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Conformational Characteristics and Unperturbed Chain Dimensions of the Oxygen-Containing Polymers $[-OCH_2CR_2CH_2-]_n$ with R = H, CH_3, and CH_2CH_3

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ABSTRACT: MM3 molecular mechanics calculations reveal that poly(3,3′-diethyloxetane) (PDEO) differs sharply from poly(3,3′-dimethyloxetane) (PDMO) and poly(trimethylene oxide) (POM_3) in terms of conformational preferences, notwithstanding the similarity of these three polymers as successive members of the homologous series $[OCH_2CR_2CH_2]_n$ where R = CH_2CH_3, CH_3, and H, respectively. Within the four-bond repeat unit $OCH_2CR_2CH_2$, POM_3 and PDMO both prefer ttgg while PDEO prefers tttt. These conformational differences are reflected in the predicted values of the characteristic ratio CR = $\langle r^2\rangle_0/nl^2$ for the unperturbed chain dimensions (after allowance for the *oxygen gauche effect*) obtained from rotational-isomeric-state (RIS) calculations: 3.9 for POM_3, 4.7 for PDMO, and 23 for PDEO. These CR values for POM_3 and PDMO are consistent with experiment (3.9 and 4.3, respectively) and with previous theoretical treatments. The larger R substituent of PDEO compared with PDMO and POM_3 imposes steric demands that offset the otherwise strong preference of the C−C backbone bonds for *gauche* states. This reversal in preference from *gauche* to *trans* causes the abrupt increase in CR since now the almost exclusively all-*trans* backbone of PDEO lacks the distinctive conformational randomness of POM_3 and PDMO. In terms of $E_\sigma = E_t - E_g$ for the focal C−C bond in these polymers, comparison of the MM2, MM3, and *Discover* (plus a variant *Discover′*) force fields reveals a wide disparity of values for E_σ and more so for the constituent energy components $E_{stretch}$, E_{bend}, $E_{torsion}$, E_{vdW}, and $E_{electrostatics}$. The preference of the focal C−C bond in PDEO for *trans* over *gauche* involves a surprising degree of interplay among these energy components; hence the conformational analysis of PDEO would represent a stringent test of any existing or prospective force field.

Introduction

The structurally related polymers poly(trimethylene oxide) (POM_3) $[-OCH_2CH_2CH_2-]_n$ and poly(3,3′-dimethyloxetane) (PDMO) $[-OCH_2C(CH_3)_2CH_2-]_n$ have attracted particular attention for their unusual conformational properties. Specifically, the experimental values of the characteristic ratio (CR) $\langle r^2\rangle_0/nl^2$ for POM_3 and PDMO are 3.86[1] and 4.34,[2] respectively, both of which are small compared with that for poly(ethylene) (PE) $[-CH_2CH_2-]_n$ (CR = 6.7).[3] This unexpected compactness of POM_3 and PDMO stems from their conformational randomness in that, within the four-bond repeat unit (Figure 1), the two C−C backbone bonds prefer *gauche* states while the two C−O bonds prefer *trans* states. In contrast, the wholly C−C backbone in PE prefers *trans* states over *gauche* states and virtually excludes successive *gauche* states. The −O−C−C−C−O−C−C−C sequence in POM_3 and PDMO is thus capable of adopting effectively random arrangements such as ...$ttg^+g^+ttg^-g^-$..., a spatially compact configuration that is virtually inaccessible energetically to PE.

The *trans*−*gauche* energy difference, $E_t - E_{g^\pm}$, for the C−O bonds in POM_3 and PDMO is actually larger than that for the C−C bonds in PE due to the shortness of the C−O bond (1.43 Å) relative to the corresponding C−C bond (1.53 Å). This shrinkage in the rotatable bond draws the attendant $CH_2\cdots CH_2$ interaction into closer proximity, thereby aggravating steric repulsions in the *gauche* state. The impact of this strong preference for the *trans* state in the C−O bonds of POM_3 and PDMO is, in effect, mitigated by the strong preference for *gauche* states in the C−C bonds. Rotation of the C−C bond in POM_3 and PDMO to a *gauche* conformation draws the $O\cdots CH_2$ interaction into close proximity. Semiempirical force-field (molecular mechanics) calculations have found this interaction to be slightly attractive in both POM_3 and PDMO.[4−7] The van der Waals radius of the O atom is small (compared with the analogous CH_2 group in PE) to lessen steric repulsions, and the polarity of the C→O bond leads to an electrostatically attractive $^{\delta+}CH_2\cdots O^{\delta-}$ interaction. Nevertheless, experimental evidence reveals that the C−C bond prefers *gauche* over *trans* even more than predicted on the basis of molecular mechanics calculations, by 0.4 kcal mol^{-1} in POM_3[4,8] and by 0.3−0.7 kcal mol^{-1} in PDMO.[5,9,10] This preference is confirmed by the X-ray diffraction studies on POM_3 by Tadokoro et al.,[11] who identified ttgg as the most stable of three crystal modifications identified for the [−O−C−C−C] sequence. This extra stabilization of *gauche* states observed for POM_3 and PDMO is an example of the more general phenomenon known commonly as the *oxygen gauche effect* operative most notably in the polyoxides $[-OCH_2-]$ and $[-OCH_2$-

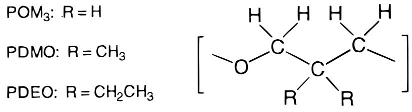

Figure 1. Four-bond repeat unit of POM_3, PDMO, and PDEO. The two C−O bonds prefer the *trans* conformation for all three polymers. The two C−C bonds prefer *gauche* in POM_3 and PDMO but, according to the present calculations, *trans* in PDEO.

