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Conformational Analysis of Poly(thiopropylene)

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ABSTRACT: Conformational energies associated with poly(thiopropylene) (PTP) chains were calculated by using semiempirical potential energy functions. Reliability of these functions was tested against the known values of conformational energies of various simple alkyl sulfides bearing somewhat related structures. The magnitude of the gauche sulfur effect associated with the $S-CH_2-CH(CH_3)-S$ moiety was estimated from the rotational isomeric state analysis of the experimental values of the unperturbed dimension, dipole moment, and their temperature coefficients observed for atactic samples of PTP. The value obtained for the gauche conformation (α) with the articulated methyl group trans to the preceding sulfur atom indicates that the gauche effect involved in such polymer systems is slightly repulsive in contrast to that found for the gauche oxygen effect of the poly(oxypropylene) (POP) chain, the oxygen analogue of PTP. The gauche sulfur effect was estimated to be zero or possibly positive for the conformation (β) in which the preceding sulfur atom is syn to both the following sulfur and the methyl group. Using the conformational energy parameters thus estimated, we were able to calculate the characteristic ratio $\langle r^2\rangle_0/nl^2$, the dipole moment ratio $\langle\mu^2\rangle/nm^2$, and their temperature coefficients for the isotactic and syndiotactic chains as well. The results compared favorably with the existing experimental data for the isotactic chain.

Conformational analyses on a series of polyoxide chains such as $(-CH_2CH(R)O-)_x$, where R = H, CH_3, CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$, have been reported in our previous papers.[1-3] Extra stabilization energies associated with the gauche conformation about the skeletal C–C bonds were estimated by taking the difference between the conformational energies (E_{calcd}) calculated by using semiempirical expressions and those (E_{exptl}) derived from the analysis of the experimental data such as the unperturbed dimensions, dipole moments, and bond conformations. The gauche oxygen effect ($\Delta E = E_{calcd} - E_{exptl}$) estimated in this manner amounts to ca. 1 kcal mol^{-1} for poly(oxyethylene) (POE) and ca. 0.7 kcal mol^{-1} for the gauche α conformation of poly(oxypropylene) (POP) in which the pendant CH_3 group is situated trans to the preceding oxygen atom of the skeletal chain. A value of $\Delta E = 0.2$ kcal mol^{-1} was obtained for the gauche conformation (β) of the latter polymer. These gauche effects play very important roles in the aforementioned polymer systems by enhancing fractions of the gauche conformation about the C–C bonds and thus rendering conformational flexibility to the polymer chain.[1-3]

A similar treatment has been extended to poly(thiopropylene) (PTP), the sulfur analogue of POP.[4] The PTP may be obtained in a highly isotactic or an atactic form depending upon the catalyst system employed in the polymerization of propylene sulfide.[5] The PTP chain differs considerably from POP in its structural features: (1) the C–S bond length is larger by ca. 30% than C–O;[6-8] (2) the bond angle CSC is less by ca. 10° than that of COC;[6-8] and (3) the van der Waals radius of the sulfur atom is larger by ca. 20% than that of oxygen.[9] These differences should manifest themselves in the conformational characteristics: e.g., it is suggested from spectroscopic studies[8,10-12] on

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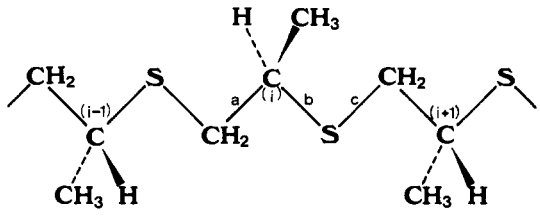


Figure 1. Schematic diagram of the isotactic poly((*R*)-thiopropylene) chain in its planar, all-trans conformation. Each skeletal bond in a repeat unit is distinguished by an alphabetical notation.

Table I
Geometrical Parameters Used for Poly(thiopropylene)

bond length, Å	bond angle,[a] deg
C-C, 1.53	CSC, 100
C-S, 1.815	SCC*, 114
C-H, 1.10	CC*S, 110
	CC*C, 110
	CCH, 110

[a] Asymmetric carbon atoms are marked with an asterisk.

various simple alkyl sulfides that the bond sequence CS⇄CC is quite flexible in contrast to the rigidity assigned to the CO⇄CC moiety of polyoxide chains.[1-3]

