taken place, the collisional relaxation of i-C_6H_6 is much faster than further reaction of i-C_6H_6. This perhaps explains why this i-C_6H_6 is not observed in condensed phases. At high pressures, as in solution, its rate of production would be vanishingly low. Finally, the eventual drop in concentration of i-C_6H_6, as shown in Figure 2, can be attributed to its secondary photolysis or sensitized decomposition by excited benzene.

This in conjunction with its low rate of production would, of course, reduce its steady-state concentration in condensed phases to unobservable levels.

Dipole Moments of Chain Molecules. I. Oligomers and Polymers of Oxyethylene

J. E. Mark and P. J. Flory

Contribution from the Departments of Chemistry, The Polytechnic Institute of Brooklyn, Brooklyn 1, New York, and Stanford University, Stanford, California. Received April 12, 1966

Abstract: Mean-square dipole moments have been calculated for oxyethylene chain molecules $RO(CH_2CH_2O)_xR$, where R = H or C_2H_5 and $x = 1$–120, using a rotational isomeric state model with neighbor dependence. In a previous study of polyoxyethylene, the mean extension of the chain and its temperature coefficient were used to obtain statistical weights for rotational states about skeletal bonds. These statistical weights, with minor modification, are shown to give dipole moments in good agreement with measured values over a wide range of molecular weight. A comparatively large, positive temperature coefficient of the dipole moment is predicted for polyoxyethylene.

The rotational isomeric state model has been notably successful in the interpretation of the random coil configurations of an impressive list of long-chain molecules: polyisobutylene,[1] polyethylene,[2,3] poly(dimethylsiloxane),[4] polyoxymethylene,[5] polyoxyethylene,[6] polypeptides,[7] and vinyl polymers of both regular and irregular steric structure.[8] In these cases, the efficacy of the model was put to test by comparison of calculated and measured values of (i) the *characteristic ratio* $\langle r^2 \rangle_0/nl^2$ of the mean-square end-to-end distance of the chain unperturbed by long-range interactions to the same mean-square dimension nl^2 in the idealization that all skeletal bonds of the chain are freely jointed, and usually also of (ii) the temperature coefficient d $\ln \langle r^2 \rangle_0/dT$ of these unperturbed dimensions. Experimental methods permit the determination of these two quantities only for high molecular weight materials. Recent advances in theory[9] permit calculation of the mean-square moment which is the resultant sum of any set of vector quantities associated with the respective skeletal bonds of a chain molecule, irrespective of its degree of polymerization. The mean-square dipole moment of a chain molecule consisting of units having

dipole moments is such a quantity. It can be measured with considerable accuracy over a wide range of molecular weight. This experimental quantity is therefore ideally suited for a test of theory in the interesting region of short chain length, where the properties of a chain molecule change most rapidly with molecular weight. An important step in this direction is the successful interpretation[10] of the dipole moments of α,ω-dibromo-n-alkanes in the low molecular weight region, using statistical weights calculated from spectroscopic investigations on n-alkanes and n-alkyl bromides and supported by the statistical analysis of the polyethylene chain.[2,3]

This paper is concerned with mean-square dipole moments of chain molecules having dipolar skeletal bonds. Specifically, dipole moments of oligomers and polymers of oxyethylene are calculated using statistical weights appropriate for the interpretation of $\langle r^2 \rangle_0/nl^2$ and d $\ln \langle r^2 \rangle_0/dT$ of polyoxyethylene. The interdependence of bond rotational states, manifested in the repression of conformations in which neighboring bonds adopt *gauche* rotational states of opposite sign, is taken into account as described previously.[6] Calculations are compared with experimental results reported in the literature.

Theory

Rotational Statistical Weights. The polyoxyethylene chain is shown in its planar *trans* conformation in Figure 1. The end groups R for the two series of homologs to be considered are C_2H_5 and H. The

(1) O. B. Ptitsyn and Yu. A. Sharanov, *Zh. Tekh. Khim.*, **27**, 2744, 2762 (1957); C. A. J. Hoeve, *J. Chem. Phys.*, **32**, 888 (1960).
(2) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961); C. A. J. Hoeve, *J. Chem. Phys.*, **35**, 1266 (1961); K. Nagai and T. Ishikawa, *ibid.*, **37**, 496 (1962).
(3) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).
(4) P. J. Flory, V. Crescenzi, and J. E. Mark, *ibid.*, **86**, 146 (1964).
(5) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).
(6) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).
(7) D. A. Brant and P. J. Flory, *ibid.*, **87**, 2791 (1965).
(8) P. J. Flory, J. E. Mark, and A. Abe, *ibid.*, **88**, 639 (1966).
(9) P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964); P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

(10) W. J. Leonard, R. L. Jernigan, and P. J. Flory, *ibid.*, **43**, 2256 (1965).

polyoxyethylene diethyl ethers ($R = C_2H_5$) will be designated by POEE, and the polyoxyethylene glycols ($R = H$) by POEG. In both cases the end-to-end length r of the chain will be measured from the atom centers (C or H) of the R groups which are joined by the R–O and O–R bonds.