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CH_2–].[4] (The *anomeric effect* in carbohydrates is a related anomalous phenomenon.[12,13]) The oxygen *gauche* effect is not simply electrostatic in nature since, as noted above, inclusion of Coulombic interactions in molecular mechanics calculations fails to account for the discrepancy between the observed and calculated conformational preferences. While its origins remain uncertain, the oxygen *gauche* effect obviously bears a pronounced influence on the conformational and configuration-dependent properties of these polymers.

Inomata et al.[9] have reported several configuration-dependent properties and their temperature coefficients for POM_3, PDMO, and another poly(oxetane) calculated using a rotational isomeric state (RIS) scheme with a three-rotational state model. The conformational energies were deduced from analysis of the NMR $^1H-^1H$ and $^{13}C-^1H$ vicinal coupling constants for small model compounds including diethyl ether, 1,3-dimethoxypropane, and 1,3-dimethoxy-2,2′-dimethylpropane. Molecular mechanics was employed as a supplementary tool to elucidate regions of high conformational energy not accessible to these experiments. Confirming the results of previous studies,[4] these workers found the CRs of POM_3 and PDMO to be nearly identical to each other and smaller than the CR of PE. The magnitude of the oxygen *gauche* effect for the C–C bonds of POM_3 and PDMO was estimated as 0.3–0.4 kcal mol^{-1}. They also noted that the CR is only slightly larger for PDMO (4.34) than for POM_3 (3.86). The effect of the increased steric bulk on the aforementioned preferences of the C–C backbone bonds for *gauche* over *trans* states is apparently negligible.

The molecular mechanics calculations of Inomata et al.[9] reveal that E_σ, the statistical-weight parameter which measures the preference of the C–C bond for *gauche* over *trans* states, is actually more negative for PDMO (–0.60 kcal mol^{-1}) than for POM_3 (–0.18 kcal mol^{-1}). The *trans* conformation is disfavored more so in PDMO by the additional $O\cdots CH_3$ interactions involving the two pendant R groups. The present study addresses the question whether this trend continues for R larger than CH_3. As demonstrated by the present calculations, larger R substituents will impose steric demands that offset the otherwise strong preference of the C–C bond for *gauche* states. This reversal in preference from *gauche* to *trans* will cause a large and abrupt increase in CR since now the almost exclusively all-*trans* backbone lacks the distinctive conformational randomness of POM_3 and PDMO. Other configuration-dependent properties besides the CR, such as the dipole moment and their respective temperature coefficients, should similarly experience dramatic changes.

The present study was therefore undertaken to examine these polymers in terms of the sensitivity of their conformational properties to the steric bulk of the substituent R. MM3[14] conformational energy calculations with full geometry relaxation were carried out on model compounds appropriate to $[-OCH_2CR_2CH_2-]_n$ in which the steric bulk of R is increased along the homologous series H, CH_3, CH_2CH_3. The structural and energetic data thus provided were used as input to compute the CR of the corresponding polymers by application of standard RIS techniques. A primary objective of this study was to determine the threshold size of R at which the CR of these polymers jumps as described above, presumably from values below 6.7 (the value for PE) to well above 6.7. The present conformational energy calculations reveal that $R = CH_2CH_3$ is sufficiently bulky to enable the C–C bond to overcome the intrinsic preference for *gauche* states over *trans* states in this series of polymers. Correspondingly, the calculated values of CR jump from 3.9 and 4.7 for POM_3 and PDMO, respectively, to 23 for poly(3,3′-diethyloxetane) (PDEO) in which case $R = CH_2CH_3$.

A secondary objective of this study was to compare the three popular force fields, namely, MM3,[14] MM2,[15] and Discover,[16] plus one variant of *Discover*, with respect to predicting the value of $E_\sigma = E_t - E_{g^\pm}$ associated with the focal C–C bonds in this series of polymers. It is found that both the magnitude and sign of E_σ are dictated by a delicate balance of the force field's bonded (i.e., stretch, bend, torsion) and nonbonded (i.e., vdW, electrostatic) energy components. All four force fields concur that the rather modest increase in steric bulk of R from CH_3 to CH_2CH_3 promotes a dramatic shift in the conformational preferences of this C–C bond in the direction of *trans*. At the same time, decomposition of E_σ into separate force-field contributions (i.e., $E_{stretch}$, E_{bend}, $E_{torsion}$, E_{vdW}, $E_{electrostatics}$) reveals striking differences among the four force fields in terms of the magnitude and sign of individual contributions. Analysis of these contributions suggests that the influence of the steric bulk of R on the conformational preferences of the C–C bond in this series of polymers is quite subtle. Consequently, the conformational analysis of these polymers poses a stringent test for any current or prospective molecular-mechanics force field. The conformational energies and CR values for POM_3 and PDMO as derived from the present MM3 calculations agree reasonably well with the results of earlier studies.[4,6,9] It is concluded that the choice of force field and the inclusion or exclusion of geometry optimization are less crucial for these two polymers whose conformational properties are similar. PDEO, whose conformational characteristics differ qualitatively from those of its homologues POM_3 and PDMO, would likely demand a more robust force field inclusive of geometry optimization.

Computational Methodology

Initial structures for the various model compounds were constructed, visualized, and prepared for conformational analysis using the molecular modeling program *Spartan*,[17] which also served as the interface to the MM2 and MM3 force fields. The *Discover* force field was accessed through the molecular modeling visualization program *Insight*.[16] The dielectric constant was set to its *in vacuo* value $\epsilon = 1.0$, and the energy was minimized using the resident Newton–Raphson algorithm. For each model compound, minima in the conformational energy were sought for the rotational states associated with the following set of bond pairs: tt, $tg^\pm$, $g^\pm g^\pm$, and $g^\pm g^\mp$. For PDMO and PDEO, a conformational search of the side-chain torsion angle(s) was conducted for each backbone conformation in order to minimize the energy corresponding to a conformational state.

