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The Model Compounds and the Conformational Analysis of Poly(thiomethylene)

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The conformational energies of model compounds of poly(thiomethylene), $CH_3(SCH_2)_nSCH_3$, (n=1—6) were calculated by the molecular-mechanics method. Based on these conformational energy differences, the configuration-dependent properties of poly(thiomethylene) were estimated under the rotational isomeric-state approximations. The first-order interaction energy of the $^{\mathrm{C}}\diagdown\mathrm{S}\diagup{}^{\mathrm{C}}\diagdown\mathrm{S}$ bond, obtained from the energy differences among the conformers of $CH_3(SCH_2)_3SCH_3$, is coincident with that estimated from the same bond sequence for poly(1,3-dithiocane). Based on this coincidence, the monomeric sequential length of the model compound, which is representative of poly(thiomethylene), was decided. The propriety of the method of coupling the molecular-mechanics with the statistical-mechanics was also demonstrated.

Because of the structural similarity between poly(oxyalkylenes) and poly(thioalkylenes), the anomalous preference of the gauche states to the trans, i.e. the "gauche effect," which had been found in poly(oxyalkylenes),[1] is expected also to be present in poly(thioalkylenes). Based on the success of the estimation of the "gauche effect" and that of the proper approximation for rotational states of poly(oxyalkylenes),[2–4] poly(thiotrimethylene) was studied by the molecular-mechanics method in a previous report.[5] This polymer has the simplest chemical structure among the analogous poly(thioalkylenes), whose configuration-dependent properties had previously been observed experimentally. In that earlier paper,[5] the dipole-moment ratio and its temperature coefficient, observed experimentally, were reproduced with satisfactory success under the isomeric-state approximation of the molecular-mechanics method. It was shown that the "gauche effect" caused by sulfur atoms is significantly different from that of poly(oxyalkylenes); in the case of poly(thiotrimethylene), a longer-range steric interaction plays an important role. It was also shown that the molecular mechanics is effective in the analysis of the anomeric gauche effect of poly(thiotrimethylene).

Poly(thiomethylene) is the simplest member of the poly(thioalkylenes) and possesses the characteristic $^{\mathrm{C}}\diagdown_{\mathrm{S}}\diagup{}^{\mathrm{C}}\diagdown_{\mathrm{S}}$ sequence. Therefore, it can be expected to exhibit the even more characteristic "sulfur gauche effect." Recently, a vibrational analysis of poly(thiomethylene) was done[6] based on the group-coordinate force-field method, which clarified that the dominant conformational state of the skeletal bonds in the crystal, liquid, and gaseous states is gauche, although the energy difference between possible conformers had not yet been estimated accurately.

In this paper, the molecular conformation and the related properties of poly(thiomethylene) are studied by the method of statistical mechanics coupled with the molecular mechanics, since the configuration-dependent properties have not been observed experimentally because of the low solubility of poly(thiomethylene) in any solvents and its high melting point. Several model compounds possessing various chain lengths are investigated in an attempt to estimate the rotational isomeric-state approximations of the polymer. The most suitable chain length for the model compound of poly(thiomethylene) should satisfy the following conditions: it gives all the statistical and geometrical parameters required in the statistical-mechanics calculations for poly(thiomethylene), and it gives a first-order interaction $(^{\mathrm{C}}\diagdown_{\mathrm{S}}\diagup{}^{\mathrm{C}}\diagdown_{\mathrm{S}})$ parameter of the same magnitude as that which has experimentally estimated for poly(1,3-dithiocane). Using the parameters thus obtained, the configuration-dependent properties of poly(thiomethylene) are calculated.

Theoretical

Molecular-Mechanics Method. The molecular-mechanics method, also called the force-field method, has become one of the most popular methods in the field of computer chemistry. In this calculation, a molecule is treated as a system of particles held to one another with classical mechanical interatomic forces. The steric energy of the molecule is obtained as a function of the bond-stretching, bending, torsional, van der Waals, and electrostatic interactions; then, the optimum conformation is searched for.

