The Model Compounds and Conformational Analysis of Poly(thiotrimethylene) Using Molecular Mechanics Method

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Several model compounds of poly(thiotrimethylene), including one to four thiotrimethylene units, were studied by means of a molecular mechanics method. The geometric and statistical weight parameters were directly derived from the results of molecular mechanics calculations concerning several conformers of these model compounds. Although the first-order interactions of poly(thiotrimethylene) were significantly larger than those of poly(oxyalkylenes), the second-order interactions of this polymer were much smaller. The "gauche effect" by sulfur atoms seemed to be mainly caused by small second-order interactions. By means of the model, compounds including more than three repeating units, the calculated configuration-dependent properties were in better agreement with the experimental ones than that calculated earlier. The better agreement was obtained by varying some of the geometric parameters. Compounds including more than three repeating units of the polymer were available as model compounds. Since this was also true in poly(oxyalkylenes), it was found that a combination of the methods of molecular and statistical mechanics was sufficiently effective to investigate the configurational properties of poly(thiotrimethylene).

Poly(thioalkylenes) have been investigated[1-8] with regard to their configurational properties in comparison with the analogous poly(oxyalkylenes),[9-13] because of their similarity in structure. In the case of poly(oxyalkylenes), it has been shown that the gauche conformations, which are associated with the O-CH_2 interactions, are much preferred to the trans state. This anomalous gauche preference is called the "oxygen gauche effect." Earlier semiempirical calculations[9] of the conformational energies for the model compounds of poly(oxyalkylenes) could not succeed in providing proper interpretations of such anomalous gauche preference, although structural studies in crystal[14,15] or vibrational spectroscopic studies[16] have been well established. In previous studies,[10-13] we undertook the first attempts to combine the molecular mechanics method[17] with the calculations involving statistical mechanics. When the lone-pair electrons on an oxygen atom were taken into consideration, molecular mechanics calculations on the model compounds of poly(oxyalkylenes) prevailed to estimate the proper amount of the gauche oxygen effect. The configuration-dependent properties of poly(oxyalkylenes), which were calculated by means of the rotational isomeric states approximations directly obtained from the results of molecular mechanics on the model compounds, were in fairly good agreement with the experimental ones.

In analogy to the poly(oxyalkylenes), it was found that poly(thioalkylenes) had a similar gauche effect,[1-8] although it was different in amount. Similarly, in poly(oxyalkylenes), earlier conformational energy calculations[6-8] of the model compounds of poly(thioalkylenes) also could not provide proper interpretations of the rotational isomeric states approximations. Moreover, molecular mechanics, which provided successful interpretations of the rotational states approximations for the model compounds of poly(oxyalkylenes), had as yet never been applied to the model compounds of poly(thioalkylenes) for such approximations, except regarding the conformational and packing stability in crystal[18] or the vibrational spectra analysis using the group coordinate force field.[19-21] Poly(thioalkylenes), which included one or two methylene groups in their repeating units, had not been experimentally investigated with regard to the configuration-dependent properties, because of their high melting points and poor solubility in solvents. The simplest poly(thioalkylenes), whose configuration-dependent properties have been experimentally observed, is poly(thiotrimethylene).[8] Therefore, in this study, molecular mechanics were applied to the model compounds of poly(thiotrimethylene), which have various chain lengths. By means of these results, the configuration-dependent properties of this polymer could be estimated. The calculated values were compared with the experimentally observed ones. Then, the most suitable length of the model compound of poly(thiotrimethylene) could be determined. Here, the propriety of the application of the molecular mechanics to the poly(thioalkylenes) is also discussed.

Theoretical

Molecular Mechanics Calculation. Molecular mechanics[17] (or force field method) is a method that allows calculations of the structure and energy of a molecule by means of several potential functions (bending, stretching, torsional, van der Waals, electrostatic, their cross terms) and their experimentally derived parameters. Then the energy is minimized. In recent years, molecular mechanics has become one of the most popular methods, occupying a significant position in the field of computer chemistry, called "applied theoretical chemistry".[22] Although many force fields have been suggested, each force field has a different object to simulate a molecule. The force

