agreement with the value of 0.5 ± 0.1 kcal mol^{-1} established in numerous experimental and theoretical studies[2a] of *n*-alkane chains, including PM.

We consider now second-order interactions, i.e., those occurring between groups separated by four bonds. In all the chains investigated here, such interactions between two methylene groups in the g$^\pm$g$^\mp$ conformation involve severe steric repulsions. Interferences of this type arise for the bond pair ab in POM, ca in POE, da, ab, and cd in POM$_3$, and ea, ab, and de in POM$_4$, respectively (see Figure 1). As pointed out originally by Flory and Mark,[6] steric conflicts are more severe than those encountered in the PM chain,[4] due to the shorter length of the C–O bond. The effect is also reflected in the marked displacements in the conformational energy minima; because of these displacements, the increments in the interaction energies over the corresponding values for *n*-alkane chains are relatively moderate. Energy minima are entirely absent in the vicinity of g$^\pm$g$^\mp$ in the case of POM (in which all skeletal bond lengths are taken to be 1.42 Å). In the other cases minima do occur and, as seen in Table III, one of the gauche bonds in the g$^\pm$g$^\mp$ pair is forced to take a nearly eclipsed position ($\varphi \cong 60°$). Accordingly, these minima are very shallow and scarcely noticeable on the shoulder of the potential curves. When one or both of the interacting groups are replaced by oxygen atoms in the g$^\pm$g$^\mp$ conformation, steric repulsions are greatly reduced.[6] Correspondingly, clearly defined minima were found on the conformational energy surface for such bond pairs; specifically, the bond pairs involved are ba in POM ab and bc in POE, bc in POM$_3$, and bc and cd in POM$_4$.

The separate interaction energies of the type E_σ and E_ω were deduced from the total conformational energies by direct summation of the various contributions. The values obtained are given in the last column of Table III. Interactions characterized by ω_1', ω_2', ω_3', ω_3'', ω_4', and ω_4'' were found to be of very high energy; each of these statistical weight factors was therefore set equal to zero. As anticipated, the energies for the first-order interactions involving oxygen atoms, i.e., $E_{\sigma 1}$, $E_{\sigma 2}$, $E_{\sigma 3}$, and $E_{\sigma 4}$ are decisively at variance with those deduced previously from the preliminary analyses of the configurational properties of the corresponding polymers,[5-13] as described in an earlier section. These energy parameters will therefore be treated as variables in the following rotational isomeric state calculations of the dimensions and dipole moments of all four of these chains. Comparison of these calculated results with the best currently available experimental results will then provide the experimentally most reliable values of the energies associated with these atypical interactions.

The Unperturbed Dimensions and Dipole Moments

Calculated values of the unperturbed dimensions $\langle r^2\rangle_0$ and dipole moments $\langle\mu^2\rangle_0$ were obtained using rotational isomeric state theory in the usual manner.[2a] The statistical weight factors required in the formulation of the statistical weight matrix defined in eq 2 were obtained from Table III, except for the parameters σ_1, σ_2, σ_3, and σ_4, as already mentioned. As is now customary,[2a] the results were expressed as the *characteristic ratio* $\langle r^2\rangle_0/nl^2$ and the *dipole moment ratio* $\langle\mu^2\rangle_0/nm^2$, where $n = (y + 1)x + 2$ is the number of skeletal bonds, and l^2 and m^2 are the averaged values of the squares of their lengths and dipole moments, respectively. Temperature coefficients of both $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ were calculated by investigating the effects of changing the temperature-dependent Boltzmann factors. In the case of the high molecular weight polymers, the calculations were carried out using sufficiently large values of x so that $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle_0/nm^2$ were essentially independent of chain length. The calculated results are presented and discussed in detail in the following sections.

Experimental values of the same configuration-dependent properties were obtained primarily from a literature survey, but also from some studies as yet unpublished. The most reliable of these experimental results are summarized in Table IV. (Because of experimental difficulties in obtaining reliable experimental results on POM (see below), some relevant results obtained for the dipole moments of the corresponding dimer ($x = 1$) and trimer ($x = 2$) are included in the case of this type of polyoxide chain.) The experimental values of $\langle r^2\rangle_0/nl^2$ were calculated from values of the intrinsic viscosity $[\eta]$, using the relationship[46]

$$[\eta] = \Phi\left[\frac{\langle r^2\rangle_0}{M}\right]^{3/2} M^{1/2}\alpha^3 \tag{4}$$

