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A Third-Order Rotational Isomeric State Model for Poly(oxyethylene) Based upon ab Initio Electronic Structure Analyses of Model Molecules

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ABSTRACT: A new three-state rotational isomeric state (RIS) model has been derived for poly(oxyethylene) (POE), based upon ab initio electronic structure analyses of the model molecules 1,2-dimethoxyethane (DME) and diethyl ether (DEE). It is demonstrated that the low energy of the $tg^{\pm}g^{\mp}$ conformation of DME, resulting from strong O$\cdots$H attractions, as indicated by the ab initio studies, necessitates the inclusion of third-order interactions (depending on three consecutive torsional angles) in the RIS model. This is realized by adopting 9 × 9 statistical weight matrices. This third-order RIS model, with all the parameters derived from the conformational geometries and energies of DME and DEE, predicts the chain dimensions, the dipole moments, and their temperature coefficients for POE in good agreement with experiments. It was also found from analysis of the energies of the O–C—C–O, O–C—C–CH_2–(O), and O–C—C–CH_2–(CH_2) gauche conformations (relative to trans) in DME, 1,3-dimethoxypropane, and methyl butyl ether, respectively, that the strength of the oxygen gauche effect for the C—C bond, i.e., the stabilization of the O–C—C–X gauche conformation relative to the trans conformation, correlates well with the degree of Coulombic repulsion or attraction between the oxygen and the "X" moiety. This explains the slightly higher energy (0.1 kcal/mol) found for the O–C—C–O gauche conformation (relative to trans) in DME from ab initio calculations while similar calculations for 1,3-dimethoxypropane and methyl butyl ether indicate that the O–C—C–CH_2 gauche conformations are significantly lower in energy than their respective trans conformations.

Introduction

Three-state rotational isomeric state (RIS) models have been adopted by several investigators to describe the conformation-dependent properties of poly(oxyethylene) (POE).[1-5] These models utilize first-order statistical weights to describe the interactions between atoms and groups separated by three bonds (hence dependent upon one torsion) and second-order statistical weights to describe the interactions between atoms and groups separated by four bonds (hence dependent upon two consecutive torsions). In general, higher order interactions, which are dependent upon more than two consecutive torsions, are ignored in RIS models. This is due to the negligible incidence of close contacts between atoms and groups separated by more than four bonds, resulting from high second-order interaction energies associated with such conformations.

Several approaches have been employed in parameterizing the RIS models for POE. In the earlier approaches,[1-3] the energy parameters for the statistical weights were determined so as to yield best agreement between calculated and experimental mean-square chain dimensions and dipole moments and their temperature dependence for the polymer. In more recent work,[4] molecular mechanics studies of the conformational energies of 1,2-diethoxyethane were used as a basis for parameterizing an RIS model for POE. The energy parameters obtained from molecular mechanics analysis of several conformations of this molecule were used without adjustment, while geometric parameters were adjusted to give best agreement with experimental mean-square dimensions and dipole moments for the polymer. Most recently,[5,6] 1,2-dimethoxyethane (DME) was used as a model compound for parameterizing an RIS model for POE. The RIS energy parameters were again obtained from molecular mechanics analysis of the model molecule. The values so determined were then adjusted so as to yield best agreement between calculated and experimental NMR vicinal coupling data for DME. Minor modifications to these energy parameters were subsequently made to improve agreement between calculated and experimental mean-square dimensions and dipole moments for the polymer, where necessary.

What is salient from comparison of the various RIS models is the wide range of predicted energies of the O–C—C–O gauche conformation relative to the trans conformation, an energy reflecting the strength of the so-called oxygen gauche effect for the O–C—C–X bond (where, in this case, the moiety X is another oxygen atom). Energy values for the gauche conformation range from −1.2[6] to +0.9[4] kcal/mol relative to the trans conformation. Previous ab initio electronic structure calculations[7,8] on DME predict the *tgt* conformer to be about 0.5 kcal/mol higher in energy than the *ttt* conformer; i.e., they predict the O–C—C–O gauche conformation to be about 0.5 kcal/mol higher in energy than the trans conformation. Additionally, a wide range of energies for the C–O—C—C–O $g^{\pm}g^{\mp}$ conformation relative to the *tt* conformation is seen from comparison of the various models. The energy of this $g^{\pm}g^{\mp}$ conformation was initially considered to be significantly higher than that of the *tt* conformation due to "pentane-like" repulsion.[1] However, some molecular mechanics and ab initio computations indicate that the $g^{\pm}g^{\mp}$ conformation is energetically favorable.[4,8]

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We have recently performed detailed ab initio electronic structure calculations on the conformational energies of diethyl ether (DEE) and DME, including a systematic study of the effect of basis set and electron correlation on the energy of the DME *tgt* conformer relative to the *ttt* conformer. The results of these ab initio investigations are presented in detail elsewhere.[9,10] We found[9] that the conformational energies for DME from the ab initio calculations yield conformational populations for the molecule which agree well with those determined from electron diffraction experiments[11] and that these populations can be used successfully in reproducing experimental dipole moments[12] and NMR vicinal coupling data[13] for DME. In this work we present only those results from the ab initio investigations relevant to the parameterization of the RIS model for POE.

