

Configurational Characteristics of Poly(oxy-1,1-dimethylethylene). III. Configuration-Dependent Properties of the Polymer Chain

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ABSTRACT: The configurational characteristics of poly(oxy-1,1-dimethylethylene) (PODME) were estimated by calculation based on the information acquired through the dipole moment and NMR analyses of 1,2-dimethoxy-2-methylpropane, and, in part, of PODME as presented in the preceding papers. By using the set of conformational energy parameters so established, the characteristic ratio $\langle r^2 \rangle_0/nl^2$ and the dipole moment ratio $\langle \mu^2 \rangle/nm^2$ were evaluated. These results were compared with those for poly(oxyethylene) and poly(oxypropylene) studied previously. The configurational entropy calculated for the temperature equivalent to the melting point (175°C) of the polymer is 4.1 cal mol⁻¹ deg⁻¹. It was pointed out that a fairly large value of the enthalpy of fusion should be required to explain this comparatively high melting temperature of PODME, unless the correction term for the entropy of fusion emerging from the volume change on melting is very small.

KEY WORDS Poly(oxy-1,1-dimethylethylene) / 1,2-Dimethoxy-2-methylpropane / Unperturbed Dimension / Dipole Moment / Configurational Entropy / Poly(oxyethylene) / Poly(oxypropylene) /

Geometrical parameters and conformational energies established in the preceding papers^{1,2} (referred to as papers I and II) enable us to evaluate various configuration-dependent properties of the poly(oxy-1,1-dimethylethylene) (PODME) chain which are otherwise quite inaccessible: PODME is a crystalline polymer with a high melting point (175°C)³ and only poorly soluble in conventional organic solvents. The results of these calculations will be compared with those of other polymers having related structures such as poly(oxyethylene)⁴ (POE) and poly(oxypropylene)⁵ (POP). The polymer chains mentioned above can be represented by a general formula $[\text{CH}_2\text{C}(\text{R}_1)(\text{R}_2)\text{O}]_x$, where R_1 and R_2 may be a proton atom or a methyl group depending upon the polymer system. The conformational flexibility of a given (skeletal) bond varies with the degree of methyl substitution. As is evident from the results presented in papers I and II, the bond rotation around the skeletal C—C bond tends to be more restricted in the order POE, POP, and PODME, while the number of conformers per-

mitted to the neighboring C(R_1)(R_2)—O bond becomes more proliferated as R becomes bulkier. Accordingly, the molar configurational partition function of PODME obtained in the preceding work² is similar in magnitude to that of POE⁴ and POP.⁵

The most stable conformations found in the crystalline state for the moiety O—CH₂—C(R_1)(R_2)—O are (*t g[±]t*), (*t t t*), and (*t[±]t t[±]*), respectively, for POE,⁶ isotactic POP,⁷ and PODME.⁸ For a better understanding of the characteristic feature at fusion, configurational contribution to the entropy change on melting will be estimated.

GEOMETRICAL PARAMETERS AND CONFORMATIONAL ENERGIES

Bond lengths and bond angles required in the description of the skeletal chain of PODME were taken from Table II of paper I, in which geometrical parameters used in the analysis of DMMP are

summarized. Unless otherwise noted, we shall adopt $\angle \text{COC} = 118^\circ$ for all ether linkages except the one associated with bonds 1 and 2, for which $\angle \text{COC} = 111.5^\circ$ was employed. The other bond lengths and bond angles are comparable to those used in the treatment of POE⁴, POP⁵ and their analogs. Configurational partition function Z for a given chain may be calculated⁹ by using eq 3—8 of paper I. The conformational energy parameters required here are given in Table III of paper I. In accordance with the experimental observations reported in papers I and II, the value of E_o is taken to be 0.5 kcal mol⁻¹.

Based on the results of the conformational energy calculations presented in paper I, rotational isomeric states t , g^+ , and g^- were taken to occur at the regularly staggered position, *i.e.*, $\phi_i = 0$ and $\phi_{g^\pm} = \pm(2/3)\pi$, for bonds like a and b (*cf.* eq 6—8 and Figure 1 of paper I). The *gauche* conformations for bond c involve prohibitively severe steric conflicts between the two $>\text{C}(\text{CH}_3)_2$ groups: a value of $\phi_i = 0$ was accordingly assigned to the remaining *trans* state.

