Unperturbed Chain Dimensions of Poly(di-*n*-hexylsilane), Poly(methyl-*n*-propylsilane), and Poly(di-*n*-butylsilane)

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ABSTRACT: Unperturbed chain dimensions of poly(di-*n*-hexylsilane) (PDHS), poly(methyl-*n*-propylsilane) (PMPrS), and poly(di-*n*-butylsilane) (PDBS) have been evaluated by a combined use of static light scattering, size exclusion chromatography (SEC), and SEC−multiangle laser light scattering. The θ solvents and characteristic ratios (C_∞'s) of the individual polysilanes were determined as follows: PDHS, a mixed solvent of *n*-hexane (58.2 wt %) and 2-propanol (41.8 wt %) at 25 °C and $C_\infty = 42.5$; PMPrS, a mixed solvent of *n*-hexane (62.6 wt %) and 2-propanol (37.4 wt %) at 25 °C and $C_\infty = 19.9$; PDBS, *n*-hexane at 19.1 °C and $C_\infty = 42.3$. These C_∞ values show that the polysilanes in the θ state are much more extended and rigid than ordinary carbon backbone polymers. On the basis of the results, the conformational characteristics of the three polysilanes are discussed by reference to their UV spectra.

1. Introduction

Polysilanes, of which main chains comprise only Si−Si bonds, have different electronic structures from carbon backbone polymers. In the main chain, bonding σ and antibonding σ* localized orbitals are formed; therefore, polysilanes show characteristic UV absorptions, of which wavelengths depend on molecular weight, backbone conformation, and side chain.[1]

The main-chain conformation of *n*-alkyl-substituted polysilanes in the crystalline state is known to vary with the side-chain length: Poly(dimethylsilane) (PDMS),[2] poly(diethylsilane),[3] and poly(di-*n*-propylsilane)[3] adopt the all-trans conformation, poly(di-*n*-butylsilane) (PDBS)[4] and poly(di-*n*-pentylsilane)[4] have a 7/3 helical structure, and poly(di-*n*-hexylsilane) (PDHS)[5] and poly(di-*n*-octylsilane)[6] also take the all-trans conformation. Solutions and fresh films of PDHS show a broad UV absorption maximum around 310−320 nm. On standing at room temperature, the film exhibits another absorption peak around 370−375 nm and its intensity increases, while the original absorption decreases.[7] In the 7/3 helix of PDBS, the dihedral angle of the Si−Si backbone deviates from that of the trans planar conformation by ca. 30°, and the helical PDBS chain shows a blue shift of ca. 60 nm relative to the all-trans PDHS chain.[4]

To reveal causes of the structural variation exhibited by the polysilanes, first of all, the inherent conformational preferences as an isolated chain, i.e., the conformational characteristics free from the long-range intramolecular and intermolecular interactions, should be elucidated by theoretical treatments such as the rotational isomeric state (RIS) scheme[8] and molecular dynamics simulations. In these analyses, reliable experimental data on configuration-dependent properties, e.g., the characteristic ratio in the θ state, C_∞, are required for comparison with theories.

For some polysilanes, the characteristic ratios have been evaluated by Cotts et al.[9−13] For example, they have estimated the C_∞ values of unperturbed PDHS as 19 from the intrinsic viscosity,[11] as 26 by static light scattering (SLS) using a mixed solvent of 2-propanol (41.3 wt %) and *n*-hexane,[12] and as 31 by size exclusion chromatography (SEC)−light scattering (LS).[13] It seems certain that polysilanes are, in general, much extended as compared with carbon backbone polymers (cf. C_∞ of polyethylene (PE), 6.6−6.8).[8]

The object of our study is to obtain the accurate experimental C_∞ values of three polysilanes, PDHS, poly(methyl-*n*-propylsilane) (PMPrS), and PDBS, by using SLS, SEC, and SEC−multiangle laser light scattering (MALLS). The reasons for selecting these three polymers are as follows. These polysilanes can be dissolved in ordinary organic solvents at room temperature. Thus, it would not be difficult to find the θ conditions. As stated above, in the crystal, the PDBS and PDHS chains adopt the 7/3 helical and all-trans conformations, respectively. Values of their unperturbed dimensions would give an insight into the structural variation. Poly(methyl-*n*-propylsilane), which has been indicated to be atactic[14] and all-trans in the crystal,[15,16] may be considered representative of polysilanes having short side chains.

