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]

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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 ($\phi = 0, \pm 120°$), 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 $E_\sigma = 0.5$ 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.

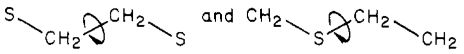
Poly(thioethylene) (PTE), or poly(ethylene sulfide), is known as a highly crystalline polymer which melts at a high temperature (215.6 °C).[1] The polymer is in practice quite intractable due to its instability at high temperatures (above the melting point) and its insolubility in conventional organic 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 $\mu_{C-S} = 1.21$ D and $\mu_{C-O} = 1.07$ D, respectively. We concluded in the preceding paper[5] (paper 1) that the poly(thiopropylene) (PTP) chain is appreciably more flexible than the poly(oxypropylene) (POP) chain in terms of the number of accessible conformations. It may be reasonable to expect that the skeletal chain of PTE is more flexible in its free state than that of POE. Based on the analysis of the X-ray crystallographic data of PTE, Takahashi, Tadokoro, and Chatani[7] pointed out that the dipoles fixed to the C–S–C groups in the chain are so arranged in the crystalline lattice as to enhance the interchain dipole–dipole interaction. Such strong polar interactions should raise the enthalpy of fusion, and in turn the melting point, of the polymer crystal.

The enthalpy of fusion has been determined experimentally on an as-made sample by differential scanning calorimetry: 1.8 ± 0.1 kcal mol^{-1} by Nicco et al.[8] and 2.1 kcal mol^{-1} by de Chirico and Zotteri.[1] The former authors estimated the enthalpy of fusion ΔH_f for perfect crystallinity to be 3.4 ± 0.5 kcal mol^{-1} by adopting the degree of crystallinity of 54% as determined by the X-ray diffraction method. This result leads to a value for the entropy of fusion of $\Delta S_f = \Delta H_f/T_m = 6.9 \pm 1.0$ cal mol^{-1} deg^{-1}. Corresponding values of ΔH_f and ΔS_f for POE are reported[3,9-11] to be 2.2 kcal mol^{-1} and 6.5 cal mol^{-1} deg^{-1}, respectively. These thermodynamic data again suggest that a large value for the enthalpy of fusion plays a major role in raising the melting point of PTE.

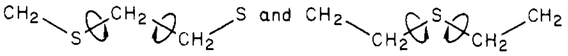
In this paper, various configuration-dependent properties of the PTE chain are evaluated. The conformational energy parameters required in these calculations are derived by using the semiempirical energy expressions established in paper 1. The configurational partition function developed in this manner should provide information regarding the configurational contribution to the entropy change on melting.[11,12] The configurational entropy thus estimated will be compared with those for some other polymer systems.[5,13,14]

Conformational Energies and Statistical Weight Matrices

Let σ and σ' denote the statistical weight parameters given to the first-order interaction involved in the gauche conformation of the moieties



respectively. (The parameter σ defined in this manner should not be confused with the one which was used in paper 1.[5] The latter one is replaced by σ' in the present treatment.) The second-order interactions associated with the bond sequences



are distinguishable in this polymer system; they are designated with the statistical weight parameters ω' and ω'', respectively. These statistical weight parameters may be defined in practice as Boltzmann factors for the corresponding conformational energies. Having defined the statistical weight parameters in this way, we can formulate the statistical weight matrices required for evaluation of the configuration partition function of the PTE chain in a conventional 3 × 3 matrix scheme.[6,15]

Conformational energy calculations were carried out for an appropriate portion of the PTE chain by using the expression established in paper 1.[5] The geometrical parameters adopted in these calculations are as follows: bond lengths $l_{CC} = 1.53$, $l_{CS} = 1.815$, and $l_{CH} = 1.10$, all being in Å; bond angles CSC = 100°, CCS = 114°, and CCH = 110°. Results of the calculations are summarized in Table I. The value of the conformational energy parameter E_σ given in the table may be somewhat less definite due to the gauche effect associated with the first-order S· · ·S interaction. The results of the conformational analysis on PTP presented in paper 1[5] suggest however that the effect on E_σ arising from this source should be only of the order of 0.1 kcal mol^{-1}. To be noted in this connection are the results reported on 1,2-bis(methylthio)ethane (1,2-BMTE), a monomer model of PTE, by Hayashi et al.[16] From the infrared analysis, they suggested that the energy difference between the *gtg'* and *ggg* forms is 1.1 kcal mol^{-1} in the gaseous state, but less than 0.1 kcal mol^{-1} in the liquid. Conformational energy calculations gave a value of 0.21 kcal mol^{-1} for the same energy difference (cf. Table III of paper 1). The values of $E_{\sigma'}$ and $E_{\omega''}$ listed in Table I compare favorably with the experimental data reported on some low molecular weight compounds of the related structures (cf. Table III of paper 1). Contribution from the conformation designated with ω' is estimated to be relatively small due to a large van der Waals radius of the sulfur atom. The same value of $E_{\omega'}$ was adopted in paper 1 for the conformational analysis of the PTP chain.

