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Conformational Fluctuations of Helical Poly(dialkyl silylene)s in Solution

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ABSTRACT: On the basis of the broken wormlike chain model, the persistence length q of helical polymers is formulated in terms of the internal rotation potential $E(\tilde{\phi})$, probabilities p_P and p_M of the right- and left-handed helical states, the average length $\overline{\langle l \rangle}$ of a helix sequence, and the kink angle $\hat{\theta}_\mathrm{V}$ at the helix reversal. Here, p_P, p_M, and $\overline{\langle l \rangle}$ can be calculated from the free energy difference $2\Delta G_\mathrm{h}$ between the right- and left-handed helical states and the free energy ΔG_r of the helix reversal; $2\Delta G_\mathrm{h}$ can be calculated from $E(\tilde{\phi})$. With assumption of an empirical functional form of $E(\tilde{\phi})$ along with using ΔG_r determined experimentally, q and $2\Delta G_\mathrm{h}$ are calculated for two optically active polysilylenes, poly[*n*-hexyl-(*S*)-3-methylpentylsilylene] (polysilylene **1**) and poly[(*R*)-3,7-dimethyloctyl-(*S*)-3-methylpentylsilylene] (polysilylene **2**), and the results are compared with experimental data obtained in previous work to determine parameters in $E(\tilde{\phi})$ and $\hat{\theta}_\mathrm{V}$. From the $E(\tilde{\phi})$ determined, standard deviations $\langle(\tilde{\phi} - \tilde{\phi}_0)^2\rangle^{1/2}$ of the torsional fluctuation in the dihedral angle $\tilde{\phi}$ are estimated for the two polysilylene chains in solution. The considerably flexible polysilylene **1** has larger $\hat{\theta}_\mathrm{V}$ and $\langle(\tilde{\phi} - \tilde{\phi}_0)^2\rangle^{1/2}$ than the rigid polysilylene **2**. While the chain flexibility of polysilylene **2** is mainly determined by the torsional fluctuation, both kink due to the helix reversal and torsional fluctuation are important in the chain flexibility of polysilylene **1**. The potential $E(\tilde{\phi})$ determined is compared with a result of molecular mechanics. It is shown that the ultraviolet absorption spectrum of polysilylene correlates not to the torsional fluctuation but to the helix reversal (or $\overline{\langle l \rangle}$).

1. Introduction

Polysilylene derivatives have unique and interesting optical, electric, and photochemical properties owing to the σ-conjugation in the silicon backbone chains.[1,2] In addition to these properties, it has been more recently revealed that polysilylenes bearing optically active side chains exhibit remarkable chiroptical properties, which give us the opportunity of their applications to chiral molecular switches or memories.[3,4]

It has been found that optical and chiroptical properties as well as global conformations of optically active polysilylenes strongly depend on their local helical conformations which are determined by chemical structures of side chains attaching to polysilylene chains.[2,5−7] Therefore the investigation of local helical conformations of optically active polysilylenes is a basically important task to understand their various interesting properties. Basic research on helical conformations of optically active polysilylenes in solution has been recently started.[8−12]

In solution, conformations of helical polymers are not usually frozen but dynamically more or less fluctuate with respect to the internal rotation angle and also occasionally change their helical sense via the helix reversal.[13−17] To understand the helical conformation of a polymer in solution, we have to characterize not only the most energetically stable helical conformation but also the torsional fluctuation and the helix reversal. For helical poly(alkyl isocyanate) chains, such characterizations were undertaken by Green and others.[16−20]

The purpose of this study is to characterize the torsional fluctuation and helix reversal of two optically active polysilylenes **1** and **2** (cf. Chart 1), recently studied by Terao et al.[8−10,12] The previous studies demonstrated that the persistence lengths q (or the intrinsic viscosity $[\eta]$)[8,9,12] and the free energy difference $2\Delta G_\mathrm{h}$ between the right- and left-handed helical states[10,12] remarkably depend on the methyl branch position on alkyl side-chains as well as the temperature T. In this study, we have calculated q and $2\Delta G_\mathrm{h}$ from the potential $E(\tilde{\phi})$ of the internal rotation and the kink angle $\hat{\theta}_\mathrm{V}$ at the helix reversal, and we have compared the results with the T dependencies of q (or $[\eta]$) and $2\Delta G_\mathrm{h}$ obtained previously, to determine $E(\tilde{\phi})$ and $\hat{\theta}_\mathrm{V}$ for the two polysilylene chains. This is a novel method of characterizing $E(\tilde{\phi})$ (or the degree of torsional fluctuation) and the helix reversal of helical polymers.

2. Theoretical Section

2.1. Persistence Length of an Intact Helix without Helix Reversals.

Since polysilylene homopolymers consist of a single type of main-chain bonds, the conformation of each repeating unit can be specified by a bond length b, a bond angle θ, and an internal rotation

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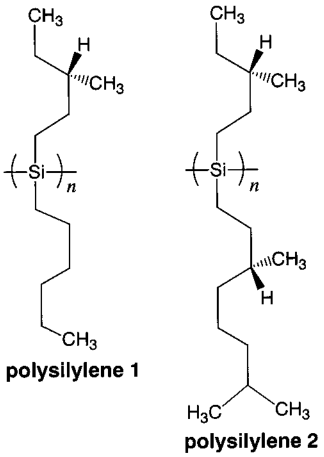
Chart 1



polysilylene 1

polysilylene 2

angle ϕ. Conventionally, ϕ is defined to be zero at the cis conformation, but in what follows, we use the angle $\tilde{\phi} \equiv \phi - \pi$ to express the internal-rotational state of polysilylene chains, because stable conformations of polysilylenes are close to the trans conformation. In this paper, we assume that b and θ are constant and consider only fluctuations of $\tilde{\phi}$.[21] If the polymer chain takes an intact helical conformation without any helix reversals, $\tilde{\phi}$ of each repeating unit fluctuates around a potential-minimum angle $\tilde{\phi}_0$. We assume that the fluctuation of all $\tilde{\phi}$ takes place independently. The characteristic ratio for such polysilylene chains at sufficiently high degree of polymerization can be written as[22]

$$C_\infty = \left(\frac{1+\cos\hat{\theta}}{1-\cos\hat{\theta}}\right)\frac{(1+\langle\cos\tilde{\phi}\rangle)^2+\langle\sin\tilde{\phi}\rangle^2}{1-\langle\cos\tilde{\phi}\rangle^2-\langle\sin\tilde{\phi}\rangle^2} \tag{1}$$

where $\hat{\theta} \equiv \pi - \theta$ and $\langle\cdots\rangle$ represents the thermal average over the fluctuation of $\tilde{\phi}$.