The skeletal bond conformations will be treated according to the rotational isomeric state model, each bond being accorded three discrete states: *trans* (t), *gauche$^+$* (g^+), and *gauche$^-$* (g^-), located at $\varphi = 0°$, and at $\varphi = \pm 120°$, respectively, where φ is the angle of rotation about the skeletal bond. The *gauche* potential minima for rotations about C–O and O–C bonds doubtlessly occur at angles $|\varphi| < 120°$ owing to steric repulsions (*cf. seq.*), but the displacement probably does not exceed 10°.[3] Relocation of the *gauche* states adopted above would have no effect of significance on the final results.

Let $u_{\zeta\eta;a}$ denote the statistical weight to be associated with assignment of a C–O bond, such as $i - 1$ in Figure 1, to rotational state η when the preceding bond $i - 2$ has been assigned to state ζ. In matrix form

$$\mathbf{U}_a = [u_{\zeta\eta;a}] \qquad (1)$$

where the three rotational states are indexed in the order t, g^+, g^-; those for bond $i - 1$ are indexed on the columns and those for bond $i - 2$ on the rows. Statistical weight matrices $\mathbf{U}_b$ and $\mathbf{U}_c$ are defined similarly for the O–C and C–C bonds, *e.g.*, bonds i and $i + 1$ in Figure 1, respectively. Bonds 2, 3, and $n - 1$ require special consideration. The statistical weight matrices applicable to them depend on the character of the end groups R.

The configuration partition function will be given by[9,11]

$$Z = \mathbf{J}^* \mathbf{U}_2 \mathbf{U}_3 (\mathbf{U}_a \mathbf{U}_b \mathbf{U}_c)^{x-1} \mathbf{U}_{n-1} \mathbf{J} \qquad (2)$$

where

$$\mathbf{J}^* = [1\ 0\ 0], \quad \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

and x is the number of repeating units, *i.e.*, $x = (n - 2)/3$.

Let the all *trans* conformation of the chain as a whole be taken as the state of reference. It is accorded a statistical weight of unity. In assigning bond i to state η, the statistical weight $u_{\zeta\eta;i}$ is then to be reckoned relative to the *trans* conformation, bond $i - 1$ having been previously assigned to state ζ. As a further convenience, we adopt the convention of assessing the interactions precipitated by the assignment of bond i to state η on the supposition that all succeeding bonds $j > i$ are (temporarily) retained in *trans* conformations. The eventual assignment of one or more of them to other states will be taken into account by statistical weights to be introduced by succeeding U matrices.

These conventions render first column elements $u_{\zeta 1;i} = 1$ for all ζ and i. Thus we obtain

$$\mathbf{U}_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \omega\sigma \\ 1 & \omega\sigma & \sigma \end{bmatrix} \qquad (3)$$

$$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \qquad (4)$$

$$\mathbf{U}_c = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \omega\sigma' \\ 1 & \omega\sigma' & \sigma' \end{bmatrix} \qquad (5)$$

as was shown previously.[6,12]

The factor σ occurring in $\mathbf{U}_a$ and $\mathbf{U}_b$ represents the interaction between two CH_2 groups separated by three skeletal bonds when the intervening C–O or O–C bond is in a *gauche* conformation. The distance between the pair of CH_2 groups is then 2.81 A, center to center. The factor σ' in $\mathbf{U}_c$ similarly takes account of the interaction $O \cdots O$ brought about by assignment of C–C bond $i + 1$ to a *gauche* state. Pairs of *gauche* rotations of like sign about consecutive bonds markedly decrease the distance between groups separated by four bonds, but do not bring them within a distance where important interactions are expected.[6] Hence, $g^\pm g^\pm$ states receive the same statistical weights as $tg^\pm$ in each of the three matrices.
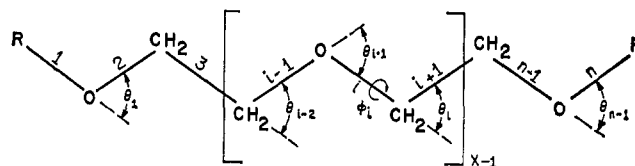

Figure 1. Specification of bonds and bond angles in the polyoxyethylene chain.