In this paper, we describe the sample preparations, the measurements, and the results for the individual polymers in detail and discuss the obtained data by reference to their UV spectra.

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2. Experimental Section

2.1. Synthesis. The polysilanes were prepared by the Wurtz-type coupling of the corresponding dichlorodialkylsilanes.[17] Toluene was dried over calcium chloride under nitrogen for a day, refluxed for 3 h, distilled, and used as the solvent in the polymerization. The monomer was distilled under reduced pressure before use to remove impurities. Bis(2-methoxyethyl) ether (diglyme), dried over lithium aluminum hydride for a day, refluxed for 3 h, and distilled, was used as the cosolvent only in the preparation of PDHS. All glassware were washed thoroughly and dried at 130 °C for a day.

To a four-necked flask (300 mL) equipped with a condenser, a dropping funnel, and a thermometer were added freshly cut sodium metal (2.2 times as much as the monomer in moles), toluene (ca. 100 mL), and diglyme under an argon atmosphere. The molar ratio of diglyme to sodium was changed from 0.14 to 0.49 to vary the molecular weight of the polymer. The mixture was heated at 110 °C to melt sodium. The monomer was added to the sodium dispersion through the dropping funnel, and the solution was refluxed under argon for 0.5−4 h. After the reaction mixture was cooled to room temperature, 2-propanol was added cautiously to quench unreacted sodium. The solution was poured into a beaker, and 2-propanol (ca. 200 mL) was added therein. The sediment was collected by filtration and dried under vacuum. The crude polymer thus obtained was dissolved in toluene to remove residual impurities, reprecipitated, collected, and dried by the same procedures. The purified polymer, shown to be bimodal by SEC, was fractionated by repeated precipitations with *n*-hexane (solvent) and 2-propanol (precipitant). The polymerization and purification were carried out in a dark room.

2.2. Size Exclusion Chromatography. Molecular weight distributions of the polymers were determined by a Shimadzu LC-6A pump coupled with two Tosoh TSKgel GMH HR-H mixed gel columns maintained at 40 °C. The mobile phase was tetrahydrofuran (THF), and the flow rate was 1.0 mL min^{-1}. The columns were calibrated with a series of 14 polystyrene standards of narrow molecular weight distributions, according to a cubic polynomial: $\log M^{PS} = A + B\tau_e + C\tau_e^2 + D\tau_e^3$, where M^{PS} is the molecular weight relative to polystyrene, A, B, C, and D are empirical parameters, and τ_e is the elution time. A Tosoh RI-8020 differential refractometer was used to detect the polymer eluted from the column. The number-average (M_n^{PS}) and weight-average (M_w^{PS}) molecular weights relative to polystyrene were calculated by the built-in software.

2.3. Density (*d*). For PDHS, Cotts[12] has found a θ solvent of *n*-hexane and 2-propanol (41.3 wt %). Thus, we have also employed mixed solvents of *n*-hexane and 2-propanol in SLS measurements for PDHS and PMPrS. Densities of the mixed solvents were determined by an Anton Parr DMA60 digital densimeter. The sample temperature, monitored by an Anton Parr DT-100-20 thermistor, was maintained at 25.00 ± 0.01 °C. As the reference for the frequency calibration, ultrapure water prepared by an Organo Model-S special purification equipment was used.

In SLS measurements for PDBS, *n*-hexane was adopted as the solvent. The reason will be stated later. The density and its temperature coefficient of *n*-hexane were taken from the literature:[18] $d = 0.659\ 42$ g cm^{-3} at 20 °C and $dd/dt = 8.91 \times 10^{-4}$ g cm^{-3} $°C^{-1}$, where t is the temperature in °C.

2.4. Refractive Index (*n*). Refractive indexes of the mixed solvents of different compositions were determined by an Atago 2T Abbe refractometer using a He−Ne laser (632.8 nm). Then the temperature was maintained at 25.0 ± 0.1 °C. Since the apparatus is designed for the measurements at 589.3 nm, it was calibrated for those at 632.8 nm.

The refractive index of *n*-hexane at each temperature was calculated from literature data:[18] $n = 1.375\ 05$ at 20 °C and $dn/dt = 5.42 \times 10^{-4}$ $°C^{-1}$.

2.5. Differential Refractive Index Increment (d*n*/d*c*). The differential refractive index increment was measured by a Chromatix KMX-16 differential refractometer using the He−Ne laser. Then the sample temperature was maintained at 25.00 ± 0.03 °C. The polymer concentration ranged from 1 to 6 mg mL^{-1}.