Our ab initio calculations reveal that a second-order RIS model is not suitable for representation of the conformations of DME and hence POE. This is due primarily to the unfavorably high energy of the C–O—C—C—O–C $g^{\pm}g^{\mp}g^{\pm}$ conformation resulting from steric interactions between the two CH_3 groups, which are separated by five bonds and hence by three consecutive torsions. The energy of this conformation is high despite the fact that the $tg^{\mp}g^{\pm}$ conformation is energetically favorable. Consideration of such "third-order" interactions, dependent upon the conformations of three consecutive torsions, is not normally necessary due to the high second-order energy of the $g^{\pm}g^{\mp}$ conformation resulting from "pentane effects" in most polymers. However, the apparent absence of pentane effects in the C–O—C—C–O $g^{\pm}g^{\mp}$ conformation requires an explicit accounting of third-order interactions. In this work we present a third-order RIS model for POE based upon the results of our ab initio investigations of the conformational energies and geometries of the model compounds given above. We compare calculated and experimental mean-square chain dimensions, dipole moments, and their temperature dependencies for the polymer with experimental values and predictions of previous RIS models. We also present some preliminary results from ab initio studies of the conformational energies of 1,3-dimethoxypropane (DMP) and methyl butyl ether (MBE) which are relevant to a discussion of the oxygen gauche effect for the O–C—C–X bond.

Results and Discussion

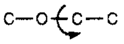
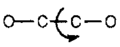
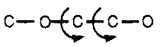
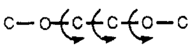
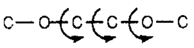
Conformational Energies. Given the conformational energies of model molecules containing the sequences of atoms occurring in the polymer, it is possible to associate an energy with each conformation-dependent interaction and hence parameterize an RIS model for the polymer. For POE, DME and DEE were used as model molecules. Ab initio energies for the various conformations of DEE and DME are presented in Table I. Energies are given with respect to the lowest energy conformation of each model molecule. In determining the conformational energies, geometries were first optimized at the SCF level using a D95** basis set, a Dunning[14] double-zeta basis set with polarization functions on all atoms. Then, using these optimized geometries, SCF and MP2 level energies were determined using the D95** basis set and the larger D95+(2df,p) basis set, which includes additional polarization functions and diffuse functions for the carbon and oxygen atoms. Comparison of SCF and MP2 energies indicates that inclusion of electron correlation effects is quite important. Comparison of D95** and D95+(2df,p) energies indicates that basis set size effects are important also, especially in regards to the DME *tgt* energy. A more detailed discussion of these basis set size and electron correlation effects can be found elsewhere.[9,10] From the D95+(2df,p) MP2 energies, it can be seen that there are three important low-energy conformations for DME, namely, *ttt*, *tgt*, and $tg^{\mp}g^{\pm}$.

Table I. DEE and DME Conformer Energies

	Δ^a D95**		Δ D95+(2df,p)	
conformation	SCF	MP2	SCF	MP2
tt(DEE)	0.0	0.0	0.0	0.0
$tg^{\pm}$(DEE)	1.63	1.24	1.79	1.45
$g^{\pm}g^{\pm}$(DEE)	3.06	2.49	3.34	2.94
$g^{\pm}g^{\mp}$(DEE)	4.24	3.70	4.45	4.08
ttt	0.0	0.0	0.0	0.0
$tg^{\pm}t$	1.31	0.75	1.52	0.14
$tg^{\pm}g^{\pm}$	3.13	1.77	2.54	1.51
$tg^{\pm}g^{\mp}$	1.63	0.24	1.78	0.23
$ttg^{\pm}$	1.89	1.24	2.00	1.43
$g^{\pm}tg^{\pm}$	3.94	2.90	4.09	3.13
$g^{\pm}tg^{\mp}$	3.53	2.61	3.80	3.08
$g^{\pm}g^{\pm}g^{\pm}$	3.97	1.69	4.00	1.64
$g^{\pm}g^{\pm}g^{\mp}$	3.65	1.68	3.89	1.86
$g^{\mp}g^{\pm}g^{\mp}$	3.82	2.53	3.85	2.41

[a] Δ indicates energy relative to either the *tt* conformer of DEE or the *ttt* conformer of DME, in kcal/mol.