fields of Scheraga[23] or Kallman[24] shows fine performances for calculations of the molecular structure of polypeptide or nucleic acids. That of Lifson/Warshel[25,26] has proven to be highly efficient for calculations of the packing of molecules in a crystal, and that of Tadokoro[27] or Williams[28] aim at estimations of crystalline structures. Matsuura et al.[18,19] developed a group coordinate force field, which had been initiated by Shimanouchi et al.,[29] and proved to be suitable for treating the vibrations of molecules. For the general force fields aimed at hydrocarbons, Schleyer's,[30] Boyd's,[31] and Allinger's[32] are very famous. Among them, Allinger's force field is available for a wide range of the problems concerning organic chemistry, since the parameters of hydrocarbons and those of various heteroatoms are made courteously. The use of this method has spread remarkably around world. In this study, the force field of Allinger[32] was selected, because of this remarkably wide spread usage and the reliability of parameters for heteroatoms. Another positive point is that a satisfactory estimation of the rotational isomeric states of poly(oxyalkylenes) had been obtained by the previous force field of Allinger, i.e. MMI;[17,33] therefore, the calculated results of poly(thioalkylenes) can be directly compared with the previous results of poly(oxyalkylenes). More recently, since computer programs for molecular mechanics, which can run on a microcomputer, have become available,[33] molecular mechanics has become easier to use. In this study we used a molecular mechanics program which was reported in 1977 by Allinger et al. (MM2[32]). This program could execute under MS-DOS[34] and be transformed so as to be able to run on a PC-9801 microcomputer.[35]

Considering structural symmetry, and for the purpose of deriving the geometric and statistical weight parameters in order to calculate the configuration-dependent properties of poly(thiotrimethylene), the following model compounds, including one to four thiotrimethylene units $CH_2CH_2CH_2S$ with terminal methyl or ethyl groups, were studied; i.e. 2,6-dithiaheptane (**4T**) $CH_3SCH_2CH_2CH_2SCH_3$, 3,7-dithianonane (**6T**) $CH_3CH_2SCH_2CH_2CH_2SCH_2CH_3$, 2,6,10-trithiaundecane (**8T**) $CH_3S\text{-}(CH_2CH_2CH_2S\text{-})_2\text{-}CH_3$, 3,7,11-trithiatridecane (**10T**) $CH_3CH_2S\text{-}(CH_2CH_2CH_2S)_2CH_2CH_3$, 2,6,10,14-tetrathiapentadecane (**12T**) $CH_3S(CH_2CH_2CH_2S)_3CH_3$, 2,6,10,14,18-pentathianonadecane (**16T**) $CH_3S(CH_2CH_2CH_2S)_4\text{-}CH_3$. The numbers with **T** in parentheses denote the number of skeletal bonds whose rotations experience a first-order interaction between CH_2 and CH_2, or CH_2 and S atoms; these abbreviations are used here instead of the full names of model compounds. Regarding these model compounds, the all-trans conformer, the conformers including one gauche state and those including consecutive two gauche states, were calculated by molecular mechanics. In molecular mechanics, the effect of any solvent was taken into account by considering the solvent as an isotropic continuum having a macroscopic dielectric constant. Under such conditions, the rotational states of molecules have a preference for gauche states as the polarity of solvents increases. The configuration-dependent properties of this polymer, which were to be compared with the results of molecular mechanics, were obtained in a nonpolar solvent, i.e. benzene.[8] Moreover, the configuration-dependent properties of the polymer were studied under an unperturbed state; therefore, no additional treatment was made regarding the effect of a solvent.

Results and Discussion

Results of Molecular Mechanics Calculations on the Model Compounds of Poly(thiotrimethylene). As the model compounds of poly(thiotrimethylene), the six compounds described in the previous section were used in molecular mechanics calculations, in which the dipole-dipole interactions with common atoms were taken into consideration. The calculated energy differences between corresponding an all-trans conformer and several conformers of each model compound are listed in Table 1.

With respect to compound **4T**, the all-trans conformer has the lowest energy and a TTTG conformer with a rotational state of CC-SC is gauche, has secondly low energy. Concerning the derivation of the statistical-weight parameters of poly(thiotrimethylene), **4T** is too short to derive all of the parameters (eight kinds of parameters are needed, although only six are obtained from **4T**).

The **6T** is the smallest model compound of poly(thiotrimethylene), which can be used to derive all of the eight statistical-weight parameters required for a calculation of the configuration-dependent properties of the polymer. The all-trans conformer of **6T** also has the lowest energy; a TTTTGT conformer with a rotational state of CC-SC is gauche, has the second lowest energy.