The major purpose of the present study is to estimate the S···S interaction energies involved in the gauche arrangements about the skeletal C–C bond from the analysis of the unperturbed dimensions[13,14] and dipole moment data[15] reported on PTP. The results should provide a quantitative estimate of the extra interaction energy (ΔE)[1-3] associated with the SC⇄CS moiety incorporated in an open chain system. The conformational energy parameters thus established will be adopted in the conformational analysis of poly(thioethylene) (PTE) in the following paper.[16]

Structural Features of the Chain

A portion of an isotactic PTP chain in its planar, all-trans conformation is shown in Figure 1. The asymmetric carbon atoms situated along the chain are taken to be in the (*R*) configuration. Distinction between the two stereochemical arrangements, *i.e*, (*R*) and (*S*), becomes important when stereoirregular chains are examined.[2]

The bond lengths and bond angles used in this study are listed in Table I. The bond length C–S and bond angles CSC and SCC*, C* denoting the asymmetric carbon atom situated along the chain, were taken from the results of spectroscopic studies on some relevant simple sulfides. Pierce and Hayashi[6b] reported the results of microwave spectroscopy on dimethyl sulfide: C–S = 1.802 Å and ∠CSC = 98.9°. Tsuchiya et al.[7] carried out electron diffraction studies on the same compound. The analysis of the electron diffraction data alone led to the results C–S = 1.805 Å and ∠CSC = 101.2°. When this analysis was supplemented with the information provided by the aforementioned microwave experiment, they obtained C–S = 1.803 Å and ∠CSC = 99.0°. Structural parameters of methyl ethyl sulfide were determined by Oyanagi and Kuchitsu[8] in the gaseous state by the electron diffraction analysis. An averaged value of the bond length C–S was found to be 1.816 Å. Bond angles CSC = 98.6° and SCC = 113.6° were also reported. In the conformational energy calculations to be presented in the following section, these bond angles will be varied tentatively within a certain range. The hydrogen atoms on the methyl and methylene carbons were fixed in the positions which conform with the tetrahedral arrangements.

Table II
Parameters for Nonbonded Interactions[a]

atom pair k,l	$a_{kl} \times 10^{-3}$	b_{kl}	c_{kl}	r_{min}
H···H	9.95	4.54	45.2	2.6
C···H	86.1	4.57	127.0	3.1
C···C	908.6	4.59	363.0	3.6
S···H	117.1	4.21	398.0	3.2
S···C	1084.0	4.23	1157.0	3.7
S···S	1354.0	3.90	3688.0	3.8

[a] Units are such as to give E in kcal mol^{-1} when r is in Å.

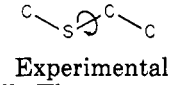
Parameters for the Conformational Energy Calculations

Conformational energies were estimated by using the conventional expression[17]

$$E(\phi_i) = (E_0/2)(1 - \cos 3\phi_i) + \sum_{k<l}[a_{kl} \exp(-b_{kl}r_{kl}) - c_{kl}/r_{kl}^6 + \delta_k\delta_l/\epsilon r_{kl}] \quad (1)$$

where ϕ_i represents the bond rotation angle measured from the trans form and r_{kl} is the distance between the centers of atoms k and l. The intrinsic torsional potential is represented by the term $(E_0/2)(1 - \cos 3\phi_i)$, in which the barrier height E_0 was assigned the values 2.8 and 1.82 kcal mol^{-1} for rotations about C–C and C–S bonds, respectively. The latter value was so chosen as to reproduce the observed rotational barrier height (2.13 kcal mol^{-1}) of dimethyl sulfide[6b] when used in combination with the nonbonded interaction parameters as given below. Values of the interatomic interaction parameters a, b, and c used in the present study are listed in Table II. The interaction parameters for the atomic pairs H···H, C···H, and C···C are those used previously in the analysis of *n*-alkanes.[18] For consistency, the rest of the parameters (S···H, S···C, and S···S) were derived in a similar manner.[1-3] The quantity r_{min} given in the last column represents the distance at which the interaction energy for the given nonbonded pair is minimum. Coulombic contributions to the conformational energy were estimated by using the last term of eq 1 by assigning partial electronic charges to the carbon ($\delta_C = 0.14$) and sulfur ($\delta_S = -0.28$) atoms joined by each C–S bond. These partial electronic charges were estimated from the bond moment of 1.21 ± 0.08 D, which corresponds to the observed dipole moments 1.55 ± 0.10 D of various aliphatic thioethers as summarized in McClellan's table.[19] (On assigning these numerical values to δ_C and δ_S, the last term in eq 1 for the Coulombic contribution should be multiplied by a factor of 332 to express the result in kilocalories per mole.) The effective dielectric constant ϵ required in eq 1 was taken to be 3.0, the same value being used in the analysis of various polyoxide chains in a series of previous papers.[1-3]