On the other hand, C_∞ is written in terms of the wormlike chain model as[22,23]

$$C_\infty = \frac{2q_0 h}{b^2} \tag{2}$$

where q_0 is the persistence length of the intact helix and h is the helix pitch per the repeating unit. The pitch h of a helical polymer can be calculated by eq A5 in the Appendix. Combining eqs 1 and 2, we have

$$q_0 = \frac{b^2}{2h}\left(\frac{1+\cos\hat{\theta}}{1-\cos\hat{\theta}}\right)\frac{(1+\langle\cos\tilde{\phi}\rangle)^2+\langle\sin\tilde{\phi}\rangle^2}{1-\langle\cos\tilde{\phi}\rangle^2-\langle\sin\tilde{\phi}\rangle^2} \tag{3}$$

If there is no fluctuation in $\tilde{\phi}$, $\langle\cos\tilde{\phi}\rangle^2 + \langle\sin\tilde{\phi}\rangle^2$ is equal to unity so that q_0 becomes infinity. The fluctuation of $\tilde{\phi}$ reduces q_0 to a finite value.

2.2. Inclusion of the Effect of Helix Reversals. If a helical polymer chain has helix reversals, the reversal points may cause kinks and the chain may not be regarded as a *regular* wormlike chain. In 1986, Mansfield[15] proposed the broken wormlike chain (BWC) model, which may be suitable to describe helical polymer chains with helix reversals. If right- and left-handed helical portions possess different stiffnesses, the BWC can be defined as a continuous limit of a freely rotating chain with three different types of bond angles, corresponding to the right-handed helix, left-handed helix, and helix reversal states. The resulting (effective) persistence length q of the BWC is given by[24]

$$\frac{1}{q} = \frac{p_{\mathrm{P}}}{q_{0,\mathrm{P}}} + \frac{p_{\mathrm{M}}}{q_{0,\mathrm{M}}} + \frac{1-\cos\hat{\theta}_{\mathrm{V}}}{\overline{\langle l\rangle}} \tag{4}$$

where $q_{0,\mathrm{P}}$ and $q_{0,\mathrm{M}}$ are persistence lengths of intact right- and left-handed helix portions in the BWC given by eq 3, p_{P} and p_{M} are probabilities of appearing the right- and left-handed helical states in the BWC, $\hat{\theta}_{\mathrm{V}}$ is the kink angle at the helix reversal, and $\overline{\langle l\rangle}$ is the arithmetic mean of average lengths of a right-handed helix sequence and a left-handed helix sequence on an infinitely long chain. The quantity $\overline{\langle l\rangle}$ is sometimes referred to as the "helical persistence length" in the literature, but it should be distinguished from q, because the contribution of the third term on the right-hand side of eq 4 is often minor.[17]

Mansfield[15] demonstrated that the mean-square end-to-end distance and radius of gyration of the BWC are identical with those of the original wormlike chain with the persistence length being equal to q given by eq 4, and the difference appears in the fourth and higher moments of the end-to-end distance R. Employing the Koyama distribution function for R, Mansfield calculated the mean reciprocal end-to-end distance $\langle R^{-1}\rangle$ of the BWC as a function of q, the contour length L, and the parameter δ defined by

$$\delta \equiv \frac{q}{2\overline{\langle l\rangle}}(1-\cos\hat{\theta}_{\mathrm{V}})^2 \tag{5}$$

The parameter δ is equal to $|(\lambda_2 - \lambda_1)/\lambda_1|$ in the original paper, and at $\delta = 0$, the kink contribution disappears in the BWC. According to his result, if $\delta = 0.3$, $\langle R^{-1}\rangle$ of the BWC is equal to that of the original wormlike chain within 3.5% error for any q and L. Thus we can expect that the intrinsic viscosity and hydrodynamic radius of the BWC, which are calculated from the mean reciprocal distance between two contour points on the BWC, are indistinguishable from those of the regular wormlike chain, if δ is small enough. Dilute solution properties of helical polymers have been so far analyzed in terms of the regular wormlike chain model to obtain q,[8,9,11,12,25-27] and the resulting q may be identified with that of the BWC in most of cases.

The average helical-sequence length $\overline{\langle l\rangle}$ as well as the probabilities p_{P} and p_{M} in eq 4 can be calculated by Lifson et al.'s theory.[17] This statistical mechanical theory describes the helical conformation of a polymer chain in terms of three free energies (per mole of repeating units) of the right- and the left-handed helical conformations and of the reversal conformation. If one chooses the average free energies of the right- and left-handed helical conformations as the reference free energy, the free energies of the three states are written as $-\Delta G_{\mathrm{h}}$, $+\Delta G_{\mathrm{h}}$, and ΔG_{r}, respectively, and $\overline{\langle l\rangle}$ is given by

$$\overline{\langle l\rangle} = h\frac{[\sinh^2(\Delta G_{\mathrm{h}}/RT) + \exp(-2\Delta G_{\mathrm{r}}/RT)]^{1/2}}{\exp(-2\Delta G_{\mathrm{r}}/RT)} \tag{6}$$

where RT is the gas constant multiplied by the absolute temperature. The probabilities p_{P} and p_{M} are given as functions of ΔG_{h}, ΔG_{r}, T, and the degree of polymerization N_0. Values of ΔG_h and ΔG_r can be determined by comparison between circular dichroism or optical rotation data in dilute solution and Lifson et al.'s theory.

