Conformational Transitions in Poly{*n*-hexyl-[(S)-3-methylpentyl]silylene} in Dilute Solution: Temperature and Molecular-Weight Dependence Detected by Circular Dichroism

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ABSTRACT: Ten narrow-distribution samples of poly{*n*-hexyl-[(S)-3-methylpentyl] silylene} (PH3MPS) ranging in weight-average molecular weight from 3.1×10^3 to 8.7×10^5 in isooctane, *n*-hexane, and methylcyclohexane were studied by circular dichroism and ultra violet absorption over a wide temperature range (from −75 to 85°C). To follow the conformational transition, Kuhn's dissymmetry factor g_{abs} as a measure of helicity was determined as a function of molecular weight and temperature from the ratio of circular dichroism to absorbency. The molecular-weight dependence of g_{abs} was analyzed by a statistical mechanical theory based on a conformational picture of an alternating sequence of right-handed and left-handed helices intervened by helix reversals. The free energy of the helix reversal was much smaller than those for polyisocyanates investigated previously [poly((R)-1-deuterio-*n*-hexyl isocyanate) and poly((R)-2-deuterio-*n*-hexyl isocyanate)] at the same temperatures although its solutions showed large circular dichroism. Therefore, it was shown that the correlation lengths of the helix for this polymer were much shorter than the polyisocyanates at the same temperature. Thus, the helix reversal is the dominant molecular process in the conformational properties of PH3MPS.

Heading: Poly{*n*-hexyl-[(S)-3-methylpentyl]silylene} in Dilute Solution

Introduction

Polysilylenes have a characteristic absorption-bands in the near-ultraviolet (UV) due to the σ-conjugation of the Si−Si backbone.[1-3] Therefore, it is expected that the cotton effects of the circular dichroism (CD) due to this conjugation may be observed for polysilylenes whose main-chains have helicity imbalanced to be right- or left-handed. Indeed, as reported by Fujiki et al.,[4-14] solutions of polysilylenes with chiroptical side groups show CD due to the excess screw-sense of the helical structure of the main chain. They have concluded that these polysilylenes have a mixture of helical senses, which change reversibly with solvent and temperature. Among the polymers studied, polydialkylsilylenes with non-racemic chiral side chains are suitable for investigating their helical structure because no absorption band exist except that due to their main chains in the wavelength range of the near UV.

A quantitative theory of the optical activity (specific rotation, circular dichroism) as a function of the absolute temperature T and the degree of polymerization N of the polymer was derived based on a simple statistical mechanical model.[15-17] The model assumes that each monomer unit can exist in either of three conformations: a right-handed helix(M), a left-handed helix(P), or a helical reversal (R) from one helical sense to the other. Indeed, it has been shown that this theory explains quantitatively the molecular-weight dependence of the optical rotation for polyisocyanates having chiral side chains.[16-19] Since the strength of the CD is a quantity related to optical rotation directly, the CD behavior for polysilylene solutions may be analyzed by this theory.

Recently, we studied two polysilylenes, poly{*n*-hexyl-[(S)-3-methylpentyl]silylene} (PH3MPS) and poly{*n*-hexyl-[(S)-2-methylbutyl]silylene} (PH2MBS) shown in Figure 1, to determine their global conformations in dilute solution from dimensional and hydrodynamic properties.[20,21] We found that the main-chain conformation of PH2MBS in isooctane is nearly rodlike (the persistence length q = 85 nm at 20°C) but that of PH3MPS in the same solvent is semiflexible (q = 6.1 nm at 25°C). In fact, the values of q for PH3MPS increase remarkably with falling temperature (q = 5.0 nm at 45°C and 11.9 nm at −15°C). This large difference in q between the two polysilylenes may be related to the helical structure, i.e., the intrinsic rigidity and the number of helix breaks in one molecule. In this study, we conducted CD and UV measurements for a number of polysilylene samples of different molecular weights in a wide temperature range. This paper presents such data and shows that they are well analyzed in terms of the statistical mechanical theory constructed by Teramoto[17] to elucidate the molecular mechanism behind the helical sense properties, yielding the important statistical mechanical parameters for the helical structure.

