

Configurational Characteristics of Poly(oxy-1,1-dimethylethylene). I. Conformational Energies Estimated from the Analysis of the Dipole Moment Data of 1,2-Dimethoxy-2-methylpropane, a Monomer Model

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ABSTRACT: Dielectric measurements were carried out on 1,2-dimethoxy-2-methylpropane (DMMP), a monomer model for poly(oxy-1,1-dimethylethylene) (PODME), in nonpolar solvents such as benzene, carbon tetrachloride, and cyclohexane. The values of the dipole moment $\langle \mu^2 \rangle^{1/2}$ derived therefrom are 1.69, 1.68, and 1.61 D, respectively, at 25°C. Theoretical calculations performed within the framework of the rotational isomeric state approximations were found to reproduce favorably these experimental results. Conformational energy parameters required in these calculations were estimated by using semiempirical potential energy expressions. The results of the analysis suggest that DMMP differs greatly from dimethoxyethane for which a *gauche* oxygen effect plays an important role in determining the relative stability of the isomeric states around the skeletal C—C bond. Such an effect is almost entirely suppressed in the former compound: the *trans* state is preferred to the *gauche* states by about 0.5 kcal mol⁻¹ in the conformational energy. Statistical weight matrices required for the analysis of the PODME chain have also been formulated.

KEY WORDS 1,2-Dimethoxy-2-methylpropane / Poly(oxy-1,1-dimethylethylene) / Dipole Moment / Potential Energy Calculation / Conformational Energy / *gauche* Oxygen Effect /

Poly(oxy-1,1-dimethylethylene) (PODME) is a crystalline polymer having a high melting point (*ca.* 175°C)¹ and quite insoluble in conventional organic solvents. The polymer prepared from isobutene oxide by using diethyl zinc–water–cyclohexylamine catalyst is known to form a good elastic hard fiber on melt spinning.² Some of the chemical and mechanical properties of the polymer have been reported.^{1–3} From the X-ray diffraction studies, Kaji and Sakurada⁴ concluded that the polymer chain possesses a somewhat distorted zigzag conformation in the crystalline state.

The conformational analysis of the PODME chain presented in this paper, and in those which will follow, constitutes a part of our studies^{5–7} on polyoxide chains having a general formula $\{CH_2C(R_1)(R_2)O\}_x$. In all these polymers, *gauche*

O···O interactions take place around the skeletal C—C bond. The major purpose of our studies is to evaluate the *gauche* oxygen effect associated with these polymers in terms of the extra stabilization energies (ΔE), which have been defined^{5–8} as the difference between the conformational energies (E_{calcd}) calculated by using semiempirical expressions and those (E_{expl}) derived from the analysis of the experimental data on some relevant conformation-dependent properties such as the unperturbed dimension, dipole moment, and bond conformations.

In the case of poly(oxyethylene) (POE),^{5,9,10} where $R_1=R_2=H$, semiempirical energy calculations failed to reproduce the observed preference for the *gauche* over the *trans* state. The theoretical value is 0.6 kcal mol⁻¹ (1 cal=4.2 J) in favor of the

Table I. Results of dielectric measurements (25°C)

| | Benzene | Carbon tetrachloride | Cyclohexane |
|--|------------------|----------------------|------------------|
| ϵ_0 | 2.27 | 2.23 | 2.02 |
| $(d\epsilon/d\omega)$ | 2.3 ₄ | 4.1 ₉ | 1.8 ₁ |
| $10^3\rho_0/\text{kg m}^{-3}$ | 0.871 | 1.58 ₄ | 0.773 |
| $10^3(d\rho/d\omega)/\text{kg m}^{-3}$ | -0.03 | -1.3 ₅ | 0.0 ₅ |
| $\langle\mu^2\rangle^{1/2}/D$ | 1.69 ± 0.04 | 1.68 ± 0.03 | 1.61 ± 0.05 |
| $\langle\mu^2\rangle/nm^2$ | 0.58 ± 0.02 | 0.56 ± 0.01 | 0.52 ± 0.02 |