2.6. Static Light Scattering. Static light scattering measurements were carried out using a Photal DLS7000 photometer. The wavelength λ of the incident light from the He−Ne laser was 632.8 nm. Five solutions of different polymer concentrations of 0.1−3.0 mg mL^{-1} were prepared. The weight fraction of the solution was evaluated gravimetrically and converted to mass concentration c using the solvent density. The solution was optically purified by filtration through a 0.2 μm Teflon membrane filter (Toyo Roshi) and introduced into the light scattering cell with a Teflon syringe. For cleaning, the cell, syringe, and glassware were exposed to acetone vapor for 2 h before use. During the measurement, the sample temperature was maintained at 25 ± 0.1 °C. The excess Rayleigh ratio was measured at each concentration in a scattering angle range of $20° \le \theta \le 150°$ at intervals of 5°.

The excess Rayleigh ratio R_θ at a concentration c is related to the weight-average molecular weight M_w, the second virial coefficient A_2, and the z-average root-mean-square radius of gyration $R_{G,z}$ as follows:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w}(1 + 2A_2c + ...)\left(1 + \frac{q^2R_{G,z}^2}{3} + ...\right) \quad (1)$$

where

$$K = \frac{4\pi^2n^2(dn/dc)^2}{N_A\lambda^4} \quad (2)$$

with N_A being Avogadro's number. The magnitude of the scattering vector, q, is given by

$$q = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) \quad (3)$$

On the assumption that the Schulz−Zimm distribution[19] of molecular weight holds for the present samples, the $R_{G,z}$ value can be converted to the weight-average value, $R_{G,w}$, by

$$R_{G,w} = R_{G,z}\left(\frac{1 + U}{1 + 2U}\right)^{1/2} \quad (4)$$

where U is the inhomogeneity factor ($= M_w/M_n - 1$),[20] which may be evaluated from the polydispersity index obtained by SEC−MALLS. The characteristic ratio can be calculated from $R_{G,w}$ by

$$C_\infty = 6R_{G,w}^2\Big/\frac{M_w}{M_0}l^2 \quad (5)$$

where M_0 is the formula weight of repeat unit and l is the bond length.

2.7. Size Exclusion Chromatography−Multiangle Laser Light Scattering. The same SEC setup as above was used. The mobile phase was THF. The eluate from the column was directed to a Dawn DSP laser photometer (Wyatt Technology Co.). The polymer concentration at each elution time may be calculated from $c = (n_{eluate} - n_{THF})/(dn/dc)_{THF}$, where n_{eluate} and n_{THF} are the refractive indexes of eluate and THF, respectively. The former can be measured with the refractometer of the SEC setup. The differential refractive index increment of the THF solution at 25 °C, $(dn/dc)_{THF}$, was independently determined: 0.150 mL g^{-1} for PDHS, 0.198 mL g^{-1} for PMPrS, and 0.175 mL g^{-1} for PDBS. The concentrations thus estimated were ca. 0.001 mg mL^{-1}, so small as to be assumed null in the analysis. The excess Rayleigh ratio was measured at 12 scattering angles in a range of $39° \le \theta \le 139°$. The molecular weight of each eluate was determined as

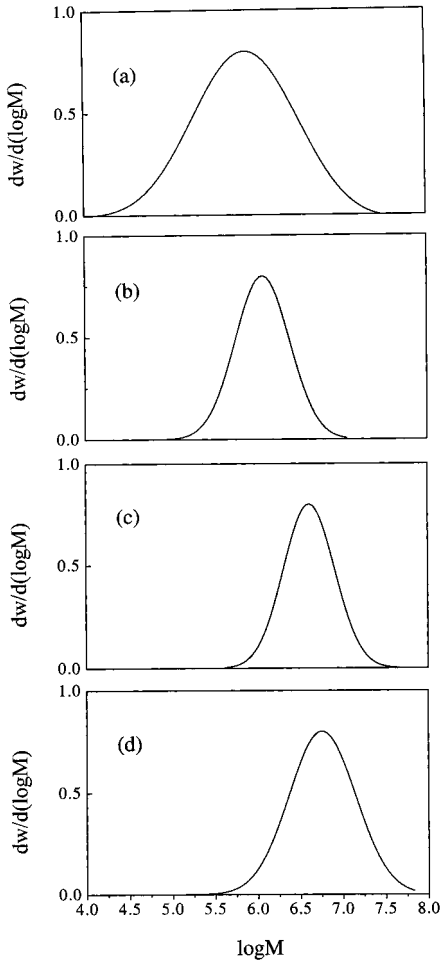

Figure 1. Molecular weight distributions of fractionated PDHS samples, obtained by SEC-MALLS: samples (a) 1, (b) 2, (c) 3, and (d) 4.

described in section 2.6, and the polydispersity index M_w/M_n was calculated from the molecular weights.