In applying the RIS approximation to calculate the configuration-dependent properties of these polymers, a standard three-state model (t, g^+, g^-) was adopted as in earlier studies[4,9] to describe the allowable rotational states of these polymers. The required statistical-weight matrix **U**, accounting for the interdependency of rotational potentials between neighbors, then assumes the familiar generalized form of a 3 × 3 matrix[3]

$$\mathbf{U} = \begin{array}{c|ccc|} & t & g^+ & g^- \\ \hline t & 1 & \sigma & \sigma \\ g^+ & 1 & \sigma\lambda & \sigma\lambda' \\ g^- & 1 & \sigma\lambda' & \sigma\lambda \end{array}$$

where the statistical-weight parameter σ is associated with first-order (three-bond) interactions $g^\pm$ and the parameters λ and λ' represent the second-order (four-bond) interactions $g^\pm g^\pm$ and $g^\pm g^\mp$, respectively. These parameters are computed from the corresponding rotational-state energies E_σ, etc., as Boltzmann factors, e.g., $\sigma = \sigma_0 \exp(-E_\sigma/RT)$, where the preexponential factor σ_0 (sometimes referred to as the "entropy" factor) accounts for the domain size and shape of that conformational state and R and T are the gas constant and Kelvin temperature, respectively. Values of the specified energies E_σ, etc., generally correspond to local minima in the conformational energy for the particular rotational state (t, g^+, g^-) taken relative to $E_t = 0.0$ kcal mol^{-1} for the *trans* state. The preexponential factors σ_o, λ_o, λ_o', etc., can be obtained from analysis of the appropriate conformational energy maps.[18] Those associated with the *trans* and *gauche* energy minima found on the energy maps for POM3, PDMO, and PDEO were of similar magnitude. As adopted by Inomata et al.,[9] one is justified in such cases to set these factors equal to unity (e.g., $\sigma_o = \lambda_o = \lambda_o' = 1$), thereby expressing differences in statistical weights as derived solely from the energies.

Standard RIS procedures were employed to deduce values of the conformational energies, the statistical-weight parameters, and the CRs.[3] The four backbone bonds in the repeat unit of the chain sequence

$$[-CH_2-CR_2-CH_2\overset{\phi_1}{-}O\overset{\phi_2}{-}CH_2\overset{\phi_3}{-}CR_2\overset{\phi_4}{-}CH_2\overset{\phi_1}{-}O-CH_2-CR_2-]$$

are designated appropriately in terms of the torsional rotations ϕ_1, ϕ_2, ϕ_3, and ϕ_4. Model compounds A, B, C, and D embedding the successive bond pairs (ϕ_1, ϕ_2), (ϕ_2, ϕ_3), (ϕ_3, ϕ_4), and (ϕ_4, ϕ_1) were constructed to carry out the conformational analysis. An illustration of each model compound is given in Figure 2, along with the corresponding statistical-weight matrix and the attendant three-bond and four-bond interactions encountered in the $g^\pm$ and $g^\pm g^\pm$ (or $g^\pm g^\mp$) states, respectively.

Inspection of the statistical-weight matrices in Figure 2 reveals that the rotational states of these polymers can be described in terms of six statistical-weight parameters: σ, ρ, ω, κ, χ', and χ''. Of these, σ, ρ, and ω were defined similar to Inomata et al.[9] Rotational states encountering prohibitively high conformational energies were assigned statistical weights of zero. The four-bond interaction parameters ω, χ', and χ'', were retained in the present analysis since their associated conformational energies were deemed only moderately high (<1.5 kcal mol^{-1} for R = H) to justify their inclusion.

Model Compound A

$$CH_3\text{-}CR_2\text{-}CH_2\overset{\phi_1}{-}O\overset{\phi_2}{-}CH_2\text{-}CR_2\text{-}CH_3$$

$$\begin{array}{c|ccc|} & t & g^+ & g^- \\ t & 1 & \rho & \rho \\ g^+ & 1 & \rho\chi'' & 0 \\ g^- & 1 & 0 & \rho\chi'' \end{array}$$

$\rho = CH_2\cdots CR_2$
$\chi'' = CR_2\cdots CR_2$

Model Compound B

$$HCR_2\text{-}CH_2\text{-}O\overset{\phi_2}{-}CH_2\overset{\phi_3}{-}CR_2\text{-}CH_2\text{-}OCH_3$$

$$\begin{array}{c|ccc|} & t & g^+ & g^- \\ t & 1 & \sigma & \sigma \\ g^+ & 1 & \sigma\chi' & 0 \\ g^- & 1 & 0 & \sigma\chi' \end{array}$$

$\sigma = O\cdots CH_2$
$\chi' = CH_2\cdots CH_2$

Model Compound C

$$CH_3\text{-}O-CH_2\overset{\phi_3}{-}CR_2\overset{\phi_4}{-}CH_2\text{-}O-CH_3$$

$$\begin{array}{c|ccc|} & t & g^+ & g^- \\ t & 1 & \sigma & \sigma \\ g^+ & 1 & \sigma\kappa & \sigma\omega \\ g^- & 1 & \sigma\omega & \sigma\kappa \end{array}$$

$\sigma = O\cdots CH_2$
$\kappa = O\cdots O$ for $g^{+/-}g^{+/-}$
$\omega = O\cdots O$ for $g^{+/-}g^{-/+}$

Model Compound D

$$CH_3\text{-}O-CH_2-CR_2\overset{\phi_4}{-}CH_2\overset{\phi_1}{-}O-CH_2-CR_2H$$

$$\begin{array}{c|ccc|} & t & g^+ & g^- \\ t & 1 & \rho & \rho \\ g^+ & 1 & \rho\chi' & 0 \\ g^- & 1 & 0 & \rho\chi' \end{array}$$

$\rho = CH_2\cdots CR_2$
$\chi' = CH_2\cdots CH_2$

Figure 2. Illustration of model compounds A−D along with the associated statistical-weight matrices and key three- and four-bond interactions.