[Figure 1]

Experimental Section

Samples. The previously investigated PH3MPS samples[20,21] with known weight-average molecular weight M_w or viscosity-average molecular weight M_v were used for the present study. Most of these samples were previously analyzed for molecular weight distribution by sedimentation equilibrium or gel permeation chromatography (GPC). Their molecular weight distributions were found to be reasonably narrow with the *z*-average molecular weight to M_w ratios M_z/M_w being in the range between 1.0_3 and 1.1_7.[21]

A fractionated sample PD1 of poly{*n*-decyl-[(S)-2-methylbutyl]silylene} (PD2MBS) was also chosen for this study and its M_w was estimated to be ca. 1.2×10^6 from GPC with the calibration curve constructed with the known M_w's for the PH2MBS samples investigated previously.[20] The global conformation of PD2MBS was estimated to be nearly rodlike from their viscosity index for tetrahydrofuran solutions,[6,7] and the detail information, for example its persistence length in isooctane, will be reported in our forthcoming publication.[22] The value of M_z/M_w for this sample was estimated to be 1.2 from the GPC.

UV-Absorption and Circular Dichroism (CD) Measurements. UV-absorption and CD measurements for 10 samples (F12, F32, ..., F72, O1, ..., O4) in isooctane, F43 (M_v = 10.7×10^4)[21] in *n*-hexane, and F61 ($M_v = 9.6 \times 10^4$)[21] in methylcyclohexane at the temperatures between −75 and 85°C were made on a JASCO J700 Circular Dichroism Spectropolarimeter using a quartz cell of 0.5-cm path length at wavelengths of the incident light between 260 and 360 nm. The solutions with concentrations whose absorbency at the peak became between 0.8 and 1.5 were prepared for this study. In order to avoid the degradation of PH3MPS by near-UV light, different solutions were used at each temperature. It was confirmed with UV-absorption and CD that PH3MPS did not degrade during the above measurements.

The UV absorption and CD spectra are expressed in terms of the extinction coefficient ε and the difference $\Delta\varepsilon$ of ε between left and right circularly polarized light, respectively, both in units of (Si-repeat-unit)$^{-1}$ dm^3 cm^{-1}. The solution density is approximated by the solvent density ρ_0. The values of ρ_0 for isooctane at temperatures between 0 and 45°C were determined using an

Anton Paar DMA 5000 density meter and expressed accurately as $\rho_0 = 0.70819 - 8.25 \times 10^{-4}(T - 273.15)$ g cm^{-3}. Polymer concentrations were evaluated from the weight fractions of the polymer and using this equation.

These two measurements were also made for isooctane solutions of the sample PD1 to estimate the standard strength of CD for perfectly one-side-handed helical polysilylene; note that this polymer whose chemical structure shown in Figure 1 was used instead of PH2MBS because phase separation was observed for dilute PH2MBS solutions at lower temperatures. Both PD1 and PH3MPS were completely soluble in isooctane down to −85°C.

Results

Isooctane Solutions. Figure 2 compares the CD (panel A) and UV (panel B) absorption spectra of indicated PH3MPS samples at −75°C. The CD profiles for high M_w samples F12, F32, and F42 overlap each other on the almost same curves, but the spectra for the lower molecular weight samples become smaller and broader with decreasing M_w. A similar trend is seen for the UV spectra as shown in Figure 2B, but the change is more gentle than that of the CD spectra. There were no thermal-history and time dependence in the CD and UV spectra for our PH3MPS samples in isooctane.

[Figure 2]

We determined the wavelength λ_{max} of the peak, full width *fwhm* at half maximum, and the peak height ε_{max} from the UV-spectra evaluated. The N_w dependence of these values in isooctane at 25 and −75°C are shown in Figure 3; N_w is the weight-average number of Si atoms per molecule defined by $N_w \equiv M_w / M_0$, where M_0 is molecular weight of an Si-unit, that is M_0 = 198.4 for PH3MPS. It is seen that these values are independent of N_w in the range of $N_w >$ 300. The same trend is seen at all temperatures studied. The asymptotic values of λ_{max}, *fwhm*, and ε_{max} at large N_w ($N_w > 500$) are shown in Figure 4. The shape of the UV-spectrum becomes broader with rising temperature, but the λ_{max} is almost independent of temperature. This finding suggests that the statistical average of the torsion angles of Si-Si-Si-Si of PH3MPS does not change much with temperature, but the fluctuation around the average changes the spectrum shape.[1−3]

[Figure 3] [Figure 4]

It is seen in Figure 2 that the CD and UV spectra for a given sample at the same temperature are similar in shape. Therefore, the Kuhn dissymmetry ratio g_{abs} defined as $g_{abs} \equiv \Delta\varepsilon / \varepsilon$ can be determined accurately from the ratio of their peak areas. The values of g_{abs} obtained for the PH3MPS samples in isooctane are summarized in Table 1 along with those of N_w determined from light scattering and/or sedimentation equilibrium reported in our previous paper.[21] These values will be used instead of the $\Delta\varepsilon$ values to quantitatively characterize the right- and left-handed helical populations of optically active polysilylenes.[5,14]