Table II. First-, Second-, and Third-Order Interactions in POE

		torsional states			
interaction	model	ϕ_1	ϕ_2	ϕ_3	statistical weight
	DEE	$g_{oc}^{\pm}$ [a]			ρ
	DEE	$g_{co}^{\pm}$	$g_{oc}^{\mp}$		ω'
	DME	$g_{cc}^{\pm}$			σ
	DME	$g_{oc}^{\pm}$	$g_{cc}^{\mp}$		ω
	DME	$g_{oc}^{\pm}$	$g_{cc}^{\pm}$	$g_{co}^{\pm}$	τ
	DME	$g_{oc}^{\pm}$	$g_{cc}^{\mp}$	$g_{co}^{\pm}$	0[b]

[a] $g^{\pm}$ refers to the g^+ and g^- torsional states. The subscripts refer to the skeletal bonds. [b] All $g^{\pm}g^{\mp}g^{\pm}$ sequences are assigned a statistical weight of 0 (see text).

First- and Second-Order RIS Energy Parameters. The first-order (one torsion) and second-order (two torsion) interactions which arise in POE are illustrated in Table II. Also given in the table is the model molecule used to parameterize each interaction. The D95+(2df,p) MP2 energies of the various conformations of DEE and DME, along with the representation of the conformational energies of the model molecules in terms of the energies of the interactions given in Table II, are shown in Table III, where E_ν is the energy associated with interaction ν. The resulting RIS energy for each conformation, given as a sum of the energies associated with all interactions present in the conformation, is also given in the table. Below we describe the procedure used in determining the values of the energy parameters.

Beginning with the ab initio energy and RIS representation for the $tg^{\pm}$ conformer of DEE given in Table III, we conclude that $E_\rho = 1.4$ kcal/mol. With this value established, the $g^{\pm}g^{\mp}$ DEE conformational energy yields $E_{\omega'} = 1.3$ kcal/mol. The $tg^{\pm}t$ energy of DME yields a value of $E_\sigma = 0.1$ kcal/mol, the positive sign reflecting that our ab initio calculations predict *ttt* to be the lowest energy conformation of DME. Although slightly higher than the energy of the *ttt* conformer, the $tg^{\pm}t$ energy is still much lower than expected considering the strong O···O electro-

Table III. RIS Representations of DEE and DME Conformers

conformation	ab initio energy[a]	RIS representation	RIS energy[b]
tt(DEE)	0.00		0.0
$tg^\pm$(DEE)	1.45	E_ρ	1.4
$g^\pm g^\mp$(DEE)	4.08	$2E_\rho + E_{\omega'}$	4.1
$g^\pm g^\pm$(DEE)	2.94	$2E_\rho$	2.8
ttt	0.00		0.0
$tg^\pm t$	0.14	E_σ	0.1
$ttg^\pm$	1.43	E_ρ	1.4
$tg^\pm g^\mp$	0.23	$E_\sigma + E_\rho + E_\omega$	0.2
$tg^\pm g^\pm$	1.51	$E_\sigma + E_\rho$	1.5
$g^\pm tg^\pm$	3.13	$2E_\rho$	2.8
$g^\pm tg^\mp$	3.06	$2E_\rho$	2.8
$g^\pm g^\pm g^\mp$	1.84	$E_\sigma + 2E_\rho + E_\omega$	1.6
$g^\mp g^\pm g^\mp$	2.41	not allowed	
$g^\pm g^\pm g^\pm$	1.64	$E_\sigma + 2E_\rho + E_\tau$	1.6

[a] SCF optimized geometries were determined using a D95** basis set; then single-point energies at the MP2 level of electron correlation were calculated using a D95+(2df,p) basis set.[9,10] Energies are in kcal/mol. [b] $E_\sigma = 0.1$, $E_\rho = 1.4$, $E_\omega = -1.3$, $E_{\omega'} = 1.3$, and $E_\tau = -1.3$, all in kcal/mol.