where $\alpha = [\langle r^2\rangle/\langle r^2\rangle_0]^{1/2}$ is the chain expansion factor characterizing the perturbing effects of excluded volume interactions, and Φ is a hydrodynamic constant. Viscometric results obtained in a theta solvent[46] are to be preferred since excluded volume effects are known to be nullified under these conditions, i.e., $\alpha = 1.0$. The value of Φ appropriate under these conditions is 2.6×10^{21} dl cm^{-3} mol^{-1}.[2a,47] Somewhat less reliable are viscometric results obtained in a thermodynamically good solvent, corrected using values of α estimated from second virial coefficients by means of the theory of Orofino and Flory.[48] A somewhat smaller value of Φ, 2.1×10^{21}, is preferred in the interpretation of such data.[47] Approximate values of the unperturbed dimensions may also be estimated from data obtained in a thermodynamically good solvent by extrapolating values of $[\eta]$ into a region of such small chain length that α should be approximately unity.[49] Values of $\langle r^2\rangle_0/nl^2$ thus obtained are probably not of high reliability,[50] but some are discussed below as preliminary results. In these cases, Φ was arbitrarily assigned the value 2.6×10^{21}; the resulting values of $\langle r^2\rangle_0/nl^2$ cited below may of course be adjusted to other values of Φ by multiplication by $(2.6 \times 10^{21}/\Phi)^{2/3}$. Because of the symmetric disposition of the bond dipoles in the polyoxide chains under consideration, the mean-square dipole moments of the chains are not affected by excluded volume interactions.[51] Experimental values of the dipole moment obtained in any (nonpolar) solvent are therefore suitable for comparison with the theoretical results and, for this reason, the restrictive zero subscript on $\langle\mu^2\rangle_0$ will henceforth be deleted.

Table IV. Observed Values of the Characteristic Ratio $\langle r^2\rangle_0/nl^2$ and Dipole Moment Ratio $\langle\mu^2\rangle/nm^2$ and Their Temperature Coefficients for the Polyoxides $CH_3O[(CH_2)_yO]_xCH_3$

Polymer	$\langle r^2\rangle_0/nl^2$	$[d \ln \langle r^2\rangle_0/dT] \times 10^3$, K^{-1}	$\langle\mu^2\rangle/nm^2$ [n]	$[d \ln \langle\mu^2\rangle/dT] \times 10^3$, K^{-1}
POM	10 ± 2.0[a]	Negative and large[a]	0.10 ($x = 1$)[b] 0.29 ($x = 2$)[b] 0.3[c]	6.0 ($x = 1$)[b]
POE	5.2[d]	0.23 ± 0.02[e]	0.51 ± 0.02[f,g]	2.6[g]
POM$_3$	3.7 ± 0.1[h]	0.08 ± 0.08[i]	0.41 ± 0.01[j]	1.5[j]
POM$_4$	6.1 ± 0.1[k]	−1.33[l]	0.50[g,m]	2.7,[g] 1.9[m]

[a] Extrapolated values from viscosity measurements in good solvents: In hexafluoroacetone–water at 25 °C, W. H. Stockmayer and L.-L. Chan, *J. Polym. Sci., Part A-2*, 4, 437 (1966); in phenol at 90 °C, V. Kokle and F. W. Billmeyer, Jr., *J. Polym. Sci., Part B*, 3, 47 (1965). [b] In n-hexane at 25 °C. Temperature coefficient ($x = 1$) observed in the gaseous state over the temperature range 34 to 199 °C: T. Uchida, Y. Kurita, and M. Kubo, *J. Polym. Sci.*, 19, 365 (1956). [c] Estimated from dielectric measurements in the molten state at 200 °C: C. H. Porter, J. H. L. Lawler, and R. H. Boyd, *Macromolecules*, 3, 308 (1970). [d] A value derived from viscosity measurements on fractionated samples in poor solvents at or near the respective theta temperatures (0.45 M aqueous K_2SO_4 at 35 °C, methyl isobutyl ketone at 50 °C, and diethylene glycol diethyl ether at 50 °C): D. R. Beech and C. Booth, *J. Polym. Sci., Part A-2*, 7, 575 (1969). [e] Thermoelastic measurements over the temperature range 30 to 90 °C: J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, 87, 1415 (1965); see also J. E. Mark and P. J. Flory, *Macromolecules*, 6, 300 (1973); S. Bluestone, J. E. Mark, and P. J. Flory, *ibid.*, 7, 325 (1974). [f] In benzene at 20 °C: J. Marchal and H. Benoit, *J. Polym. Sci.*, 23, 223 (1957). Somewhat smaller values, in the range 0.46–0.49, have been observed in dioxane at 25 °C: A. Kotera et al., manuscript in preparation. [g] Dipole moments observed in benzene at 20 °C; temperature coefficient determined over the temperature range 20 to 60 °C: K. Bak, G. Elefante, and J. E. Mark, *J. Phys. Chem.*, 71, 4007 (1967). [h] Preliminary result obtained from measurements in a theta solvent (cyclohexane, 27 °C): D. S. Chiu, Y. Takahashi, and J. E. Mark, manuscript in preparation. [i] Thermoelastic measurements over the temperature range 35 to 80 °C: Y. Takahashi and J. E. Mark, manuscript in preparation. [j] Preliminary results obtained in carbon tetrachloride at 20 °C; temperature coefficient over the range 20 to 50 °C: J. E. Mark and D. S. Chiu, manuscript in preparation. [k] Values of $\langle r^2\rangle_0/nl^2$ obtained from viscosity measurements in theta solvents (2-propanol at 44.6 °C and diethyl malonate at 33.5 °C): J. M. Evans and M. B. Huglin, *Makromol. Chem.*, 127, 141 (1969). (A value estimated from measurements in a mixed solvent (6.6 at 30.4 °C) is not included in the average value cited.) [l] Thermoelastic measurements over the temperature range 60 to 100 °C; see reference cited in footnote *g*. [m] Dipole moments observed in methylcyclohexane at 20 °C; temperature coefficient over the range 6.2 to 60 °C: H. Okamoto, presented at the 19th meeting, "Discussion on High Polymers," Kyoto, 1970. [n] Calculated for bond dipole moment $m_{C-O} = 1.07$ D and $m_{C-C} = 0$.