The theoretical expressions thus established were first tested against some simple alkyl sulfides for which experimental values of the conformational energy difference among the isomers are known from the literature. The results are summarized in Table III, where the pertinent rotational isomeric states of the molecules are indicated by the suffix to the E values in the second column. Values given in the last column are those obtained by adjusting the adjoining bond rotations as well, to minimize the energies. For the first two compounds, relative stability of the gauche conformation about the



bond was examined. Experimental values[10-12] are reproduced reasonably well. The agreement with the observed

Table III
Comparison of Observed and Calculated Values of Conformational Energies for Some Simple Sulfides

compd	ΔE	conformational energy, kcal mol^{-1} obsd[a]	calcd[b]
$CH_3S\overset{\frown}{\underset{\smile}{}}CH_2CH_3$	$E_{g\cdot t}$	−0.03 ± 0.05 (g)[c] −0.14 ± 0.05 (l)[d]	0.01 (−0.09)
$CH_3CH_2\overset{\frown}{\underset{\smile}{}}S\overset{\frown}{\underset{\smile}{}}CH_2CH_3$	$E_{gg\cdot tg}$	0.04 ± 0.05 (g, l)[e]	0.26 (0.03)
	$E_{tg\cdot tt}$	−0.46 ± 0.1 (g, l)[e]	−0.01 (−0.09)
$(CH_3)_2CH\overset{\frown}{\underset{\smile}{}}SCH_3$	$E_{C_s-C_1}$	1–1.5 (l)[f]	1.17 (0.65)
$(CH_3)_3CS\overset{\frown}{\underset{\smile}{}}CH_2CH_3$	$E_{g\cdot t}$	1.40 ± 0.16 (l)[g]	1.90 (1.46)
$CH_3S\overset{\frown}{\underset{\smile}{}}CH_2\overset{\frown}{\underset{\smile}{}}CH_2\overset{\frown}{\underset{\smile}{}}SCH_3$	$E_{ggg\cdot gtg'}$	1.1 (g), <0.1 (l)[h]	0.21

[a] Values obtained for the gaseous state are indicated by (g) and those for the liquid state by (l). [b] Geometrical parameters required in these calculations are given in Table I. Values in parentheses are those calculated by using ∠CSC = 102°. [c] Reference 11. From the results of the electron diffraction analysis, Oyanagi and Kuchitsu[8] elucidated the population of the trans isomer to be 20 ± 10%. This leads to a value of $E_{g\cdot t} = -0.4 \pm 0.3$ kcal mol^{-1}. [d] Reference 10. [e] Reference 12. [f] Reference 20. [g] Reference 21. [h] Reference 22.

values may be further improved by adopting a slightly larger bond angle for the sulfur linkage (∠CSC = 102°) as indicated in parentheses. Higher energy conformations of $(CH_3)_2CH\rightarrow SCH_3$ and $(CH_3)_3CS\rightarrow CH_2CH_3$ involve severe steric repulsions.[20,21] Also included in the table are the results obtained for 1,2-bis(methylthio)ethane, $CH_3SCH_2CH_2SCH_3$. Hayashi et al.[22] suggested from infrared studies that the energy difference between the *ggg* and *gtg'* form is 1.1 kcal mol^{-1} in the gaseous state while it becomes very small (<0.1 kcal mol^{-1}) in the liquid state. Calculations using potential energy parameters given in Table II lead to a value of 0.21 kcal mol^{-1}. The result of these calculations is however quite sensitive to the choice of the bond angle SCC: adoption of a slightly smaller value ∠SCC = 112° raises the conformational energy $E_{ggg\text{-}gtg'}$ to 0.70 kcal mol^{-1}.