Figure 5 shows the temperature dependence of g_{abs} for the PH3MPS samples (circles). The triangles in this figure show the data for the sample PD1 of PD2MBS in the same solvent. The value of g_{abs} for PD1 increases with lowering temperature above –40°C and come to an asymptotic value of $2.6_7 \times 10^{-4}$ at lower temperatures. This result suggests that the conformation of PD2MBS in isooctane below –40°C is fixed to a single helical sense. The data for four PH3MPS samples of $N_w > 500$ approach the PD1 curve at low temperatures; those for (F12 ~ F52) are almost indistinguishable each other, and fitted by a smooth curve which drops sharply at temperatures between –30 and 20°C, and levels off without crossing 0 at high temperatures. The temperature dependence of g_{abs} for the samples of $N_w < 200$ become gentle with decreasing N_w. Figure 6 illustrates the molecular weight dependence of g_{abs} for PH3MPS samples at temperatures between –75°C and 45°C. It is seen that g_{abs} tends to approach an asymptotic value at high N_w but decreases with decreasing N_w for $N_w < 200$ at all the temperatures investigated. It is noted however that it changes remarkably with temperature even for the lowest N_w of 15.5, and is not zero even at 45°C.

[Figure 5] [Figure 6]

Solvent Dependence for Circular Dichroism. The results of the CD measurements for the sample F43 in *n*-hexane and F61 in methylcyclohexane are summarized in Table 2 along with their N_v values ($N_v \equiv M_v / M_0$). Figure 7 shows the temperature dependence of the g_{abs} values for these two solutions with the data for the samples F52 and F62 in isooctane. F52 has an N_w value, that is larger than those for F43 and F61, and the N_w value of F62 is smaller than those for these two samples as shown in Table 1. The data points for the three solvents are seen to follow the solid curve, and g_{abs} is the same for the same N_w irrespective of solvents. This finding suggests that the helical structure of PH3MPS is not affected by this solvent difference.

[Figure 7]

Discussion

Analysis of g_{abs} Data for PH3MPS in Isooctane. As described in the previous section, it seems that the main-chain of PH3MPS in solution has a helical conformation with both left and right-handedness because the values of λ_{max} are almost independent of temperature while the g_{abs} values decrease as temperature increases. We introduce the statistical mechanical theory for the helix reversal model which considers that the local conformation of a helical molecule consists of the following three units, i. e., a large number n_P of P-helix units, a small number n_M of M-helix units, and a much smaller number n_V of helix reversal units *v*.

(1) Theoretical Background of the Statistical Mechanical Theory. The partition function of the chain based on this model is calculated for homopolymer with *N* monomeric units by the matrix method as[17]

$$Z_N = \begin{pmatrix} u_M & u_P \end{pmatrix} \begin{pmatrix} u_M & vu_P \\ vu_M & u_P \end{pmatrix}^{N-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{1}$$

This expression is exact if the end segments do not have a special screw sense. Here, u_M, u_P, and v are functions of only absolute temperature T in the given solvent, which may be related to the two independent free energy functions ΔG_h and ΔG_r as follows:

$$\begin{aligned} u_M &= \exp[-\Delta G_h / RT] \\ u_P &= u_M^{-1} \\ v &= \exp[-\Delta G_r / RT] \end{aligned} \tag{2}$$

where R is the gas constant. $2\Delta G_h$ is defined by $2\Delta G_h \equiv G_M - G_P$, where G_M and G_P are the free energies of Si units in the left handed and right handed helices, respectively. On the other hand, ΔG_r is the free energy of the reversal unit measured from $(1/2)(G_M+G_P)$.

The average number n_X in the molecule is given by

$$n_X = \frac{\partial(\ln Z_N)}{\partial(\ln u_X)} \tag{3}$$

In our case X may be M or P. In a similar way the average number n_V of helix reversals in the molecule is calculated from

$$n_{\mathrm{V}} = \frac{\partial(\ln Z_N)}{\partial(\ln v)} \tag{4}$$

Numerical solutions of eqs 3 and 4 with eqs 1 and 2 can be calculated directly by computer or using the analytical equations reported by Teramoto.[17] The approximate solution for n_{M} (or n_{P}) derived by Lifson et al.[15] is correct only for large N and small $\Delta G_{\mathrm{h}}/\Delta G_{\mathrm{r}}$; but the difference between these two solutions is marginal to our analysis of the data for PH3MPS in isooctane.