POM Chains. High molecular weight POM has not been studied extensively with regard to its configurational characteristics because of its high melting point, 190 °C.[52] For this reason, the results of dipole moment measurements on two oligomers ($x = 1$ and 2) by Uchida, Kurita, and Kubo[5] have

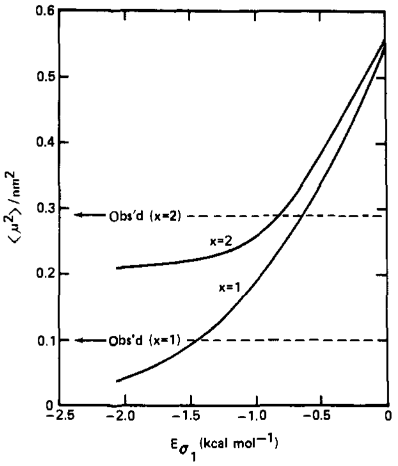


Figure 2. Values of the dipole moment ratio for dimers (x = 1) and trimers (x = 2) of $CH_3O[CH_2\text{-}O\text{-}]_xCH_3$ at 25 °C. The calculated values were obtained using E_{ω_1} = 1.5 kcal mol, $\varphi_g = \pm 115°$, and illustrative values of E_{σ_1}. The experimental values, shown by the arrows, were taken from ref 5.

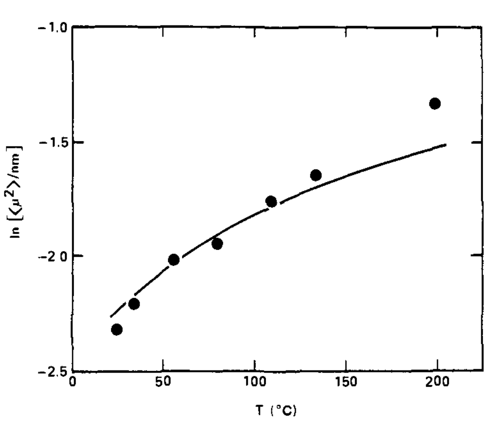


Figure 3. The variation of the dipole moment ratio of dimethoxymethane (x = 1) with temperature. The curve shown was calculated using the parameters $E_{\sigma_1} = -1.4$ kcal mol^{-1}, $E_{\omega_1} = 1.5$ kcal mol^{-1}, and $\varphi_g = \pm 115°$. The observed values[5] are located by the open circles.

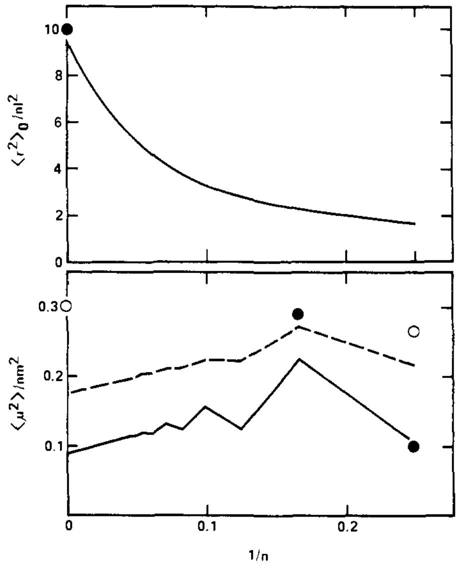


Figure 4. Statistical properties of POM chains shown as a function of the reciprocal of the number of skeletal bonds. The results for the characteristic ratio, shown in the upper part, pertain to 25 °C. The curve represents the calculated results, obtained using the parameters given in the legend to Figure 3: the single point shown represents the experimental result[53,54] for very large n. Calculated and experimental values of the dipole moment ratio are shown in the lower portion. Results at 25 °C are represented by the solid curve and filled circles[5] and at 200 °C by the broken curve and open circles.[5,56]

long been regarded as the most reliable source for the configurational energies of such polyoxide chains.[2a] The energy difference $E_g - E_t$ between the gauche and trans isomeric states thus estimated, −1.7 kcal mol^{-1}, was employed in the calculation of the characteristic ratio $\langle r^2\rangle_0/nl^2$ by Flory and Mark[6] and shown to be consistent with approximate results estimated from intrinsic viscosities measured in good solvents.[53,54]