2.3. Potential of the Internal Rotation. If a polysilylene chain bears bulky side chains, the trans conformation may cause steric hindrance between side chains attaching to the second nearest silicon atoms along the main chain, which makes the trans conformation unstable, as in the case of poly(tetrafluoroethylene).[28] Similarly, the gauche conformation may be excluded, because steric hindrance between side chains and monomer units attaching to the second-nearest main-chain silicon atoms. As a result, the potential $E(\tilde{\phi})$ of the internal rotation of the polysilylene chain (per mole of repeating units) becomes a double-well type, so that the chain takes a right- or left-handed helical conformation.

Recently, Fujiki et al.[3,7] obtained double-well potentials for some optically active polysilylenes by molecular mechanical calculations. Referring to their results, we express $E(\tilde{\phi})$ for polysilylenes with bulky side chains by the following empirical function[29]

$$E(\tilde{\phi}) = E_T - C + Ce^{-(\tilde{\phi}_0/\beta)^2}(\tilde{\phi}/\beta)^2 + Ce^{-(\tilde{\phi}/\beta)^2} \qquad (7)$$

where

$$C \equiv \frac{E_T - E_0}{1 - [1 + (\tilde{\phi}_0/\beta)^2]e^{-(\tilde{\phi}_0/\beta)^2}}$$

and E_T and E_0 are potential energies at $\tilde{\phi} = 0$ (the trans conformation) and $\tilde{\phi}_0$ (the potential-minimum angle), respectively, and β is a parameter relating the steepness of the well. For optically active polysilylenes, the mirror image of the right-handed helix is not energetically identical with the left-handed helix due to chiral pendant groups. This dissymmetry can be expressed by eq 7, if different values of E_0, $\tilde{\phi}_0$, and β are used at $\tilde{\phi} > 0$ and < 0. In what follows, E_0, $\tilde{\phi}_0$, and β at $\tilde{\phi} < 0$ are denoted as $E_{0,P}$, $\tilde{\phi}_{0,P}$, and β_P, those at $\tilde{\phi} > 0$ as $E_{0,M}$, $\tilde{\phi}_{0,M}$, and β_M, and helices with the negative and positive $\tilde{\phi}$ are referred to as the P-helix and M-helix, respectively. When the average of $E_{0,P}$ and $E_{0,M}$ is chosen as the reference energy, $E_{0,P}$ is equal to $-E_{0,M}$.

Using $E(\tilde{\phi})$ given by eq 7, statistical weights of the P- and M-helices are written as

$$u_P = \int_{-\pi}^{0} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi},$$
$$u_M = \int_{0}^{\pi} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi} \qquad (8)$$

and the free energy difference $2\Delta G_h$ between the M- and P-helices are given by

$$\frac{u_M}{u_P} = \exp(-2\Delta G_h/RT) \qquad (9)$$

On the other hand, the persistence length q is calculated from $E(\tilde{\phi})$ given by eq 7 through eqs 3 and 4, where the averages $\langle\cos \tilde{\phi}\rangle$ and $\langle\sin \tilde{\phi}\rangle$ for the P-helix are given by

$$\langle\cos \tilde{\phi}\rangle_P = \frac{1}{u_P}\int_{-\pi}^{0} \cos \tilde{\phi} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi},$$
$$\langle\sin \tilde{\phi}\rangle_P = \frac{1}{u_P}\int_{-\pi}^{0} \sin \tilde{\phi} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi} \qquad (10a)$$

and those for the M-helix by

$$\langle\cos \tilde{\phi}\rangle_M = \frac{1}{u_M}\int_{0}^{\pi} \cos \tilde{\phi} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi},$$
$$\langle\sin \tilde{\phi}\rangle_M = \frac{1}{u_M}\int_{0}^{\pi} \sin \tilde{\phi} \exp[-E(\tilde{\phi})/RT]d\tilde{\phi} \qquad (10b)$$

Furthermore, standard deviations of the torsional fluctuation in the P- and M-helices are calculated by

$$\langle(\tilde{\phi} - \tilde{\phi}_0)^2\rangle_P^{1/2} = \left\{\frac{1}{u_P}\int_{-\pi}^{0} (\tilde{\phi} - \tilde{\phi}_0)^2 \exp[-E(\tilde{\phi})/RT]d\tilde{\phi}\right\}^{1/2} \qquad (11a)$$

$$\langle(\tilde{\phi} - \tilde{\phi}_0)^2\rangle_M^{1/2} = \left\{\frac{1}{u_M}\int_{0}^{\pi} (\tilde{\phi} - \tilde{\phi}_0)^2 \exp[-E(\tilde{\phi})/RT]d\tilde{\phi}\right\}^{1/2} \qquad (11b)$$

3. Results and Discussion

Throughout the following discussion about polysilylene chains, we adopt standard values for the Si−Si bond length b (= 0.235 nm) and the Si−Si−Si bond angle θ (=111°).[2] At present, there is no decisive value for the most stable internal rotation angle $\tilde{\phi}_0$ for the polysilylene chain in solution. If the most stable conformation of polysilylene chains is identical with the 7/3 helix proposed for poly[(di-*n*-butyl)silylene] and poly[(di-*n*-pentyl)silylene] in the crystalline state,[1,30] $|\tilde{\phi}_0|$ is calculated to be 31.3° from the condition that ρ given by eq A4 in the Appendix is equal to $6\pi/7$. On the other hand, recent molecular mechanical calculations of polysilylene chains gave us slightly smaller values (20°) for $|\tilde{\phi}_0|$.[3,7] These two values of $|\tilde{\phi}_0|$, however, provide almost identical helix pitch h per repeating unit (=0.19 nm, calculated by eq A5 in the Appendix), which is consistent with h obtained from previous intrinsic viscosity analyses for polysilylenes **1** and **2**.[9,12] We assume $|\tilde{\phi}_0|$ to be 20° in the following discussion, but numerical results shown below are approximately the same even if estimated from the 7/3 helix model.

For some polysilylenes, right- and left-handed helices exhibit the circular dichroism (CD) at slightly different wavelengths,[31] which indicates that pitches of the right- and left-handed helices are not identical for such polysilylenes. However, CD peaks of polysilylenes **1**[10] and **2**[7,12] in solution is essentially unaltered with changing the right- and left-handed helical population, so that we assume that $\tilde{\phi}_{0,M} = -\tilde{\phi}_{0,P}$ in the following discussion.