dard expressions

$$\langle\mu^2\rangle^{1/2} = 0.0128\sqrt{(p - 1.05R_D)T} \quad (1)$$

and

$$p = M \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{1}{\rho_0} \left(1 + \frac{3(d\epsilon/d\omega)}{(\epsilon_0 - 1)(\epsilon_0 + 2)} - \frac{(d\rho/d\omega)}{\rho_0} \right) \quad (2)$$

where p is the molar polarization, R_D the molar refractivity ($3.35 \times 10^{-5} \text{ m}^3$)¹⁶, T the absolute temperature, M the molar mass of the solute, ϵ and ϵ_0 the dielectric constants of solution and solvent, respectively, ω the weight fraction of the solute, and ρ and ρ_0 the densities of solution and solvent, respectively.

RESULTS

Experimental values of the coefficients $d\epsilon/d\omega$ and $d\rho/d\omega$, obtained at 25°C, and the RMS dipole moments $\langle\mu^2\rangle^{1/2}$ calculated therefrom are given in Table I, where the values of ϵ_0 and ρ_0 used in the calculations are also included. For later convenience, the results were recast into the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where n is the number of the skeletal bonds, and m^2 is the mean-square of the bond moments of the molecule: for DMMP, $n=5$ and $m^2=0.996$ (cf. seq.), the unit of m being expressed in Debye ($3.34 \times 10^{-30} \text{ Cm}$).

Variation of the dipole moment with temperature was studied over the range 25–40°C. From the plot $\ln[\langle\mu^2\rangle/nm^2]$ vs. temperature, the thermal coefficients $d\ln\langle\mu^2\rangle/dT$ were estimated to be $3.5 (\pm 3.8) \times 10^{-3}$ (benzene), $1.7 (\pm 2.9) \times 10^{-3}$ (carbon tetrachloride), and $4.4 (\pm 4.8) \times 10^{-3} \text{ K}^{-1}$ (cyclohexane). The range of temperature over which these experiments were carried out is insufficient to claim much precision for the results.

CONFORMATIONAL ANALYSIS OF DMMP

A schematic representation of DMMP in its all *trans* conformation is given in Figure 1, where skeletal bonds and bond angles are numbered from left to right. The bond lengths and bond angles used in this study are listed in Table II. The two bond angles COC denoted by θ_1 and θ_4 may not be sterically equivalent. A value of 111.5° was assigned to the former (θ_1), the same value being used previously in the treatment of the POE⁵ and POP chains.⁶ A somewhat larger bond angle 118° was

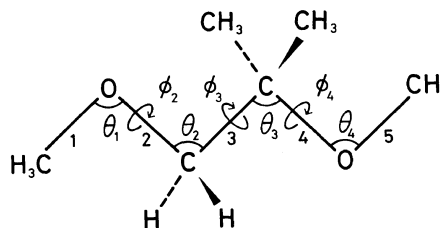


Figure 1. Schematic diagram of 1,2-dimethoxy-2-methylpropane (DMMP) in its extended form, a monomer model for the poly(oxy-1,1-dimethylethylene) (PODME) chain.

Table II. Geometrical parameters used for DMMP

| Bond length | | Bond angle | |
|-------------|------|---------------------|-------|
| | Å | | deg |
| C-C | 1.53 | θ_1 | 111.5 |
| C-O | 1.43 | θ_2 | 112 |
| C-H | 1.10 | θ_3 | 109.5 |
| | | θ_4 | 118 |
| | | $\angle \text{CCH}$ | 110 |
| | | $\angle \text{OCH}$ | 110 |

adopted for the latter (θ_4) in consideration of the results of the conformational analysis presented in a later part of this section. The bond angles at the carbon atom carrying two methyl substituents may be assumed to be tetrahedral. The angle OCC at the primary carbon atom was taken to be 112° .⁵