Following the previous treatment,[6] values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ were calculated for dimethoxymethane ($x = 1$) and dioxymethylene dimethyl ether ($x = 2$) at 25 °C. Rotational isomeric states were assumed to occur at $\varphi_t = 0°$ and $\varphi_g = \pm 115°$, the latter value being supported by the results of electron diffraction studies on dimethoxymethane.[31] The value of E_{ω_1} was taken to be 1.5 kcal mol^{-1} in this calculation, as suggested by the relevant entry in Table III. The results are plotted as a function of the parameter E_{σ_1} in Figure 2. As expected, increase in E_{σ_1} greatly increases $\langle\mu^2\rangle/nm^2$ since group dipoles are essentially parallel in the all-trans configuration. Observed values, shown by the arrows, were reproduced with $E_{\sigma_1} \approx -1.4$ ($x = 1$) and −0.8 kcal mol^{-1} ($x = 2$), respectively. Adoption of a larger displacement for the gauche rotational state as suggested by crystallographic data[55] on POM does not improve the agreement (e.g., calculations at $\varphi_g = \pm 110°$ yielded $E_{\sigma_1} \approx -1.5$ and −0.8 kcal mol^{-1}). The effect of E_{ω_1} on $(\langle\mu^2\rangle/nm^2)_{x=2}$ was found to be negligible for $E_{\omega_1} \geq 1.0$ kcal mol^{-1}. By taking $E_{\sigma_1} = -1.4$ kcal mol^{-1}, the observed temperature dependence[5] of $(\langle\mu^2\rangle/nm^2)_{x=1}$ was satisfactorily reproduced over the temperature range 2 to 150 °C, as is shown in Figure 3.

The dependence of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and dipole moment ratio $\langle\mu^2\rangle/nm^2$ on the reciprocal $1/n$ of the number of skeletal bonds is shown in Figure 4; pertinent experimental data are included. The characteristic ratio $(\langle r^2\rangle_0/nl^2)_\infty = 9.5$ calculated at 25 °C is in good agreement with the value estimated[2a] from the experimental data,[53,54] as shown in the upper part of the figure. These experimental data apparently also support the expectation[6] that $\langle r^2\rangle_0$ decrease significantly with increasing temperature (d ln $\langle r^2\rangle_0/\mathrm{d}T$(calcd) = -6.0×10^{-3} K^{-1} at 25 °C). The dipole moment ratio $\langle\mu^2\rangle/nm^2$ of the polymer was estimated to be ca. 0.3 at 200 °C, using dielectric data obtained on molten POM samples by Boyd and co-workers.[56] This value is somewhat higher than the calculated values, shown in the lower portion of Figure 4, but at least part of the disagreement may be due to experimental difficulties involved in obtaining reliable dielectric data at very high temperatures.

POE Chains. Results pertaining to high molecular weight POE are shown in Figure 5; the left and right ordinates indicate values of the characteristic ratio and dipole moment ratio, respectively. (To facilitate the analysis, the scales on the two ordinates in this and the following figures have been located so that the observed values for $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ meet at the same height.) The solid curves were obtained using the values of $E_{\sigma_2'}$ and E_{ω_2} given in Table III, with rotational isomeric states at φ_g(C-O) = ±100° (for bonds a, c) and φ_g(C-C) = ±120° (for bond b). These parameters were termed "set I". Both here and below, the temperatures used to obtain the calculated values were the same as those employed in the corresponding experiments, in order to facilitate the desired comparisons. At $E_{\sigma_2} \approx -0.2$ kcal mol^{-1}, calculated values of $\langle r^2\rangle_0/nl^2$ fall within the range of experimental values which have been reported.[57] The temperature coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ at this point is 0.19×10^{-3} K^{-1} in the vicinity of 60