Conformational Energies and Statistical Weight Matrices

Following the procedure previously employed in the analysis of the POP chain,[2] statistical weight matrices required for evaluating the configurational partition function for PTP may be expressed in a 3 × 3 matrix scheme:

$$\mathbf{U}_a^R = \begin{bmatrix} 1 & \alpha & \beta \\ \omega & \alpha & \beta\omega' \\ 1 & \alpha\omega' & \beta\omega \end{bmatrix} \quad (2)$$

$$\mathbf{U}_b^R = \begin{bmatrix} 1 & \tau & \gamma \\ 1 & \tau & \gamma\omega' \\ 1 & \tau\omega' & \gamma \end{bmatrix} \quad (3)$$

$$\mathbf{U}_c^R = \begin{bmatrix} 1 & \sigma & \sigma\omega'' \\ 1 & \sigma\omega'' & \sigma\omega'' \\ 1 & \sigma\omega'' & \sigma \end{bmatrix} \quad (4)$$

where subscripts a, b, and c denote the type of bond to which each matrix should be applicable (cf. Figure 1). The stereochemical configuration of the asymmetric center with which these bonds are associated is indicated by superscripts *R*. Thus, for an (*R*) unit incorporated in a polymer chain, we have

$$\mathbf{U}^R = \mathbf{U}_a^R\mathbf{U}_b^R\mathbf{U}_c^R \quad (5)$$

Statistical weight matrices $\mathbf{U}^S$ applicable to the (*S*) unit may be easily derived from eq 5 in the usual manner.[2]

Conformational energies associated with the rotation about the skeletal C–C bond (bond a in Figure 1) were calculated for (*R*)-1,2-bis(methylthio)propane [$CH_3SCH_2CH(CH_3)SCH_3$], a monomer model. Three rotational minima *t*, g_α, and g_β occur at $\phi_{C\text{-}C}$ = 9, 111, and −120°, respectively, when the adjoining S–C and C–S bonds are kept trans. For a C–C bond joined with the (*R*) center, the g_α conformation is identified with g^+ and g_β with g^-. The opposite applies to the bond associated with the (*S*) center. Energies expressed relative to that of the trans state are E_α = 0.2 and E_β = 1.3 kcal mol^{-1}, respectively, for the g_α and g_β forms. The Coulombic interaction between the two sulfur atoms was found to be appreciable in the gauche arrangement. Contribution from this source amounts to ca. 0.4 kcal mol^{-1} in both E_α and E_β. In the analysis of the configuration-dependent properties of the POP chain presented in a previous paper,[2] the conformational energy parameters E_α and E_β were treated as variables in an effort to elucidate the gauche oxygen effect quantitatively. Employing the same procedure for the PTP chain, we let

$$E_\alpha = 0.2 - \Delta E_\alpha \quad (6)$$

$$E_\beta = 1.3 - \Delta E_\beta \quad (7)$$

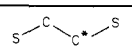
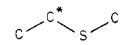
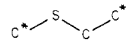
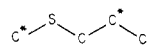
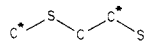
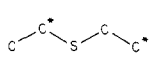
both being expressed in kilocalories per mole. Values E_α and E_β so chosen as to reproduce the experimental results for the dimension and dipole moment should provide the most reliable estimate of the "gauche sulfur effect" (i.e., ΔE_α and ΔE_β), if any exists, for the PTP system.

Steric interactions taking place around bond b (Figure 1) should be approximately equivalent to those encountered in isopropyl methyl sulfide $CH(CH_3)_2SCH_3$ (cf. Table III). Conformational energy calculations for this model yielded two identical minima for the C_1 form with a displacement $\Delta\phi$ = 13° from the regularly staggered position. The energy minimum calculated for the symmetrical C_s form (E_τ) is higher by ca. 1.2 kcal mol^{-1} than those of the C_1 form. In these calculations, rotations about the adjoining C–C bonds were adjusted to minimize the energy: e.g., displacement of the rotation angle ($\Delta\phi$) by as much as 7° from the regular staggering is required for the high energy C_s form. The value of E_τ thus derived is in agreement with the experimental observations (1–1.5 kcal mol^{-1}).[20] In the PTP chain, Coulombic interactions occurring between partially charged carbon atoms may enhance the energy of the conformation in which two methylene groups joined by bonds a and c, respectively, are gauche. The energy contribution from this origin (E_γ) is estimated to be ca. 0.1 kcal mol^{-1}.

Interactions between $(CH)_i$ and $(CH)_{i+1}$ occur for rotations about bond c (Figure 1). Conformational energy parameter E_σ assigned to the gauche states may be zero or slightly negative in view of the experimental results reported on some relevant alkyl sulfides (cf. Table III). Displacement of the rotational minima from the regular positions $\phi = \pm^2/_3\pi$ is estimated to be 7° by the calculation. Rotational angles for the isomeric states of each constituent bond and the corresponding conformational energy parameters chosen based on these considerations are summarized in Table IV.