The relation between signs of circular dichroism (CD) and stable internal rotation angle $\tilde{\phi}_0$ has not been established yet. In previous experimental papers,[7,10,12] polysilylene chains exhibiting positive CD were tentatively assigned as the P-helix, and we obey this assignment in the following.

3.1. Polysilylene 1. Figure 1 shows experimental results of $2\Delta G_h/RT$ (unfilled circles) and $\Delta G_r/RT$ (filled circles) for polysilylene **1** in isooctane, which were recently estimated by Terao et al.[10] from CD (or the *g*-factor) data. The free energy difference between the M- and P-helical states per monomer unit is much lower than the thermal energy, but large ΔG_r amplifies the difference to provide measurable CD signal. It turns out from the temperature T dependence of $2\Delta G_h/RT$ that the enthalpic contribution ($2\Delta H_h/RT = 0.029$) is much larger than the entropic contribution ($2T\Delta S_h/RT = -0.001$) at −25 °C for this polysilylene. Figure 2 shows

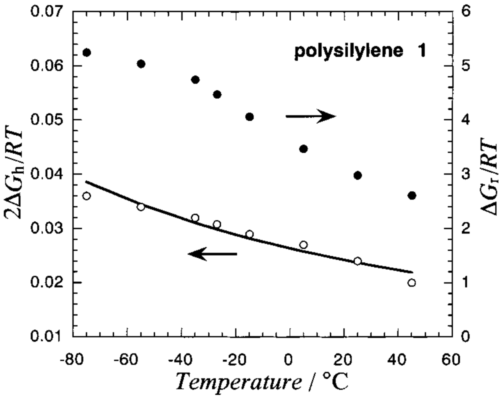


Figure 1. Temperature dependencies of $2\Delta G_h/RT$ and $\Delta G_r/RT$ for polysilylene **1** in isooctane.[10] Solid curve, $2\Delta G_h/RT$ calculated by eqs 8 and 9.

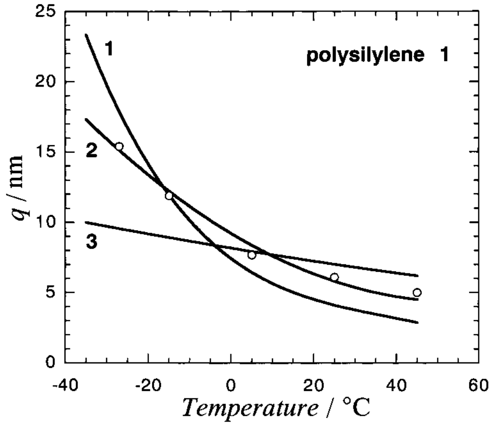


Figure 2. Temperature dependence of the persistence length q for polysilylene **1** in isooctane.[10] Key: solid curves, q calculated by eqs 3, 4, 6, and 10; curve 1, with $E_T = 4$ kJ/mol, $E_{0,M} = 37.5$ J/mol, $\beta_M = 13.2°$, $\beta_P = 13.165°$, and $\hat{\theta}_V = 80°$; curve 2, with $E_T = 4$ kJ/mol, $E_{0,M} = 37.5$ J/mol, $\beta_M = 11.3°$, $\beta_P = 11.28°$, and $\hat{\theta}_V = 55°$; curve 3, with $E_T = 4$ kJ/mol, $E_{0,M} = 37.5$ J/mol, $\beta_M = 9.87°$, $\beta_P = 9.86°$, and $\hat{\theta}_V = 30°$.

experimental T dependence of the persistence length q for polysilylene **1** in isooctane by circles, determined by Terao et al.[9] from intrinsic viscosity and radius of gyration data. Although q is rather small at a room temperature, its T dependence is so strong that polysilylene **1** becomes a semiflexible polymer at low T.

As explained in section 2, ΔG_h and q can be calculated from the potential $E(\tilde{\phi})$ of the internal rotation and the kink angle $\hat{\theta}_V$ at the helix reversal. The potential $E(\tilde{\phi})$ given by eq 7 contains four adjustable parameters, E_T, $E_{0,P}$ ($= -E_{0,M}$), β_P, and β_M, and eq 4 of q contains one more unknown parameter, $\hat{\theta}_V$; $\langle l \rangle$ can be calculated from eq 6 using ΔG_h estimated by eq 9 and experimental ΔG_r.[32] Thus we have totally five adjustable parameters to calculate $2\Delta G_h$ and q. The magnitude and T dependence of ΔG_h are mainly determined by $E_{0,P}$ and the difference $\beta_M - \beta_P$. On the other hand, the magnitude and T dependence of q are predominantly affected by β_P (or β_M) and $\hat{\theta}_V$. Both ΔG_h and q depend on E_T only weakly. Therefore, if E_T is rather arbitrarily chosen, the remaining parameters can be determined by fitting theoretical results to experimental ΔG_h and q shown in Figures 1 and 2.

Solid curves in Figures 1 and 2 indicate theoretical values of $2\Delta G_h/RT$ and q calculated with E_T chosen to be 4 kJ/mol and three different sets of $E_{0,P}$, β_P, β_M, and $\hat{\theta}_V$; integrations including in eqs 8 and 10 were made numerically. The three different parameter sets provide almost identical values of $2\Delta G_h/RT$ indicated by the solid curve in Figure 1 but different T dependence of q indicated by the three solid curves in Figure 2. The curve for $\hat{\theta}_V = 55°$ most closely fits the data of q. When choosing different values of E_T, we have to slightly change the remaining parameters to fit the theory to the experiment. The fitting results are summarized in Table 1; all the parameter sets provide the fitting as good as those shown in Figures 1 and 2. The parameter δ calculated by eq 5 using the fitting parameters is listed in the sixth column of the table. The small value of δ guarantees the identification of q of the broken and regular wormlike chain models. Values of $E_{0,P}$ and $\hat{\theta}_V$ determined are almost independent of choice of E_T, but the potential steepness parameter β_P or β_M slightly decreases with increasing E_T.