Although many force fields have been suggested, Allinger's force-field[7] can be used for a wide range of problems in organic chemistry because its parameters for hydrocarbons and some hetero atoms are made carefully. An old type of this type of force field, i.e., MMI,[7] has been successfully used in a series of our studies of the conformational analysis of poly(oxyalkylenes); a newer version, i.e., MM2[8] has also been used in our previous reports on a similar analysis of poly(thiotrimethylene). In the present calculation, we used the new version of MM2,[9] which can run on a microcomputer.

In order to ascertain the optimal length of model compounds used as representative poly(thiomethylenes), the following compounds including one to six $-SCH_2-$ units with terminal methyl and methylthio groups were selected for study; 2,4-dithiapentane [**2T**] $CH_3-SCH_2-SCH_3$, 2,4,6-trithiaheptane [**4T**] $CH_3-(SCH_2)_2-SCH_3$, 2,4,6,8-tetrathianonane [**6T**] $CH_3-(SCH_2)_3-SCH_3$, 2,4,6,8,10-pentathiaundecane [**8T**] $CH_3-(SCH_2)_4-SCH_3$, 2,4,6,8,10,12-hexathiatridecane [**10T**] $CH_3-(SCH_2)_5-SCH_3$, and 2,4,6,8,10,12,14-heptathiapentadecane [**12T**] $CH_3-(SCH_2)_6-SCH_3$. Here ***n*T** in square brackets denotes the number of skeletal bonds whose internal rotations experience the butane interaction between CH_2 groups and S atoms; these abbreviations will be used hereafter instead of the full names of the model compounds. The all-trans conformer, the conformers including one gauche state, and those including two consecutive gauche bonds with the same or opposite signs are calculated by means of the molecular-mechanics.

Results and Discussion

Model Compounds of Poly(thiomethylene). The results of molecular-mechanics calculations on the six above-mentioned kinds of model compounds of poly(thiomethylene) are listed in Table 1, where the energy differences between the conformers including one or two consecutive gauche states and the corresponding all-trans conformer are also shown.

In the case of the simplest model compound, **2T**, the GG conformer has the lowest energy, the TG conformer is next, and the TT has the highest. In the vibrational analysis of this model compound, more than two conformers were found in the liquid or gaseous states.[6] These results can be compared with those for the corresponding model compounds of poly(oxymethylene),[2] i.e. 2,4-dioxapentane, in which the energy differences of the TG, GG, and GḠ conformers from TT are −10.84, −18.45, and −3.18 kJ mol^{-1} respectively. Comparing these values with the values of **2T** shows that the energy of TG, i.e., −4.01 kJ mol^{-1}, is much higher than that of 2,4-

Table 1. The Energy Differences between the All-Trans State and Other Conformers (in kJ mol^{-1})

2,4-Dithiapentane	E/kJ mol^{-1}	2,4,6-Trithiaheptane	E/kJ mol^{-1}	2,4,6,8-Tetrathianonane	E/kJ mol^{-1}	2,4,6,8,10-Pentathiaundecane	E/kJ mol^{-1}
TT	0.0	TTTT	0.0	TTTTTT	0.0	TTTTTTTT	0.0
TG	−4.012	TTTG	−4.289	TTTTTG	−4.376	TTTTTTTG	−4.427
GG	−8.209	TTGT	−5.142	TTTTGT	−5.540	TTTTTTGT	−5.745
GḠ	−1.950	TTGG	−9.703	TTTGTT	−5.590	TTTTTGTT	−5.728
		TGGT	−10.196	TTTTGG	−10.188	TTTTGTTT	−6.138
		TTGḠ	−7.895	TTTGGT	−11.088	TTTTTTGG	−10.414
		TGḠT	−9.644	TTGGTT	−11.531	TTTTTGGT	−11.431
				TTTTGḠ	−2.481	TTTTGGTT	−12.184
				TTTGḠT	−4.531	TTTGGTTT	−12.226
				TTGḠTT	−9.309	TTTTTTGḠ	−2.435
						TTTTTGḠT	−4.682
						TTTTGḠTT	−5.280
						TTTGḠTTT	−4.757