Following the procedure customarily employed in the conformational statistics of chain molecules,¹⁷ statistical weight matrices may be defined for the three internal bonds of the DMMP molecule as

$$U_2 = \begin{bmatrix} 1 & \sigma' & \sigma' \end{bmatrix} \quad (3)$$

$$U_3 = \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & 0 & \sigma\omega \\ 0 & \sigma\omega & 0 \end{bmatrix} \quad (4)$$

$$U_4 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega' \\ 1 & \omega' & 1 \end{bmatrix} \quad (5)$$

where subscripts specify the bond with which the corresponding statistical weight matrix is associated, and rows and columns of each matrix are indexed to rotational states in the order t , g^+ , and g^- for the bond pair under consideration. Since it is not necessary to define the rotational isomeric states for the first bond, U_2 may be expressed in a row form. Statistical weight parameters σ' and σ are defined respectively for the first-order interactions¹⁷ taking place about bonds 2 and 3. Similarly, ω and ω' are those for the second-order interactions as specified. Each statistical weight factor is normalized to the weight of unity for the corresponding *trans* state. Following the conventional procedure,¹⁷ statistical weight parameters are taken to be simple Boltzmann factors in the corresponding conformational energies. With the statistical weight matrices thus defined, the configurational partition function Z for DMMP can be given by¹⁷

$$Z = U_2 U_3 U_4 J \quad (6)$$

where J is a 3×1 column matrix with all elements equal to unity.

Theoretical values of the conformational energies were calculated as a function of bond rotation angles by adopting the expressions used previously

for the analyses of polyoxide chains.⁵⁻⁸ As inspection of a model reveals, rotation around bond 4 involves severe steric repulsions between the terminal methyl and the preceding methyl or methylene groups irrespective of the rotational isomeric states. The bond angle θ_4 tends to be widened by such steric effects. However, the angle deformation thus induced must be opposed by the angle strain energy customarily expressed¹⁸ as

$$E(\theta) = A(\pi/180)^2(\theta_4 - 109.5)^2 \quad (7)$$

Following Shimanouchi *et al.*,¹⁹ the force constant A for the \angle COC bending was taken to be 88 kcal mol⁻¹. The equilibrium position for θ_4 was estimated by calculating the conformational energy as a function of θ_4 , the other bond angles being kept invariable. When all the internal bonds are kept *trans* ($\phi_2 = \phi_3 = \phi_4 = 0$), the energy was found to be minimum at about $\theta_4 = 118.6^\circ$. This value reduces slightly to 117.4° if adjustments of rotation angles (ϕ_s) for the articulated methyl groups are additionally permitted: displacements of $\Delta\phi_s = 6^\circ$ from the regularly staggered position are required. We adopt a value of 118° in Table II and also in the following study.

In the previous treatment of POE⁵ and POP⁶, a value of 1.20 (± 0.10) D was set forth for the dipole moment of the ether group. According to McClellan's table,²⁰ the dipole moment of methyl *t*-butyl ether, a model for the $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_2-$ moiety, was found to be similar in magnitude, indicating that the dipole moment of the aliphatic ether is not affected much by the bulkiness of the alkyl groups. In view of these experimental observations, we adopt an identical value (1.20 \pm 0.10 D) for both ether groups of DMMP. The combined use of the bond angle $\theta_4 = 118^\circ$ (see above) leads to a value of 1.16 D for the bond dipole moment applicable to bonds 4 and 5. The corresponding partial electronic charges assigned to the carbon and oxygen atoms are respectively $\delta_C = 0.17$ and $\delta_O = -0.34$.