If repeating units along the polymer chain directly transform from one sense to the opposite sense of helical conformation at the helix reversal, without passing through any intermediate conformations (the *two-state approximation*), we may calculate $\hat{\theta}_V$ from the geometrical consideration, as explained in the Appendix. For polysilylene chains, this approximation gives us $\hat{\theta}_V$ to be 11° from eq A9. This result is not consistent with the above estimate for polysilylene **1**. This implies that the polysilylene **1** chain takes some intermediate conformation at the helix reversal. Lifson et al.[18] demonstrated by an empirical force field calculation for polyisocyanates that two or three repeating units in the vicinity of the helix reversal of a polyisocyanate chain take some intermediate conformations other than the right- nor left-handed helical conformations. (For polysilylene chains, such a force field calculation has not been performed yet.)

Standard deviations of $\tilde{\phi}$ due to the torsional fluctuation in the P- and M-helical portions of the polysilylene **1** chain can be calculated by eq 11. The results at two different T are also listed in Table 1, which slightly depend on the choice of E_T but the uncertainties are not so large. Even with the considerable chain flexibility of polysilylene **1**, the average fluctuation of $\tilde{\phi}$ is less than 20° below 45 °C. It is noted that differences in the torsional fluctuation as well as the potential minimum between the P- and M-helical states ($2E_{0,M} = 70-80$ J/mol) are small, indicating a weak chiral interaction among optically active side chains in the polysilylene **1** chain.

Figure 3 shows the ratio of q to the average $\overline{q_0}$ of $q_{0,P}$ and $q_{0,M}$, where $\overline{q_0} \equiv [(p_P/q_{0,P}) + (p_M/q_{0,M})]^{-1}$, calculated with the internal potential parameters determined. At low T, $q/\overline{q_0}$ for polysilylene **1** is large and the chain flexibility is mainly determined by the torsional fluctuation of the internal rotation. On the other hand, the ratio decreases with increasing T, demonstrating that the kink due to the helix reversal plays an important role in the chain flexibility.

3.2. Polysilylene 2. This polysilylene is known to undergo a thermal helix-sense inversion at 3 °C.[7] Figure 4 shows $2\Delta G_h/RT$ and $\Delta G_r/RT$ for this polysilylene in isooctane determined by Teramoto et al.[12] from CD (or the g-factor) data. The T dependence of $2\Delta G_h/RT$ for polysilylene **2** is stronger than that for polysilylene **1**. From this dependence, both enthalpic and entropic contributions ($2\Delta H_h/RT$ and $2T\Delta S_h/RT$) are estimated to be ca. 0.20 at the inversion temperature for this polysilylene.

Table 1. Parameters of the Internal Rotation Potential $E(\tilde{\phi})$ and Standard Deviations of the Torsional Fluctuation for Polysilylene 1[a]

						$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_M^{1/2}$		$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_P^{1/2}$	
E_T/J mol^{-1}	$E_{0,M}$/J mol^{-1}	β_M/deg	β_P/deg	$\hat{\theta}_V$/deg	δ[b]	−35 °C	45 °C	−35 °C	45 °C
2000	40	13.5	13.395	55	≤0.157	14.4	16.9	14.3	16.8
4000	37.5	11.3	11.28	55	≤0.156	15.3	18.1	15.2	18.0
6000	37	10.4	10.397	55	≤0.155	16.0	19.0	15.9	18.9
8000	36	9.9	9.901	55	≤0.156	16.4	19.4	16.3	19.3
10000	36	9.55	9.553	55	≤0.156	16.8	19.9	16.7	19.8

[a] Assuming that b (the bond length) = 0.235 nm, θ (the bond angle) = 111°, and $|\tilde{\phi}_0|$ (the most stable internal rotation angle) = 20°. [b] Below 45 °C.

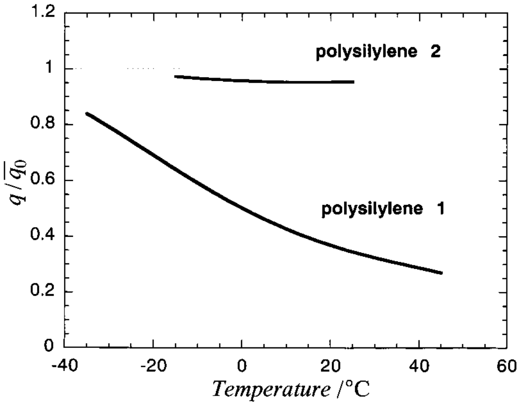


Figure 3. Ratio of q to $\overline{q_0} \equiv [(p_P/q_{0,P}) + (p_M/q_{0,M})]^{-1}$ for polysilylenes **1** and **2**.

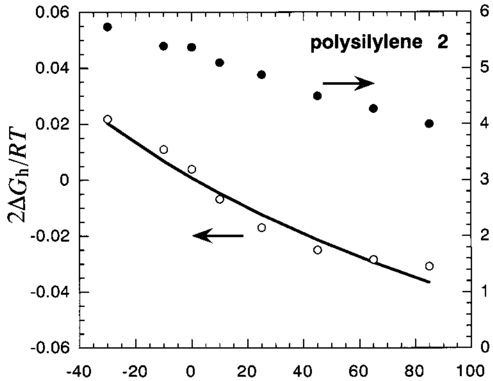


Figure 4. Temperature dependencies of $2\Delta G_h/RT$ and $\Delta G_r/RT$ for polysilylene **2** in isooctane.[12] Solid curve: $2\Delta G_h/RT$ calculated by eqs 8 and 9.

Teramoto et al.[12] analyzed the molecular weight dependence of the intrinsic viscosity $[\eta]$ for polysilylene **2** in isooctane at 25 °C by the theory of Yamakawa, Fujii, and Yoshizaki[33,34] (the YFY theory) for the wormlike cylinder model to estimate q = 103 nm, the molar mass per unit contour length M_L = 1270 nm^{-1}, and the diameter d = 3.0 nm at 25 °C. They did not estimate q at different T, but measured $[\eta]$ for one polysilylene **2** sample with a high molecular weight of 9.14 × 10^5 as a function of T. As shown in Figure 5, $[\eta]$ of this sample in isooctane decreases monotonically with T and exhibits no significant singularity at the inversion temperature 3 °C.