3. Results

3.1. PDHS. 3.1.1. Molecular Weight Distribution. Molecular weight distributions of four fractionated PDHS samples, obtained by SEC−MALLS, are shown in Figure 1. All the four samples were shown to have unimodal molecular weight distributions and hence employed in the SLS measurements.

3.1.2. Photodegradation. As stated in the Introduction, polysilanes show characteristic UV absorptions. The photodegradation of polysilanes was reported in the previous study.[9] Thus, we investigated the effect of room light on the molecular weight quantitatively.

A hexane solution of PDHS (sample 1, see Table 1) was prepared in a glass tube with 10 mm i.d., 12 mm o.d., and 35 mm height, and the PDHS concentration was 1.2 mg mL^{-1}. The sample tube was placed under room light. The UV lights of 320−390 nm, corresponding to the absorption band of PDHS, were counted at several points around the sample by using a UVA-365 UV meter (N.T. Corporation). The illuminances were estimated to be 1.2−1.3 μW cm^{-2}. In Figure 2a, the M_n^{PS} and M_w^{PS} values, obtained by SEC, are shown as a function of the exposure time τ.

From the figure, it can be seen that PDHS is easily damaged by room light. After 3 h, the weight-average molecular weight was reduced to ca. 15% of the initial value. For comparison, the fresh solution was placed in a dark place, and the time dependence of the molecular weight was examined. In Figure 2b, the M_n^{PS} and M_w^{PS} values are plotted against log τ. Although the data are slightly scattered, it may be concluded that the polymer kept its original molecular weight. In dark rooms free from UV lights, we have carried out all of our experiments.

Next, the effects of the He−Ne laser radiation of our SLS apparatus on the molecular weight and radius of gyration were investigated for the same solution as above. The SLS measurement was repeated five times, and the M_w and $R_{G,z}$ values were evaluated each time. An SLS measurement took ca. 2.5 h. During the experiment, the sample was exposed to the laser beam. Nevertheless, both M_w and $R_{G,z}$ values were shown to be essentially invariant. Therefore, it can be concluded that the He−Ne laser radiation does no damage to PDHS on the time scale of ordinary SLS measurements. It has been assumed that PMPrS and PDBS are also stable in the laser beam.

Table 1. Molecular Parameters of Fractionated PDHS Samples

sample no.	SLS		SEC−MALLS			
	M_w[a]	$R_{G,z}$[a] (Å)	M_w[b]	M_w/M_n[b]	$R_{G,w}$[c] (Å)	C_∞[d]
1	5.38×10^5	430	6.00×10^5	3.76	327	42.9
2	5.21×10^5	383	5.75×10^5	1.65	324	43.4
3	1.71×10^6	653	1.90×10^6	1.40	576	41.9
4	2.21×10^6	788	2.69×10^6	1.79	656	41.8

[a] From SLS measurements using the mixed θ solvent of *n*-hexane (58.2 wt %) and 2-propanol (41.8 wt %) at 25 °C. [b] From SEC-MALLS measurements for the THF solutions at 25 °C. [c] From eq 4, using M_w/M_n obtained by SEC−MALLS. [d] From eq 5, using M_w obtained by SLS.