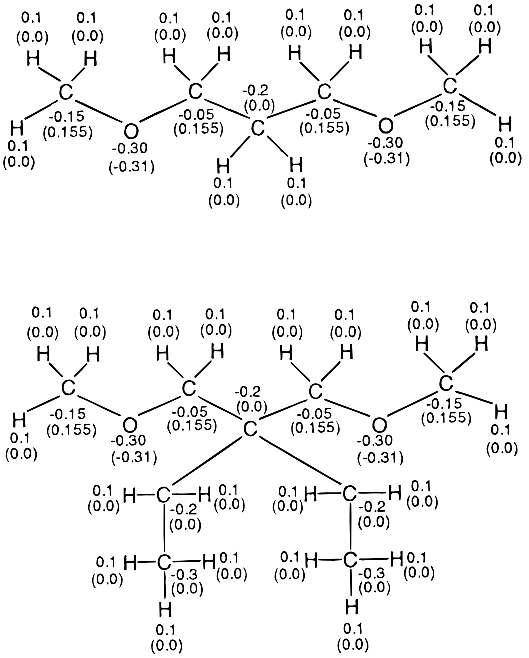

Figure 3. Comparison of the atomic partial charges for model compound C with R = H and R = CH_2CH_3, as assigned by *Discover* and (in parentheses) by the force field employed in refs 4 and 9.

To explore the sensitivity of E_σ to the computational methodology, four different force fields were compared to calculate the conformational energies for model compound C with R = H, CH_3, and CH_2CH_3. Besides MM3,[14] the other standard force fields included MM3's predecessor MM2[15] and Biosym's *Discover*.[16] Both MM2 and MM3 calculate the electrostatic energy $E_{electrostatic}$ directly from bond dipole moments using the Jeans' formula.[18−20] *Discover* employs a Coulomb's law expression $E_{electrostatic} = kq_Aq_B/\epsilon r_{AB}$, where q_A and q_B are the atomic partial charges, r_{AB} is the interatomic distance, ϵ is the dielectric constant, and k is a parameter for adjusting units. As illustrated in Figure 3, the distribution of atomic partial charges in model compound C differs considerably between *Discover* and the force field adopted by Inomata et al.[9] as well as by previous workers.[4] These earlier workers assigned $q_O = -0.31$ to the O atom and $q_C = 0.155$ to the C atom based on a bond dipole moment of $\mu_{C-O} = 1.07$ D derived from analysis of dipole moment measurements in nonpolar

Table 1. Calculated Values of the Rotational-State Energies *E*[a] for POM$_3$, PDMO, and PDEO.

	POM$_3$ (R = H)				PDMO (R = Me)		PDEO (R = Et)
	MM3[b]	ref 9	ref 4	ref 6[f]	MM3[b]	ref 9	MM3[b]
E_σ	−0.11	−0.18	−0.14	−0.40	−0.47	−0.60	0.68
E_ρ	1.50	1.0	1.18	0.78	high	high	high
$E_{\chi''}$	0.17	*c*	*c*	0.11	high	*e*	high
$E_{\chi'}$	−0.11	*c*	*c*	−0.15	high	*e*	high
E_ω	0.99	0.82 (0.4)[d]	0.90	2.36	2.07	1.05	2.39
E_κ	0.031	*c*	*c*	0.26	0.19	*c*	0.29

[a] Energies are in kcal mol^{-1}, normalized to $E = 0.0$ kcal mol^{-1} for the *trans* ($\phi = 0°$) conformation. [b] Present work. [c] Not explicitly reported by ref 9; the energy is presumed to be 0.0 kcal mol^{-1}. [d] E_ω was reduced from 0.82 to 0.4 kcal mol^{-1} to improve agreement between calculated and observed values of the CR. [e] Not explicitly reported; the energy is presumed to be prohibitively high. [f] Reference 6 also included explicit conformational energies for the four-bond interactions encountered in g$^\pm$g$^\mp$ states of the C−O−C−C−C sequence (1.59 kcal mol^{-1}) and C−C−O−C− sequence (0.77 kcal mol^{-1}). The present calculations found these interactions to have prohibitively high energies and assigned them statistical weights of zero. References 3, 4, and 9 also assigned statistical weights of zero to these states

solvents. The remaining atoms were assigned values of zero. The corresponding *Discover* charges are virtually identical to these values except that the $q_C = 0.155$ charge (technically, 0.15) is dispersed over the entire CH$_2$ group attached to an O atom by assigning $q_H = 0.1$ to both H atoms and $q_C = -0.05$ to the C atom. In a similar fashion, any CH$_2$ group not connected to an O atom is assigned $q_H = 0.1$ and $q_C = -0.2$. As a consequence, the key attractive electrostatic interaction found in the *gauche* conformation will be H···O for *Discover* as opposed to C···O for the previous studies cited above.[4,9] In light of the critical importance of these electrostatic attractions in the evaluation of E_σ, such differences in partial-charge distribution may exert an overwhelming influence on the conformational properties of the subject polymers. To assess the significance of these differences in more quantitative terms, a variant of the *Discover* force field was employed in which the atomic partial charges were assigned according to the earlier scheme (Figure 3).[4,9] This modification is designated *Discover′* in subsequent discussions.[21]