static repulsion (see discussion below). The $ttg^\pm$ DME energy yields a value of $E_\rho = 1.4$ kcal/mol, which agrees well with the value obtained from analysis of DEE given above. With E_σ and E_ρ determined, a value of $E_\omega = -1.3$ kcal/mol is deduced from the $tg^\pm g^\mp$ energy. The E_ω parameter represents the second-order (two torsion) O···C "pentane" type interaction. From our ab initio results it appears that strong attraction between the oxygen atom and the hydrogen atoms on the "pentane" eclipsed carbon greatly stabilizes the $tg^\pm g^\mp$ conformation, resulting in a large negative value of E_ω. Another recent ab initio study of DME,[8] which utilized a smaller basis set than the present study, also yields a similar negative value of E_ω. In addition, a similar negative value for E_ω was predicted by one of the earlier molecular mechanics studies using 1,2-diethoxyethane as a model molecule.[4] However, both of these studies found E_σ to be greater than 0.5 kcal/mol, whereas we find it to be about 0.1 kcal/mol. As detailed elsewhere,[9] conformational populations of DME resulting from the energies predicted by these other studies[4,8] fail to successfully reproduce NMR vicinal coupling constants in DME and their temperature dependence primarily due to the large positive E_σ, which leads to an increase in the gauche fraction of the O–C—C–O bond with increasing temperature. A decrease in the gauche fraction with increasing temperature is required to successfully reproduce the temperature dependence of the NMR coupling coefficients.[9] Our DME conformational energies, with the much smaller (although still positive) E_σ, were successful in reproducing the NMR coupling constant data.[9] Using the above values for E_σ, E_ρ, and E_ω, we reproduce the energies of the $g^\pm tg^\pm$, $g^\pm tg^\mp$, and $g^\pm g^\pm g^\mp$ conformations well, as shown in Table III.

Third-Order Effects. At this point we consider the DME $g^\mp g^\pm g^\mp$ conformation. As the DME $tg^\pm g^\mp$ conformation is low in energy, due primarily to attractive O···H interactions, a second-order model predicts the C–O—C—C—O–C $g^\mp g^\pm g^\mp$ conformation also to be low in energy. Invoking our previously defined first-order and second-order interactions, we obtain an RIS energy for the DME $g^\mp g^\pm g^\mp$ conformation of $E_\sigma + 2E_\rho + 2E_\omega = 0.3$ kcal/mol. Actually, the DME $g^\mp g^\pm g^\mp$ conformation is high in energy due to the steric interaction between the terminal methyl groups. This is a third-order effect, meaning the interaction depends on the conformation of all three intervening torsions. To adequately represent the higher energy of this conformation in the RIS model, it is necessary to extend the RIS model to include such third-order interactions. Because this conformation is of relatively high energy even for DME and would become even higher for longer chains due to steric crowding involving chain segments attached to the sequence, we concluded chain properties would be most accurately represented by assigning a statistical weight of 0 to this conformation for the polymer. For DME, the conformation may be included in an RIS model by assigning to the conformation, in addition to the second-order representation given above, a third-order parameter with an energy of 2.1 kcal/mol.

Explicit consideration of third-order effects in $g^\mp g^\pm g^\mp$ conformations is generally unnecessary due to the fact that the $g^\pm g^\mp$ sequences are usually high in energy, resulting in $g^\mp g^\pm g^\mp$ conformations very high in energy (and hence of negligible population) without explicit inclusion of a third-order term. Such is the case for C–C—O—C—C–O $g^\mp g^\pm g^\mp$ conformations, where the high energy of the $g^\pm g^\mp$ conformation of DEE makes it unnecessary to explicitly consider third-order effects in such conformations.

Finally, we consider the $g^\pm g^\pm g^\pm$ conformation of DME. Representing the $g^\pm g^\pm g^\pm$ conformation using the first-order and second-order interactions already described yields an RIS energy of $E_\sigma + 2E_\rho = 2.9$ kcal/mol, well above the ab initio value of 1.64 kcal/mol. Since it is already necessary to consider third-order interactions in the model, we can assign an additional third-order energy parameter, E_τ, with a value of −1.3 kcal/mol, to the $g^\pm g^\pm g^\pm$ conformation, thereby bringing the RIS conformation energy in line with the ab initio value. This interaction requires a $g^\pm g^\pm g^\pm$ three-torsion sequence (see Table II) and may result from a unique combination of attractive interactions between oxygen lone-pair electrons and the hydrogen atoms of the opposite methyl groups and an alleviation of repulsive interactions between lone-pair electrons of the opposing oxygen atoms. While this adjustment is included in our RIS model, its influence on polymer properties was found to be insignificant.

The resulting 9 × 9 statistical weight matrices for an RIS model for POE which includes these third-order effects are shown in Figure 1, where the statistical weights are given as

$$\sigma = \exp(-E_\sigma/kT) \quad (1)$$

$$\rho = \exp(-E_\rho/kT) \quad (2)$$

$$\omega = \exp(-E_\omega/kT) \quad (3)$$

$$\omega' = \exp(-E_{\omega'}/kT) \quad (4)$$

$$\tau = \exp(-E_\tau/kT) \quad (5)$$

Each column of a statistical weight matrix represents an isomeric state of the current bond (bond i in Figure 1), given the state of the bond previous (bond $i-1$). Each row represents the state of the bond previous ($i-1$) to the current bond, given the state of the bond preceding it ($i-2$), hence allowing consideration of third-order interactions. In this model, all $g^\mp g^\pm g^\mp$ sequences have been explicitly disallowed.