Consecutive *gauche* rotations of opposite sign, however, were shown to bring about interactions of foremost importance. In the case of such rotations about CH_2–O–CH_2 bonds, CH_2 groups separated by four bonds are brought within 2.37 A of one another. Since the van der Waals radius of the methyl group is 2.0 A,[13] the resulting severe steric overlaps warrant assignment of a statistical weight of zero to the offending conformations, g^+g^- and g^-g^+ in $\mathbf{U}_b$. *Gauche* rotations of opposite sign about CH_2–CH_2–O and O–CH_2–CH_2 bond pairs precipitate less severe interactions between CH_2 groups and O atoms, which are represented by the factor $\omega \leqslant 1$ in $\mathbf{U}_a$ and $\mathbf{U}_c$. Because of the smaller domain of the O atom,[13] these conformations are depressed but not excluded.[6]

Dipole–dipole interactions, not cited explicitly in the foregoing rationalization of the statistical weights, will of course contribute to the parameters. Their effect is presumed to be small in view of the fairly small magnitude of the CH_2–O bond dipole moment. These dipolar effects are conveniently considered in terms of equivalent partial charges assigned to the various atoms and groups.[6]

Yet to be constructed are $\mathbf{U}_2$, $\mathbf{U}_3$, and $\mathbf{U}_{n-1}$. In the case of POEE, the R ($= C_2H_5$) groups are involved in

(11) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941); G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

(12) The factors α and γ occurring in the 2,2 and 3,3 elements of the statistical weight matrices as represented in ref 6 are here set equal to unity in light of results there reported. Also, in the present notation ω replaces the previous β.

(13) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964); L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

interactions identical with those already described. Hence, $U_2 = U_b$, $U_3 = U_c$, and $U_{n-1} = U_a$.[14]

For POEG, a *gauche* rotation about bond 2 brings the terminal H atom within 2.45 A of one of the H atoms on the CH_2 group between bonds 3 and 4 (assuming bond 3 to be *trans*). Since the van der Waals radius of the H atom is *ca.* 1.1 to 1.2 A,[13,15] there should be little interaction, and therefore weights of unity may be assigned to each of the three states for bond 2. These may be incorporated in the first row of U_2 (other elements being immaterial[14]). Pairs of *gauche* rotations of opposite sign about bonds 2 and 3 decrease the distance between the terminal H atom and the O atom four bonds removed to 2.50 A. The van der Waals radius of an O atom is 1.4 A.[13] Neither repulsions nor attractions should be large at this distance. Rotation of bond 3 should therefore be nearly independent of its predecessor; hence, we take

$$U_3 = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma' \end{bmatrix} \quad (6)$$

Similarly, and to an approximation corresponding to that offered in formulating U_2

$$U_{n-1} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (7)$$

The approximations involved in adopting these simple forms for U_2, U_3, and U_{n-1} may be significant, of course, only for short chains.

The Mean-Square Dipole Moment. The orthogonal transformation matrices **T** required for the calculation of this quantity[9] are formulated using cartesian coordinate systems defined for each skeletal bond in the following manner: (i) the x axis is taken along bond i; (ii) the y axis is taken in the plane determined by bonds i and $i - 1$, the positive direction making an acute angle with bond $i - 1$; and (iii) the z axis is chosen so as to make the coordinate system right-handed. The matrix

$$T_i = \begin{bmatrix} \cos \theta_i & \sin \theta_i & 0 \\ \sin \theta_i \cos \varphi_i & -\cos \theta_i \cos \varphi_i & \sin \varphi_i \\ \sin \theta_i \sin \varphi_i & -\cos \theta_i \sin \varphi_i & -\cos \varphi_i \end{bmatrix} \quad (8)$$

where θ_i is the bond angle supplement (see Figure 1), will effect the transformation of a vector in the reference frame for bond $i + 1$ into that of bond i. Bond angles $\angle COC$ and $\angle CCO$ are very nearly tetrahedral;[16] so also is $\angle COH$ required in the analysis of the POEG chain.[16] All bond angle supplements (*e.g.*, θ_1, θ_{i-2}, θ_{i-1}, and θ_i in Figure 1) may therefore be assigned the same value (70°), and no indices on θ are required in the construction of the **T** matrices.