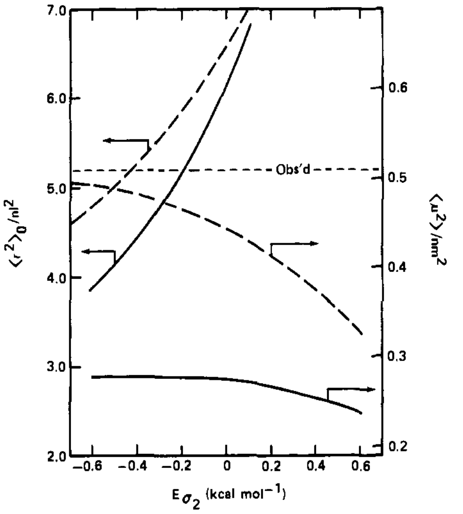


Figure 5. The characteristic ratio and dipole moment ratio for POE chains having $x = 161$ ($n = 485$) calculated as a function of E_{σ_2} for temperatures of 30 and 20 °C, respectively. The two solid curves were obtained using parameter set I ($E_{\sigma_2'} = 1.3$ kcal mol^{-1}, $E_{\omega_2} = 0.4$ kcal mol^{-1}, φ_g(C-O) = ±100°, and φ_g(C-C) = ±120°); the two broken curves were obtained from set II ($E_{\sigma_2'} = 0.9$ kcal mol^{-1}, $E_{\omega_2} = 0.4$ kcal mol^{-1}, φ_g(C-O) = φ_g(C-C) = ±110°). The horizontal dashed line indicates the appropriate observed values for both ordinates, as taken from Table IV.

Table V. Dipole Moments of Two POE Oligomers[d] $CH_3O(CH_2CH_2O)_xCH_3$

	$\langle\mu^2\rangle/nm^2$		d ln $\langle\mu^2\rangle$/dT × 10^3, K^{-1}	
x	Calcd[a]	Obsd[b]	Calcd[a]	Obsd[c]
1	0.65	0.64 (0.55)	0.3	0.6
4	0.58	0.52 (0.52)	1.3	2.0

[a] Calculated using conformational energy parameter set II and $E_{\sigma_2} = -0.5$ kcal mol^{-1}. [b] Determined in benzene at 25 °C; the alternative values in parentheses are those measured in n-hexane. [c] Estimated over the temperature range 25–45 °C using the values measured in benzene. [d] Observed values reported by K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Jpn.*, 39, 608 (1966).

°C, which is also in good agreement with experiment.[7] Within the range of E_{σ_2} examined, however, calculated values of the dipole moment reach only 50-60% of the observed values.[2a,13,58]

As has been pointed out by Mark and Flory,[8] the characteristic ratio $\langle\mu^2\rangle/nm^2$ varies markedly with $E_{\sigma_2'}$ and φ_g (both of which pertain to the C-O bond). Choice of $E_{\sigma_2'} = 0.9$ kcal mol^{-1} and φ_g(C-O) = ±110° raises the curve enough to attain agreement with observations for the range $E_{\sigma_2} = -0.2$ to -0.6 kcal mol^{-1}. On the other hand, $E_{\sigma_2} \leq -0.4$ kcal mol^{-1} is required to reproduce the positive experimental value of the temperature coefficient d ln $\langle r^2\rangle_0$/dT after such modifications. As a final adjustment, the gauche rotation angle φ_g(C-C) about the C-C bond was adjusted by 10° to meet the requirement imposed on $\langle r^2\rangle_0/nl^2$. A displacement of 8.4° in φ_g(C-C) is, in fact, suggested from the x-ray analysis of the most stable crystalline form $(tg^{\pm}t)_x$, as reported by Takahashi and Tadokoro.[59] All these adjustments are included in what is termed parameter set II; the results obtained using it are shown by the dotted curves in Figure 5. The agreement with observed values is satisfactory in the range of $E_{\sigma_2} = -0.4$ to -0.5 kcal mol^{-1}. For example, at $E_{\sigma_2} = -0.5$ kcal mol^{-1}, $\langle r^2\rangle_0/nl^2 = 5.0$ (at 30 °C), d ln $\langle r^2\rangle_0$/d$T = 0.14 \times 10^{-3}$ K^{-1} (at 60 °C), $\langle\mu^2\rangle/nm^2 = 0.49$ (at 20 °C), and d ln $\langle\mu^2\rangle$/dT = 2.9×10^{-3} K^{-1} (at 40 °C).

There is also a great deal of relevant information[2a,13,60] on the dipole moments of POE oligomers, essentially all of which is in satisfactory agreement with theory. One[60] of these studies, involving the oligomers corresponding to $x = 1$-4, is particularly pertinent as a check of the parameters of set II which, in conjunction with $E_{\sigma_2} = -0.5$ kcal mol^{-1}, gave a good account of all of the experimental results on high molecular weight POE, as described above. In this experimental study, the results reported for $x = 1$ and 4 are representative and are summarized here in Table V. As can be seen, calculated and experimental values of both the dipole moment ratio and its temperature coefficient are in satisfactory agreement. It is of particular interest to note that the calculated results predict that increase in degree of polymerization x in this region of short chain length should decrease the dipole moment ratio but increase its temperature coefficient. This is verified by the experimental results reported in this study, as illustrated in Table V.