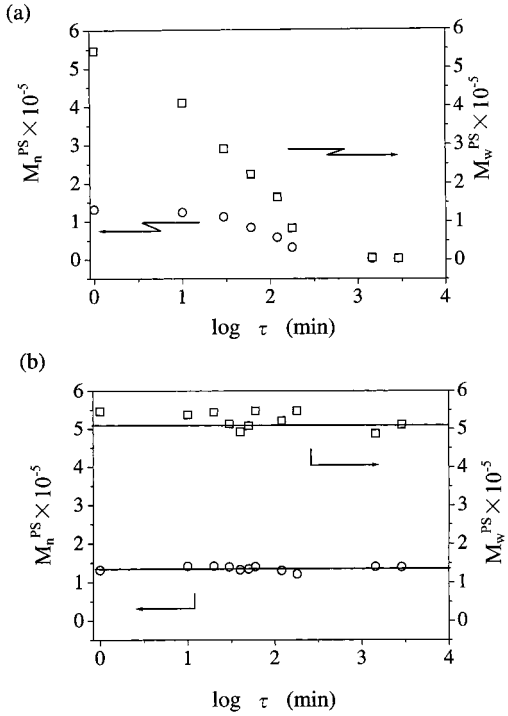

Figure 2. Number-average (M_n^{PS}) and weight-average (M_w^{PS}) molecular weights of PDHS (sample 1, dissolved in *n*-hexane) (a) exposed to room light and (b) placed in a dark room free from UV lights, as a function of τ, where τ is the time after the first measurement.

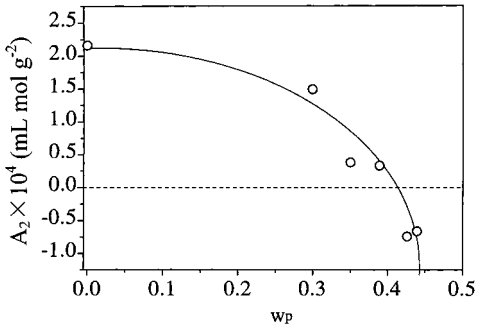

Figure 3. Second virial coefficients (A_2's) of the ternary system of PDHS (sample 2), *n*-hexane, and 2-propanol at 25 °C, as a function of the weight fraction of 2-propanol, w_p.

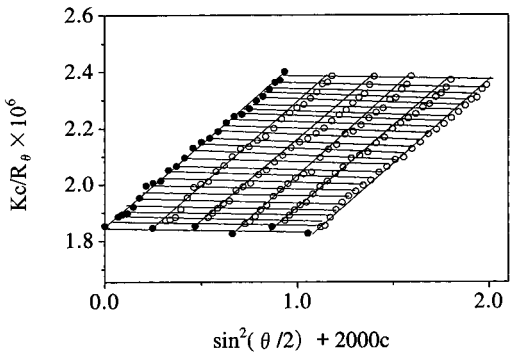

Figure 4. Zimm plot for PDHS (sample 2) in the mixed θ solvent of *n*-hexane and 2-propanol at $w_p = 0.418$ and 25 °C.

3.1.3. Determination of the θ Condition. Our experiments indicated that the density of the mixed solvent can be expressed as follows:

$$d\ (\mathrm{g\ cm^{-3}}) = -0.0101w_p^3 + 0.0494w_p^2 + 0.0856w_p + 0.6559 \quad (0 \le w_p \le 1) \quad (6)$$

where w_p is the weight fraction of 2-propanol. The composition dependence of the refractive index was found to be given by

$$n = -0.0117w_p^3 + 0.0242w_p^2 - 0.0096w_p + 1.3675 \quad (0 \le w_p \le 1) \quad (7)$$

The differential refractive index increment d*n*/d*c* of the dilute solution was also represented as a function of w_p.

Using sample 2 of PDHS, we have attempted to determine the θ composition of the mixed solvent at 25 °C. The optical constant *K*, defined in eq 2, was calculated for each w_p from the *d*, *n*, and d*n*/d*c* values. In Figure 3, the A_2 values estimated from Zimm plots[19] are plotted against w_p. A positive A_2 of 3.53×10^{-5} at $w_p = 0.389$ indicates that the mixed solvent is somewhat good, while a negative A_2 of -7.91×10^{-5} at $w_p = 0.426$ represents the solvent as rather poor. Thus, the θ composition is expected to exist between the two w_p's. As shown in Figure 3, the experimental data can be found on or around the cubic curve fitted by a least-squares method. The convex curve intersects with the horizontal line $A_2 = 0$ at $w_p = 0.418$. Therefore, we have determined the θ composition as $w_p = 0.418$. This value is very close to that (0.413) reported by Cotts.[12] The d*n*/d*c* value for $w_p = 0.418$ was obtained as 0.1902 mL g^{-1}. The Zimm plot of sample 2 at $w_p = 0.418$ and 25 °C, shown in Figure 4, gave an A_2 value of -8.09×10^{-6}.