The Oxygen Gauche Effect. It is of interest to compare energies obtained from the ab initio calculations for the gauche conformation of the O–C—C–X as a function of X for DME, 1,3-dimethoxypropane (DMP), and methyl butyl ether (MBE) to gain insight into the nature of the oxygen gauche effect. We begin by considering the energy of the O–C—C–X gauche conformation (relative to trans) to be due to an intrinsic torsional energy difference (E_t) plus a Coulombic electrostatic energy

C-O—C-C Bond

$$\begin{array}{cc|ccc|ccc|ccc|l}
 & & & t & & & g^+ & & & g^- & & \text{bond i-1} \\
 & & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & \text{bond i} \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 & \\
t & g^+ & 0 & 0 & 0 & 1 & \rho & \rho\omega' & 0 & 0 & 0 & \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \rho\omega' & \rho & \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 & \\
g^+ & g^+ & 0 & 0 & 0 & 1 & \rho & \rho\omega' & 0 & 0 & 0 & \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho & \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 & \\
g^- & g^+ & 0 & 0 & 0 & 1 & \rho & 0 & 0 & 0 & 0 & \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \rho\omega' & \rho & \\
\text{bond i-2} & \text{bond i-1} & & & & & & & & & &
\end{array}$$

O-C—C-O Bond

$$\begin{array}{cc|ccc|ccc|ccc}
 & & & t & & & g^+ & & & g^- & \\
 & & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\hline
 & t & 1 & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
t & g^+ & 0 & 0 & 0 & 1 & \sigma & \sigma\omega & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma\omega & \sigma \\
\hline
 & t & 1 & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+ & g^+ & 0 & 0 & 0 & 1 & \sigma & \sigma\omega & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma \\
\hline
 & t & 1 & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
g^- & g^+ & 0 & 0 & 0 & 1 & \sigma & 0 & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma\omega & \sigma
\end{array}$$

C-C—O-C Bond

$$\begin{array}{cc|ccc|ccc|ccc}
 & & & t & & & g^+ & & & g^- & \\
 & & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\
t & g^+ & 0 & 0 & 0 & 1 & \rho & \rho\omega & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \rho\omega & \rho \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+ & g^+ & 0 & 0 & 0 & 1 & \rho\tau & \rho\omega & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho \\
\hline
 & t & 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\
g^- & g^+ & 0 & 0 & 0 & 1 & \rho & 0 & 0 & 0 & 0 \\
 & g^- & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \rho\omega & \rho\tau
\end{array}$$

Figure 1. Statistical weight matrices for the three-state, third-order RIS model for POE.

difference due to changes in the O···X distance. The gauche energies (in kcal/mol) are represented by

$$E_\sigma = nE_t + 332.08q_Oq_X\left[\frac{1}{R_{O\cdots X}(\text{gauche})} - \frac{1}{R_{O\cdots X}(\text{trans})}\right] \tag{6}$$

Here, n is the number of oxygen atoms adjacent to the C—C bond, q_O and q_X are the partial atomic charges for the O and X moieties determined from standard Mulliken analyses of the D95+(2df,p) SCF wave functions,[9] and $R_{O\cdots X}$ is the O···X distance. The charges are illustrated for DME, DMP, and MBE in Figure 2. The $R_{O\cdots X}$ values are given in Table IV. A least-squares fit of the ab initio gauche energies yields a value of $E_t = -0.38$ kcal/mol. The resulting energies are compared with the ab initio values in Table IV, where good agreement is indicated. We therefore conclude that there is an intrinsic stabilization of the gauche conformation of the O-C—C-X sequence due to the presence of the oxygen adjacent to the C—C bond. In species containing the sequence A-O-C—C-X-B, the energy of the gauche conformation about the C—C bond depends not only upon the nature of the X moiety but also upon the electronegativity of the moieties A and B and may be of higher or lower energy than the trans conformation. Interestingly, the OC—C-X gauche energies found from molecular mechanics analysis of 1,2-diethoxyethane (0.92 kcal/mol), 1,3-diethoxypropane (−0.40 kcal/mol), and 1,4-diethoxybutane (+0.33 kcal/mol)[4,15] show a similar trend to those we found from ab initio analysis of DME (0.14 kcal/mol), DMP (−1.06 kcal/mol), and MBE (−0.53 kcal/mol), with the former averaging 0.77 kcal/mol higher than the latter. Previous RIS analyses of DMP and 1,4-dimethoxybutane,[16] based upon NMR vicinal coupling experiments, yield O-C—C-X gauche energies of −0.5 and −0.2 kcal/mol, respectively, in qualitative agreement with our ab initio results. RIS models for poly(oxytrimethylene) (POM$_3$) and poly(oxytetramethylene) (POM$_4$), along with a detailed comparison with previous studies, will be presented upon completion of the ab initio studies of DMP and MBE.