As mentioned in section 3.1, ΔG_h and q can be calculated as functions of T, if the five parameters, E_T, $E_{0,P}$, β_P, β_M, and $\hat{\theta}_V$, are given. Using q calculated, the T dependence of $[\eta]$ at the molecular weight of 9.14 × 10^5 can be obtained using the YFY theory if M_L and d are assumed to be independent of T. Solid curves in Figures 4 and 5 indicate $2\Delta G_h/RT$ and $[\eta]$ calculated in such a way with three different parameter sets at E_T fixed to be 8 kJ/mol. The parameter sets provide almost identical values of $2\Delta G_h/RT$ indicated by the solid curve in Figure 4 but a different T dependence of $[\eta]$ indicated by the three solid curves in Figure 5. Although not shown, the fitting at $\hat{\theta}_V$ = 0° was as good as the curve for $\hat{\theta}_V$ = 10°. Thus, we determine $\hat{\theta}_V$ to be equal to or less than 10° for polysilylene **2**, which is much smaller than $\hat{\theta}_V$ for polysilylene **1**. The fit with different E_T provides parameter sets listed in Table 2.[35] When choosing E_T less than 6 kJ/mol, we could not fit the $2\Delta G_h/RT$ and $[\eta]$ data simultaneously. As listed in the sixth column, the value of δ calculated by eq 5 using the fitting parameters is so small that $[\eta]$ of the broken and regular wormlike chain models with the same q are indistinguishable.

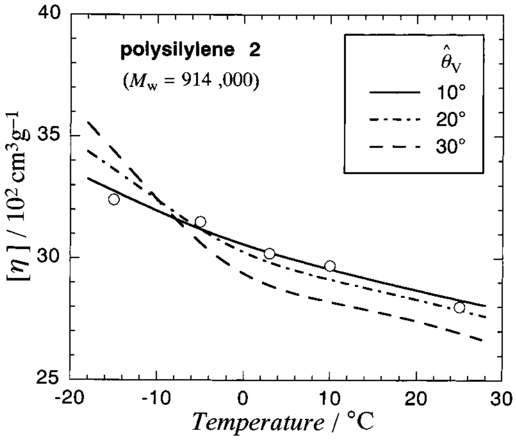


Figure 5. Temperature dependence of the persistence length q for polysilylene **2** in isooctane.[12] Curves: q calculated by eqs 3, 4, 6, and 10; solid curve, with E_T = 8 kJ/mol, $E_{0,M}$ = 170 J/mol, β_M = 14.9°, β_P = 17.93°, and $\hat{\theta}_V$ = 10°; dot−dash curve, with E_T = 8 kJ/mol, $E_{0,M}$ = 180 J/mol, β_M = 16.2°, β_P = 21.45°,and $\hat{\theta}_V$ = 20°; dashed curve, with E_T = 8 kJ/mol, $E_{0,M}$ = 190 J/mol, β_M = 21.4°, β_P = 200°, and $\hat{\theta}_V$ = 30°.

For polysilylene chains, the two-state approximation gives us $\hat{\theta}_V$ to be 11°, which is consistent with the above estimate for polysilylene **2**. This implies that the chain of polysilylene **2** may directly transform from the right- to left-handed helices, without passing through any intermediate conformation at the helix reversal for this polysilylene, unlike polysilylene **1**. However, this conjecture must be confirmed, for example, by a force field calculation, as made for polyisocyanate chains.[18,36]

Standard deviations of the torsional fluctuation in the P- and M-helical portions of the polysilylene **2** chain, calculated by eq 11 for two different T are listed in Table 2. The degree of the torsional fluctuation is considerably reduced in the polysilylene **2** chain in comparison with that in the polysilylene **1** chain (cf. Table 1). Moreover the difference in the degree of fluctuation in the M- and P-helix portions is much larger in the polysilylene **2**

Table 2. Parameters of the Internal Rotation Potential $E(\tilde{\phi})$ and Standard Deviations of the Torsional Fluctuation for Polysilylene 2[a]

E_T/J mol^{-1}	$E_{0,M}$/J mol^{-1}	β_M/deg	β_P/deg	$\hat{\theta}_V$/deg	δ^b	$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_M{}^{1/2}$ −15 °C	$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_M{}^{1/2}$ 25 °C	$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_P{}^{1/2}$ −15 °C	$\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_P{}^{1/2}$ 25 °C
8000	170	14.9	17.93	10	$\leq 3.5 \times 10^{-4}$	6.04	6.58	5.26	5.74
10000	169	13.15	14.8	10	$\leq 3.4 \times 10^{-4}$	6.18	6.77	5.18	5.66
15000	168	11.52	12.44	10	$\leq 3.4 \times 10^{-4}$	6.45	7.09	5.24	5.73
20000	167	10.78	11.47	10	$\leq 3.4 \times 10^{-4}$	6.62	7.30	5.35	5.87

[a] Assuming that b (the bond length) = 0.235 nm, θ (the bond angle) = 111°, and $|\tilde{\phi}_0|$ (the most stable internal rotation angle) = 20°. [b] Below 25 °C.

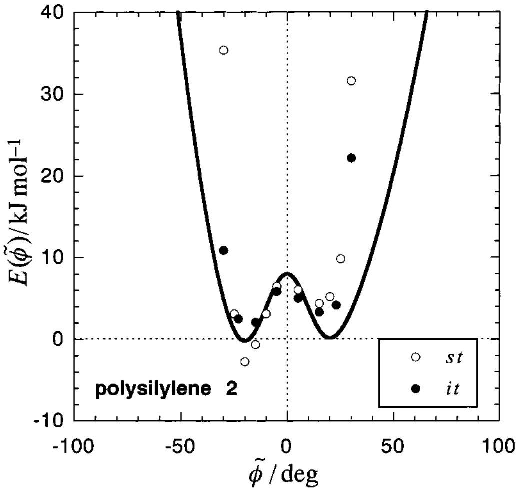


Figure 6. Comparison of the internal rotation potential given by eq 7 with parameters listed on the first line in Table 2 (solid curve) with the result of the molecular mechanics[7] (unfilled circles for the syndiotactic polymer and filled circles for the isotactic polymer).

chain than in the polysilylene **1** chain. The difference in the potential minimum between the P- and M-helical states ($2E_{0,M}$ = 330−340 J/mol) is also larger in the polysilylene **2** than in the polysilylene **1**. These results indicate that the (R)-3,7-dimethyloctyl side-chain attaching to polysilylene **2** not only severely restricts the internal rotation but also enhances the dissymmetry between the P- and M-helices.