2,4,6,8,10,12-Hexathiatridecane	E/kJ mol^{-1}	2,4,6,8,10,12,14-Heptathiapentadecane	E/kJ mol^{-1}
TTTTTTTTTT	0.0	TTTTTTTTTTTT	0.0
TTTTTTTTTG	−4.464	TTTTTTTTTTTG	−4.523
TTTTTTTTGT	−5.879	TTTTTTTTTTGT	−6.017
TTTTTTTGTT	−5.879	TTTTTTTTTGTT	−6.033
TTTTTTGTTT	−6.443	TTTTTTTTGTTT	−6.724
TTTTTGTTTT	−6.217	TTTTTTTGTTTT	−6.561
TTTTTTTTGG	−10.535	TTTTTTGTTTTT	−6.657
TTTTTTTGGT	−11.652	TTTTTTTTTTGG	−10.640
TTTTTTGGTT	−12.552	TTTTTTTTTGGT	−11.862
TTTTTGGTTT	−12.740	TTTTTTTTGGTT	−12.887
TTTTGGTTTT	−12.912	TTTTTTTGGTTT	−13.175
TTTTTTTTGḠ	−2.377	TTTTTTGGTTTT	−13.489
TTTTTTTGḠT	−4.837	TTTTTGGTTTTT	−13.422
TTTTTTGḠTT	−6.092	TTTTTTTTTTGḠ	−2.330
TTTTTGḠTTT	−4.887	TTTTTTTTTGḠT	−5.000
TTTTGḠTTTT	−11.301	TTTTTTTTGḠTT	−6.276
		TTTTTTTGḠTTT	−4.619
		TTTTTTGḠTTTT	−14.322
		TTTTTGḠTTTTT	−4.920

dioxapentane. The energies of the two consecutive gauche states of 2,4-dioxapentane (E_{GG} and $E_{\mathrm{G\bar{G}}}$) are larger than twice the energy difference in the conformer including one gauche state ($2E_{\mathrm{TG}}$), while the energy of E_{GG} of **2T** is smaller than $2E_{\mathrm{TG}}$. Such a difference may be caused by the difference in the skeletal-bond length: the long C–S bond and the short C–O bond. The energy differences between the conformers of **2T** are mainly caused by the difference in the torsional and electrostatic interactions. These interactions also play an important role in the energy difference among the conformers of 2,4-dioxapentane. However, the energy difference between **2T** and 2,4-dioxapentane may also be caused by the electrostatic interactions: the electrostatic attraction in 2,4-dioxapentane is much larger than that in **2T**. This model compound, **2T**, is too short in length to give all the statistical-weight parameters required in the statistical-mechanics calculations for poly(thiomethylene). The smallest model compound giving the five required statistical-weight parameters is **4T**.

The conformers of **4T** including the two consecutive gauche bonds with the same sign are the lowest in energy, those including one gauche bond are the next lower, and the all-trans conformer is the highest. In the case of the corresponding model compounds of poly(oxymethylene),[2] i.e., 2,4,6-trioxaheptane, the order of the conformers in terms of energetic stability are the same as in **4T**, although the energy of the conformer including one gauche is lower by a factor of about 2.7 than that of the corresponding conformer of **4T**. The energy difference among the conformers is mainly caused by the torsional and electrostatic interactions. Especially the electrostatic interaction plays an important role in the steric-energy difference between **4T** and 2,4,6-trioxaheptane. The vibrational and normal-coordinate analysis of poly(thiomethylene) and its model compounds[10] made it clear that the lone-pair electrons on the sulfur atoms in the trans form are all located in the same direction and that the repulsion force between the lone-pairs becomes large (rabbit-ear effect), resulting in the stability of the gauche state.[10] This stability of the gauche state is consistent with the calculated results for the model compounds in this study.