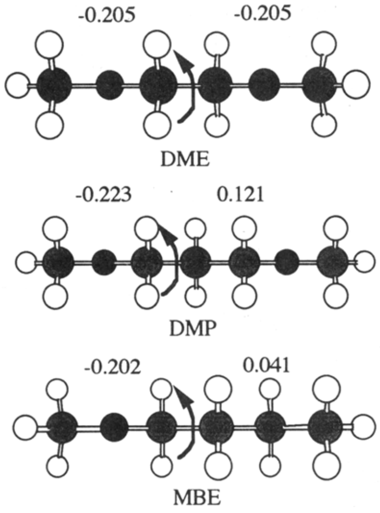


Figure 2. Partial atomic charges (esu) from Mulliken analyses for the O and X moieties of the O-C—C-X conformation in DME, DMP, and MBE. For DME, X = O, while in DMP and MBE, X = CH$_2$.

Table IV. O-C—C-X Gauche Energies

model (X)	$R_{O\cdots X}$ (Å)[a] gauche	$R_{O\cdots X}$ (Å)[a] trans	O-C—C-X gauche energy (kcal/mol)[b] ab initio[c]	O-C—C-X gauche energy (kcal/mol)[b] intrinsic + electrostatic[d]	conformations
DME (O)	2.92	3.57	0.14	0.12	*tgt* − *ttt*
DMP (CH$_2$)	2.97	3.74	−1.06	−1.00	*tggt* − *tgtt*
MBE (CH$_2$)	2.98	3.75	−0.53	−0.57	*tgt* − *ttt*

[a] When X = CH$_2$, the distance is to the backbone carbon atom. [b] Energy difference between the indicated conformers. [c] Energies determined at the MP2 level with a D95+(2df,p) basis set using optimized geometries found at the SCF level using a D95** basis set. Details of the calculations for DME are in ref 9. Details for calculations for DMP and MBE will be presented in a future paper. [d] From eq 6.

Table V. RIS Geometric Parameters

parameter	value
C—C bond length (Å)	1.52
C—O bond length (Å)	1.40
C—C—O angle (deg)	111
C—O—C angle (deg)	115
C—O—C—C gauche angle (deg)	100
O—C—C—O gauche angle (deg)	105

RIS Predictions. Standard matrix multiplication methods were utilized to determine mean-square chain dimensions and dipole moments from the statistical weights and matrices given above.[2] The geometric parameters utilized in our RIS analyses, obtained from conformational averages of ab initio optimized conformational geometries of DME,[9] are shown in Table V.

Calculated properties of POE (at temperatures corresponding to those given in ref 3), using the third-order model and geometric and energy parameters described above, are presented in Table VI, assuming preexponential factors of unity for all statistical weights (case I). Con-

Table VI. Conformation-Dependent Properties of POE

case	properties[a]			
	$\langle r^2\rangle_0/nl^2$	1000 × $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ (K^{-1})	$\langle\mu^2\rangle_0/n\mu_0^2$	1000 × $\mathrm{d}\ln\langle\mu^2\rangle_0/\mathrm{d}T$ (K^{-1})
I[b]	4.5	0.08	0.29	1.9
II[c]	5.0	0.11	0.27	2.4
III[d]	3.8	−0.01	0.25	1.4
IV[e]	4.0	0.12	0.58	2.5
V[f]	5.0	0.14	0.49	2.9
VI[g]	5.2	0.74	0.35	3.0
VII[h]	3.6	0.16	0.17	2.7
VIII[i]	5.5	−0.71	0.22	2.1
IX[j]	4.9	−0.45	0.21	2.5
exp	4.0–5.6[1,17–19]	0.2,[20] 0.23[1]	0.48[21] (0.27),[k] 0.53[22] (0.30)	2.6[22]