Throughout the calculated results of all the model compounds, the gauche state about CC-SC is lower in energy than that about SC-CC. In poly(oxytrimethylene), the gauche state about the central bond in the sequence CC-CO has been found to be lower in energy than that in the sequence CC-OC. This is caused by the fact that a C-O bond (1.407 Å) is considerably shorter than a C-C bond; therefore, the van der Waals interactions of a gauche in CC-OC become larger than those in CC-CO and is caused by the large electrostatic attractions of a gauche in CC-CO. On the contrary, the gauche of poly(thiotrimethylene) in CC-SC has been found to be lower in energy than that in CC-CS. The preference of the former is mainly due to stabilizations by van der Waals and torsional interactions owing to the long bond length of C-S, i.e. $l_{C\text{-}S}$=1.815 Å. These contributions to the steric energy are larger

Table 1. The Results of Molecular Mechanics Calculations on Several Model Compounds of Poly(thiotrimethylene)

2,6-Dithiaheptane		3,7-Dithianonane		2,6,10-Trithiaundecane		3,7,11-Trithiatridecane	
Conformer	ΔE / kJ mol^{-1}	Conformer	ΔE / kJ mol^{-1}	Conformer	ΔE / kJ mol^{-1}	Conformer	ΔE / kJ mol^{-1}
TTTT	0.0	TTTTTT	0.0	TTTTTTTT	0.0	TTTTTTTTTT	0.0
TTTG	0.406	TTTTTG	0.603	TTTTTTTG	0.398	TTTTTTTTTG	0.544
TTGT	1.506	TTTTGT	0.297	TTTTTTGT	1.389	TTTTTTTTGT	0.360
TTGG	1.481	TTTGTT	1.439	TTTTTGTT	1.410	TTTTTTTGTT	1.289
TGGT	3.155	TTTTGG	0.598	TTTTGTTT	0.084	TTTTTTGTTT	1.552
TTG$\bar{G}$	10.694	TTTGGT	1.234	TTTTTTGG	1.272	TTTTTGTTTT	0.038
TG$\bar{G}$T	12.381	TTGGTT	2.983	TTTTTGGT	2.808	TTTTTTTTGG	0.510
		TTTTG$\bar{G}$	4.301	TTTTGGTT	0.854	TTTTTTTGGT	0.967
		TTTG$\bar{G}$T	10.523	TTTGGTTT	−0.557	TTTTTTGGTT	2.715
		TTG$\bar{G}$TT	12.021	TTTTTTG$\bar{G}$	6.134	TTTTTGGTTT	0.854
				TTTTTG$\bar{G}$T	12.209	TTTTGGTTTT	−0.615
				TTTTG$\bar{G}$TT	5.594	TTTTTTTTG$\bar{G}$	4.356
				TTTG$\bar{G}$TTT	3.523	TTTTTTTG$\bar{G}$T	10.590
						TTTTTTG$\bar{G}$TT	12.021
						TTTTTG$\bar{G}$TTT	146.633
						TTTTG$\bar{G}$TTTT	3.498