Based on the calculated results for the various conformers from **2T** to **12T**, it was clarified that the conformation energy is smaller for the compound which includes the gauche bond in the inner position of the skeletal chain. This is always true for the conformers with a gauche state located within the fourth position from the terminal point, except for the sequence of TTTTTTGT and TTTTTGTT of **8T**. On the contrary, the conformers of **10T** and **12T**, which include a gauche bond at a position more inward than the fourth from the terminal point, show larger energies than those of the conformers which include a gauche bond at the fourth position. It seems that, when the length of the chain becomes long, the gauche state of the central position experiences a severe steric interaction because of the large substituent groups being brought close to each other. Therefore, the **10T** and **12T** molecules seem too long to be adopted as suitable model compounds of poly(thiomethylene). For the conformers including two consecutive gauche bonds of the same sign, the energy becomes lower as the two gauche bonds are positioned at the inner part of the chain, except for the cases of the TTTTTTGGTTTT and TTTTTGGTTTTT of **12T**.

Statistical-Mechanics Calculation of Configuration-Dependent Properties. A parameter of the first-order interaction and the four parameters of the second-order interactions are required to make statistical-mechanics calculations of configuration-dependent properties of poly(thiomethylene). The statistical-weight parameter of the first-order interaction for a gauche in the $^{\mathrm{C}}\diagdown_{\mathrm{S}}\diagup^{\mathrm{C}}\diagdown_{\mathrm{S}}$ bond sequence is denoted by σ. The parameters of the second-order interaction in the $^{\mathrm{S}}\diagdown_{\mathrm{C}}\diagup^{\mathrm{S}}\diagdown_{\mathrm{C}}\diagup^{\mathrm{S}}$ sequence are denoted by ϕ and ω for the two consecutive gauche bonds with the same and with opposite signs respectively. The second-order interaction parameters of the two other consecutive gauches in the $^{\mathrm{C}}\diagdown_{\mathrm{S}}\diagup^{\mathrm{C}}\diagdown_{\mathrm{S}}\diagup^{\mathrm{C}}$ sequence are defined by ϕ' and ω' for the $\mathrm{GG}(\overline{\mathrm{GG}})$ and $\mathrm{G\bar{G}}(\mathrm{\bar{G}G})$ respectively. These parameters are obtained from the above-mentioned results of the molecular-mechanics calculation of the conformers of each model compound. The first-order interaction energy E_σ is calculated as the averaged value of the conformational-energy differences between the conformers including one gauche state and the all-trans conformer. The second-order interaction energy is obtained as the energy increment upon the introduction of one additional gauche state into the corresponding conformation with one gauche bond; for example, $E_{\phi'}=E_{\mathrm{TTGG}}-E_{\mathrm{TTGT}}-E_{\mathrm{TTTG}}$. These energy values are averaged over all the model compounds. The energies of the first- and second-order interactions thus obtained are plotted for the number of skeletal bonds of model compounds in Fig. 1. The first-order interaction energy E_σ decreases with the increase in the chain length: -4.02 kJ mol^{-1} in **2T** and -6.11 kJ mol^{-1} in **12T**. In contrast, E_ϕ and $E_{\phi'}$ are held at almost the same level; E_ϕ is nearly zero, and $E_{\phi'}$ is between -0.17 and -0.33 kJ mol^{-1}. The second-order interaction energies for the two consecutive oppositely signed gauche sequences, i.e., E_ω and $E_{\omega'}$, vary significantly. The E_ω increases with an increase in the chain length, while the $E_{\omega'}$ tends to decrease slightly with some vibration. The conformations of poly(thiomethylene) are estimated from these energy parameters. The gauche state occurs most frequently because of a large negative value of E_σ. The