Table I
Conformational Energy Parameters
Calculated for the PTE Chain

parameter	conform. energy, kcal mol^{-1}
E_σ	0.4
$E_{\sigma'}$	−0.1
$E_{\omega'}$	1.1
$E_{\omega''}$	0.4

Table II
Calculated Values[a] of the Characteristic Ratio $\langle r^2\rangle_0/nl^2$ and Dipole Moment Ratio $\langle\mu^2\rangle/nm^2$ and Their Temperature Coefficients for Poly(thioethylene) and a Monomer Model, 1,2-Bis(methylthio)ethane

	PTE[b]	1,2-BMTE
$\langle r^2\rangle_0/nl^2$	4.2	
10^3 d ln $\langle r^2\rangle_0/dT$	−0.33	
$\langle\mu^2\rangle/nm^2$	0.42	0.70
10^3 d ln $\langle\mu^2\rangle/dT$	2.8	0.64

[a] Temperatures are taken to be 25 °C. [b] Calculated for a chain $CH_3S(-CH_2CH_2S-)_xCH_3$ with $x = 200$ units.

With the reasons stated above, except as otherwise noted, a value of $E_\sigma = 0.5$ kcal mol^{-1} will be adopted in the following treatment. The other parameters will be taken from Table I as indicated.

Theoretical Estimation of the Unperturbed Dimension, Dipole Moment, and Configurational Entropy

Structural parameters required in these calculations were given in the preceding section. In accordance with the previous treatment[5] of the PTP chain, a value of $\mu_{C-S} = 1.21$ D was adopted for the bond dipole moment. Results of the conformational energy calculations suggest that the displacements $\Delta\phi$ of the rotational minima from the regularly staggered gauche position are in the range 5–10° for both the C–C and C–S bonds. For the first approximation, therefore, the rotational minima were assumed to occur at $\phi = 0, \pm 110°$ for both bonds.

Listed in Table II are the results obtained for the unperturbed dimension and the dipole moment, being expressed customarily[15] as the characteristic ratios $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$, respectively. These calculations were carried out for a chain $CH_3S(-CH_2CH_2S-)_xCH_3$ with $x = 200$ units for the temperature of 25 °C. The temperature coefficients d ln $\langle r^2\rangle_0/dT$ and d ln $\langle\mu^2\rangle/dT$ derived for the

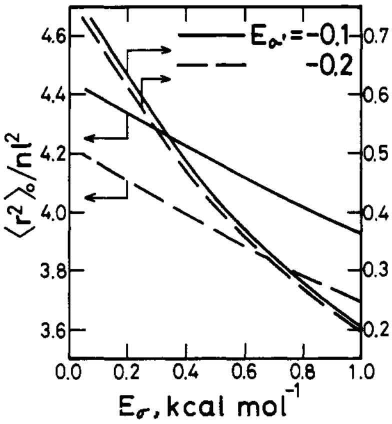


Figure 1. The characteristic ratio and dipole moment ratio for the PTE chains having $x = 200$ ($n = 602$) calculated as a function of E_σ for the temperature of 25 °C. Values of $E_{\sigma'}$ employed in these calculations are indicated in the figure, the other parameters being kept invariable ($E_{\omega'} = 1.1$ and $E_{\omega''} = 0.4$ kcal mol^{-1}).

same temperature are also included. For comparison, the dipole moment ratio and its temperature coefficient calculated for the monomer model, 1,2-BMTE, are given in the third column. It may be interesting to note here that the results given in Table II resemble in general those reported for POE[6] inspite of the fact that the conformational characteristics of these two polymers are quite dissimilar. (The temperature coefficients $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ calculated for these two polymers are opposite in sign, but they are small in magnitude.) Both $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ reach quite rapidly their asymptotic values for $x = \infty$. At around $x = 10$, these ratios come into the range within 10% of the limiting values.