2,6,10,14-Tetrathiapentadecane		2,6,10,14,18-Pentathianonadecane	
Conformer	ΔE / kJ mol^{-1}	Conformer	ΔE / kJ mol^{-1}
TTTTTTTTTTTT	0.0	TTTTTTTTTTTTTTTT	0.0
TTTTTTTTTTTG	0.389	TTTTTTTTTTTTTTTG	0.406
TTTTTTTTTTGT	1.398	TTTTTTTTTTTTTTGT	1.385
TTTTTTTTTGTT	1.418	TTTTTTTTTTTTTGTT	1.460
TTTTTTTTGTTT	0.280	TTTTTTTTTTTTGTTT	0.389
TTTTTTTGTTTT	0.239	TTTTTTTTTTTGTTTT	0.481
TTTTTTGTTTTT	1.460	TTTTTTTTTTGTTTTT	1.615
TTTTTTTTTTGG	1.222	TTTTTTTTTGTTTTTT	1.598
TTTTTTTTTGGT	2.728	TTTTTTTTGTTTTTTT	0.921
TTTTTTTTGGTT	0.921	TTTTTTTTTTTTTTGG	1.197
TTTTTTTGGTTT	−0.561	TTTTTTTTTTTTTTGGT	2.703
TTTTTTGGTTTT	0.741	TTTTTTTTTTTTTGGTT	0.866
TTTTTGGTTTTT	2.678	TTTTTTTTTTTTGGTTT	−0.594
TTTTTTTTTTG$\bar{G}$	6.347	TTTTTTTTTTTGGTTTT	0.703
TTTTTTTTTG$\bar{G}$T	12.368	TTTTTTTTTTGGTTTTT	2.523
TTTTTTTTG$\bar{G}$TT	10.297	TTTTTTTTTGGTTTTTT	1.013
TTTTTTTG$\bar{G}$TTT	91.994	TTTTTTTTGGTTTTTTT	−0.398
TTTTTTG$\bar{G}$TTTT	15.414	TTTTTTTTTTTTTTTG$\bar{G}$	6.343
TTTTTG$\bar{G}$TTTTT	12.339	TTTTTTTTTTTTTTG$\bar{G}$T	12.397
		TTTTTTTTTTTTTG$\bar{G}$TT	10.531
		TTTTTTTTTTTTG$\bar{G}$TTT	83.881
		TTTTTTTTTTTG$\bar{G}$TTTT	12.347
		TTTTTTTTTTG$\bar{G}$TTTTT	13.021
		TTTTTTTTTG$\bar{G}$TTTTTT	8.046
		TTTTTTTTG$\bar{G}$TTTTTTT	4.356

than those from electrostatic interactions in these conformers.

A similar tendency was also found in a report by Tai et al.[18] Their conformational analysis of the crystal states of poly(oxytrimethylene) showed that the molecular chain, consisting of the sequence $C\overset{O}{\overset{\diagdown}{\overset{\diagup}{\tau_1}}}\tau_2 C\tau_3\overset{C}{\overset{\diagdown}{\overset{\diagup}{\tau_4}}}C$, was stable when the C-O bonds were trans and the C-C bonds were gauche, namely $(T_2G_2)_2$ helix ($\tau_1=\tau_2\simeq180°$ and $\tau_3=\tau_3\simeq60°$). It emphasized the preference of GG of the $\overset{O}{\diagdown}C\overset{C}{\diagup}\overset{C}{\diagdown}\overset{O}{\diagup}$ bond and coincided with our previous results. The same report also showed that the conformations in the crystal states of poly(thiotrimethylene) about the molecular chain consisted of the sequence $\overset{C}{\diagdown}S\overset{C}{\diagup}\overset{C}{\diagdown}C\overset{C}{\diagup}$. It showed that the lowest energy conformation was the $(G_2T_2)_2$-type helix, though it has not yet been observed. The next lowest energy conformation was the G_4-type of

the actual existence. The following low-energy conformations were T_4 planar zigzag and a $(T_2G_2)_2$ helix. It demonstrated that the conformer which contained the two consecutive gauche in the bond sequence C–C–S–C–C was the most stable. This result is coincident with the present study, though details are somewhat different because of the premises of the molecular state, namely in the crystal state and in a dilute solution. More recently, Matsuura et al.[20] studied the vibrational spectra of the model compound of poly(thiotrimethylene), $CH_3S(CH_2)_3SCH_3$, by a normal coordinate calculation. This study had helped to clarify that the terminal GT+ and GG+ conformations, namely gauche about the CH_3S-CH_2 axis, were more stable than the TT+ and TG+ conformations, namely trans about the same axis (in the liquid state). Our results are contrary to these owing to a different assumption concerning the molecular state (in crystal or liquid against in gaseous or isolated molecule in some solvent). The propriety of our results were examined in terms of the configuration-dependent properties, which are discussed in following sections.

In the case of model compounds which are longer than **6T**, conformers with rotational states of CC-S-CC in the central positions are two consecutive gauche of the same sign ($G^{\pm}G^{\pm}$), are the lowest in energy among the respective conformers; for example, TTTGGTTT of **8T**, TTTTGGTTTT of **10T**, TTTTTTTGGTTT of **12T**, TTTTTTTTTTTGGTTT and TTTTTTTGGTTTTTTT of **16T**. Because these conformers which include two consecutive gauche of same signs, form a helical structure, the steric repulsions between bulky terminal groups are greatly reduced. Therefore, the van der Waals, torsional and electrostatic interaction energies of these conformers are much smaller than those of others. Contrary to this, the conformers which include two successive gauche about CC-S-CC in the terminal position are not so stable; i.e. TTTTGG of **6T** or TTTTTTTTGG of **10T**. It seems that the helix formation with the terminal part of these conformers does not cause a large reduction in the energy since one of the terminal groups is much larger than the previously mentioned conformers. The conformers containing two successive gauche of the opposite signs about CC-S-CC ($G^{\pm}G^{\mp}$) are also lower in energy than other consecutive gauche of the opposite signs with some exceptions.