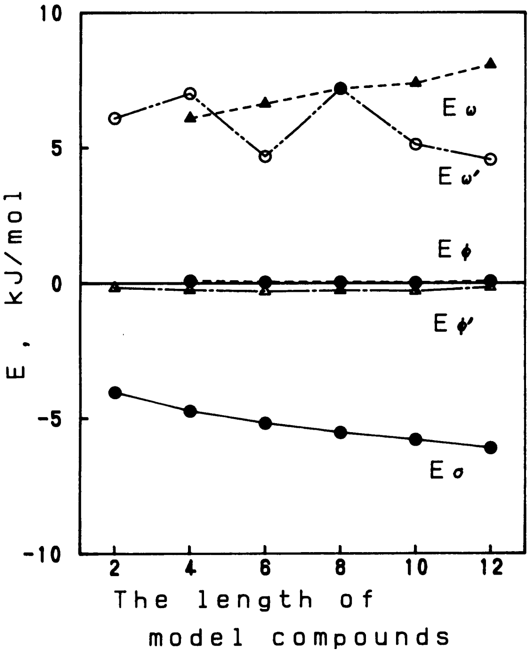

Fig. 1. The variation of statistical-weight parameters plotted against the chain length of model compounds of poly(thiomethylene).

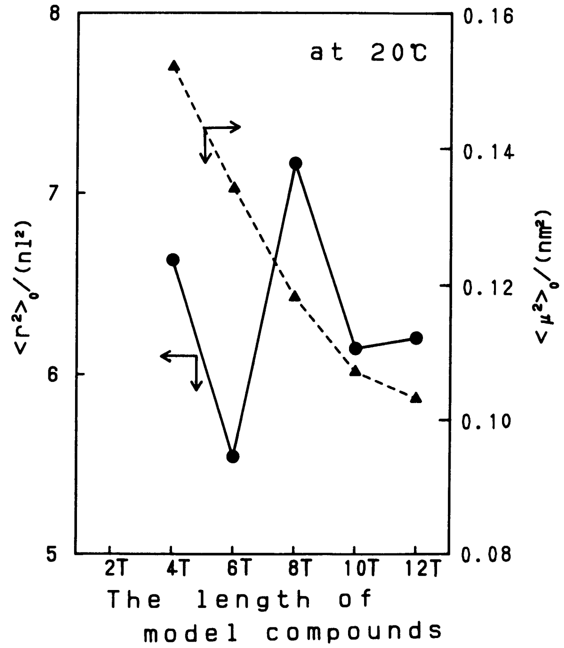

Fig. 2. The dependence of the characteristic ratio and the dipole-moment ratio of poly(thiomethylene) on the chain length of model compounds. Filled circles represent the characteristic ratios and filled triangles represent the dipole-moment ratios.

conformers containing two consecutive gauche states with the same sign in the $\mathrm{C}\diagdown_{\mathrm{S}}\diagup\mathrm{C}\diagdown_{\mathrm{S}}\diagup\mathrm{C}$ bond sequence occur more frequently than those in $\mathrm{S}\diagdown_{\mathrm{C}}\diagup\mathrm{S}\diagdown_{\mathrm{C}}\diagup\mathrm{S}$ because the value $E_{\phi'}$ is negative and smaller than $E_{\phi}(\simeq 0)$. The $E_{\omega'}$ value is apparently smaller than E_{ω} in **6T**, **10T**, and **12T**; therefore, the conformers containing two consecutive gauche states with the opposite signs in the $\mathrm{C}\diagdown_{\mathrm{S}}\diagup\mathrm{C}\diagdown_{\mathrm{S}}\diagup\mathrm{C}$ bond sequence occur more frequently than those in $\mathrm{S}\diagdown_{\mathrm{C}}\diagup\mathrm{S}\diagdown_{\mathrm{C}}\diagup\mathrm{S}$. Such an estimation can be compared with the experimental results of poly(thiomethylene) and its model compounds. The crystal structure of this polymer had been investigated,[11] and the molecular form in the solid state has been confirmed to be the [G] form. However, this X-ray study was carried out in the solid state, and so the results could not be directly compared with the present results, for in this study the conformation of poly(thiomethylene) in a liquid (dilute solution) or an isolated molecule has been investigated. A recent study of the vibrational analysis of poly(thiomethylene) and its model compounds[10] pointed out that many forms coexist in a liquid or gaseous state: for example, GG, TT, TG in **2T**. Their results correspond well with those obtained in this study.