Various second-order interactions taking place in the PTP chain were estimated in the usual manner from the corresponding energy map.[17] Conformational energy parameters E_ω, $E_{\omega'}$, and $E_{\omega''}$ thus obtained are also included

Table IV
Conformational Energy Parameters Calculated for the Poly((*R*)-thiopropylene) Chain

bond[a]	rotat. state	rotat. angle (ϕ), deg	conform. energy, kcal mol^{-1}
	t	9	$E_\alpha = 0.2$
	g^+	111	$E_\beta = 1.3$
	g^-	−120	
	t	−12	$E_\tau = 1.2$
	g^+	120	$E_\gamma = 0.1$
	g^-	−108	
	t	0	
	g^+	113	$E_\sigma = 0.0$
	g^-	−113	
			$E_\omega = 1.5$
			$E_{\omega'} = 1.1$
			$E_{\omega''} = 0.4$

[a] Asymmetric carbon atoms are marked with an asterisk.

Table V
Observed Values of the Characteristic Ratio $\langle r^2\rangle_0/nl^2$, Dipole Moment Ratio $\langle\mu^2\rangle/nm^2$, and Their Temperature Coefficients for the Poly(thiopropylene)s (25 °C)

polymer	$\langle r^2\rangle_0/nl^2$	10^3 d ln $\langle r^2\rangle_0$/dT, K^{-1}	$\langle\mu^2\rangle/nm^2$	10^3 d ln $\langle\mu^2\rangle$/dT, K^{-1}
isotactic		−2.8[b]	0.33[c]	2.1[c]
			0.39[d]	2.0[d]
atactic	4.0[a]	−2.0[b]	0.37[c]	4.0[c]
			0.44[d]	1.5[d]

[a] A value obtained from viscosity measurements in a mixed solvent at 25 °C, ref 13. [b] Estimated from viscosity data in an athermal solvent over a temperature range 10–40 °C, ref 14. [c] Dielectric measurements in carbon tetrachloride over a range 20–50 °C, ref 15. [d] Dielectric measurements in benzene over a range 20–60 °C, ref 15.

in Table IV. The statistical weight parameters requried in eq 2–4 may be defined as Boltzmann factors for the conformational energies given in the table.

Unperturbed Dimensions and Dipole Moments

Experimental values reported in the literature for the isotactic and atactic samples of PTP are listed in Table V. The unperturbed dimension and dipole moment are expressed as the characteristic ratio $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$, respectively, where n is the number of the skeletal bonds, and l^2 and m^2 are the averaged values of the square of their bond lengths and dipole moments.

Nash and Pepper[13] carried out viscosity measurements on fractionated samples of PTP prepared with cadmium bis(phenyl alkyl thiolate) as the initiator. The polymer prepared in this manner was found to be nearly atactic (isotacticity 55%) by the NMR analysis. The intrinsic viscosity–molecular weight relation[17] determined in a Θ mixture (31% *n*-heptane/toluene at 25 °C) leads to a value of $\langle r^2\rangle_0/nl^2 = 4.0$. Recently Rahalkar, Mark, et al.[14] estimated the temperature coefficient of the unperturbed dimension from viscosity measurements in an athermal solvent (propylene sulfide) over the temperature range 10–40 °C. Values of d ln $\langle r^2\rangle_0$/dT obtained for a highly isotactic (prepared by using cadmium thiolate as the initiator; isotacticity 95–100% by NMR) and an atactic sample (prepared with a carbazyl sodium initiator) are −2.8 × 10^{-3} and −2.0 × 10^{-3} K^{-1}, respectively.

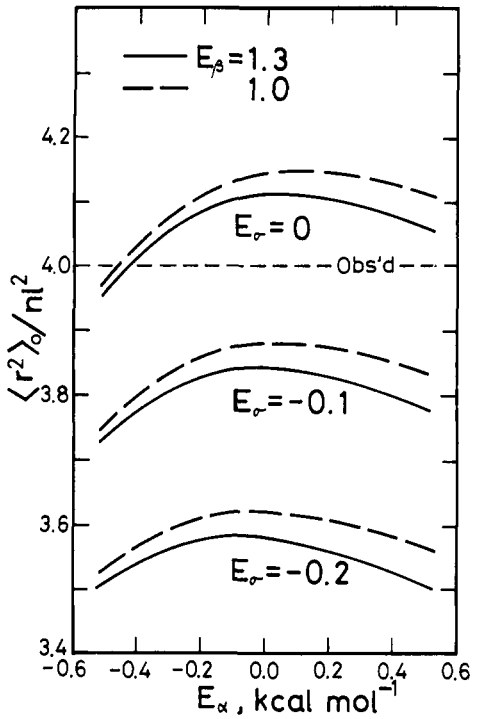


Figure 2. The characteristic ratio $\langle r^2\rangle_0/nl^2$ for an atactic PTP chain having x = 200 (n = 602) calculated as a function of E_α, values of E_β and E_σ being indicated in the figure. The other parameters were taken from Table IV. Calculations were carried out for the temperature of 25 °C. The experimental value observed at this temperature is indicated by the dashed line.