Geometric and Statistical Weight Parameters of Poly(thiotrimethylene). From the results of molecular mechanics calculations on the model compounds of poly(thiotrimethylene), the geometric parameters obtained by Boltzmann averaged values over each conformer in Table 1 are shown in Table 2. In any case, the bond lengths are stretched and the bond angles are widened from those in a state of equilibrium, i.e. $l_{C\text{-}S}$=1.815 Å, $l_{C\text{-}C}$=1.523 Å, ∠CSC=96.3°, ∠SCC=109.0°, ∠CCC=109.5°. The bond angle of CSC is especially widened. In this study, the dihedral angles are defined as zero when the rotational state of a skeleton is in an ideal trans state. It is clear from Table 2 that the amount of twisting from the original trans position is small; on the other hand, those from gauche are somewhat large. The differences of the geometric parameters among the model compounds are slight.

The statistical-weight parameters of poly(thiotrimethylene) are constructed by two kinds of first-order interactions and six kinds of second-order interactions (Fig. 1). The skeleton of a repeating unit of poly(thiotrimethylene) consists of four kinds of bonds; each bond is distinguished by an alphabetic notation. Namely, σ and σ' are defined for a first-order interaction due to a rotation around the C-C (*b* and *c*) and C-S (*a* and *d*) bond, respectively. When the gauche sequence of the same sign, $G^{\pm}G^{\pm}$, are consecutive, the second-order interaction parameter ϕ is defined for *bc*, ϕ' for *ab* and *cd*, ϕ'' for *da*. For the consecutive gauche sequence of opposite sign, $G^{\pm}G^{\mp}$, ω with a corresponding number of primes are defined in the same way as ϕ.

For each model compound, the conformers listed in

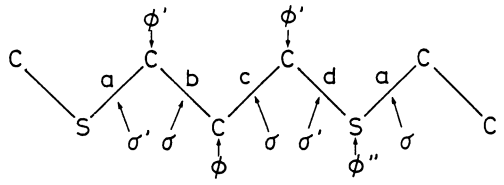

Fig. 1. Alphabetical notation of the skeletal bond and the statistical weight parameters of poly(thiotrimethylene).

Table 2. Geometric Parameters of Poly(thiotrimethylene) Obtained from Various Model Compounds; for Abbreviations of Compounds See Text

Compound	$l_{C\text{-}S}$/Å	$l_{C\text{-}C}$/Å	∠CSC/°	∠SCC/°	∠CCC/°	$\psi_{CC\text{-}SC}$/°		$\psi_{SC\text{-}CC}$/°	
						T	G	T	G
4T	1.829	1.539	101.4	109.9	112.5	−0.1	112.7	2.6	112.8
6T	1.832	1.536	101.6	109.5	111.9	1.0	114.0	1.8	115.0
8T	1.830	1.539	101.3	109.5	111.8	0.3	111.9	1.0	115.0
10T	1.833	1.537	101.2	109.4	111.6	0.2	114.7	0.7	116.0
12T	1.831	1.538	101.2	109.5	111.5	0.0	114.3	0.6	115.4
16T	1.831	1.538	101.0	109.5	111.4	−0.3	114.4	0.3	115.4

Table 1 and include the same first- or second-order interactions are averaged: for example, $E_\sigma+E_{\sigma'}+E_{\phi'}=$ 1.063 kJ mol^{-1} is obtained from TTTTTTGG and TTTTGGTT of **8T**, etc.; then, the obtained simultaneous equations containing eight variables are solved.[10] The obtained statistical-weight parameters are listed in Table 3. Figure 2 shows the variation of E_σ and E_ϕ with no or one prime, and E_ϕ with two primes against the chain length of the model compounds. From Table 3 and Fig. 2, it is clear that the averaged values of first-order interactions, E_σ and $E_{\sigma'}$, assume minima in **8T**; these values increase gradually. This may be caused by a progressive increase of the steric repulsions between bulky substituents when the sole gauche happens to appear in the inner position of the chains. The second-order interaction parameters, E_ϕ, $E_{\phi'}$, and $E_{\phi''}$, decrease with an increase in the chain length with some vibrations. Comparing the first-order interaction energies of poly(oxytrimethylene), i.e. $E_\sigma=-1.67$, $E_{\sigma'}=3.26$ kJ mol^{-1},[13] they are significantly different from those of poly(thiotrimethylene). Even the sequence of E_σ and $E_{\sigma'}$, is reverse. This is due