Following the procedure adopted previously in the analysis of POE[6] and other related polymers,[5,13] values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ are plotted in Figure 1 against the conformational energy parameter E_σ over the range E_σ = 0–1.0 kcal mol^{-1}. As E_σ increases, the trans conformation tends to be more stabilized around the C–C bond. The negative slope of the $\langle \mu^2\rangle/nm^2$ vs. E_σ curve may be explicable on the basis of the fact that the value of $\langle \mu^2\rangle/nm^2$ should be nil for the all-trans conformation of the chain. The characteristic ratio $\langle r^2\rangle_0/nl^2$ of the PTE decreases slightly but definitely with an increase in E_σ in contrast to the tendency found for POE.[6] Such $\langle r^2\rangle_0/nl^2$ vs. E_σ relations reflect implicitly the divergence in the conformational characteristics between these two polymers. The results obtained by using $E_{\sigma'} = -0.2$ kcal mol^{-1} are also shown in Figure 1 (the dotted curves). With such a modification, $\langle r^2\rangle_0/nl^2$ decreases by ca. 5% while the effect on $\langle \mu^2\rangle/nm^2$ is negligibly small. Calculated values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle/nm^2$ should vary with the choice of rotational angles. Reduction of $\Delta\phi$ for the C–S bond from 10° to 0, the other parameters being kept constant, causes a decrease in $\langle r^2\rangle_0/nl^2$ by ca. 15% and similarly a decrease in $\langle \mu^2\rangle/nm^2$ by ca. 5%.

The configurational entropy of the chain was evaluated according to the expression[11,12]

$$S_{\mathrm{conf}} = R[\ln z + \mathrm{d}\ln z/\mathrm{d}\ln T] \qquad (1)$$

where z is the configurational partition function for an internal monomer residue, calculated by assigning a weight of unity to the lowest-energy conformation (i.e., $tg^\pm g^\pm$ for the bond sequence CH$_2$–CH$_2$–S–CH$_2$). A value of z thus defined represents by itself the conformational flexibility of the chain, or more exactly the relative number of conformations allowed to a monomer residue.[17] Calculations using the parameter set set forth above yield $z = 13.8$ and $S_{\mathrm{conf}} = 6.1$ cal mol^{-1} deg^{-1} for a chain of 200 units at the temperature (215 °C) equivalent to the melting point of the polymer.[1] Values of z and S_{conf} vary somewhat with the choice of the conformational energy parameter E_σ; e.g., with $E_\sigma = 1.0$ kcal mol^{-1}, we get $z = 11.0$ and $S_{\mathrm{conf}} = 5.8$ cal mol^{-1} deg^{-1}, and with $E_\sigma = 0.1$ kcal mol^{-1}, we get $z = 16.0$ and $S_{\mathrm{conf}} = 6.2$ cal mol^{-1} deg^{-1}. Judging from these results, both z and S_{conf} should not be much affected by a small increment (0.1–0.2 kcal mol^{-1}) in E_σ associated with the gauche sulfur effect around the C–C bond. The configurational entropy obtained in this manner corresponds to the entropy of fusion at constant volume. The correction factor for the volume change on melting is however unknown for PTE because of the lack of information on the thermal pressure coefficient of the polymer.[11] A direct comparison of the theoretical and experimental values is therefore not permitted.

Table III
Conformational Partition Function for a Monomer Residue[a], Estimated by Assigning a Weight of Unity to the Lowest-Energy State

polymer	preferred conformation[b] C–C	C–O or C–S	O–C or S–C	z
POE	$g^\pm$	t	t	4.3
PTE	t	$g^\pm$	$g^\pm$	10.2
	(t	$g^\pm$	t)	
	(t	t	$g^\pm$)	
POP[c]	g^+	t	t	3.6[d]
PTP[c]	t	t	t	4.8[d]
	(t	g^-	g^-)	
	(t	g^-	t)	

[a] Calculated for chains with $x = 200$ units. Temperatures were taken to be 25 °C. [b] Alternative conformations with slightly higher energies are indicated in parentheses. [c] Preferred conformations are shown for the (R) residue. [d] The value of z varies quite insensitively with the tacticity of the chain. The value cited here is the one calculated for the isotactic chain. See ref 5 and 14.