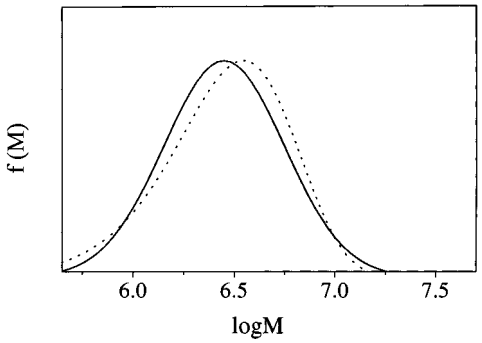

Figure 5. Theoretical (dotted line) and experimental (solid line) molecular weight distributions of PDHS (sample 3).

3.1.4. Characteristic Ratio. Using the θ mixed solvent at 25 °C, we carried out SLS measurements for the four fractionated PDHS samples. The M_w and $R_{G,z}$ values determined are listed in Table 1, together with M_w's and M_w/M_n's obtained by SEC−MALLS.

According to the Schulz−Zimm distribution,[19] the mass distribution function $f(M)$ is given by

$$f(M) = \frac{h^h}{\Gamma(h)} \frac{M^h}{M_n^{h+1}} \exp\left(-\frac{hM}{M_n}\right) \quad (8)$$

where $h = 1/U$ and Γ is the gamma function. Using the U and M_n values obtained by SEC−MALLS, we may directly compare the theoretical and experimental molecular weight distributions. In Figure 5, both calculated and observed $f(M)$ functions of sample 3 are shown. The former was calculated from eq 8, and the latter was obtained by normalizing the distribution curve in Figure 1c. The good agreement between theory and experiment indicates the applicability of the Schulz−Zimm distribution to the present samples.

Listed in Table 1 are the $R_{G,w}$ and the C_∞ values calculated from eqs 4 and 5, respectively. The characteristic ratios, which were obtained using $M_0 = 198.4$ and $l_{Si-Si} = 2.35$ Å,[1] are found within a narrow range of 41.8−43.4, and the average is 42.5. This value indicates that the PDHS chain is much more extended than ordinary carbon backbone polymers. Between $R_{G,w}$ and M_w, the follwoing relation was found:

$$R_{G,w}\ (\text{Å}) = 0.519M_w^{0.49} \quad (9)$$

Because the exponent is nearly equal to 0.5, the PDHS chain can be considered to be in the θ state.[21]

3.2. PMPrS. In the SLS measurements, the mixed solvents of *n*-hexane and 2-propanol at 25 °C were also employed for PMPrS. Accordingly, the density and refractive index of the mixed solvent were calculated from eqs 6 and 7, respectively. The w_p dependence of d*n*/d*c* was also determined. Since molecular weight distributions of four fractionated samples (Table 2) were unimodal, all the samples were adopted in SLS measurements.

3.2.1. Determination of the θ Condition. Determination of the θ composition for PMPrS was attempted using sample 2. The A_2 versus w_p plot formed a convex curve intersecting with the line $A_2 = 0$ at $w_p = 0.374$. There the d*n*/d*c* value was obtained as 0.2359 mL g^{-1}, and the Zimm plot gave a small A_2 value of 3.14×10^{-6}. Thus, we have determined the θ composition as $w_p = 0.374$.

Table 2. Molecular Parameters of Fractionated PMPrS Samples

sample no.	SLS		SEC−MALLS			
	M_w[a]	$R_{G,z}$[a] (Å)	M_w[b]	M_w/M_n[b]	$R_{G,w}$[c] (Å)	C_∞[d]
1	1.91×10^5	240	1.71×10^5	1.46	209	21.4
2	2.75×10^5	285	2.81×10^5	1.80	237	19.2
3	3.42×10^5	306	3.59×10^5	1.76	256	18.0
4	7.44×10^5	480	7.71×10^5	1.62	408	21.0

[a] From SLS measurements using the mixed θ solvent of *n*-hexane (62.6 wt %) and 2-propanol (37.4 wt %) at 25 °C. [b] From SEC−MALLS measurements for the THF solutions at 25 °C. [c] From eq 4, using M_w/M_n obtained by SEC−MALLS. [d] From eq 5, using M_w obtained by SLS.