The characteristic dipole moment ratio can then be expressed by[9]

$$\langle \mu^2 \rangle_0 / nm^2 = 1 + (2/Znm^2)[1\ 0 \cdots 0] \cdot$$

$$\begin{bmatrix} \prod_{i}^{n-1} G_i \end{bmatrix} \begin{bmatrix} J \times m_n \\ J \end{bmatrix} \quad (9)$$

where the G_i's are defined by

$$G_i = \begin{bmatrix} U_i & (E_3 \times m_i^T)(U_i \times E_3)\|T\| & 0 \\ 0 & (U_i \times E_3)\|T\| & (E_3 \times m_i)U_i \\ 0 & 0 & U_i \end{bmatrix} \quad (10)$$

The matrix U_1 required in the construction of G_1 is the unit matrix E_3 of order three. The symbol $\times$ denotes the direct product. For example

$$A \times B = \begin{bmatrix} A_{11}B & A_{12}B \\ A_{21}B & A_{22}B \end{bmatrix} \quad (11)$$

where **A** is taken to be of second order. The bond moment vectors are of the form

$$m_i = \begin{bmatrix} m_i \\ 0 \\ 0 \end{bmatrix} \quad (12)$$

since the dipoles considered lie along the bonds. Finally

$$\|T\| = \begin{bmatrix} T(\varphi = 0°) & & \\ & T(\varphi = 120°) & \\ & & T(\varphi = -120°) \end{bmatrix} \quad (13)$$

is the pseudo-diagonal matrix of ninth order comprising the submatrices **T** defined by eq 8 and evaluated for the indicated values of φ. Other quantities are $\langle \mu^2 \rangle_0$, the mean-square dipole moment in the absence of long-range interactions, and $m^2 = (1/n)[x(m_a^2 + m_b^2 + m_c^2) + 2m_n^2]$, the average of the squares of the bond moments. For oxyethylene chains having the structure shown in Figure 1, eq 9 takes the form

$$\langle \mu^2 \rangle_0 / nm^2 = 1 + (2/Znm^2)[1\ 0 \cdots 0]G_1G_2G_3 \cdot$$

$$(G_aG_bG_c)^{x-1}G_{n-1} \begin{bmatrix} 0 \\ \vdots \\ J \times m_n \\ J \end{bmatrix} \quad (9')$$

Experimental Dipole Moments. The dipole moments of oxyethylene molecules have been determined by Marchal and Benoit,[17] by Uchida, *et al.*,[18] by Rossi and Magnasco,[19] and by Kotera, *et al.*[20] Measurements were carried out using good solvents in which long-range interactions increase the mean-square dimensions of very long chains as a result of the effect of volume exclusion. Marchal and Benoit[17] have shown that the mean-square dipole moment is unaffected by this perturbation of the configuration if the resultant moment for each repeating unit lies in the plane bisecting the bond angle of a skeletal atom of the chain.[21] It is

(14) It will be observed that only the first row of U_2 is required in eq 2, as follows from premultiplication by J^*. This is consistent with the absence of a rotational assignment preceding bond 2.

(15) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(16) H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

(17) J. Marchal and H. Benoit, *J. Chim. Phys.*, **52**, 818 (1955); *J. Polymer Sci.*, **23**, 223 (1957).

(18) T. Uchida, Y. Kurita, N. Koizumi, and M. Kubo, *ibid.*, **21**, 313 (1956).

(19) C. Rossi and V. Magnasco, *ibid.*, **58**, 977 (1962).

(20) A. Kotera, K. Suzuki, K. Matsumura, T. Nakano, T. Oyama, and U. Kambayashi, *Bull. Chem. Soc. Japan*, **35**, 797 (1962).
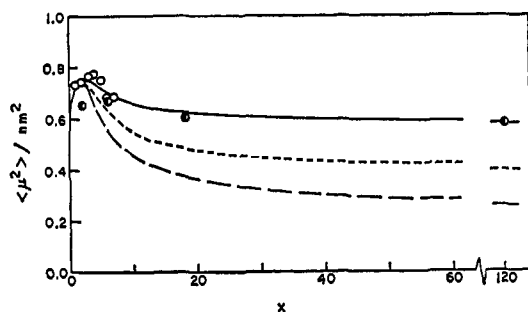
Figure 2. The dipole moment ratio $\langle \mu^2 \rangle /nm^2$ vs. the degree of polymerization x for POEG. The experimental results of Uchida, et al.,[18] are represented by open circles, and those of Marchal and Benoit[17] by half-filled circles. The short-dashed line refers to results obtained using the first set of parameters of Table I, the long-dashed line the fifth set, and the solid line the last set.