(2) Comparison of Theory and Experiment. We assumed that a PH3MPS chain consists of three parts or conformers P, M, and V. However, the UV spectra show only one species. This is reconciled if the right-handed and left-handed helical conformers are nearly of the same energies but symmetric, and a helix reversal is a junction between the two kinds of conformers. Therefore $N = n_{\mathrm{P}} + n_{\mathrm{M}}$ and the optical activity is proportional to $n_{\mathrm{P}} - n_{\mathrm{M}}$. These theoretical values can be related to the experimental values as

$$\frac{n_{\mathrm{P}} - n_{\mathrm{M}}}{n_{\mathrm{P}} + n_{\mathrm{M}}} = \frac{g_{\mathrm{abs}}}{g_{\mathrm{m}}} \tag{5}$$

where g_{m} is the g_{abs} when all monomeric units have only one-side helical sense.

According to eq 5, g_{abs} is expressed as a known function of N with the three parameters g_{m}, ΔG_{h}, and ΔG_{r}, which are independent of N under a given solvent condition. If the validity of the theory is verified by comparing eq 5 with experimental g_{abs} vs N relationship, then it is possible to determine the values of the parameters involved under the specified condition. The first parameter g_{m} can be estimated from the discussion in the Results section to be $g_{\mathrm{m}} = 2.6_7 \times 10^{-4}$.

Trial-and-error procedures were repeated with the data in Figure 6 at each temperature until the difference between experimental and theoretical values were minimized, and the resulting values of $2\Delta G_{\mathrm{h}}$ and ΔG_{r} were taken as optimal. The parameters estimated for PH3MPS in isooctane at temperatures between –75 and 45°C are summarized in Table 3. The solid curves in Figure 6 show the theoretical values calculated by eq 5 for the parameter values shown in this table. It can be seen that the curves closely fit the data points for PH3MPS in isooctane at the respective temperatures, thus validating the theory for this system.

Temperature Dependence of ΔG_{h} and ΔG_{r}. Figure 8 illustrates the plots of $2\Delta G_{\mathrm{h}}/RT$ and $\Delta G_{\mathrm{r}}/RT$ against temperature for PH3MPS in isooctane. It is seen that the values of $2\Delta G_{\mathrm{h}}/RT$ and $\Delta G_{\mathrm{r}}/RT$ change significantly within the range of T investigated for either solvent and are represented by

$$\Delta G_{\mathrm{h}} / RT = 0.0135 - 6.5\times10^{-5}(T - 273.15) \tag{6}$$

$$\Delta G_{\mathrm{r}} / RT = 3.7 - 0.028(T - 273.15) + 1\times10^{-6}(T - 273.15)^3 \tag{7}$$

The solid lines illustrated in Figure 8 represent the values calculated by these equations. Figure 9 shows that the theoretical solid curves calculated with eqs from 5 to 7 for the indicated PH3MPS samples closely fit the data points over the entire temperature range studied; note that the data for the three lower molecular weight samples are compared with the theoretical values for couples of N encompassing their N_{w}.

[Figure 8] [Figure 9]

Previously, optical rotation data of polyisocyanates were analyzed by the statistical mechanical theory as described in the Introduction section.[15-19] Figure 10 compare our free energy data evaluated in this work and the previous data for poly((R)-1-deuterio-*n*-hexyl isocyanate) (αPdHIC) and poly((R)-2-deuterio-*n*-hexyl isocyanate) (βPdHIC) in various solvents. The absolute values of ΔG_h for PH3MPS illustrated with circles in panel A of this figure are much larger than those for polyisocyanates. On the other hand, the values of ΔG_r illustrated in Figure 10B are smaller than those for the polyisocyanates at the same temperature. Thus we see that ΔG_r is of primary importance for PH3MPS in the conformational transitions whereas ΔG_h is more important for polyisocyanates. In other words, the helix reversal is the major molecular process in the transition for PH3MPS. It is emphasized that these conformational characteristics are disclosed only by invoking the molecular-weight dependence of quantities related to the helical structure.

[Figure 10]

Correlation Length. According to eq 4, the values of n_v can be calculated easily when two energies of ΔG_h and ΔG_r are given. The correlation number of helices $N_{C,X}$ (X = M or P) at large number of N is calculated by

$$N_{C,X} = \frac{2n_X}{n_v} \qquad (N >> 1) \tag{8}$$

Figure 11 shows $N_{C,X}$ calculated in this manner for PH3MPS compared with those for the polyisocyanates; circles, $N_{C,X}$ calculated using the free energy functions in Table 3 and solid curves, by eqs 6 and 7. The values of $N_{C,X}$ become much larger with decreasing temperature and exceed 1000 at –75°C. It is tempting to consider that this change is due to the chain stiffness. In fact, the values of q for PH3MPS in isooctane are 11.9, 7.7, 6.1, and 5.0 nm at –15, 5, 25, and 45°C, respectively. However, a quantitative comparison between the helix structure and the global conformation is difficult because several parameters, for example the angle between adjoining helices, could not be determined by our experimental results to allow calculation of the global conformation from the free energy functions of the helix. The data for αPdHIC and βPdHIC both in *n*-hexane are plotted in the same figure as the triangles and squares, respectively. It is seen that compared at the same temperature the correlation length for these polymers are much longer than PH3MPS. This is because the helix reversal is less frequent in the polyisocyanates than in PH3MPS.