Table 3. Molecular Parameters of Fractionated PDBS Samples

sample no.	SLS		SEC−MALLS			
	M_w[a]	$R_{G,z}$[a] (Å)	M_w[b]	M_w/M_n[b]	$R_{G,w}$[c] (Å)	C_∞[d]
1	3.83×10^5	419	3.88×10^5	2.50	331	44.3
2	8.45×10^5	580	8.45×10^5	1.73	486	43.3
3	8.97×10^5	581	9.38×10^5	1.92	478	39.4
4	2.40×10^6	929	2.34×10^6	1.46	810	42.3

[a] From SLS measurements using the θ solvent of *n*-hexane at 19.1 °C. [b] From SEC−MALLS measurements for the THF solutions at 25 °C. [c] From eq 4, using M_w/M_n obtained by SEC−MALLS. [d] From eq 5, using M_w obtained by SLS.

3.2.2. Molecular Parameters in the θ State. Values of M_w and $R_{G,z}$ of the four PMPrS samples, determined from the SLS measurements using the θ mixed solvent at 25 °C, are listed in Table 2. The weight-average radius of gyration, $R_{G,w}$, was obtained from eq 4 using M_w/M_n by SEC−MALLS, and the characteristic ratio, C_∞, was calculated from eq 5 with $M_0 = 86.21$ and $l_{Si-Si} = 2.35$ Å. The C_∞ values were averaged to be 19.9. This is in good agreement with that (19 ± 7) reported by Cotts et al.[9,22] The relationship between $R_{G,w}$ and M_w was obtained as

$$R_{G,w}\,(\text{Å}) = 0.446 M_w^{0.50} \qquad (10)$$

The exponent of 0.50 indicates that the PMPrS chain is in the θ state.

3.3. PDBS. 3.3.1. Determination of the θ Condition. All four fractionated samples of PDBS, found to be unimodal, were used in SLS measurements (see Table 3).

First, we attempted an SLS measurement with an *n*-hexane solution of sample 2 at 25 °C. Then the second virial coefficient A_2 was evaluated to be 6.18×10^{-5}, being so small that the solution might be considered in the θ state. Next, we prepared a mixed solvent of *n*-hexane (90 wt %) and 2-propanol (10 wt %) at 25 °C and dissolved a small amount of PDBS powder therein. After a while, however, the polymer was sedimented. Therefore, we have employed only *n*-hexane as the solvent for the SLS measurements and treated the solution temperature as the parameter to find the θ condition for PDBS.

The d*n*/d*c* data for PDBS were approximated as a function of temperature to calculate the optical constant *K* of eq 2. In Figure 6, the A_2 values, estimated from the Zimm plots, are plotted against the reciprocal of the absolute temperature *T*. The straight line fitted to the experimental data crosses the horizontal line $A_2 = 0$ at $T^{-1} = 3.422 \times 10^{-3}$ K^{-1}; therefore, the θ temperature could be determined as 19.1 °C. The d*n*/d*c* value was 0.2100 mL g^{-1} at 19.1 °C.

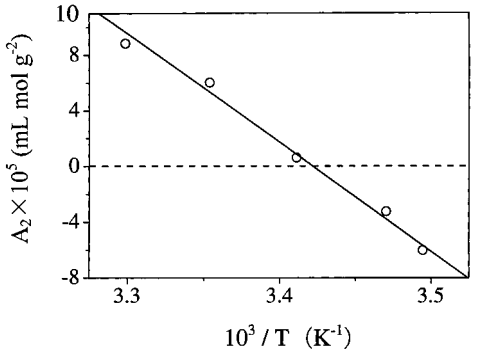

Figure 6. Second virial coefficients of the PDBS (sample 2)/*n*-hexane system as a function of the reciprocal of the absolute temperature.

3.3.2. Molecular Parameters in the θ State. Listed in Table 3 are values of M_w and $R_{G,z}$ of the four PDBS samples in *n*-hexane at 19.1 °C. The $R_{G,w}$ and C_∞ values were calculated from eqs 4 and 5 with $M_0 = 142.3$ and $l_{Si-Si} = 2.35$ Å. The C_∞ values were averaged to be 42.3.[24] The relationship between $R_{G,w}$ and M_w is expressed by

$$R_{G,w}\,(\text{Å}) = 0.613 M_w^{0.49} \qquad (11)$$

4. Discussion

The characteristic ratios of PMPrS, PDBS, and PDHS were evaluated to be 19.9, 42.3, and 42.5, respectively. The C_∞ value tends to increase with the side-chain length. The difference in side-chain length between PMPrS and PDBS, on average, corresponds to two methylene units, being the same as that between PDBS and PDHS. However, the C_∞ value of PDBS is largely different from that of PMPrS but in good agreement with that of PDHS.