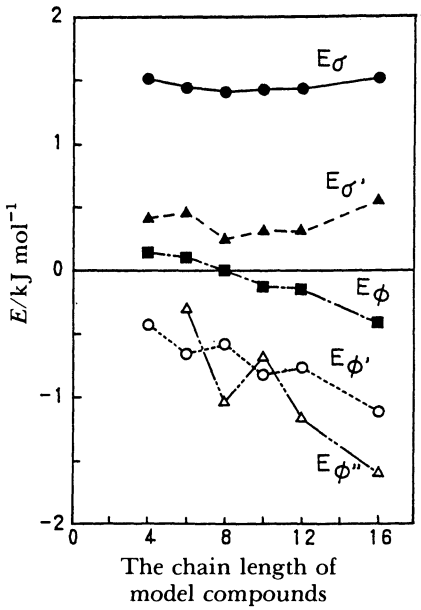

Fig. 2. The variation of statistical weight parameters plotted against the chain length of model compounds of poly(thiotrimethylene).

to the same reason mentioned in the previous section. These results show the characteristic fact that the "sulfur gauche effect" is significantly different from the "oxygen gauche effect." The "oxygen gauche effect" causes gauche states about the central bond of CC-CO to be much lower in energy than trans. Compared with this, the "gauche effect" by a sulfur atom seems to be diminished. The second-order interaction energies of poly(oxytrimethylene), i.e. $E_\phi=1.09$, $E_{\phi'}=-0.63$, $E_{\phi''}=0.46$, $E_\omega=9.87$, $E_{\omega'}=6.65$, and $E_{\omega''}=3.22$ kJ mol^{-1},[13] are also different from those of poly(thiotrimethylene). The second-order interaction energies for $G^\pm G^\pm$ of poly(thiotrimethylene), i.e. E_ϕ, $E_{\phi'}$, and $E_{\phi''}$, are all smaller and almost all have negative values. The small values of the second-order interaction energies are caused by the long bond length of C-S, and the stabilization by the helical structure formation (as mentioned before). These small second-order interaction energies are regarded as a metamorphosed "gauche effect." Namely, although an isolate gauche of poly(thiotrimethylene) is unstable, the conformers which include consecutive gauche states lower the conformation energy. These results are strongly supported by the fact that the crystalline-state configuration of poly(thiotrimethylene) has been reported to be $[G^\pm G^\pm G^\pm G^\pm]$.[36]

Unperturbed Dimensions and Dipole Moment. The characteristic ratios, dipole moment ratios and their temperature coefficients, which are calculated by means of the geometric and statistical weight parameters listed in Tables 2 and 3, are plotted in Figs. 3 and 4 against the chain length of the model compounds. Figure 3 shows the unperturbed dimension and its temperature coefficient of poly(thiotrimethylene) with infinite chain length; i.e. more than 500 in degree of polymerization. Figure 4 shows the dipole moment ratio and its temperature coefficient. The characteristic ratio takes a minimum at **8T**, then increases until **12T** and remains on the same level at **16T**. Although its temperature coefficient also takes a minimum at **8T** and shows a similar tendency, its variation with the chain length is larger than that of the characteristic ratio. Because these configuration-dependent properties have not been observed experimentally, the quality of the calculated results could not be ascertained. The

Table 3. Statistical Weight Parameters of Poly(thiotrimethylene) Obtained from Various Model Compounds; for Notation of Statistical Weight Parameters E_σ, E_ϕ, E_ω with and without Primes, See Text