[Figure 11]

Conclusions We have determined the Kuhn dissymmetry factor g_{abs} as a function of temperature and weight-average number of Si atoms for poly{*n*-hexyl-[(S)-3-methylpentyl]silylene} (PH3MPS) in isooctane. Analyses of the data obtained in terms of the statistical mechanical theory gave the free energies ΔG_h and ΔG_r for the difference between the two helices and the helix reversal, respectively, as functions of temperature. The values of ΔG_h and ΔG_r are much smaller and larger, respectively, than those for polyisocyanates investigated with the same method previously at the same temperature. These parameters suggest that the number of helix breaks in much larger in PH3MPS than in polyisocyanates and increases with rising temperature. Thus the helix reversal is the dominant molecular process in the helical sense properties of PH3MPS.

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Table 1. Results of Circular Dichroism for the PH3MPS Samples in Isooctane

Sample	N_w[a]	g_{abs} / 10^{-4}								
		−75°C	−55°C	−35°C	−15°C	5°C	25°C	45°C	65°C	85°C
F12	4400	2.6_0	2.5_0	2.3_0	1.6_5	1.0_3	0.7_0	0.3_5	−	−
F32	2570	2.6_0	2.5_5	2.3_5	1.6_5	1.1_0	0.6_4	0.3_8	0.2_5	0.2_0
F42	1290	2.5_8	2.4_5	2.3_0	1.6_8	1.0_3	0.5_9	0.3_3	−	−
F52	635	2.5_0	2.4_0	2.2_5	1.7_0	1.0_2	0.6_3	0.4_0	−	−
F62	333	2.4_0	2.3_5	2.2_0	1.6_5	1.0_0	0.6_5	0.4_0	−	−
F72	185	2.3_5	2.3_0	2.1_0	1.5_5	1.0_0	0.5_8	0.3_5	−	−
O1	103	2.2_0	2.1_0	1.9_0	1.4_0	0.9_0	0.4_9	0.3_0	−	−
O2	55.4	1.6_0	1.7_0	1.5_5	1.2_5	0.7_7	0.4_4	0.3_0	−	−
O3	34.5	1.4_0	1.3_5	1.2_0	0.9_0	0.7_0	0.4_0	0.2_5	−	−
O4	15.5	0.7_0	0.7_0	0.7_5	0.6_0	0.4_5	0.3_0	0.2_0	−	−

[a] Determined by the equation $N_w = M_w / M_0$ from the M_w values were reported in ref. 21.

Table 2. Results of Circular Dichroism for the PH3MPS Samples in Different Solvents

Sample	Solvent	N_v[b]	g_{abs} / 10^{-4}						
			−75°C	−55°C	−35°C	−15°C	5°C	25°C	45°C
F43	*n*-hexane	539	2.6_0	2.5_5	2.2_5	1.7_5	1.2_0	0.5_5	0.5_0
F61	MCH[a]	484	−	2.4_0	−	1.7_0	1.1_5	−	−

[a] Methylcyclohexane, [b] $N_v = M_v / M_0$: the M_v values were reported in ref. 21.

Table 3. Free Energy Parameters for PH3MPS in Isooctane at Various Temperatures

Temperature	$2\Delta G_h$ / $10^{-2}RT$	$\Delta G_r / RT$
−75°C	3.6	5.2_5
−55°C	3.4	5.0_4
−35°C	3.2	4.7_5
−15°C	2.9	4.0_6
5°C	2.7	3.4_7
25°C	2.4	2.9_8
45°C	2.0	2.6_1

Figure Captions.

Figure 1. Chemical structures of PH3MPS **1**, PH2MBS **2**, and PD2MBS **3**.

Figure 2. CD (panel A) and UV absorption (panel B) spectra for the indicated PH3MPS samples in isooctane at −75°C.

Figure 3. N_w dependence of the UV-spectra for PH3MPS in isooctane at 25°C (unfilled circles) and −75°C (filled circles). (A) wavelength of the peak λ_{max}, (B) width at the half height *fwhm*, and (C) the maximum of the peak ε_{max}.