Figure 3. The dipole moment ratio $\langle \mu^2 \rangle /nm^2$ plotted against the degree of polymerization for POEE. The open circles refer to the results of Kotera, et al.,[20] and the half-filled circles to the results of Marchal and Benoit.[17] The curve was calculated using the last set of parameters of Table I.

readily apparent that the oxyethylene chains are of this type. The experimental results to be considered here pertain to POE chains of degrees of polymerization not exceeding 120 units. Long-range perturbations of the configurations of chains of this length, even as manifested in $\langle r^2 \rangle$, are small.[22] In light of these considerations, dipole moments of oxyethylene molecules determined in good solvents may be compared, without correction, with those calculated as described in the preceding sections. We therefore drop the subscript on $\langle \mu^2 \rangle_0$ as being superfluous for these molecules.

In keeping with the mode of expression of the results of the theoretical calculations, the reported value of $\langle \mu^2 \rangle$ for each chain molecule has been divided by nm^2, the mean-square dipole moment of that chain in the idealization that the skeletal bonds are freely jointed. That is, nm^2 is the sum of the squares of the bond dipole moments for all bonds of the chain, terminal bonds (e.g., O–H) included. Figure 2 presents experimental results obtained by Marchal and Benoit[17] for hydroxyl-terminated oxyethylene molecules in benzene at 20°,[23] and by Uchida, et al.,[18] in dioxane at 25°. Measurements on lower chain homologs carried out by Rossi and Magnasco[19] in benzene at 25° lead to values of $\langle \mu^2 \rangle /nm^2$, not included here, which are considerably higher than the corresponding points shown in Figure 2. Their results show a monotonic increase in the dipole moment ratio as the degree of polymerization x decreases, a value of $\langle \mu^2 \rangle /nm^2 = 1.03$ being reached at $x = 4$. It would be difficult to reconcile their results with a limiting value for $x = 0$ of approximately 0.6, the dipole moment ratio for H_2O vapor.[24] The theoretical curves for oxyethylene glycols calculated as described in the following section meet this requirement.

Results of Marchal and Benoit for long chains ($x \cong 120$) yield $\langle \mu^2 \rangle /nm^2 = 0.58$, which may be taken as

representative of the asymptotic limit for $x = \infty$. This result is corroborated both by the value $\langle \mu^2 \rangle /nm^2 = 0.59$ at $x = 176$ found by Rossi and Magnasco[19] and by measurements of Svirbely and Lander[25] giving $\langle \mu^2 \rangle /nm^2 = 0.57$ for an unfractionated POEG of average $x \cong 85$ dissolved in benzene at 44°.

Experimental results for diethyl-terminated oxyethylene molecules, obtained in benzene at 20°[17,23] and in benzene at 25°,[20] are presented in Figure 3.

Theoretical Calculations. The C–O bond moment m_{C-O}, calculated from the dipole moment (1.15 D.)[24] of diethyl ether in the vapor state and the bond angle $\angle COC = 108°,$[16] is 0.99 D. This bond moment, in conjunction with the dipole moment (1.70 D.)[24] of ethanol and the bond angle $\angle COH = 106$ to $110°,$[16] give 1.7 D. for the bond moment m_{H-O}. The C–C bond dipole moment is take to be zero. These scalar bond moments were used in eq 9' in the manner dictated by the chain structure of Figure 1. Thus, $m_a = m_{n-1} = -m_b = -m_2 = m_{C-O}, m_c = m_3 = m_{C-C} = 0; m_1 = -m_n = m_{C-O}$ for POEE, and $m_1 = -m_n = m_{H-O}$ for POEG. Dipolar inductive effects should be small and for simplicity are neglected in these calculations.

The range of statistical weight parameters found acceptable in the interpretation of the chain dimensions and their temperature coefficient at 60° have been reported.[6] The energies corresponding to these parameters were calculated on the assumption that each parameter may be expressed as a Boltzmann factor, e.g., by

$$\sigma = \exp(-E_\sigma/RT) \qquad (14)$$

They are listed in columns 3, 5, and 7 of the first five rows of Table I for representative sets of values of the parameters falling within the aforementioned range.

(21) J. Marchal and C. Lapp, J. Polymer Sci., 27, 571 (1958), have determined the dipole moments for poly(methyl methacrylate) chains in a series of solvents at the same temperature. Although the solvents were sufficiently different in their thermodynamic interactions with this polymer to cause $\langle r^2 \rangle /nl^2$ to change by a factor of 3, $\langle \mu^2 \rangle /nm^2$ was constant within experimental error.