As shown in Figure 3, q is almost equal to $\overline{q_0}$ for polysilylene **2**, demonstrating that the kink due to the helix reversal little contributes to the chain flexibility for this polymer unlike for the more flexible polysilylene **1**. This comes from long $\overline{\langle l\rangle}$ and small $\hat{\theta}_V$ for this polysilylene. The minor contribution of the helix reversal to q was also indicated for polyisocyanates theoretically[17] and by viscosity and light scattering experiment.[37]

Recently, Fujiki et al.[7] calculated the internal rotation potential $E(\tilde{\phi})$ for polysilylene **2** by molecular mechanics. Figure 6 compares their result for polysilylene **2** (unfilled circles for the syndiotactic polymer and filled circles for the isotactic polymer)[7] with our potential function with the parameters determined above at E_T fixed to be 8 kJ/mol (solid curve). The molecular mechanics provides slightly steeper potential well and also larger difference ($2E_{0,P}$) in the potential minimum between the P- and M-helical states than $E(\tilde{\phi})$ determined above. Since the standard deviation of $\tilde{\phi}$ for polysilylene **2** is only a few degrees, the disagreement of $E(\tilde{\phi})$ in the high energy region may not so important in calculations of ΔG_h and q. However, ΔG_h and q are so sensitively dependent on $2E_{0,P}$, that the molecular mechanics cannot properly predict the thermal inversion of CD or the side-chain dependence of the global conformation of optically active polysilylenes.

4. Concluding Remarks

The fluctuation of the helical polymer conformation in solution is characterized by the torsional fluctuation of the internal rotation angle and by the helix reversal. We have estimated the degree of the torsional fluctuation and the kink angle at the helix reversal for two optically active polysilylenes **1** and **2**, from temperature T dependencies of the persistence length (or the intrinsic viscosity) and the free energy difference between the right- and left-handed helical states. The two kinds of the conformational fluctuation contribute to various molecular properties in different ways. For example, the chain flexibility of polysilylene **1** is mainly affected by the torsional fluctuation at low temperatures but by the helix reversal at high temperatures.

Fujiki[5] found that the maximum ϵ_{max} and the half-width fwhm of ultraviolet (UV) absorption spectra of various polysilylenes closely correlate to their chain stiffness (or the Mark−Houwink−Sakurada exponent). Now we ask ourselves whether the UV absorption spectrum is directly related to the torsional fluctuation or to the helix reversal.

The torsional fluctuation and the helix reversal may be characterized in terms of the arithmetic mean of the standard deviation $\overline{\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle^{1/2}}$ [$\equiv(\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_M{}^{1/2}+\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle_P{}^{1/2})/2$] and the average helical-sequence length $\overline{\langle l\rangle}$, respectively. Figure 7a shows T dependencies of both quantities for polysilylenes **1** and **2**, which are calculated from eqs 6 and 11 using parameters determined in sections 3.1 and 3.2. The T dependence of $\overline{\langle l\rangle}$ is much stronger than that of $\overline{\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle^{1/2}}$ for both polysilylenes.

On the other hand, T dependencies of ϵ_{max} and fwhm for polysilylenes **1**[10] and **2**[12] at sufficiently high molecular weights are shown in Figure 7b. Both quantities strongly depend on T. When those ϵ_{max} and fwhm are plotted against $\overline{\langle l\rangle}$, data points almost follow a universal curve, as shown in Figure 8. Since we could not obtain a composite curve when plotting ϵ_{max} and fwhm for polysilylenes **1** and **2** at different T against $\overline{\langle(\tilde{\phi}-\tilde{\phi}_0)^2\rangle^{1/2}}$, although not shown here, we may say that not the torsional fluctuation but the helix reversal directly affects the UV absorption of polysilylene chains.

Abe[38] demonstrated by a quantum mechanical calculation that in conjugated polymeric systems, the fluctuation in the interatomic distance (or the quantum lattice fluctuation) makes the absorption spectrum broader. Hasegawa et al.,[6] on the other hand, showed both experimentally and theoretically that absorption spectra of polysilylene depend on the backbone helical conformation. From those results, we may expect the

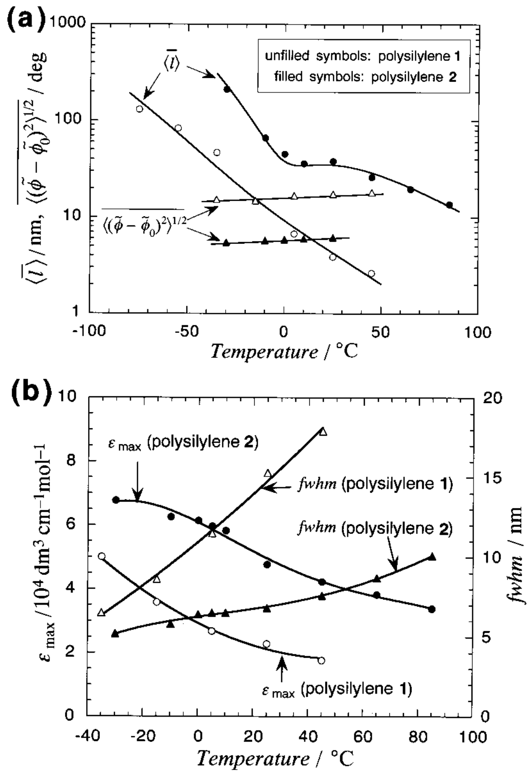


Figure 7. Temperature dependencies of (a) the average helical-sequence length $\langle \overline{l} \rangle$ and the average standard deviation of the torsional angle $\overline{\langle(\tilde\phi-\tilde\phi_0)^2\rangle^{1/2}}$ for polysilylenes **1** (at E_T = 4000 J/mol) and **2** (at E_T = 8000 J/mol) and (b) the maximum $\epsilon_{\max}$ and the half-width fwhm of UV absorption spectra polysilylenes **1**[10] and **2**[12] at sufficiently high molecular weight.