Figure 4. Temperature dependence of the UV-spectra for PH3MPS with infinite large molecular weight. Circles, $\varepsilon_{max,\infty}$; triangles, $fwhm_{\infty}$; squares, $\lambda_{max,\infty}$.

Figure 5. Temperature dependence of g_{abs} for the indicated PH3MPS samples (unfilled and filled circles) and the sample PD1 of PD2MBS (triangle) in isooctane.

Figure 6. Plots of g_{abs} vs N_w for PH3MPS in isooctane at the indicated temperatures. Solid lines, theoretical values calculated from eq 5 with the parameter shown in Table 3.

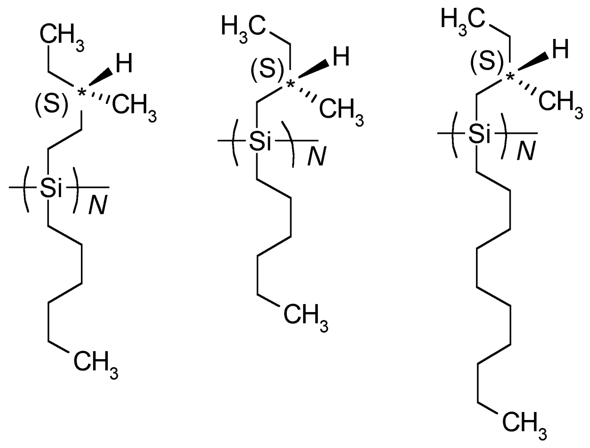
Figure 7. Temperature dependence of g_{abs} for F43 in *n*-hexane (unfilled circles), for F61 in methylcyclohexane (unfilled triangles), and F52 and F62 in isooctane (filled circles).

Figure 8. Temperature dependence of $2\Delta G_h / RT$ and $\Delta G_r / RT$. Solid curves for $\Delta G_h / RT$ and $\Delta G_r / RT$ represent calculated values of eqs 6 and 7, respectively.

Figure 9. Comparison between the measured g_{abs} (circles) for indicated PH3MPS samples in isooctane and the theoretical curves calculated by eqs 5, 6, and 7 for N shown on the left side of each curve. For clarity, the ordinate values of g_{abs}, are shifted by A in the parenthesis.

Figure 10. Comparison of $2\Delta G_h / RT$ (panel A) and $\Delta G_r / RT$ (panel B) among PH3MPS (unfilled circles), αPdHIC (filled marks), and βPdHIC (unfilled marks without circles). The different symbols refer to different solvents, i.e., circles, triangles, squares, and pentagons to isooctane, n-hexane, 1-chlorobutane, dichloromethane, respectively.

Figure 11. Temperature dependence of the correlation length for PH3MPS in isooctane (circles), αPdHIC in *n*-hexane (triangles), and βPdHIC in *n*-hexane (squares), and unfilled and filled symbols for P and M helices, respectively.



1 **2** **3**

Figure 1. Terao et al.

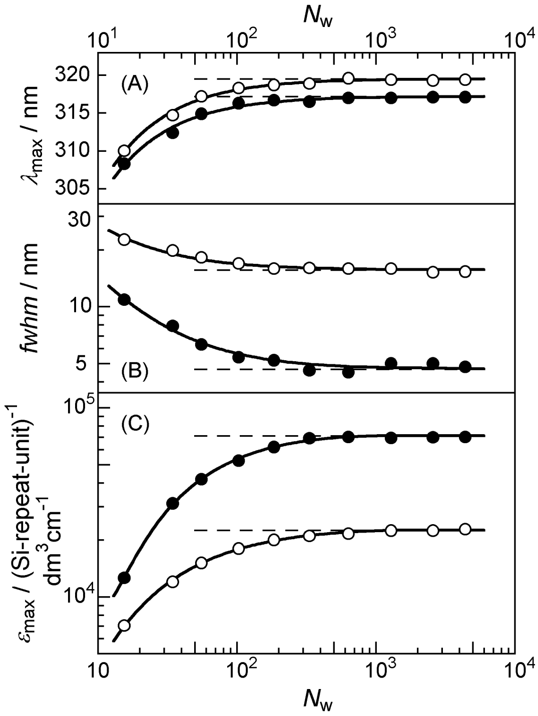
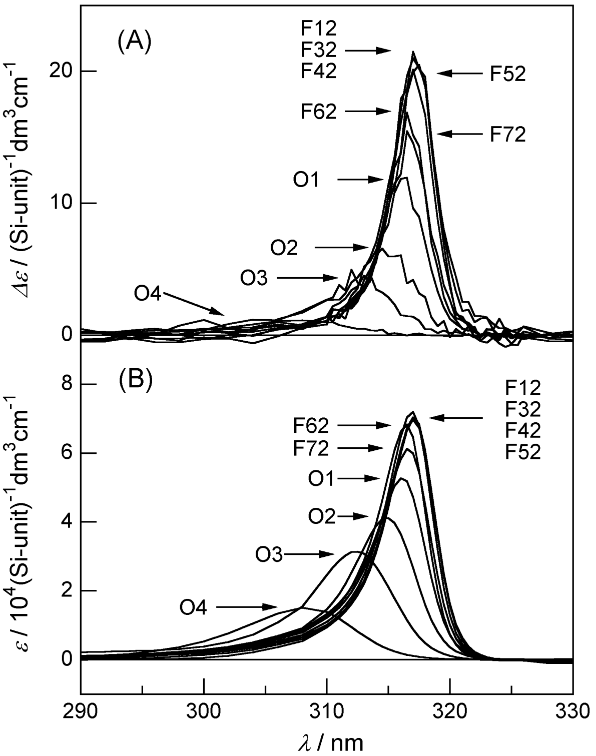