Dielectric measurements on the same samples were reported by Riande et al.[15] Dipole moment ratios $\langle\mu^2\rangle/nm^2$ determined in carbon tetrachloride and in benzene at 25 °C are listed in Table V. Temperature coefficients d ln $\langle\mu^2\rangle$/dT cited in the table are those obtained over the temperature range 20–60 °C.

Theoretical Calculations and Comparison with the Experimental Data

As shown in Table V, a complete set of experimental data for the dimension and dipole moment is available for the atactic PTP. Comparison between theoretical calculations and experimental observations will therefore be made most critically for the atactic chain. Values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ were computed for atactic chains $CH_3S(-CH_2CH(CH_3)S-)_xCH_3$ with x = 200 (n = 602) according to the conventional procedure;[2,17] for this purpose, Monte-Carlo chains were generated from a series of random numbers with the replication probability P_r = 0.5. Results are shown in Figures 2 and 3, respectively, for $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ as a function of E_α. Values of E_β and E_σ used in these calculations are indicated in the figures. The other parameters were kept invariable: E_τ = 1.2, E_γ = 0.1, E_ω = 1.5, $E_{\omega'}$ = 1.1, and $E_{\omega''}$ = 0.4, all being in kilocalories per mole. In order to facilitate comparison with observations, calculations were carried out for the same temperature (25 °C) as that employed in the corresponding experiments. The observed values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ are shown by the dotted line in each figure. Since the experimental values of $\langle\mu^2\rangle/nm^2$ observed in benzene and in carbon tetrachloride are somewhat divergent, the average is taken for the comparison.

The characteristic ratio $\langle r^2\rangle_0/nl^2$ varies quite insensitively with E_α over the range from −0.5 to 0.5 kcal mol^{-1} (Figure 2). All curves reach the maximum around E_α = 0. The ratio $\langle r^2\rangle_0/nl^2$ increases as E_σ become less negative.

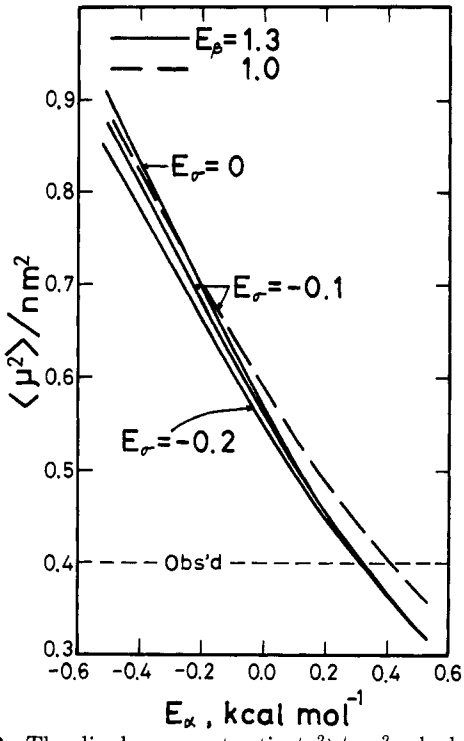


Figure 3. The dipole moment ratio $\langle\mu^2\rangle/nm^2$ calculated as a function of E_α. See legend to Figure 2.

On the contrary, the dipole moment ratio $\langle\mu^2\rangle/nm^2$ depends very sensitively on E_α, but little on E_σ (Figure 3). Variation of E_β from 1.3 to 1.0 kcal mol^{-1} raises both ratios slightly. Ranges of conformational energy parameters E_α and E_σ which reproduce the experimental values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ for the atactic chain are therefore quite restricted. We adopt values of E_α = 0.33 and E_σ = −0.05 kcal mol^{-1} for the following course of the analysis. Since the results (cf. Figures 2 and 3) are quite insensitive to E_β, the calculated value of E_β = 1.3 kcal mol^{-1} will be used as it stands. The unperturbed dimension, dipole moment, and their temperature coefficients for the atactc chain (P_r = 0.5) calculated by using the parameter set thus derived are as follows: $\langle r^2\rangle_0/nl^2$ = 4.0, 10^3 d ln $\langle r^2\rangle_0/dT$ = −0.63 K^{-1}, $\langle\mu^2\rangle/nm^2$ = 0.39, and 10^3 d ln $\langle\mu^2\rangle/dT$ = 2.2 K^{-1}. Agreement with the observed data (Table V) is assured.