POM$_3$ Chains. Of the pertinent experimental results obtained on high molecular weight, POM$_3$, those expected to be the most reliable[61-63] are as yet unpublished. Some details regarding their origin and relative reliability are therefore included here. Very recent measurements[61] of POM$_3$ fractions in a theta solvent, cyclohexane at 27 °C, yield $\langle r^2\rangle_0/nl^2 = 3.7$ ± 0.1. This result presumably supersedes the value[62] 3.9 obtained using the approximate Orofino-Flory method[48] on viscosity data obtained in very good solvent, where values of α estimated by this method are frequently somewhat in error.[64] It would also be expected to be of considerably greater reliability than the value 4.1[65] obtained by approximate extrapolation methods.[49] The value of the temperature coefficient of $\langle r^2\rangle_0$ was obtained by thermoelastic measurements on amorphous networks of POM$_3$,[62] and the values of the dipole moment ratio and its temperature coefficient were obtained in carbon tetrachloride, over the temperature range 20-50 °C.[63] All of these experimental results are listed in Table IV.

Values of the characteristic ratio and dipole moment ratio calculated for chains with $x = 129$ ($n = 518$) as a function of E_{σ_3} for the other appropriate energies given in Table III are shown by the solid curves in Figure 6. Experimental values of the dipole moment ratio and its temperature coefficient are well reproduced at $E_{\sigma_3} = -0.2$ kcal mol^{-1} (d ln $\langle\mu^2\rangle$/ dT(calcd) = 1.4×10^{-3} K^{-1} at 20 °C). A value of $E_{\sigma_3} \approx -0.7$ kcal mol^{-1} is however required to reproduce the observed value of the characteristic ratio $\langle r^2\rangle_0/nl^2$; the corresponding temperature coefficient (d ln $\langle r^2\rangle_0$/dT) computed for such set of parameters is 0.7×10^{-3} K^{-1}, being an appreciable overestimate of that observed.

The agreement can be barely improved by adopting similar alterations as made in the case of POE. That is, calculations with a set of revised parameters such as $E_{\sigma_3'} = 0.9$ kcal mol^{-1} and φ_g(C-O) = ±110° raise the curve for the dipole moment ratio $\langle\mu^2\rangle/nm^2$ by ca. 11% while that for $\langle r^2\rangle_0/nl^2$ remains almost unaltered.

A better agreement may be obtained by adjusting the second-order interaction parameter E_{ω_3} for the conformation in which two oxygen atoms are brought into close contact. In this conformation, as estimated from energy calculations, the electrostatic contribution including the repulsion between the two oxygen atoms at the separation of 2.75 Å amounts to ca. 0.7 kcal mol^{-1} whereas that attributable to the noncoulombic interaction terms is ca. 0.2 kcal mol^{-1}. With decrease in E_{ω_3}, the characteristic ratio $\langle r^2\rangle_0/nl^2$ decreases while the corresponding temperature coefficient increases, both to an appreciable extent. An optimum agreement among the quantities under consideration may be found at $E_{\omega_3} \approx 0.6$ and $E_{\sigma_3} \approx -0.4$ kcal mol^{-1}. Results of calculations[73] with $E_{\omega_3} = 0.6$ kcal mol^{-1} are shown by the broken curves in Figure 6. At a value of E_{σ_3} = -0.4 kcal mol^{-1}, calculated values are $\langle r^2\rangle_0/nl^2 = 4.3$ (at

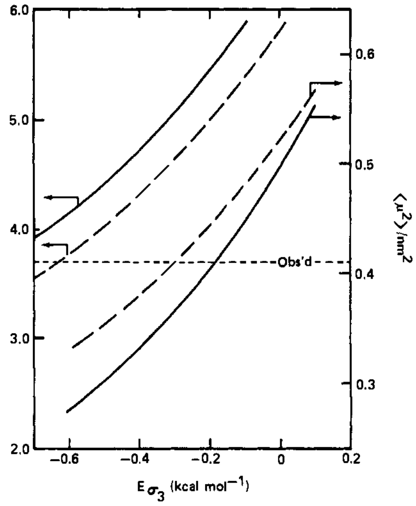


Figure 6. Values of $\langle r^2\rangle_0/nl^2$ at 30 °C and $\langle \mu^2\rangle/nm^2$ at 20 °C for POM$_3$ chains having $x = 129$ ($n = 518$). Results are shown as a function of the parameter $E_{\sigma 3}$. Those obtained using parameter set I ($E_{\sigma 3'} = 1.2$ kcal mol^{-1}, $E_{\omega 3} = 0.9$ kcal mol^{-1}, φ_g(C-O) = ±100°, and φ_g(C-C) = ±120°) are represented by the solid curves. Those from parameter set II ($E_{\sigma 3'} =$ 0.9 kcal mol^{-1}, $E_{\omega 3} = 0.6$ kcal mol^{-1}, φ_g(C-O) = ±110°, and φ_g(C-C) = ±120°) are given by the broken curves. Observed values are specified by the single horizontal line.