The geometrical parameters necessary for the statistical-mechanics calculations were also obtained from the results of the molecular-mechanics calculations on each model compound. All the geometrical parameters for the conformers of each model compound were then averaged, taking the weight of their energy differences and occurrence into account. The Boltzmann-averaged geometric parameters thus obtained were found to be scarcely influenced at all by the chain length of the model compounds; $\angle\mathrm{CSC}=80.6°-81.2°$, $\angle\mathrm{SCS}=64.2°-66.4°$, $\phi^{\mathrm{T}}_{\mathrm{CS\text{-}CS}}=-0.8°-0.7°$, $\phi^{\mathrm{G}}_{\mathrm{CS\text{-}CS}}=109.3°-112.5°$, $l_{\mathrm{C\text{-}S}}=1.819$ Å, and $m_{\mathrm{C\text{-}S}}=1.20$ D, where ϕ^{T}, ϕ^{G}, and m are the torsional angles of the trans and gauche states, and the bond dipole-moment, respectively.

The configuration-dependent properties of poly(thiomethylene) that is, the characteristic ratio, the dipole-moment ratio, and their temperature coefficients were calculated as functions of the chain length of the model compound by using these statistical-mechanics parameters; the results are shown in Figs. 2 and 3. Although the characteristic ratios $\langle r^2\rangle_0/(nl^2)$ ($\langle r^2\rangle_0$: an unperturbed dimension, n: the number of skeletal bonds, l: the length of the bond) show some variation (from 5.5 to 7.2) for **6T** and **8T**, those of **4T**, **10T**, and **12T** are all at almost the same level (6.1—6.3). The dipole-moment ratio $\langle\mu^2\rangle_0/(nm^2)$ decreases from 0.17 to 0.10 with the increase in the chain length, although the decrement rate becomes small. As is shown in Fig. 3, the temperature coefficient of the dipole-moment ratio $\mathrm{d}\log_e\langle\mu^2\rangle_0/\mathrm{d}T$ is positive and increases with the increase in the chain length. The temperature coefficients of the characteristic ratio $\mathrm{d}\log_e\langle r^2\rangle_0/\mathrm{d}T$ are all negative and show a rapid decrease from -3.2×10^{-3} K^{-1} at **4T**

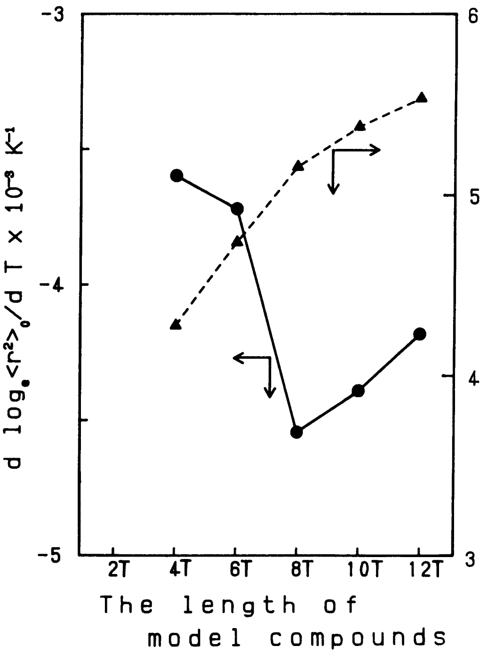

Fig. 3. The dependence of the temperature coefficients of the configuration-dependent properties of poly(thiomethylene) on the chain length of model compounds. Filled circles represent the temperature coefficients of characteristic ratios and filled triangles represent those of dipole-moment ratios.