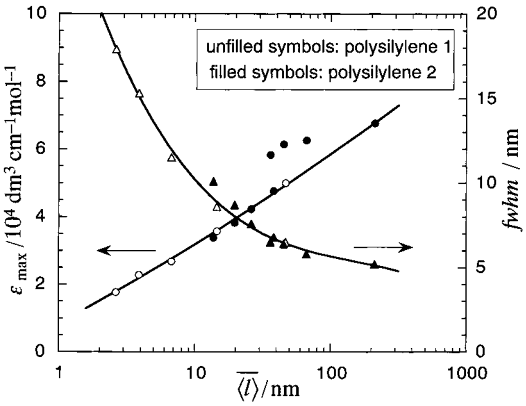


Figure 8. Plots of the maximum $\epsilon_{\max}$ and the half-width fwhm of UV absorption spectra[10,12] against $\langle \overline{l} \rangle$ for sufficiently high molecular weight samples of polysilylenes **1** and **2**.

UV spectra of polysilylene chains to depend on the fluctuation in the internal rotation angle, though such a dependence has not been demonstrated theoretically yet. This dependence must play a key role in the interrelation between the global conformation and optical-electronic properties of polysilylenes.

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Appendix. Geometrical Consideration of Helical Polymers

Let us assume that each repeating unit in the polymer chain consists of a single type of the main-chain bond, and the rotational angle ϕ around the bond can take only two values, ϕ_M and ϕ_P ($=-\phi_M$), corresponding to the left-handed (M) and right-handed (P) helical states, respectively (the *two-state approximation*). The direction of the helix axis can be defined by three sequential bonds taking the same helical sense.[18,39] When the first three bonds $\mathbf{b}^{(1)}$, $\mathbf{b}^{(2)}$, and $\mathbf{b}^{(3)}$ form the M helix, we can write the three bonds as

$$\mathbf{b}^{(1)} = \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \; \mathbf{b}^{(2)} = \mathbf{T}_M \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \; \mathbf{b}^{(2)} = {\mathbf{T}_M}^2 \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \qquad \text{(A1)}$$

where b is the bond length and $\mathbf{T}_M$ is the transformation matrix defined by

$$\mathbf{T}_M \equiv \begin{bmatrix} -\cos\tilde\phi_M \cos\hat\theta & \sin\tilde\phi_M & \cos\tilde\phi_M \sin\hat\theta \\ -\sin\tilde\phi_M \cos\hat\theta & -\cos\tilde\phi_M & \sin\tilde\phi_M \sin\hat\theta \\ \sin\hat\theta & 0 & \cos\hat\theta \end{bmatrix} \qquad \text{(A2)}$$

with the bond angle θ ($\hat\theta \equiv \theta - \pi$; $\tilde\phi_M \equiv \pi - \phi_M$). Using the three bond vectors, we can construct a unit vector $\mathbf{h}^{(1)}$ in the direction of the M helix axis by

$$\mathbf{h}^{(1)} = \frac{(\mathbf{b}^{(2)} - \mathbf{b}^{(1)}) \times (\mathbf{b}^{(3)} - \mathbf{b}^{(2)})}{|\mathbf{b}^{(2)} - \mathbf{b}^{(1)}|\,|\mathbf{b}^{(3)} - \mathbf{b}^{(2)}|\sin\rho} \qquad \text{(A3)}$$

where ρ is the rotational angle about the helix axis from one repeating unit to the next given by

$$\cos\rho = \frac{(\mathbf{b}^{(2)} - \mathbf{b}^{(1)})\cdot(\mathbf{b}^{(3)} - \mathbf{b}^{(2)})}{|\mathbf{b}^{(2)} - \mathbf{b}^{(1)}|\,|\mathbf{b}^{(3)} - \mathbf{b}^{(2)}|} \qquad \text{(A4)}$$

The pitch h per repeating unit is calculated by

$$h = \mathbf{h}\cdot\mathbf{b}^{(1)} = \mathbf{h}\cdot\mathbf{b}^{(2)} = \mathbf{h}\cdot\mathbf{b}^{(3)} \qquad \text{(A5)}$$

When the next fourth to sixth bonds along the chain form the P helix, we can write

$$\mathbf{b}^{(4)} = \mathbf{T}_P{\mathbf{T}_M}^2 \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \; \mathbf{b}^{(5)} = {\mathbf{T}_P}^2{\mathbf{T}_M}^2 \begin{bmatrix} 0 \\ 0 \\ b \end{bmatrix} \; \mathbf{b}^{(6)} = {\mathbf{T}_P}^3{\mathbf{T}_M}^2 \begin{bmatrix} 0 \\ 0 \\ b \end{bmatrix} \qquad \text{(A6)}$$

where

$$\mathbf{T}_P \equiv \begin{bmatrix} -\cos\tilde\phi_P \cos\hat\theta & \sin\tilde\phi_P & \cos\tilde\phi_P \sin\hat\theta \\ -\sin\tilde\phi_P \cos\hat\theta & -\cos\tilde\phi_P & \sin\tilde\phi_P \sin\hat\theta \\ \sin\hat\theta & 0 & \cos\hat\theta \end{bmatrix} \qquad \text{(A7)}$$

Just like above, the unit vector $\mathbf{h}^{(4)}$ in the direction of the P helix axis connected with the M helix is given by

$$\mathbf{h}^{(4)} = \frac{(\mathbf{b}^{(5)} - \mathbf{b}^{(4)}) \times (\mathbf{b}^{(6)} - \mathbf{b}^{(5)})}{|\mathbf{b}^{(5)} - \mathbf{b}^{(4)}||\mathbf{b}^{(6)} - \mathbf{b}^{(5)}|\sin\rho} \qquad \text{(A8)}$$

The kink angle $\hat\theta_V$ in the two-state approximation is calculated from

$$\hat\theta_V = \cos^{-1}(-\mathbf{h}^{(1)}\cdot\mathbf{h}^{(4)}) \qquad \text{(A9)}$$

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