Using the set of geometrical parameters given in Table II, we calculated energies for several representative conformations. Locations of the energy minima and the associated energies (expressed relative to the *ttt* state) are summarized in Table III. Statistical weight factors assigned to these conformations are also given in the preceding column. The separate interaction energies were deduced from

Table III. Results of semiempirical energy calculations for DMMP: low-energy conformations, their statistical weight factors, locations of energy minima, and separate interaction energies

| Conformation | Statistical weight factor | ϕ_2 | ϕ_3 | ϕ_4 | E_{\min} | Conformational energy parameter |
|-----------------|---------------------------|----------|-----------|-----------|------------------------|------------------------------------|
| | | deg | deg | deg | kcal mol ⁻¹ | |
| $t t g^\pm$ | γ | 0 | ± 4 | ± 118 | 0.1 | $E_\gamma = 0.1$ |
| $t g^\pm t$ | σ | 0 | ± 120 | 0 | 0.5 | $E_\sigma = 0.5$ |
| $t g^\pm g^\mp$ | $\sigma\gamma\omega'$ | 0 | ± 102 | ∓ 121 | 1.5 | $E_{\omega'} = 0.9^a$ |
| $t g^\pm g^\pm$ | $\sigma\gamma$ | 0 | ± 122 | ± 120 | 0.6 | |
| $g^\pm g^\mp t$ | $\sigma'\sigma\omega$ | ± 87 | ∓ 116 | 0 | 2.0 | $E_{\sigma'} + E_{\omega} = 1.5^b$ |

^a $E_{\omega'} = E_{t g^\pm g^\mp} - E_\sigma - E_\gamma$. ^b $E_{\sigma'} + E_{\omega} = E_{g^\pm g^\mp t} - E_\sigma$.

these results in a usual manner,⁵ and are listed in the last column of the table. The theoretical value of E_σ estimated in this manner is 0.5 kcal mol⁻¹. In the following section, the parameter E_σ is alternatively determined so as to reproduce the observed values of the dipole moment. Contributions from the $g^\pm t$ and $g^\pm g^\pm$ conformations for the bond pair (2, 3) are entirely neglected in consideration of the very severe steric conflicts taking place between the terminal methyl and one of the articulated methyl groups. Steric repulsions become less severe in the $g^\pm g^\mp$ states for the same bond pair: in this conformation, the articulated methyl group mentioned above is replaced by the oxygen atom of the skeletal chain. The sum of the conformational energies $E_{\sigma'}$ and E_{ω} is the relative energy assigned to these states and can be obtained from the calculation for the $g^\pm g^\mp t$ conformation (*cf.* Table III). As is evident from the expression given in eq 3 and 4, a further separation of the energy parameter into $E_{\sigma'}$ and E_{ω} is unnecessary in the present treatment. If a value of 1.2–1.3 kcal mol⁻¹ is assigned^{5,6} to $E_{\sigma'}$, however, the other parameter E_{ω} should bear 0.2 to 0.3 kcal mol⁻¹, a similar value being adopted in the analysis of the POE chain.⁵ The parameter E_γ comprises mainly the electrostatic contribution involved in the g^\pm conformation about bond 3. An increment in energy from this source was estimated to be only 0.1 kcal mol⁻¹. Accordingly, the statistical weight of unity is assigned to these states ($\gamma = 1$) in the following treatment.

ESTIMATION OF E_σ FROM THE ANALYSIS OF THE DIPOLE MOMENT DATA

The values of $\langle \mu^2 \rangle / nm^2$ were computed for the

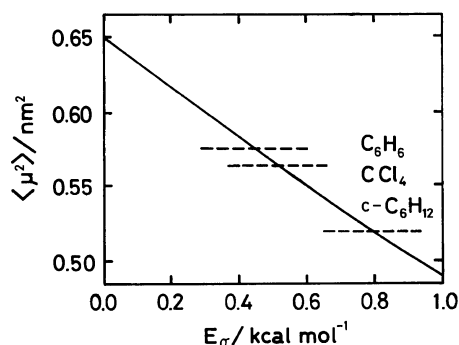


Figure 2. The dipole moment ratio for DMMP calculated as a function of E_σ for the temperature of 25°C. The horizontal dashed lines specify the experimental values observed in the solvents indicated.