Results and Discussion

Conformational Energies. Values of the rotational-state energies E_σ, E_ρ, E_ω, E_κ, $E_{\chi'}$, and $E_{\chi''}$ for POM$_3$, PDMO, and PDEO were extracted from the MM3 calculations on the appropriate model compounds A, B, C, and D (Figure 2). Table 1 summarizes the present results in comparison to other published calculated data. The values of the first-order interaction energies E_σ and E_ρ for both POM$_3$ and PDMO are reasonably consistent over the various studies. The values reported by Miyasaka et al.[6] deviate somewhat from the rest in that E_σ is more negative and E_ρ is less positive. They also employed an Allinger-based force field but of earlier vintage than MM3, and it is uncertain whether geometry optimization was carried out. The energies listed in Table 1 were all obtained from molecular mechanics calculations; hence it can be assumed that the E_σ values do not reflect the extra stabilization of *gauche* states derived from the oxygen *gauche* effect. At the same time, the value $E_\sigma = -0.4$ kcal mol^{-1} from Miyasaka et al.[6] appears to factor in some portion of this observed effect.

The values of E_ω for both POM$_3$ and PDMO vary considerably across the various studies. For POM$_3$, the values range from 0.82 kcal mol^{-1} from ref 9 to 2.36 kcal mol^{-1} from ref 6. The energy of this interaction appears to be sensitive to the choice of force field but not to the inclusion or exclusion of geometry optimization. By reducing E_ω from 0.82 kcal mol^{-1} as calculated to 0.4 kcal mol^{-1}, Inomata et al.[9] were able to reproduce the experimental value of the CR (3.9) using the RIS scheme. This adjustment of 0.42 kcal mol^{-1} can be viewed as compensating for the oxygen *gauche* effect even though it was applied to E_ω rather than to E_σ.

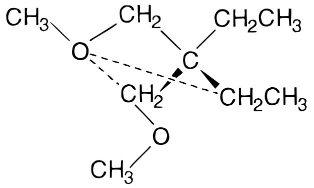

Figure 4. Illustration of model compound C for the cases R = H and R = CH$_2$CH$_3$ with one of the backbone C−C bonds in the *gauche* conformation. The electrostatically attractive O···CH$_2$ interaction and the sterically repulsive O···R interaction are indicated by dashed lines.

Abe et al.[22] recently reported conformational energies for POM$_3$ analogue 1,3-dimethoxypropane in the gas phase (corresponding to $\epsilon = 1$) based on interpretation of NMR vicinal coupling constants. Adopting $E_\rho = 1.03$ kcal mol^{-1} invoking ample precedent, they found that several combinations of E_σ and E_ω were consistent with the experimental findings. Two such combinations mentioned explicitly are $E_\sigma = -0.84$ kcal mol^{-1}, $E_\omega = 1.97$ kcal mol^{-1} and $E_\sigma = -0.58$ kcal mol^{-1}, $E_\omega = 0.40$ kcal mol^{-1}. The value $E_\omega = 0.82$ kcal mol^{-1} reported in ref 9, based on semiempirical energy calculations with $\epsilon = 3.0$ to simulate conditions in nonpolar organic solution, leads to $E_\sigma = -0.5 \rightarrow -0.3$ kcal mol^{-1}. Abe et al.[22] deduced that $E_\omega > 1$ kcal mol^{-1} for the gas phase, corresponding to $E_\sigma = -0.9 \rightarrow -0.7$ kcal mol^{-1}. After proper correction for the *oxygen gauche effect*, the present MM3 results for E_σ and E_ω are reasonably consistent with these latter values (Table 1).

Besides the present study, only Miyasaka et al.[6] have reported explicit values for $E_{\chi''}$, $E_{\chi'}$, and E_κ (see footnote *f* in Table 1) for POM$_3$. In close agreement, both studies find that $E_{\chi''}$ is small and positive while $E_{\chi'}$ is small and negative. Both studies also find that E_κ is small yet positive for POM$_3$, although the magnitude of this energy is much less using MM3 due likely to the inclusion of geometry optimization. This result is as expected since geometry optimization will permit the adjustment of bond lengths, bond angles, and torsion angles so as to enhance attractive interactions and diminish repulsive interactions.[18−20]

Comparison of the rotational-state energies (Table 1) among the three polymers indicates appreciable variation in some instances. Most revealing is E_σ, which first decreases from −0.11 kcal mol^{-1} for POM$_3$ to −0.47 kcal mol^{-1} for PDMO only to change sign and rise dramatically to 0.68 kcal mol^{-1} for PDEO (MM3 values). In terms of conformational preferences, the key C−C bond favors *gauche* in POM$_3$ and even more so in PDMO yet favors *trans* in PDEO. Inspection of model compound C in Figure 4 reveals that rotation about the backbone C−C bond draws the electrostatically attractive O···CH$_2$ interaction into proximity, which in turn stabilizes *gauche* relative to *trans* for all three cases R = H, CH$_3$, and CH$_2$CH$_3$. The further stabilization of *gauche* states for R = CH$_3$ relative to R = H is indirect in that the alternative *trans* state is disfavored by the mildly repulsive steric interactions between the two pendant CH$_3$ groups and the O atom.