Compound	E_σ	$E_{\sigma'}$	E_ϕ	E_ω	$E_{\phi'}$	$E_{\omega'}$	$E_{\phi''}$	$E_{\omega''}$
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
4T	1.506	0.406	0.142	9.368	−0.431	8.782	—	—
6T	1.439	0.452	0.150	9.142	−0.657	8.632	−0.305	3.397
8T	1.402	0.243	−0.004	9.406	−0.582	4.222	−1.042	3.050
10T	1.423	0.314	−0.130	9.176	−0.824	76.877	−0.682	3.301
12T	1.427	0.301	−0.151	9.502	−0.766	8.958	−1.163	91.391
16T	1.515	0.548	−0.414	9.681	−1.117	7.255	−1.594	43.024

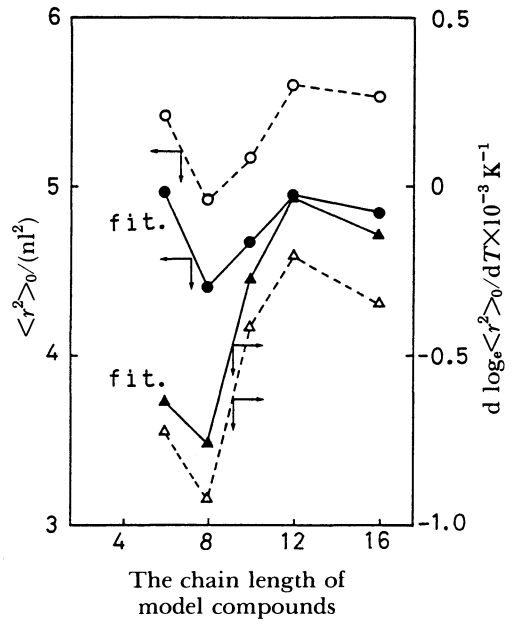

Fig. 3. The dependence of the characteristic ratio and its temperature coefficient of poly(thiotrimethylene) on the chain length of model compounds. Filled circles and filled triangles denote the results after fitting procedure, see text.

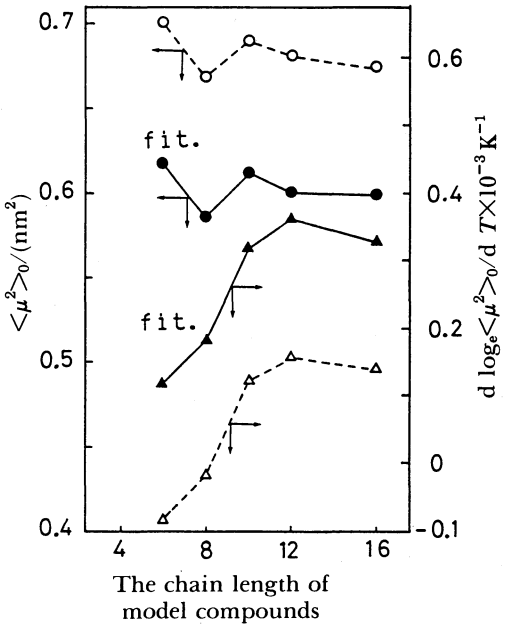

Fig. 4. The dependence of the dipole moment ratio and its temperature coefficient of poly(thiotrimethylene) on the chain length of model compounds. Filled circles and filled triangles denote the results after fitting procedure, see text.

dipole moment ratio becomes minimum at **8T** and increases at **10T**, then slightly decreases with an increase in the chain length to **16T**. Although its temperature coefficient increases from **6T** to **12T**, and remains on the same level at **16T**, the differences between the model compounds from **10T** to **16T** are small. From the variation of configuration-dependent properties with the chain length of model compounds, because these values become almost same at more than **10T** or **12T** and near to observed values, such sizes of molecules seem to be appropriate to the model compound of poly(thiotrimethylene).