(22) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

(23) Since correction to 25° by use of the temperature coefficient of $<\mu^2>$ (see below) would amount to only about 1%, these values have been included in Figure 2 without modification.

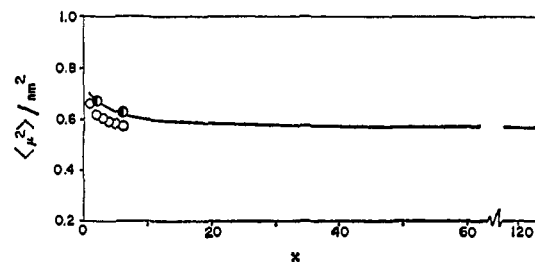(24) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, MIT, Cambridge, Mass., 1948.

Table I. Parameters (at 25°) and Corresponding Energies for Oxyethylene Chains

	ω	E_ω, cal mole^{-1}	σ	E_σ, cal mole^{-1}	σ'	$E_{\sigma'}$, cal mole^{-1}
1	0.566	338	0.118	1270	2.07	−430
2	0.672	236	0.113	1290	1.93	−390
3	0.779	148	0.084	1470	1.93	−390
4	0.889	70	0.070	1580	1.93	−390
5	1.00	0	0.055	1720	1.93	−390
6	0.566	338	0.220	900	2.07	−430

(25) W. J. Svirbely and J. J. Lander, J. Am. Chem. Soc., 67, 2189 (1945).

The statistical weights used in the present calculations were calculated from these energies taking $T = 298\,°K$, the temperature of most of the dipole moment measurements. They are given in the columns to the left of the energies from which they have been calculated.

The bond dipole moments, the bond angle supplements $(70°)$, and the first five sets of parameters listed in Table I were used to calculate $\langle \mu^2 \rangle / nm^2$ as a function of the degree of polymerization for hydroxyl-terminated oxyethylene chains. The middle and lowest curves in Figure 2 represent calculations from the first and fifth sets of parameters, respectively; curves calculated from the second, third, and fourth sets fell in order between these two. These theoretical curves follow the trends suggested by the experimental points: an asymptotic limit of $\langle \mu^2 \rangle / nm^2$ at high values of x, and a maximum in this ratio in the vicinity of $x = 2$ to 3. This latter feature is related to the increasing importance of the atypical ultimate and penultimate bonds as the degree of polymerization decreases. Although reasonable agreement between theory and experiment is found in the region of very short chain length, the two lower curves lie considerably below the experimental points for larger values of x. Since the disparity is least for calculations from the first set of parameters, attention is restricted to them for the present. Partial derivatives of $\langle \mu^2 \rangle$ and of $\langle r^2 \rangle_0$ with respect to σ, ω, and σ', calculated using the first set of parameters with $x = 120$, are given in the second column of Table II. The

Table II. Coefficients Calculated for Two Sets of Parameters from Table I

Coefficient[a]	From set 1[b]	From set 6[b]
$\partial \ln \langle \mu^2 \rangle / \partial \ln \sigma$	0.691	0.558
$\partial \ln \langle \mu^2 \rangle / \partial \ln \omega$	0.122	0.041
$\partial \ln \langle \mu^2 \rangle / \partial \ln \sigma'$	0.043	0.085
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma$	−0.039	−0.059
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \omega$	−0.108	−0.167
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma'$	−0.380	−0.320

[a] Coefficients for $\langle \mu^2 \rangle$ refer to $25°$, and those for $\langle r^2 \rangle_0$ to $60°$, these being the temperatures representative of experimental measurements on the respective quantities. Parameters ω, σ, and σ' given for $25°$ in the first and last rows of Table I were corrected to $60°$ for the purpose of calculating coefficients of $\langle r^2 \rangle_0$ at the latter temperature. The corrections were carried out on the basis of Boltzmann expressions, eq 14, the required energies having been included in Table I. [b] See Table I.

mean-square dipole moment depends strongly on σ; it is more than 15 times as sensitive as $\langle r^2 \rangle_0$ to this parameter according to the calculations in the second column.

The last set of parameters in Table I differs from the first only in the value of σ, which is increased from 0.118 to 0.220 for the calculation of $\langle \mu^2 \rangle$ at $25°$, or, correspondingly, from 0.147 to 0.257 for the calculation of $\langle r^2 \rangle_0$ at $60°$. With this alteration the experimental value of $\langle \mu^2 \rangle / nm^2$ for long oxyethylene chains, i.e., 0.58 for $x = 120$ and a temperature of $25°$, is reproduced by the calculations. Inasmuch as $\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma$ is small, the value of the characteristic ratio is little affected by this revision. Thus, we obtain $\langle r^2 \rangle_0 / nl^2 = 4.0$, in good agreement with the experimental result,[6,26] 4.1 ± 0.4.