Variation of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ with the stereoregularity of the chain was examined over the range P_r = 1.0–0.0 by using the conformational energy parameters set forth above. Both ratios tend to increase very slightly with P_r. The results obtained for the perfectly isotactic (P_r = 1.0) and syndiotactic chains (P_r = 0.0) are as follows: (isotactic) $\langle r^2\rangle_0/nl^2$ = 4.3, 10^3 d ln $\langle r^2\rangle_0/dT$ = −1.1 K^{-1}, $\langle\mu^2\rangle/nm^2$ = 0.41, 10^3 d ln $\langle\mu^2\rangle/dT$ = 2.2 K^{-1}; (syndiotactic) $\langle r^2\rangle_0/nl^2$ = 3.7, 10^3 d ln $\langle r^2\rangle_0/dT$ = −0.24 K^{-1}, $\langle\mu^2\rangle/nm^2$ = 0.38, 10^3 d ln $\langle\mu^2\rangle/dT$ = 2.3 K^{-1}, all being calculated with chains of 200 units for the temperature of 25 °C. Experimental values of d ln $\langle r^2\rangle_0/dT$, $\langle\mu^2\rangle/nm^2$, and d ln $\langle\mu^2\rangle/dT$ are available for the isotactic polymer (Table V) from the work of Rahalkar et al.[14] and Riande et al.[15] The agreement is reasonable within the uncertainties involved in the experimental error as well as in the rotational isomeric state approximation.

Asymptotic behaviors of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ for the degree of polymerization (x) were also examined. While the former ratio increases rapidly with x, the latter decreases as x increases. A similar tendency has been observed in the case of POP.[2] Both ratios reach 90% of their asymptotic values around x = 15, regardless of the tacticity of the chain. In the study of the excluded volume effect on the dipole moment, Riande et al.[23] confirmed that the value of $\langle\mu^2\rangle/nm^2$ of the atactic PTP stays invariable over a wide range of molecular weight (M_n = 5 × 10^3–5 × 10^5). Finally values of the dipole moment ratio and its temperature coefficient calculated for the monomer model (1,2-bis(methylthio)propane) (25 °C) are as follows: $\langle\mu^2\rangle/nm^2$ = 0.68 and 10^3 d ln $\langle\mu^2\rangle/dT$ = 0.45 K^{-1}, respectively.

Discussion

The value of E_σ derived from the critical analysis of the experimental data of the dimension and dipole moment was found to differ little from that calculated by eq 1. A slightly negative value of E_σ obtained in this manner is also consistent with the spectroscopic data reported on some low molecular weight sulfides (cf. Table III). It should be recalled here that due to a shorter length of the C–O bond, a large positive value (0.9–1.3 kcal mol^{-1}) was assigned to the corresponding bond sequence CO⇝CC of polyoxides.[1-3] Similarly, the value of E_τ estimated for PTP is 1.2 kcal mol^{-1} while the effect of this conformation was entirely neglected in the conformational analysis of POP.[2] Another difference to be noted between PTP and POP[2] is the effect of the second-order interaction designated with the statistical weight parameter ω''; frequent occurrence of such conformation (CC⇜S⇝CC) in PTP is assured by spectroscopic measurements.[12]

The magnitude of ΔE_α defined according to eq 6 was found to be −0.13 kcal mol^{-1}, suggesting that the S···S interaction in the g_α conformation is slightly more repulsive than that obtained from the conformational energy calculations. Since values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ vary quite insensitively with E_β, the magnitude of ΔE_β (eq 7) cannot be determined explicitly from the present analysis: ΔE_β may thus be zero or possibly negative. These results indicate that the gauche sulfur effects as defined by eq 6 and 7 may be somewhat repulsive in contrast to the decisively attractive gauche oxygen effects of POP, for which we have found[2] values of ΔE_α = 0.7 and ΔE_β = 0.2 kcal mol^{-1}. These results parallel those reported on various low molecular weight cyclic compounds.[24] Zefirov et al.[25] studied conformational equilibria for 1,2-trans-disubstituted cyclohexanes. They assumed a repulsive gauche effect for the S···S interaction in excess to that predicted on the basis of van der Waals and Coulombic forces. Under the same condition, the O···O interaction was found to be attractive. Eliel and Juaristi[26] reached an analogous conclusion from the conformational analysis on 5-substituted 1,3-dioxanes and 1,3-dithianes. The term gauche effect, whether it is attractive or repulsive, has been introduced phenomenologically.[25-27] Although details are not yet known, they may arise from the same origin.[28]