Discussion

Values of z evaluated for polymer chains such as POE,[6] PTE, POP,[14] and PTP[5] are summarized in Table III. For the purpose of comparison, values calculated for an identical temperature (25 °C) are cited. The preferred conformation in the free state is listed for the individual chains in the preceding column. Except in the case of POP, these conformations may be identified with those found in the crystalline state.[18] From the X-ray crystallographic analysis on an isotactic POP sample derived from a racemic monomer mixture, Cesari et al.[19] proposed a slightly distorted planar conformation for this chain. As reported by Takahashi et al.,[20] POE may take a planar zigzag conformation as well under a special condition. For the two sulfide polymers, two alternative conformations which differ only slightly from the lowest-energy arrangement in the free energy are available (cf. Table III). In each case, however, only a single crystalline conformation has been reported.[21,22] It may be noticed here that the lowest-energy conformation of POE ($g^\pm tt$) is excluded from the list of the low-energy arrangements of PTE. The same applies to the relation between POP and PTP. The flexibility of a polymer chain as represented by z decreases in the order PTE ≫ PTP > POE > POP. A large value of z for PTE indicates that the skeletal chain of this polymer should be highly flexible. The differences in z values among the rest of the polymers are less marked.

The configurational entropies S_{conf} calculated according to eq 1 for the temperature equivalent to the melting point

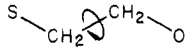
Table IV
Thermodynamic Data for Fusion and Configurational Entropy

	exptl				calcd
polymer	mp, °C	ΔH_f[g]	ΔS_f[h]	$(\Delta S_f)_v$[h]	S_{conf}[h]
POE	67.9[a]	2.2[a]	6.5[a,b]	4.9[b]	5.0
PTE	215.6[c]	3.4[d]	6.9[d]		6.1
POP	73[e]	2.0[e]	5.8[e]		4.0
PTP	53[f]				4.8

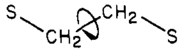
[a] Reference 3. [b] Reference 9. [c] Reference 1. [d] Reference 8. [e] Reference 23. [f] Reference 24. [g] kcal mol^{-1}. [h] cal mol^{-1} deg^{-1}.

of the respective polymers are listed in Table IV. Also included herein are the thermodynamic data such as the enthalpy ΔH_f and entropy of fusion ΔS_f taken from the literature. The entropy of fusion at constant volume $(\Delta S_f)_v$ is given only for POE, for which the correction term for the volume change on melting is available from the work of Malcolm and Ritchie.[10] As pointed out by Tonelli,[12] the agreement between S_{conf} and $(\Delta S_f)_v$ is reasonably good in this case. Among polymers listed in Table IV, PTE is unique in the sense that it possesses large values of ΔH_f and ΔS_f and exhibits a high melting point as a consequence. As pictured by Takahashi et al.,[7] the intermolecular dipole–dipole interactions should play an important role in enhancing the value of ΔH_f. The magnitude of ΔS_f (6.9) given in Table IV is at least qualitatively consistent with the calculated value of S_{conf} (6.1). The high flexibility of the chain may contribute to such strong intermolecular interactions by promoting the packing efficiency. PTE differs markedly from its oxygen analogue, POE, in these thermodynamic behaviors. In the cases of POP and PTP, as has been reported previously,[5,14] the value of z varies quite insensitively with the tacticity of the polymer chain. Similarly, the values of S_{conf} given in Table IV may apply to polymers with any tacticity. The experimental values of ΔH_f as well as ΔS_f are not known for PTP. By judging from the melting points and the magnitude of S_{conf}, however, the disparity between POP and PTP is not as large as that found between the other two polymers (cf. Table IV).

Recently Riande and Guzmán[25] reported the rotational isomeric state treatment of the poly(thiodiethylene glycol) chain, an alternating copolymer of ethylene oxide and ethylene sulfide. From the analyses of the mean-square dipole moment, they estimated the magnitude of the conformational energy difference between the gauche and trans states for the moiety



A value of 0.4 kcal mol^{-1} thus obtained is rather close to that (E_σ = 0.5 kcal mol^{-1}) adopted for the



of PTE in this paper, but quite different from the corresponding value (−0.4 kcal mol^{-1}) estimated for POE.[6]

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