In earlier calculations, Guzman et al.[8] obtained $\langle\mu^2\rangle_0/(nm^2)=0.691$ and $d \log_e(\langle\mu^2\rangle_0)/dT=-0.08\times10^{-3}\ K^{-1}$ by means of a three-state approximation and $\langle\mu^2\rangle_0/(nm^2)=0.63$, $d \log_e(\langle\mu^2\rangle_0)/dT=-0.2\times10^{-3}\ K^{-1}$ by means of a five-state approximation. Although the dipole moment ratio $\langle\mu^2\rangle_0/(nm^2)$ calculated by means of the five-state approximation is closer to the observed value, i.e. $\langle\mu^2\rangle_0/(nm^2)=0.598$ (at 20 °C), than that calculated by their three-state approximation, the temperature dependence of the dipole moment by five-state is more different from the observed value ($d \log_e(\langle\mu^2\rangle_0)/dT=1.2\times10^{-3}\ K^{-1}$) than that by their three-state. Their first-order interaction energies are $E_\sigma=0.38$ and $E_{\sigma'}=0.46$ kJ mol^{-1}, which had been derived by Welsh et al.[2] They had concluded that all of the skeletal bonds of poly(thiotrimethylene) should have gauche and trans states of essentially the same energy (within 0.4 kJ mol^{-1}); therefore, this molecule may be an interesting approximation to the "freely-rotating" chain used as a highly idealized reference state in configurational analysis.[2] If this polymer is regarded as an ideal "freely-rotating" chain, the temperature coefficients of square moments should be almost zero because of an equal probability of rotational states about the skeletal bonds. The observed temperature coefficient of the dipole moment is, however, too large to regard this polymer as such a chain. Thus, the discrepancy between the observed and their calculated temperature coefficients (almost zero in their three-state approximation) are large.

In contrast to these results, the values of the dipole moment ratio calculated in this study lies between the value calculated by the earlier three-state approximation and that by the five-state calculation. These calculated ratios agree better than that of the previous three-state. The temperature coefficients calculated by the earlier three- and five-state approximations are different, even in the sign. On the other hand, the calculated values in this study become close to the observed one. Considering that the dipole moments are not experimentally observed in the exact unperturbed state, and comparing the results obtained in this study with those obtained by an earlier three- or five-state approximation, the calculations in this study give much more satisfactory results.

As a trial, the geometric parameters obtained from the model compound **8T** were changed while seeking a parameter set which gives a better agreement with the experimentally observed configuration-dependent properties. The bond angles and the dihedral angles of trans and gauche are changed alone or in combination with them by ±5° or ±10° from the original angles

of Table 2, respectively. When the bond angle of CCS decrease by 5° and the torsional angles of CC-SC with both trans and gauche increase by 10°, the best agreement is obtained. Likewise by adding 5° to the bond angle of CCS and 10° to the torsional angles of the trans and gauche of CC-SC, the dipole moment ratios and the temperature coefficients of each model compound calculated by the new geometric parameters and are also shown in Fig. 4. The characteristic ratio and its temperature coefficient are shown in Fig. 3. The calculated values using revised geometric parameters are denoted by "*fit.*" in Figs. 3 and 4. Although the general tendencies are similar to those obtained by unchanged geometric parameters, the characteristic ratios and dipole moment ratios become small and their temperature coefficients become large. Using the parameters obtained from the model compounds which are longer than **12T**, the calculated dipole moment ratios, i.e. $\langle\mu^2\rangle_0/(\mathrm{nm}^2)=0.612$ at **10T**, 0.600 at **12T** and 0.599 at **16T**, are in fairly good agreement with the observed value of 0.598 at 20 °C and 0.608 at 30 °C. Although the temperature coefficients of the dipole moment, $d\log_e\langle\mu^2\rangle_0/dT=0.32\times10^{-3}\,K^{-1}$ at **10T**, $0.36\times10^{-3}\,K^{-1}$ at **12T**, and $0.33\times10^{-3}\,K^{-1}$ at **16T** are even smaller than the experimentally obtained value of $1.2\times10^{-3}\,K^{-1}$, they are much larger and closer to the experimental value than that previously calculated. It is noteworthy that the statistical weight parameters are left unchanged throughout this rough fitting procedure. In this case, the model compounds of **10T** to **16T** also seems to be suitable; especially the model compound of **12T** gives the best results. The model compound of **10T** includes two thiotrimethylene units with terminal ethyl groups. Model compounds **12T** and **16T** include, respectively, three and four repeating units with terminal methyl groups. Therefore, model compounds of the polymer containing more than three repeating units are available. When model compounds containing two repeating units are used, the larger terminal groups are recommended. From these discussions, it is found that the parameters directly derived from the results of molecular mechanics calculations on the model compounds lead to a good agreement between experimental and calculated configuration-dependent properties. Also, a better agreement is obtained by varying the geometric parameters to fit the calculated configuration-dependent properties to the experimental values. Then, a method combining molecular and statistical mechanics is successful for poly(thioalkylenes), just as is the case for poly(oxyalkylenes).

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