to $-4.5\times10^{-3}\,K^{-1}$ at **8T**, after which they slightly increase to $-4.2\times10^{-3}\,K^{-1}$ for **12T**. The reliability of these forecast values depends upon the reliability of the statistical-mechanics parameters obtained from the molecular-mechanics calculations on the model compounds. No experimentally obtained value of the configuration-dependent properties of poly(thiomethylene) has yet been reported. The configurational study of poly(1,3-dithiocane)[12] is the only experimental report available for comparison with the calculated values of poly(thiomethylene). The experimental values of the dipole-moment ratio and its temperature coefficient of poly(1,3-dithiocane) were reproduced by using the value of $E_\sigma=-5.02$ kJ mol^{-1}. This value of the first-order interaction energy is very close to those obtained from the model compounds of poly(thiomethylene); $E_\sigma=-4.73$ kJ mol^{-1} for **4T**, and -5.19 kJ mol^{-1} for **6T**. This fact suggests the reliability of the results obtained by the molecular-mechanics calculations on these model compounds of poly(thiomethylene). Our previous report[5] on poly(thiotrimethylene) showed that the approximate model compound of this polymer contains two or three repeating units with proper terminal groups. According to this conclusion, the appropriate model compounds of poly(thiomethylene) may be either **6T** or **8T**. The present calculation also supports this result, because: (1) the E_σ value of the model compound is of the same magnitude as that of poly(1,3-dithiocane), and (2) the gauche states in the central position of the long model compounds (above the **10T**) experience a severe steric interaction. When the **6T** is adopted as the model compound of poly(thiomethylene), the configuration-dependent properties are calculated as follows; $\langle r^2\rangle_0/(nl^2)=5.54$, $\langle\mu^2\rangle_0/(nm^2)=0.13$, $d\log_e\langle r^2\rangle_0/dT=-3.72\times10^{-3}\,K^{-1}$ and $d\log_e\langle\mu^2\rangle_0/dT=4.73\times10^{-3}\,K^{-1}$.

In an earlier report on poly(1,3-dithiocane),[12] the energy of the first-order interaction for the  bond sequence was estimated as $E_\sigma=-1.42$ kJ mol^{-1} on the basis of the calculation of the model compound, but the experimental data of the dipole-moment ratio and its temperature coefficient could not be reproduced well by this energy value. The E_σ was, therefore, modified so as to fit the experimentally obtained configuration-dependent properties; then $E_\sigma=-5.02$ kJ mol^{-1} was obtained, as has been reported above. This energy variation of E_σ, 3.60 kJ mol^{-1}, was named the "extra stabilization energy" and assumed to be the first evidence for a large attractive sulfur gauche effect in poly(sulfides).[12] In the present study, this energy difference between the trans and gauche states was estimated to be 5.19 kJ mol^{-1} for the **6T** molecule by the molecular-mechanics method.

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References

1) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).

2) T. Miyasaka, Y. Kinai, and Y. Imamura, *Makromol. Chem.*, **182**, 353 (1981).

3) T. Miyasaka, T. Yoshida, and Y. Imamura, *Makromol. Chem.*, **184**, 1285 (1983).

4) T. Miyasaka, T. Yoshida, and Y. Imamura, *Makromol. Chem.*, **187**, 1515 (1986).

5) T. Miyasaka and T. Yoshida, *Bull. Chem. Soc. Jpn.*, **61**, 4231 (1988).

6) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 113 (1972); H. Matsuura and H. Murata, *Bull. Chem. Soc. Jpn.*, **55**, 2853 (1982).

7) N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.*, **98**, 6798 (1976).

8) N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).

9) This revised program was provided to us by Prof. Dr. Eiji Osawa of Hokkaido University.

10) M. Ohsaku, *Bull. Chem. Soc. Jpn.*, **47**, 965 (1974).

11) G. Carazzolo and G. Valle, *Makromol. Chem.*, **90**, 66 (1966).

12) W. J. Welsh, *Makromol. Chem.*, **183**, 2565 (1982).