Table 2. Key Structural Data Obtained from *Discover* Calculations on Model Compound C in the *Gauche* Conformation with R = H, CH_3, and CH_2CH_3

	R = H	R = CH_3	R = CH_2CH_3
$d(O\cdots CH_2)$ (Å)	3.03	2.97	2.95
$OCH_2-CR_2CH_2$ torsion angle (deg)	64.2	58.3	53.2
$\angle CH_2CR_2CH_2$ (deg)	113.9	110.2	110.0

For the case R = CH_2CH_3, the preference for *trans* over *gauche* entails a more diverse combination of bonded and nonbonded interactions. Some explanation is provided in Table 2, which compares some key structural data on model compound C for the cases R = H, CH_3, and CH_2CH_3 as calculated by *Discover*. Of particular note is that, in the *gauche* state, the contact distance of the electrostatically attractive $O\cdots CH_2$ interaction shortens and the C−C torsion angle increases (away from *trans*) as the steric bulk of R enlarges from H to CH_2CH_3. These displacements suggest that electrostatics actually favor the *gauche* state more in PDEO than in either POM_3 or PDMO. Based on electrostatics alone, the C−C bonds in PDEO should be *gauche*, not *trans* as is the case. The preference for *trans* over *gauche* in PDEO stems from a combination of several bonded interactions and nonbonded steric interactions which in essence offset these electrostatic interactions. This interpretation is supported by the calculated CH_2-CR_2CH_2 bond angles (Table 2) in the *gauche* state, which close from a relatively unconstrained value of 113.9° for R = H to 110.0° for R = CH_2CH_3. The increase in steric bulk of R causes the $-CR_2-$ valence angles to distort commensurably to reduce congestion. As discussed in the following section, an explanation for the dramatic reversal in conformational properties between PDMO and PDEO can be deduced by analysis of the individual energetic contributions to the force field itself.

Decomposition of E_σ According to Force-Field Contributions. The four force fields MM3, MM2, *Discover*, and *Discover′* were applied on model compound C to calculate E_σ for the cases R = H, CH_3, and CH_2CH_3. The separate force-field contributions to E_σ are summarized in Table 3. For each case, the calculated values of E_σ vary considerably among the four force fields. An example of extreme variation is found for the case R = H, for which MM2 and *Discover* gave positive values of E_σ, in qualitative disagreement with the experimental evidence and with the MM3 and *Discover′* computations. Notwithstanding these and other inconsistencies, all four force fields uniformly predict that E_σ is a minimum for the case R = CH_3. Inspection of the signs of the individual contributions for the case R = CH_3 reveals negative values (i.e., favorable to *gauche*) for four out of the five terms: bond stretching, bond-angle bending, van der Waals, and electrostatics. In sharp contrast, with one exception (i.e., the MM2 bending term for R = CH_2CH_3) only the electrostatic term is negative for the cases R = H and R = CH_2CH_3.

This preceding body of theoretical evidence argues that R = CH_3 represents the optimal size in terms of favoring *gauche* as opposed to *trans* for this series of polymers. Relative to R = CH_3, R = H is not bulky enough and R = CH_2CH_3 is too bulky. For the case R = CH_2CH_3, these calculations suggest that the cumulative effect of the positive stretch, bend, torsion, and vdW energies more than offsets the negative electrostatic energy. The repulsive effects of the bulky R = CH_2CH_3 group are not manifested by the force fields exclusively in the van der Waals term even though these effects are steric in the strict sense. Instead, the force fields disperse these effects over the various bonded terms, particularly bending and torsion. For the case R = H, the negative electrostatic term is essentially counterbalanced by the combined effects of the other terms. As a general rule, the individual contributions to E_σ are larger in magnitude for R = CH_2CH_3 than for R = H. This is interpreted to mean that both electrostatic and steric interactions are of greater significance for PDEO than for POM_3.

Configuration-Dependent Properties. To implement the present RIS calculations, values of the calculated energies and associated torsion angles were required for the following seven rotational-state matrix elements: ρ, $\rho\chi''$, σ, $\sigma\chi'$, $\sigma\omega$, $\sigma\kappa$, and $\rho\chi'$ (Figure 2). The appropriate energetic data and statistical weights for POM_3, PDMO, and PDEO are compiled in Table 4 both from the present MM3 calculations and from Inomata et al.[9] The rotational-state energies provided here by MM3 and earlier by Inomata et al.[9] are reasonably consistent despite some quantitative differences. Values of the torsion angles obtained from MM3 are listed in Table 5. As noted above, the torsion angle associated with E_σ is larger for PDEO than for POM_3. As a consequence, the *gauche* conformation about the C−C bond is slightly more compact spatially in PDEO than in POM_3.

Inomata et al.[9] estimated the magnitude of the oxygen *gauche* effect in POM_3 to be 0.3−0.4 kcal mol^{-1}. They were able to reproduce the observed CR (3.9) by reducing E_ω from 0.82 to 0.4 kcal mol^{-1}, an adjustment which essentially compensated for the oxygen *gauche* effect. In a similar manner, the present MM3 results were corrected for the oxygen *gauche* effect by adjusting E_σ from −0.11 to −0.5 kcal mol^{-1}. Values of the CR derived from the present MM3 calculations on POM_3, PDMO, and PDEO are listed in Table 6. Experimental and calculated values extracted from the literature are included for comparison.

The values of CR calculated for POM_3 and PDMO in the present study are consistent with previous calculated values[4,6,9] and, after correcting for the oxygen *gauche* effect, with the observed values.[2,5,9,10] Most significant is the sharp rise in CR for PDEO relative to POM_3 and PDMO. This occurrence is a direct consequence of the reversal of the C−C bond from favoring *gauche* in POM_3 and PDMO to favoring *trans* in PDEO. The evidence provided here of a conformational transformation of such a dramatic nature for PDEO (and presumably higher members of this homologous series) should encourage future experimental investigations of this phenomenon. Concerning the preferred conformation of the key C−C bonds in PDEO, a search of the Cambridge structural database[23] failed to provide any crystallographic data on small-molecule analogues of PDEO which might substantiate or dispute the present interpretation based on theoretical considerations.