Figure 3. Terao et al.



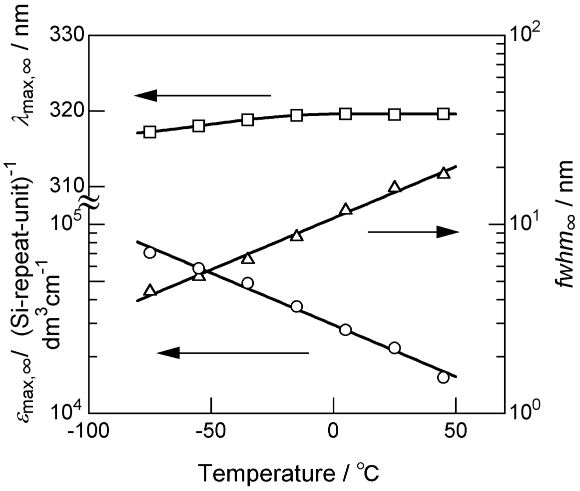


Figure 4. Terao et al.

Figure 2. Terao et al.

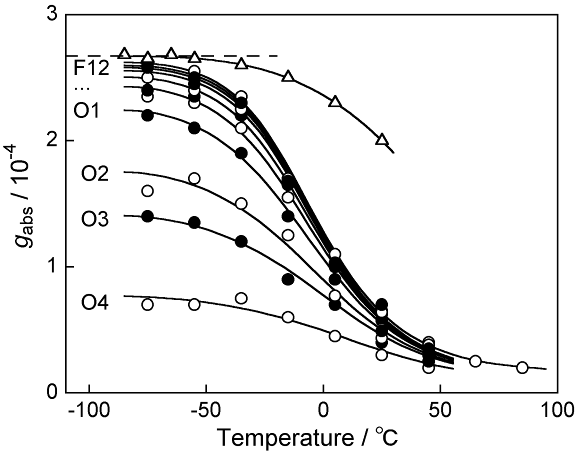


Figure 5. Terao et al.

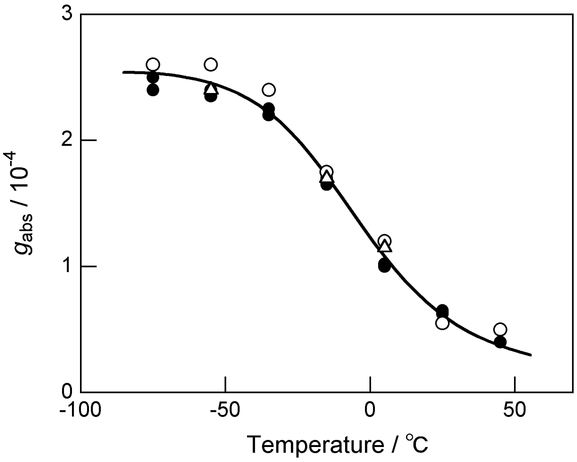


Figure 7. Terao et al.