[a] $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance. nl^2 is a sum over all backbone bonds of the bond length squared. $\langle\mu^2\rangle_0$ is the mean-square dipole moment of the unperturbed chains. $n\mu_0^2$ is a sum over all backbone bonds of the dipole moment of the bond squared. T is temperature. [b] Third-order model, no prefactor weighting. [c] Third-order model, with prefactor weighting. [d] Second-order model, no prefactor weighting. [e] Reference 2. [f] Reference 3. [g] Reference 5. [h] Reference 4, second-order model, parameter set I (ϕ_g = 100°). [i] Third-order model ($g^{\mp}g^{\pm}g^{\mp}$ sequences suppressed), using parameter set I (ϕ_g = 100°) of ref 4. [j] Calculated as for case I using energy parameters derived from the ab initio conformational energies of DME reported in ref 8. Following the representations given in Table III, these energies yield $E_\sigma = 0.5$, $E_\rho = 1.7$, $E_\omega = -1.7$, and $E_\tau = -1.9$, all in kcal/mol. A value of $E_{\omega'} = 1.3$ kcal/mol was used. [k] The mean-square dipole moment ratio values calculated from experimental mean-square dipole moment measurements using a C–O bond dipole moment of 1.07 D. Values using a bond dipole moment of 1.43 D are given in parentheses.

sideration of the conformational energy contours in DME indicates that a preexponential factor of 0.7 should be associated with statistical weight of the $g^{\pm}g^{\mp}$ C–O—C—C–O conformation,[10] and these results are also shown (case II). The influence of this preexponential factor on predicted polymer properties can be seen by comparing case II with case I. The primary effect is an expansion of the chain, while the other properties show only minor differences. Also shown in the table are predictions obtained using a second-order model with our first-order and second-order parameters (case III). These results are discussed below.

Experimental values for polymer properties are also given in Table VI. The experimental characteristic ratio values for POE were obtained from viscosity measurements at Θ conditions in polar organic and aqueous inorganic salt solutions. Comparison of NMR vicinal coupling in DME from gas phase,[13] neat liquid,[5] and solution[6] experiments indicates that the conformations of DME in the neat liquid, gas phase, and some polar organic solutions do not differ greatly. We would therefore expect RIS predictions of the characteristic ratio of POE to lie within the range of experimental values, which cover a wide variety of polar solvents. A value of 5.2 for the characteristic ratio of POE, obtained for a pair of polar organic solvents,[17] may be the best value for comparison with RIS predictions. The temperature dependence of the characteristic ratio was determined from thermoelasticity measurements on POE networks. The mean-square dipole moment data were obtained in nonpolar solutions, and the reported mean-square dipole moment ratios were determined assuming a C–O bond dipole moment of 1.07 D.[3]

Results from our third-order model (cases I and II) for the mean-square end-to-end distance of POE and its temperature dependence agree as well or better with experiments as predictions from the previous models,[1–5] which are also summarized in Table VI. The importance of including third-order terms in our model, i.e., explicit exclusion of $g^{\mp}g^{\pm}g^{\mp}$ C–O—C—C—O–C conformations when C–O—C—C–O $g^{\pm}g^{\mp}$ conformations are energetically favorable, is illustrated by comparing properties obtained from the second-order model utilizing our parameters (case III) with predictions of the third-order model (case I). The incorrectly high population of $g^{\mp}g^{\pm}g^{\mp}$ conformations obtained in the second-order model results in a considerable reduction in the end-to-end dimensions of the chain. This effect is also seen in the RIS model based upon molecular mechanics calculations for 1,2-diethoxyethane,[4] a model which also favors the C–O—C—C–O $g^{\pm}g^{\mp}$ conformation (case VII). In this second-order model inclusion of the $g^{\mp}g^{\pm}g^{\mp}$ C–O—C—C—O–C conformation dramatically decreases the characteristic ratio, an effect which is somewhat offset by the high O–C—C–O gauche energy, which tends to expand the polymer. If the energy and geometry parameters from this model are used in our third-order RIS model which suppresses the high-energy $g^{\mp}g^{\pm}g^{\mp}$ C–O—C—C—O–C conformation (case VIII), the predicted characteristic ratio increases significantly. The decrease in the characteristic ratio with increasing temperature seen in case VIII is due to the high fraction of O–C—C–O bonds predicted to be in the trans conformation, which results in an increase in gauche character of the bond with increasing temperature and hence a decrease in the characteristic ratio. Similar behavior is seen if the ab initio DME conformer energies calculated by Hirano and coworkers[8] are used to parameterize an RIS model (case IX). This is due primarily to the fact that the DME $tg^{\pm}t$ and $tg^{\pm}g^{\mp}$ conformer energies are 0.5 kcal/mol higher than the *ttt* conformer energy, which again results in a high fraction of O–C—C–O bonds in the trans conformation.