Concluding Remarks

The results of the present study reveal that the conformational properties of this series of polymers arise from a complex interplay of bonded and nonbonded interactions. This complexity manifests itself in Table 3 by comparing the contributions to E_σ for a given polymer among the four different force fields. Most striking is the wide disparity among the four force fields in terms of the magnitude and, in some cases, the sign of the individual energy contributions. Among the four force fields surveyed here, none appears to match

Table 3. Decomposition of E_σ into Contributions from Calculations on Model Compound C with R = H, CH_3, and CH_2CH_3 Using Four Different Force Fields[a]

	R = H				R = CH_3				R = CH_2CH_3			
contributions	MM3	MM2	Discover	Discover′	MM3	MM2	Discover	Discover′	MM3	MM2	Discover	Discover′
stretch	0.005	0.003	0.044	0.036	−0.014	−0.010	−0.044	−0.019	0.047	0.010	0.150	0.125
bend	0.042	0.081	0.008	0.105	−0.030	−0.030	0.001	−0.031	0.095	−0.150	0.668	0.700
torsion	0.162	0.167	0.041	0.027	0.026	0.017	0.023	0.010	0.310	0.240	0.130	0.123
vdW	0.130	0.046	0.187	0.113	−0.021	−0.008	−0.027	−0.051	0.420	0.290	0.325	0.256
electrostatics	−0.413	−0.059	−0.146	−0.509	−0.430	−0.060	−1.506	−0.524	−0.500	−0.070	−1.060	−0.559
$E_\sigma = E_g - E_t$	−0.07	0.24	0.13	−0.23	−0.47	−0.09	−1.55	−0.61	0.37	0.32	0.21	0.64

[a] Energies in kcal mol^{-1}.

Table 4. Elements for Statistical-Weight Matrices *U* for POM_3, PDMO, and PDEO

matrix elements	POM_3 (R = H)		PDMO (R = CH_3)		PDEO (R = CH_2CH_3)
	MM3[a]	ref 9	MM3[a]	ref 9	MM3[a]
E_σ	−0.50[b]	−0.18	−0.472	−0.60	0.676
σ	2.30	1.35	2.20	2.72	0.324
E_ρ	1.50	1.00	high	high	high
ρ	0.08	0.185	0.0	0.0	0.0
$E_{\rho\chi''}$	1.67	1.00	high	high	high
$\rho\chi''$	0.06	0.185	0.0	0.0	0.0
$E_{\sigma\chi''}$	−0.61[b]	−0.18	high	high	high
$\sigma\chi'$	2.76	1.35	0.0	0.0	0.0
$E_{\sigma\kappa}$	−0.47[b]	−0.18	−0.28	−0.60	0.97
$\sigma\kappa$	2.19	1.35	1.60	2.72	0.20
$E_{\sigma\omega}$	0.49[b]	0.22[c]	1.60	0.45	3.07
$\sigma\omega$	0.44	0.69	0.70	0.47	0.006
$E_{\rho\chi'}$	1.39	1.00	high	high	high
$\rho\chi'$	0.096	0.185	0.0	0.0	0.0

[a] Present study. [b] Corrected for oxygen *gauche* effect by adjusting E_σ from −0.11 to −0.5 kcal mol^{-1}. [c] Includes reduction of E_ω from 0.82 to 0.4 kcal mol^{-1} as suggested in ref 9 to improve agreement between calculated and experimental values of CR for POM_3.

Table 5. Placements of Torsion Angles[a] **for the Various Rotational States as Calculated by MM3**[b]

	POM_3 (R = H)	PDMO (R = CH_3)	PDEO (R = CH_2CH_3)
σ	118°	121°	129°
ρ	104°		
$\rho\chi''$	(97°) 97°		
$\sigma\chi'$	(104°) 124°		
$\sigma\kappa$	(118°) 118°	(120°) 120°	(129°) 129°
$\sigma\omega$	(−111°) 111°	(−114°) 114°	(−118°) 118°
$\rho\chi'$	(124°) 104°		

[a] Values shown in parentheses refer to the torsion angle of the bond preceding the one in question. [b] Values of torsion angles based on defining the *trans* conformation as $\phi = 0°$.

Table 6. Summary of Calculated and Observed CR Values for POM_3, PDMO, and PDEO

	calcd			
R	ref 4	ref 9	present study	obsd
H	4.3	4.6	6.0 (3.9)[a]	3.9[b]
CH_3		3.9	4.7	4.3[c]
CH_2CH_3			23	

[a] Value in parentheses includes correction for the oxygen *gauche* effect by adjusting E_σ to −0.5 kcal mol^{-1}. [b] From ref 1. [c] From ref 2.

another reasonably well in terms of the relative magnitude of each energy contribution for the same polymer. Considering that MM2 is the predecessor of MM3, the disparity in results for these two force fields may be viewed as surprising. Relative to the other force fields, MM2 grossly underestimates the magnitude of the electrostatic term for all three polymers. The dissimilarity between *Discover* and MM3 is equally surprising in that, in a recent study of the antineoplastic drug trimetrexate, these two force fields yielded nearly identical conformational-energy profiles.[24]