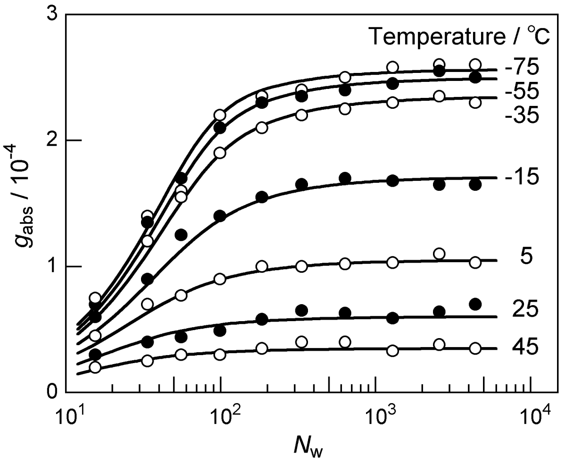


Figure 6. Terao et al.

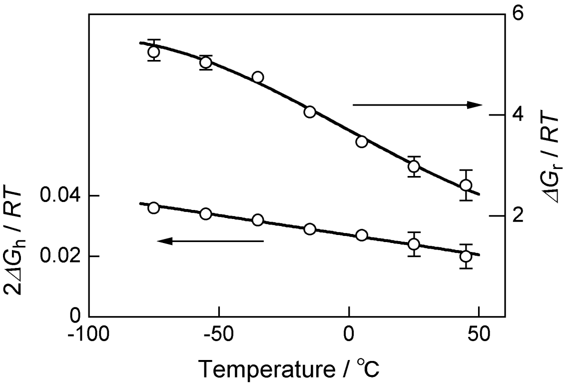


Figure 8. Terao et al.

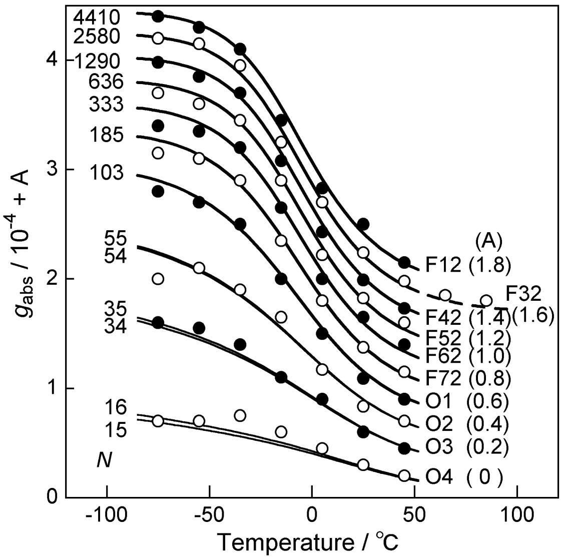


Figure 9. Terao et al.

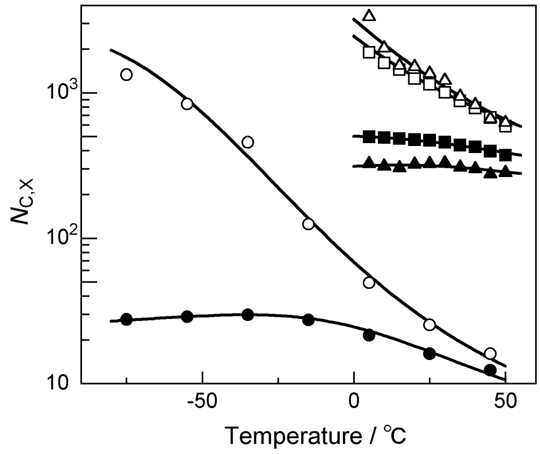


Figure 11. Terao et al.

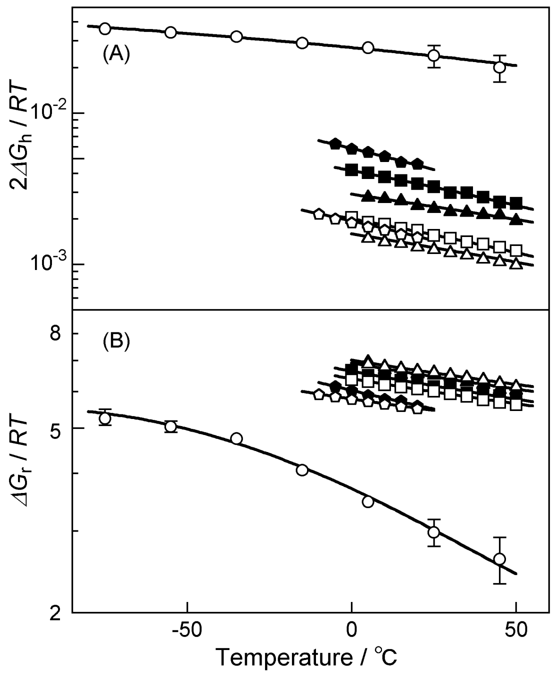


Figure 10. Terao et al.