30 °C), d ln $\langle r^2\rangle_0/\mathrm{d}T = 0.32 \times 10^{-3}$ K^{-1} (at 60 °C), $\langle \mu^2\rangle/nm^2 = 0.38$ (at 20 °C), and d ln $\langle \mu^2\rangle/\mathrm{d}T = 2.1 \times 10^{-3}$ K^{-1} (at 20 °C), all being in fair agreement with experiment.

POM$_4$ Chains. The calculations for POM$_4$ chains were carried out as a function of $E_{\sigma 4}$, using $x = 97$ ($n = 487$) and the conformational energy parameters given in Table III. Rotational states for the central C-C bond in the sequence C-C$\curvearrowleft$C-C should be essentially the same as those in n-alkanes and the gauche states for such bonds were therefore located at ±112.5°[4] in all of the calculations. For the first series of calculated results, shown by the solid lines in Figure 7, the other gauche states were located according to the assignments φ_g(C-O) = ±100° and φ_g(C-C$\curvearrowleft$C-O) = ±120°. (As shown in the figure, increase in $E_{\sigma 4}$ increases the characteristic ratio but decreases the dipole moment ratio for $E_{\sigma 4} > 0.3$ kcal mol^{-1}. This is due to the fact that when there are an even number of CH$_2$ groups between the O atoms, the all-trans form, although of high spatial extension, is of zero dipole moment because of the antiparallel dispositions of the group dipoles or pairs of bond dipoles.) The closest agreement between theory and experiment[11,66] is seen to be obtained at $E_{\sigma 4} = -0.15 \pm 0.05$ kcal mol^{-1}, where the calculated values are $\langle r^2\rangle_0/nl^2 = 6.4 \pm 0.1$ (at 30 °C) and $\langle \mu^2\rangle/nm^2 = 0.48 \pm 0.01$ (at 20 °C).

For purposes of illustration, a second parameter set (II) was obtained from the first set described above by the same revisions used to improve the agreement between theory and experiment in the case of POE. These results, shown by the broken lines in Figure 7, do not differ greatly from those calculated from parameter set I. Agreement with experiment is again found to be satisfactory, at $E_{\sigma 4} = -0.25 \pm 0.05$ kcal mol^{-1}, where $\langle r^2\rangle_0/nl^2 = 5.9 \pm 0.1$ and $\langle \mu^2\rangle/nm^2 = 0.51 \pm$ 0.01.

The temperature coefficients calculated at $E_{\sigma 4} = -0.2$ kcal mol^{-1} using parameter set I are d ln $\langle r^2\rangle_0/\mathrm{d}T = -1.0 \times 10^{-3}$ K^{-1} (at 60 °C) and d ln $\langle \mu^2\rangle/\mathrm{d}T = 1.6 \times 10^{-3}$ K^{-1} (at 40 °C). Both are in satisfactory agreement with experiment.[11,67]

Discussion

In each of the four types of polyoxide chains considered, there was found to be internal consistency in that the same set of parameters gave a satisfactory account of all of the experimental information available on the chain dimensions and dipole moments. The conformational energies thus established should obviously be useful for predicting other configuration-dependent properties of these chain molecules. One notable example of such an extension of the present type of study is the successful calculation, by Patterson and Flory,[12] of the mean-square optical anisotropies of a number of POE oligomers. Furthermore, many of the intramolecular interactions occurring in the first four members of the $[(\mathrm{CH_2})_y\text{-O-}]_x$ series occur in the other members as well. Their configuration-dependent properties should therefore also be directly calculable from the energies established in the present investigation.

The values of the energies $E_{\sigma 1}$, $E_{\sigma 2}$, $E_{\sigma 3}$, and $E_{\sigma 4}$ calculated from the semiempirical potential energy functions are not, however, in agreement with the values established by the statistical analysis of the dimensions and dipole moments. The pertinent information is given in Table VI, in which the last column shows the extent to which the semiempirical calculations overestimate the energies of each of the anomalous interactions. In the case of POM and POE, the values of this energy difference ΔE are well beyond the uncertainties in the theoretical and experimental methods employed in their de-

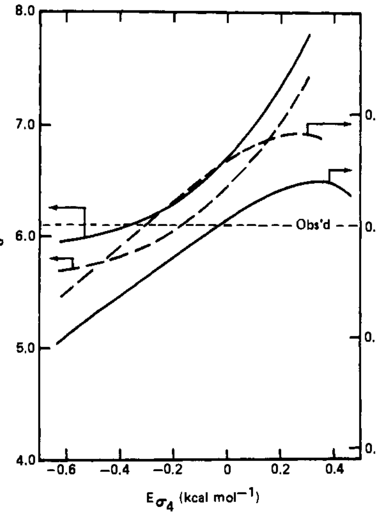
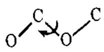
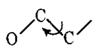
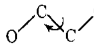
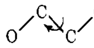