The temperature coefficient of $\langle r^2 \rangle_0$ may be calculated from the equation[6]

$$d \ln \langle r^2 \rangle_0 / dT = -(1/T)[\ln \sigma\,(\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma) + \ln \omega\,(\partial \ln \langle r^2 \rangle_0 / \partial \ln \omega) + \ln \sigma'\,(\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma')] \quad (15)$$

Using the coefficients given in the last column of Table II, we find $d \ln \langle r^2 \rangle_0 / dT = 0.12 \times 10^{-3}$ at $60°$ which is to be compared with the experimental result 0.23 $(\pm 0.02) \times 10^{-3}$ deg^{-1}. The difference, amounting to only 0.1×10^{-3} deg^{-1}, is relatively unimportant since the calculated value represents the small difference between two large quantities.[27]

As these comparisons show, the last set of parameters in Table I satisfactorily reproduces the experimental results for $\langle r^2 \rangle_0 / nl^2$, $d \ln \langle r^2 \rangle_0 / dT$, and $\langle \mu^2 \rangle / nm^2$, each quantity referring to chains of large n. Additionally, the solid curve in Figure 2 calculated from this set, affords improved agreement with values of $\langle \mu^2 \rangle / nm^2$ for short-chain oligomers. The similarly calculated curve for ethyl-terminated oxyethylene chains is shown in Figure 3. Available experimental results, unfortunately confined to the low range of x, confirm the initial portion of the calculated curve.

Temperature coefficients of the mean-square dipole moments of POEE chains, calculated after the manner of eq 15, are given in Table III. Also included are

Table III. Temperature Coefficients of Mean-Square Dipole Moments of POEE Chains

x	$10^3 d \ln \langle \mu^2 \rangle / dT$ Calcd[a]	Obsd[b]
1	0.25	0.0
2	0.69	1.2
3	1.12	1.1
4	1.47	1.6
5	1.64	1.2
6	1.71	2.0
120	2.51	

[a] Calculated for $25°$ using parameter set 6 of Table I. [b] From experimental results of Kotera, et al., in benzene at 25 and $50°$.

experimental values deduced from measurements of μ^2 for the lower oligomers of POEE carried out by Kotera, et al.,[20] at 25 and $50°$.

A large positive temperature coefficient is predicted for the dipole moment for long chains. The trend of the experimental values for lower homologs supports this prediction. Additionally, the calculated dependence of the temperature coefficient on chain length finds substantial confirmation in this set of experimental data.

Attempts to fit the array of experimental data using values of ω, σ, or σ' differing substantially from those given in the sixth row of Table I were unsuccessful.

(26) F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polymer Sci.*, **1**, 56 (1959); F. E. Bailey, Jr., J. L. Kucera, and L. G. Inhof, *J. Polymer Sci.*, **32**, 517 (1958).

(27) Exact agreement can be obtained by alteration of ω from 0.60 ($E_\omega = 338$ cal mole^{-1}) to 0.45 ($E_\omega = 530$ cal mole^{-1}). This change would not significantly affect the agreement between theory and experiment obtained for the other quantities; the calculated values would be $\langle r^2 \rangle_0 / nl^2 = 4.13$ and $\langle \mu^2 \rangle / nm^2 = 0.575$. Refinement to this extent should properly be postponed, pending more definitive experiments on the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ and on the temperature coefficient of the dipole moment ratio (see below).

Retention of the lower value of σ (0.118 at 25°) and adjustment of either ω or σ' as required to obtain the correct asymptote for $\langle \mu^2 \rangle / nm^2$ yields unacceptable values for $\langle r^2 \rangle_0/nl^2$ and/or for d ln $\langle r^2 \rangle_0/dT$. Similar modifications of the parameters in rows two through five and introduction of additional parameters to account for possible interactions between atoms separated by a pair of *gauche* states of like sign ($g^{\pm}g^{\pm}$) were abandoned for the same reason.