Predictions of the second-order RIS models of refs 1, 2, 3, and 5 are not significantly altered by adopting a third-order model with explicit exclusion of $g^{\mp}g^{\pm}g^{\mp}$ C–O—C—C—O–C conformations. This is due to the fact that the populations of the C–O—C—C–O $g^{\pm}g^{\mp}$ conformation are negligible in these models. These predictions, however, are not consistent with gas-phase electron diffraction experiments that find the $tg^{\pm}g^{\mp}$ conformer of DME to be predominant.[11]

Results from our third-order model for the mean-square dipole moment ratio (at temperatures given in ref 3) are not in as good agreement with reported experimental values as was found for the characteristic ratio, although the predicted temperature dependence of the mean-square dipole moment agrees quite well with the experimental value. The discrepancy in mean-square dipole moment ratio values may be due in part to the representation of local dipoles by assigning bond dipoles to the C–O and O–C bonds only, without consideration of conformation-dependent polarization effects and C–C and C–H dipoles. Another possible source of discrepancy is the choice of the C–O bond dipole moment used in calculating the mean-square dipole moment ratio from the experimentally determined mean-square dipole moment. Values of 0.99[2,21,22] and 1.07 D[3] have been utilized. Utilizing conformational geometries determined from ab initio analyses,[10] we find that a C–O bond dipole moment of 1.07 D reproduces the experimental dipole moment for DEE. However, again using the conformational geometries and populations determined from our ab initio analyses,[9] we find that this bond dipole moment cannot be used to reproduce the experimental dipole moment for DME nor can it reproduce the dipole moments of the individual DME conformations as determined from the electronic structure calculations. A bond dipole moment of 1.28 D is required to reproduce the ab initio dipole moment of DME of 1.58 D, which is obtained from a conformational average of the individual conformer dipole moments as determined from electronic structure calculations.[9] This bond dipole moment also reproduces the ab initio dipole moments of the important individual conformer to within 15%. A bond dipole moment of 1.43 D yields a conformational average dipole moment for DME of 1.71 D, the experimental value as determined in benzene.[12] Mean-square dipole moment ratios determined from experimental data using a C–O bond dipole moment of 1.43 D are shown in Table VI. Our RIS predictions are in good agreement with these values. Additionally, applying our third-order RIS model (with the preexponential factor of 0.7 for the $g^{\pm}g^{\mp}$ C–O—C—C–O conformation) to DME (POE dimer) and POE pentamer yields mean-square dipole moment ratios of 0.41 and 0.33, respectively, which are in good agreement with experimental values if a C–O bond dipole moment of 1.43 D is used in determining the ratios (0.36 and 0.29, respectively[12]). We obtain $d \ln \langle \mu^2 \rangle_0 / dT$ values of 1.2×10^{-3}/K and 1.8×10^{-3}/K for the dimer and pentamer, respectively, in reasonable agreement with experimental estimates of 0.6×10^{-3}/K and 2.0×10^{-3}/K.[3]

A final point regarding solvent effects in DME and POE should be made. As is well known, experimental measurements of conformation-dependent properties of DME and POE, such as NMR vicinal coupling constants[6] and characteristic ratio,[5] indicate a significant solvent effect on the conformations of these molecules in very polar solvents. These effects have not been considered in the parameterization of the RIS model presented here.

Conclusions

In our previous work[9] we have shown that conformational populations of DME determined from a detailed ab initio electronic structure analysis of conformational energies of DME, determined using MP2-level calculations with a D95+(2df,p) basis set, agree well with those determined from electron diffraction experiments and reproduce experimental dipole moments and NMR vicinal coupling data. Here, we have developed a simple three-state third-order RIS model for POE and have established all parameter values based upon the ab initio conformational energies of model molecules. Unlike previous RIS models, in which the statistical weights were parameterized to yield best agreement of polymer properties with experiments or where energy and/or geometric parameters were adjusted to improve agreement, our parameter values were not systematically adjusted from those obtained from ab initio electronic structure analysis of model compounds. Our RIS model for POE includes low-energy $g^{\pm}g^{\mp}$ C–O—C—C–O conformations and concomitant explicit consideration of $g^{\mp}g^{\pm}g^{\mp}$ C–O—C—C—O–C conformations. The energy of the O–C—C–O gauche conformation is considered to be slightly higher than that of the trans conformation. We find good agreement between predicted and experimental mean-square chain dimensions, dipole moments, and their temperature dependencies for POE using this model. We also find that the energy of the O–C—C–X gauche conformation in DME, DMP, and MBE can be well represented by a sum of an intrinsic torsional energy plus electrostatic energy due to interactions between the O and X moieties. This oxygen gauche effect, as expressed by a lowering of the intrinsic O–C—C–X gauche torsional energy, while evident in DMP and MBE, is masked in DME by the strong O···O electrostatic repulsion.

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