THEORETICAL ESTIMATION OF THE UNPERTURBED DIMENSION, DIPOLE MOMENT, AND CONFIGURATIONAL ENTROPY

Calculations were carried out⁹ for chains such as $\text{CH}_3\text{O}[\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}]_x\text{CH}_3$ for the temperature of 25°C. As is now customary,⁹ the calculated values of the unperturbed dimensions and dipole moments were expressed as the characteristic ratios $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle/nm^2$, respectively, where n is the number of skeletal bonds, and l^2 and n^2 are the averaged values of the squares of their lengths and dipole moments, respectively. The asymptotic behaviors estimated for these ratios with the degree of polymerization x are given in Figures 1a and 1b. Also shown for comparison in these figures are the results obtained by using $\angle \text{COC} = 111.5^\circ$ for all the ether linkages in the chain, with the other parameters kept invariable. Such an alteration causes a decrease of as much as *ca.* 5% in $\langle r^2 \rangle_0/nl^2$ and an increase of *ca.* 10% in $\langle \mu^2 \rangle/nm^2$, but generally the effect is only trivial. Both $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle/nm^2$ reach quite rapidly their asymptotic values for $x \rightarrow \infty$: *e.g.* at $x \cong 10$, the former ratio comes into the range within 10% of the limiting

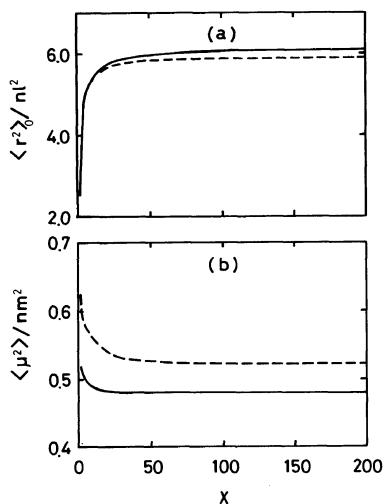


Figure 1. Dependence of the characteristic ratios (a) $\langle r^2 \rangle_0/nl^2$ and (b) $\langle \mu^2 \rangle/nm^2$ on the degree of polymerization x for the PODME chain ($T = 25^\circ\text{C}$). The solid curves indicate the results obtained by using $\angle \text{COC} = 118^\circ$ for the internal ether linkages as established in this work. The broken curves represent the results derived by adopting a value of 111.5° for all the COC angles.

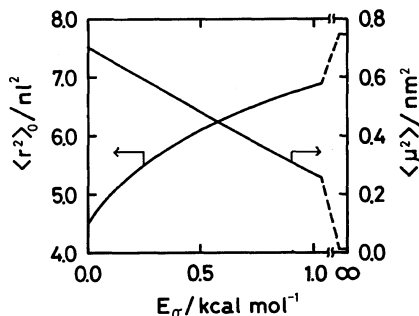


Figure 2. The characteristic ratios $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle/nm^2$ for the PODME chains having $x = 200$ ($n = 602$) calculated as a function of E_o for the temperature of 25°C. The other statistical weight parameters were kept invariable (*see text*).

value, while the latter finds itself within a few % of its limit.

In accordance with the procedure adopted previously in the treatment of polyoxide chains,^{4,5} variations of $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle/nm^2$ with the conformational energy parameter E_o were investigated over the range $E_o > 0$ (Figure 2). As E_o increases, the *trans* conformation tends to be more stabilized

around the skeletal C–C bond. The value of $\langle r^2 \rangle_0/nl^2$ increases from 5.0 to 7.0 over the range $E_\sigma=0$ to 1.0 kcal mol⁻¹, beyond which the ratio varies very slowly toward its limiting value 7.5. At this limit, the flexibility of the PODME chain arises solely from the bond rotation around the C(CH₃)₂–O bond. The value of $\langle \mu^2 \rangle/nm^2$ decreases rapidly with an increase of E_σ . Although the chain is still quite flexible around the aforementioned bond, the ratio becomes nearly zero at the limit $E_\sigma = \infty$.

The temperature coefficients calculated for a polymer chain with $x=200$ by using the parameters set forth above are as follows: $10^3 d \ln \langle r^2 \rangle_0/dT = -0.87$ K⁻¹ and $10^3 \ln \langle \mu^2 \rangle/dT = 0.81$ K⁻¹ (at 25°C).

Following the treatment previously employed in the analysis of POE and related polymers,¹⁰ the configurational partition function for an internal monomeric residue

$$z = Z^{1/x} \quad (1)$$

and the configurational entropy

$$S_{\text{conf}} = R [\ln z + d \ln z/d \ln T] \quad (2)$$

were evaluated. The values obtained for a chain of 200 units at the temperature equivalent to the melting point of the polymer are as follows: $z=5.6$ and $S_{\text{conf}}=4.1$ cal mol⁻¹ deg⁻¹. The configurational entropy obtained in this manner corresponds to the entropy of fusion at constant volume. However, no relevant experimental data are yet available.

COMPARISON WITH POE AND POP

Extra stabilization energies (ΔE) associated with the *gauche* oxygen effect have been defined previously as the difference between the conformational energies (E_{calcd}) calculated by using semi-empirical expressions and those (E_{exptl}) derived from the analysis of the experimental data such as $\langle r^2 \rangle_0/nl^2$, $\langle \mu^2 \rangle/nm^2$, and bond conformations.^{4,5} The values of ΔE thus established for the *gauche* conformations about the C–C bonds are summarized in Table I for the aforementioned polymer systems. It should be noted here that nearly the same values of E 's, and thus ΔE 's have been obtained from the analysis of the corresponding monomeric model compounds (dimethoxy derivatives)^{1,2,4,5,11} in all these cases, indicating that the results shown in the table are inherent in the chemical structure and therefore valid regardless of chain length. In Table I, the magnitude of ΔE varies from 1.0 kcal mol⁻¹ (for POE) to zero (for PODME). The two *gauche* states around the skeletal C–C bond of POP are unequivalent to each other with regard to steric environment. It is interesting to note here that the value of ΔE for this polymer falls into either of these two extremes: one ($\Delta E_\alpha=0.7$ kcal mol⁻¹) close to the value of POE and the other ($\Delta E_\beta=0.2$ kcal mol⁻¹) to that of PODME, depending on the steric requirements of the conformation. Further penetration into this problem has been attempted within the framework of the molecular orbital theory.¹² The results show success only in certain limited cases, however.