The preferred set of parameters was also used to calculate $\langle r^2 \rangle_0/nl^2$ as a function of the degree of polymerization for POEE and POEG. The characteristic ratios divided by their limiting values for $n = \infty$ are shown in Figure 4. The solid line refers to POEE and the short-dashed line to POEG; the long-dashed line, representing results calculated for polyethylene by Flory and Jernigan,[9] is included here for comparison. The characteristic ratios of the oxyethylene chains are seen to approach their limiting values more rapidly than does the characteristic ratio of polyethylene; the reverse has been found in the analogous comparison of random coil polypeptides with polyethylene.[7] This, of course, is directly related to "chain extension" as indicated by $[\langle r^2 \rangle_0/nl^2]_{n \to \infty}$, which increases from polyoxyethylenes to polyethylene to polypeptides.

Discussion

The general conclusions regarding the configuration of oxyethylene chains, which were previously reached on the basis of the chain dimensions and their temperature coefficient,[6] are given strong support by the present analysis of the dipole moments of such chains over a wide range of molecular weight. Firstly, the energy of a *gauche* state about a CH_2–O or a O–CH_2 bond considerably exceeds that of *trans*. Because the conflicting CH_2 groups are both positively charged and brought to a distance of separation less than the analogous distance in polyethylene, this energy must be appreciably greater than that (400 cal mole⁻¹) found for the polyethylene chain.[3] The value (900 cal mole⁻¹) obtained in the present analysis of the dipole moments as well as chain dimensions of oxyethylene chains is thus in accord with this prediction, though below the range (1300 to 1700 cal mole⁻¹) previously suggested[6] on the basis of analysis of the chain dimensions alone. *Gauche* rotational states about CH_2–CH_2 bonds are approximately 400 cal mole⁻¹ *lower* than *trans*. Pairs of *gauche* rotational states of opposite sign about CH_2–O–CH_2 bonds are excluded, but those for the bond pairs CH_2–CH_2–O and O–CH_2–CH_2 are only moderately disfavored. According to the present analysis, the energy E_ω attributable to the latter four-bond interaction is only about 300 cal mole⁻¹.
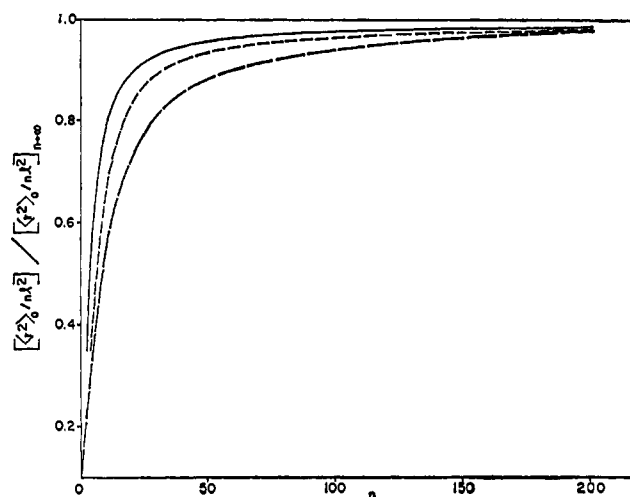

Figure 4. The dependence of the characteristic ratio $\langle r^2 \rangle_0/nl^2$ on the number n of skeletal bonds. The solid line represents POEE, the short-dashed line POEG, and the long-dashed line polyethylene.

It is also of interest to consider qualitatively the basis for the positive temperature coefficients of $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle$. The planar, all-*trans* form of an oxyethylene chain has a large end-to-end distance, but an exceedingly small mean-square dipole moment because of the mutual cancellation of the bond dipoles in this conformation; more precisely, for this conformation

$$\lim_{n \to \infty} \langle r^2 \rangle_0/nl^2 = \infty \quad \text{and} \quad \lim_{n \to \infty} \langle \mu^2 \rangle/nm^2 = 0$$

Therefore, "transitions" from *trans* to *gauche* states can be expected to decrease $\langle r^2 \rangle_0$, but to increase $\langle \mu^2 \rangle$. An increase in temperature, as pointed out previously,[6] increases the *gauche* population about CH_2–O and O–CH_2 bonds, but decreases the *gauche* population about CH_2–CH_2 bonds. In the case of the chain dimensions, the latter effect slightly exceeds the former and a small, positive temperature coefficient for $\langle r^2 \rangle_0$ consequently prevails. Comparison of the magnitudes of $\partial \ln \langle \mu^2 \rangle / \partial \ln \sigma$ and $\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma$, however, indicates that *trans* to *gauche* transitions about CH_2–O and O–CH_2 bonds are much more effective in increasing $\langle \mu^2 \rangle$ than in decreasing $\langle r^2 \rangle_0$. The effect of these transitions on $\langle \mu^2 \rangle$ predominates, and a large, positive temperature coefficient of $\langle \mu^2 \rangle$ is predicted.