geometry given in Table II according to the conventional procedure.¹⁷ The bond dipole moments for the C–O bonds were assumed to be 1.07 D for the ether group associated with the primary carbon atom (bonds 1 and 2), and 1.16 D for that of the tertiary carbon atom (bonds 4 and 5). The bond dipole moment for the C–C bond was assumed to be null.^{5–8} Results of calculations for the temperature of 25°C are shown in Figure 2 as a function of E_σ over a range 0–1.0 kcal mol⁻¹. Conformational energy parameters required in these calculations (other than E_σ) were deduced in the preceding section. Also shown in Figure 2 are the experimental values of $\langle \mu^2 \rangle / nm^2$ (the dashed lines) observed in the solvents as indicated. The values of E_σ which reproduce these experimental observations are as follows; 0.4 ± 0.1 (benzene), 0.5 ± 0.1 (carbon tetrachloride), and 0.8 ± 0.1 (cyclohexane), units being kcal mol⁻¹. The temperature coefficient $d \ln \langle \mu^2 \rangle / dT$ calculated by using $E_\sigma = 0.5$ kcal mol⁻¹ is 0.5×10^{-3}

K^{-1} (30°C). Positive values of the temperature coefficient were suggested from studies over the range 25–40°C. Experimental uncertainties involved in the measurements are however too large to allow a quantitative comparison (see above).

DISCUSSION

The conformational energy parameter E_σ deduced from the analysis of the experimental values of the dipole moment was found to be in the range 0.4–0.8 kcal mol⁻¹, indicating that the *trans* form is more stable than the *gauche* arrangement for the moiety O–CH₂–C(CH₃)₂–O. The theoretical value of the same energy obtained in the previous section is 0.5 kcal mol⁻¹ (Table III). The close agreement between theory and experiment as seen above suggests that the *gauche* oxygen effect^{11,21} is nearly suppressed in DMMP.

Observed values of the dipole moment ratio $\langle \mu^2 \rangle / nm^2$ for 1,2-dimethoxyethane (DME)²² and 1,2-dimethoxypropane (DMP)²³ were reported to be in the range 0.55–0.64 and 0.54–0.59, respectively. These values were favorably reproduced by calculations carried out using conformational energy parameters derived from the analysis of various configuration-dependent properties of the polymers. The corresponding values for DMMP were found to be 0.52–0.57 as given in Table I. In this series of compounds, which may be represented by a general formula CH₃OCH₂C(R₁)(R₂)OCH₃, the internal rotation for the central C–C bond tends to be more restricted in the order DME (R₁=R₂=H),⁵ DMP (R₁=H, R₂=CH₃),⁶ and DMMP (R₁=R₂=CH₃), while that for the succeeding C–O bond follows the opposite trend. In spite of these variations in conformational aspects, the values of the square of the dipole moment averaged over all conformations remain quite invariable for the class of molecules under consideration. The same seems to hold for the temperature coefficient $d \ln \langle \mu^2 \rangle / dT$.

The statistical weight matrices U_1 and U_2 defined respectively by eq 3 and 4 should be applicable, as they stand, to the 2nd and 3rd bond of the polymeric chain CH₃O{CH₂C(CH₃)₂O}_xCH₃. The repeat unit of the chain comprises three bonds: (a) CH₂–C(CH₃)₂, (b) C(CH₃)₂–O, and (c) O–CH₂. Due to very severe steric conflicts associated with the interaction taking place between the two

C(CH₃)₂ groups, both *gauche* states for the O–CH₂ bond may be entirely suppressed: the *trans* state remains to be the only choice for the bond. Thus we have a column expression for bond c:

$$U_c = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (6)$$

and consequently, a row form for bond a:

$$U_a = \begin{bmatrix} 1 & \sigma & \sigma \end{bmatrix} \quad (7)$$

The matrix U_4 in eq 5 is effective, without any modification, for all internal CH₂–O bonds (*i.e.* bond b):

$$U_b = U_4 \quad (8)$$

The statistical weight matrices having been defined in this manner, conformational energy parameters obtained from the analysis of DMMP should serve for the theoretical estimation of various configuration-dependent properties of the PODME chain. This subject will be treated in paper III.

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