Shown in Table II are the results of calculations

Table I. *gauche* Oxygen effects associated with *gauche* conformations around the skeletal C–C bond for the POE, POP, and PODME chains^a

	POE ^b	POP ^c		PODME
		<i>gauche</i> α^d	<i>gauche</i> β^e	
E_{calcd}	0.6	0.4	0.6	0.5
E_{exptl}	-0.4	-0.3	0.4	0.5
ΔE	1.0	0.7	0.2	0.0

^a Units in kcal mol⁻¹. ^b Reference 4. ^c Reference 5.

^d

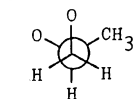
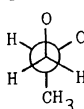


Table II. Characteristic ratio $\langle r^2 \rangle_0/nl^2$, dipole moment ratio $\langle \mu^2 \rangle/nm^2$, and their temperature coefficients for the POE, POP, and PODME chains

Polymer	$\langle r^2 \rangle_0/nl^2$	$10^3 d \ln \langle r^2 \rangle_0/dT$	$\langle \mu^2 \rangle/nm^2$	$10^3 d \ln \langle \mu^2 \rangle/dT$
		K ⁻¹		K ⁻¹
POE ^a	5.0	0.14	0.49	2.9
Isotactic ^b POP	6.1	-1.59	0.50	0.43
PODME	6.1	-0.87	0.48	0.81

^a Reference 4. ^b Reference 5.

for $\langle r^2 \rangle_0/nl^2$ and $\langle \mu^2 \rangle/nm^2$, and their temperature coefficients for POE⁴, POP⁵, and PODME. These ratios were derived by taking statistical mechanical averages over all configurations of the chain. The conformational characteristics of individual chains such as those discussed above do not manifest themselves explicitly in the final results.

The value of configurational entropy calculated above may be compared with those of other polymers as tabulated in a previous paper.¹⁰ The value of $S_{\text{conf}}=5.0$ cal mol⁻¹ deg⁻¹ given for POE in this table (Table IV of ref 10) should be substituted by a newer one (5.3 cal mol⁻¹ deg⁻¹) as a more reliable value¹³ of the melting temperature ($79 \pm 1^\circ\text{C}$) is adopted for this polymer. The value of the configurational entropy of PODME is similar in magnitude to that (4.0 cal mol⁻¹ deg⁻¹) of POP.

CONCLUDING REMARKS

The value of $S_{\text{conf}}=4.1$ cal mol⁻¹ deg⁻¹ for PODME calculated above remains nearly invariable even when $E_\gamma=0.5$ kcal mol⁻¹ is tentatively assigned to the rotation around the C(CH₃)₂-O bond (*cf.* Table III of paper I): with an increase in E_γ , the value of z , thus the first term of the right-hand side of eq 2 ($\ln z$), decreases while the contribution from the second term ($d \ln z/d \ln T$) increases as compensation. Unless the correction term in the entropy of fusion for the volume change on melting is very small,¹⁴ a fairly large value of the enthalpy of fusion should be required to explain the comparatively high melting temperature of PODME.

Crystallographic studies of PODME have been carried out by Kaji and Sakurada,⁸ who reported that the polymer chain takes a *trans* zigzag conformation, but distorted somewhat from the perfect

planarity, in the crystalline state. This conformation has been represented by $t^\pm t t^\mp$ for the sequence O-CH₂-C(CH₃)₂-O, where the rotational minima for the C-O and O-C bonds are displaced by *ca.* $\pm 27^\circ$ from the regular *trans* position. Thus, the chain has a 1/2 helix axis. The crystalline unit cell is orthorhombic, comprising four monomeric units. As these authors pointed out,⁸ PODME is quite similar to POP⁷ and poly(thiopropylene)¹⁵ not only in chain conformation but also in crystalline arrangement. No particular reasons may be noticed in this arrangement why the enthalpy of fusion should be enhanced.¹⁶ In fact, a preliminary study by Ikawa¹⁷ yielded a value of the enthalpy of fusion $\Delta H_f=2.2-2.5$ kcal mol⁻¹, and accordingly, the corresponding entropy $\Delta S_f=4.6-5.3$ cal mol⁻¹ deg⁻¹ for the equilibrium melting temperature of 202°C. This value of ΔH_f is only slightly higher than that ($\Delta H_f=2.0$ kcal mol⁻¹) of POP.¹⁸ These results are therefore somewhat inconsistent with those derived above. Further investigation is now being carried out on this subject.

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