The present results for PDEO reveal that the magnitude of the electrostatic term obtained from *Discover* (−1.06 kcal mol^{-1}) is more than twice that obtained from MM3 (−0.500 kcal mol^{-1}). This disparity is in large part offset by the bond-bending term, which is a sizable 0.668 kcal mol^{-1} for *Discover* yet only 0.095 kcal mol^{-1} for MM3. Both the bond stretching (0.047 vs 0.150 kcal mol^{-1}) and torsion terms (0.310 vs 0.130 kcal mol^{-1}) are also very different for *Discover* and MM3, although the absolute magnitude of these differences is not so large. It is clear that, at least for the atom types found in these polymers, the force fields are parameterized quite distinctly. In light of the conspicuous discrepancies among these force fields in terms of their individual energy terms, the reasonable degree of agreement in terms of their E_σ values is remarkable. The so-named *Discover′* force field, in which the standard *Discover* partial charges are replaced by those adopted by Inomata et al.,[9] stands out among these four force fields in that its E_σ values are internally consistent and appear to reasonably reflect inclusion of the oxygen *gauche* effect. Still, it is conceivable that these impressive results are fortuitous.

It should be pointed out that one should exercise care when interpreting the decomposition of calculated conformational energies into individual force-field components. As discussed elsewhere,[25] the relative magnitude of the individual energy terms comprising a calculated conformational energy cannot be taken too literally since most contemporary force fields are not parameterized to isolate, for example, E_{vdW} from E_{bend} unambiguously. The separate terms comprising a particular force field are highly correlated in the sense that imposition of a purely steric perturbation in a molecule will likely manifest itself over several terms in the force-field energy besides E_{vdW} including perhaps E_{tor}, E_{bend}, and $E_{stretch}$ as found in the present case The analysis of POM_3, PDMO, and PDEO provides a dramatic example illustrating the high degree of overlap among the individual terms of a force field. Yet it remains curious that nominally similar force fields like MM2, MM3, and *Discover* differ so much with respect to the magnitude and, in some instances, the sign of these individual contributions for a given molecule.

As noted by one reviewer of this paper, the ethyl substituent groups in PDEO may be expected to influence the spatial configuration of PDEO. Specifically, the CH_3 terminus of each ethyl side chain can presumably adopt one of three possible conformations (i.e., t, g^+, g^-) with respect to rotation about the $C_{main\ chain}-CH_2(CH_3)$ bond. The resulting nine combinations of side-chain conformations in each PDEO repeat unit will, to varying degrees, influence the minimum-energy conformations and, hence, the statistical weights of the backbone rotational states. Issues pertaining to the influence of side chain···side chain and/or side chain···

main chain interactions on the statistics of the polymer's backbone conformation have been addressed in detail by Abe,[26] by Abe and co-workers,[27] and by Wittwer and Suter[28] for cases involving assorted vinyl and related polymers with sterically-demanding substituents. Also, Brant and co-workers[29] reported an unusually strong correlation between the magnitude of the RIS-calculated CR and the glycosidic valence bond angle for the polysaccharides. Other workers have commented on the occurrence of such interactions in a variety of polymers, including poly(methyl methacrylate),[30] polyisobutylene and vinyl polymers $[-CH_2CRH-]$ with R = CH_3, C_2H_5, C_6H_5, $COOCH_3$, etc.,[3] polypropylene,.[31] the ethylene−propylene copolymers,[32] the aromatic polycarbonates,[33] and the polysilanes.[34] In the present case, the possible relevance of side chain···main chain interactions on the configuration-dependent properties of PDEO was estimated using *Discover* by calculating the Boltzmann-weighted energies $\langle E \rangle$ at 300 K of the rotational states for model compound C ($CH_3OCH_2C(CH_2CH_3)_2CH_2OCH_3$) (Figure 2) averaged over seven conformational states (i.e., tt, $tg^{\pm}$, $g^{\pm}g^{\pm}$, $g^{\pm}g^{\mp}$) of the ethyl side chains. While these $\langle E \rangle$ values were higher by ca. 0.4 kcal mol^{-1} than the rotational-state energies reported in Table 4, the increase was uniform across all of the rotational states except $g^{\pm}g^{\mp}$, for which the increase was 0.1 kcal mol^{-1}. Consequently, the ethyl side chains of PDEO do influence the backbone conformations but apparently to the same degree for each rotational state of consequence. The relative energies of the rotational states and, thus, the chain statistics of the PDEO backbone are not affected by this uniform elevation in conformational energy.

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(21) Noting that the partial atomic charges $q_C = +0.15$ and $q_O = -0.15$ in the *Discover′* force field were obtained from dipole moment measurements in nonpolar solvents, a reviewer has suggested that, for the sake of self-consistency, one should scale the electrostatic term for this force field by a dielectric constant more appropriate to a nonpolar solvent (e.g., $\epsilon \cong 2-3$) rather than use the *in vacuo* value ($\epsilon = 1$) as was done here. The proper treatment of solvent dielectric effects in such calculations remains a salient issue in contemporary science, so the reviewer's concern is reasonable. Perhaps the best approach would be to scale the solution dipole moment $\mu = 1.07$ D to *in vacuo* conditions using the expression proposed by Sharp et al. (Sharp, K.; Jean-Charles, A.; Honig, B. *J. Phys. Chem.* **1992**, *96*, 3822): $\mu_{vacuum} = 3\mu_{solution}/(2 + \epsilon_{solution})$. For $\epsilon_{solution} = 2$, $\mu_{vacuum} = 0.80$ D, yielding $q_C = +0.113$ and $q_O = -0.113$. These adjustments were not implemented since they would have obscured comparisons with the *Discover* force field. As they stand, the *Discover* and *Discover′* force fields differ only with respect to the distribution of these partial charges among the constituent atoms.
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