Conformational flexibility around a given bond may be evaluated in terms of the number of conformations allowed to the bond.[3,29] Let Z denote the molecular configurational partition function for a polymer chain. Then for a large x, the configurational partition function defined for a monomeric residue by

$$z = Z^{1/x} \tag{8}$$

should serve for the present purpose. In these calculations, each element of the statistical weight matrices (eq 2–4) should be taken relative to the most preferred state of the given bond. A value of z thus derived represents the average flexibility attributable to a monomeric residue incorporated in a polymer chain. For PTP chains (x = 200, T = 25 °C), we obtained z = 4.80 (isotactic), 4.87 (atactic), and 4.94 (syndiotactic). The result is quite insensitive to

variation of the stereoregularity of the chain. These values should be compared with those estimated for the POP chain (x = 200, T = 30 °C):[3] z = 3.65, being nearly independent of the stereoregularity. Higher flexibility of the PTP chain arises mainly from the larger C–S bond length in comparison with that of the C–O bond. More detailed discussion on a related subject will be given in the following article.[16]

Acknowledgment. The author wishes to express his gratitude to Professor J. E. Mark for kindly supplying the experimental data of his laboratory prior to publication.

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(24) In the open chain system, the repulsive interaction between two sulfur atoms in a gauche arrangement may be alleviated by adjusting the location of the rotational energy minima.[17] When the rotational isomeric states are strictly restricted to the regularly staggered position (ϕ = 0, ±120°), the S· · ·S distance is 3.34 Å for the molecular geometry adopted in this paper. With a displacement of $\Delta\phi$ = 10°, the distance increases to 3.47 Å. Similar adjustments of rotational angles are not permitted in the cyclic compounds cited herein. The characteristic feature of the S· · ·S interaction seems to manifest itself in either case, but to a different degree.
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Configuration-Dependent Properties of the Poly(thioethylene) Chain

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ABSTRACT: The configurational characteristics of poly(thioethylene) were estimated by calculation based on the information acquired through the analysis of the poly(thiopropylene) chain as presented in the preceding paper. Assigning a value of E_σ = 0.5 kcal mol^{-1} to the gauche conformation about the C–C bond, the characteristic ratio $\langle r^2\rangle_0/nl^2$ = 4.2 and the dipole moment ratio $\langle\mu^2\rangle/nm^2$ = 0.42 were obtained. The configurational entropy evaluated for the temperature equivalent to the melting point of the polymer is 6.1 cal mol^{-1} deg^{-1}. This value may be compared favorably with the observed entropy of fusion 6.9 ± 1.0 cal mol^{-1} deg^{-1}, the value being however uncorrected for the volume change on melting. All these results suggest that the polymer chain is quite flexible. The flexibility of the chain estimated in terms of the number of allowed conformations for a monomeric residue may be arranged in the order, poly(thioethylene) > poly(thiopropylene) > poly(oxyethylene) > poly(oxypropylene). The results of the present analysis are consistent with the view presented by Takahashi et al., who demonstrated that the strong (intermolecular) dipole–dipole interactions play a key role in enhancing the enthalpy of fusion and thus the melting point of the polymer.

Poly(thioethylene) (PTE), or poly(ethylene sulfide), is known as a highly crystalline polymer which melts at a high temperature (215.6 °C).[1] The polymer is in practice quite intractable due to its instability at high temperatures (above the melting point) and its insolubility in conventional organic solvents. In these respects, this polymer differs remarkably from its oxygen analogue, poly(oxyethylene) (POE),[2] which has a relatively low melting temperature (67.9 °C)[3] and exhibits high solubility in various solvents. The major differences in their molecular structure may be summarized as follows: the bond length C–S is longer than C–O by ca. 30%, while the bond angle CSC is smaller than that of COC by ca. 10°. The values of the van der Waals radii used most frequently[4] are in the range 1.8–1.9 Å for the sulfur and 1.4–1.6 Å for the oxygen atom. The bond dipole moments estimated in the usual manner[5,6] are μ_{C-S} = 1.21 D and μ_{C-O} = 1.07 D, respectively. We concluded in the preceding paper[5] (paper 1) that the

0024-9297/80/2213-0546$01.00/0