Figure 7. The characteristic ratio and dipole moment ratio for POM$_4$ chains having $x = 97$ ($n = 487$) calculated as a function for $E_{\sigma 4}$ for 30 and 20 °C, respectively. The two solid curves correspond to parameter set I ($E_{\sigma 4'} = 0.5$ kcal mol^{-1}, $E_{\sigma 4''} = 1.2$ kcal mol^{-1}, $E_{\omega 4} = 0.6$ kcal mol^{-1}, φ_g(C-O) = ±100°, φ_g (C-C$\curvearrowleft$C-O) = ±120°, and φ_g (C-C$\curvearrowleft$C-C) = ±112.5°) and the two broken curves to parameter set II ($E_{\sigma 4'} = 0.5$ kcal mol^{-1}, $E_{\sigma 4''} = 0.9$ kcal mol^{-1}, $E_{\omega 4} = 0.6$ kcal mol^{-1}, φ_g(C-O) = ±110°, φ_g(C-C$\curvearrowleft$C-O) = ±120°, and φ_g(C-C$\curvearrowleft$C-C) = ±112.5°). The horizontal line locates the observed values, as usual.

Table VI. Conformational Energies Associated with the Atypical Gauche Conformations Which Involve Oxygen Atoms

Polymer	Bond	E_σ, kcal mol^{-1} Calcd[a]	Exptl[b]	$\Delta E = E_{\sigma,\mathrm{calcd}} - E_{\sigma,\mathrm{exptl}}$
POM		−0.3	−1.4	1.1
POE		0.6	−0.4	1.0
POM$_3$		−0.1	−0.4	0.3
POM$_4$		0	−0.2	0.2

[a] Calculated using semiempirical methods; see eq 1. [b] Obtained by comparison of theoretical and experimental values of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and the dipole moment ratio $\langle \mu^2\rangle/nm^2$.

termination. The values of ΔE are smaller in the case of POM_3 and POM_4 but are probably significant nonetheless. These energy discrepancies are comparable to those which have been observed for various halogenated hydrocarbons. For example, gauche states involving interactions between F atoms in 1,2-difluoroethane should be significantly disfavored by coulombic repulsions, in the same manner as those involving interactions between O atoms in POE; they are found, however, to be of essentially the same energy as the alternative trans states.[68] Similarly, the energy of −0.2 kcal mol^{-1} favoring gauche states in POM_4 is similar in magnitude to the energies favoring gauche states in *n*-propyl fluoride (−0.47 ± 0.31 kcal mol^{-1})[28] and *n*-propyl chloride (−0.05 ± 0.15 kcal mol^{-1}),[69] in which the $CH_2 \cdots O$ interactions in POM_4 are replaced by $CH_3 \cdots F$ and $CH_3 \cdots Cl$ interactions, respectively.

Of considerable importance now is the question of whether or not these energy differences stabilizing gauche states in linear polyoxide chains can be used as simple correction terms to bring calculated conformational energies of other molecules into better agreement with experiment. This possibility is investigated in the following paper,[30] which reports conformational energy calculations on 2-methoxytetrahydropyran, an important cyclic molecule containing essentially the same $CH_2 \cdots O$ interactions as the linear POM chains.

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(71) The twofold potential arising from this source has not been specifically taken into account in the aforementioned semiempirical formulation. Such contribution may distort to some extent the threefold symmetry of the torsional potential given by the first term in eq 1. The effect estimated is however only of minor importance in the systems under consideration.
(72) Electrostatic interactions, as expressed by the last term in eq 1, are "long range" in nature. Results of energy calculations may therefore depend on the length of the chain section over which the calculations are performed. The possible importance of such an effect was examined using the POM chain, in which all skeletal atoms bear partial electronic charges $\delta_C = -\delta_O = 0.31$. Calculations were carried out for chain sequences comprising 3, 4, 6, and 8 bonds in the conformations of $g^{\pm}$, $tg^{\pm}$, $tg^{\pm}tt$, and $ttg^{\pm}ttt$, respectively. The minimum energies obtained were −0.5, −0.2, −0.3, and −0.5 kcal mol^{-1}, respectively, relative to the corresponding all-trans conformations. The location of the conformation of minimum energy does not vary significantly with the chain length. For the purposes at hand, interactions between groups separated by more than 7 bonds are unimportant in general,[2a] and furthermore, such neighboring group effects as do exist should be much smaller in the other polyoxide chains.
(73) Such a revision in E_{ω_3} (from 0.9 to 0.6 kcal mol^{-1}) corresponds to an alteration in the effective dielectric constant ϵ from 3.0 to 5.0 in eq 1.