Figure 7 shows UV spectra from PMPrS, PDBS, and PDHS in the θ solutions. The absorption maxima are found at 306 nm for PMPrS, 314 nm for PDBS, and 314 nm for PDHS; PDBS has an absorption at the same position as PDHS. Our experiments have shown that the unperturbed PDBS chain has a spatial configuration ($C_\infty = 42.3$) similar to that ($C_\infty = 42.5$) of PDHS.

In Figure 7, UV spectra observed from the solid-state polysilanes are also shown. The absorption maxima of solid PMPrS, PDBS, and PDHS are found at 329, 314, and 312 and 363 nm, respectively. For PDBS, the peak profile from the film is sharper than that from the θ solution, while the position (314 nm) is invariant. The solid PDHS exhibits an absorption at a close position (312 nm). In the crystal the PDBS chain adopts the 7/3 helical conformation.[4] As stated in the Introduction, another UV absorption (363 nm) of solid PDHS stems from the all-trans conformation,[5,7] which has been suggested to be formed owing to the side-chain crystallization. Semiempirical force field calculations on a single PDHS chain,[27] providing information on the unperturbed chain, have indicated that the all-trans conformation is higher in energy than the 7/3 helical one. Therefore, we can conclude that the unperturbed PDBS and PDHS chains adopt almost the same backbone conformations; in the θ state, the difference in side-chain length between PDBS and PDHS is little effective on the backbone structure. It has been suggested that chromophores of polysilanes are all-trans segments separated by gauche defects.[28] The first singlet excitation energy tends to decrease with increasing length of the all-trans segment. Accordingly, it should be signifi-

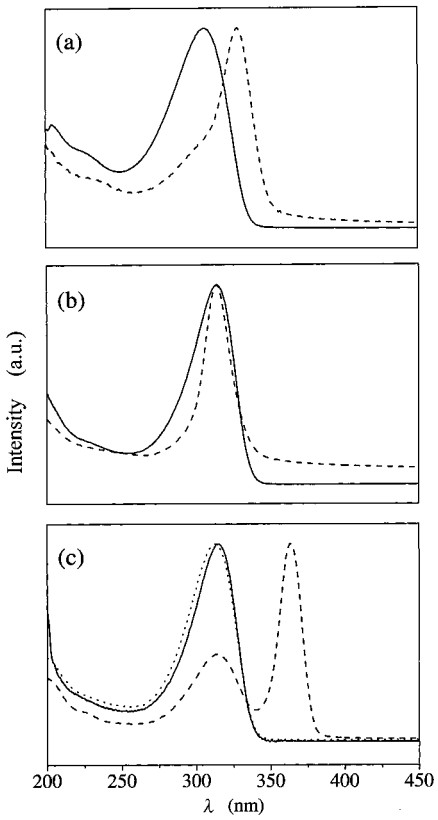

Figure 7. Ultraviolet absorption spectra of (a) PMPrS, (b) PDBS, and (c) PDHS: solid line, the θ solution; dotted line, fresh film; dashed line, film after standing at room temperature for a day.

cant to find the similarity between PDBS and PDHS in the unperturbed dimension (rigidity of the main chain) and UV absorption.

For systematic understanding of backbone conformations of polysilanes, sophisticated theoretical treatments are indispensable. Our data are hopefully helpful for such studies.

5. Summary

The characteristic ratios of PDHS, PMPrS, and PDBS in the θ state have been evaluated by a combined use of SLS, SEC, and SEC−MALLS. To acquire the accurate experimental data, particular attention has been paid. The polymer as synthesized, having a bimodal molecular weight distribution, was subjected to a repeating fractional precipitation. The molecular weight change due to photodegradation by room light was investigated for PDHS; the exposure of only 3 h was found to reduce the molecular weight to ca. 15 % of the initial value. Therefore, all of our experiments were carried out in dark rooms. On the other hand, the He−Ne laser radiation used in the SLS apparatus was shown to be harmless to PDHS.

To determine the θ conditions for PDHS and PMPrS, mixed solvents of *n*-hexane and 2-propanol at 25 °C were used, and the composition was treated as the parameter. The density and refractive index of the mixed solvent were measured, expressed as a function of w_p, and used in the calculation of the optical constant. The θ conditions for PDHS and PMPrS were determined as $w_p = 0.418$ and 0.374, respectively. The characteristic ratios of PDHS and PMPrS in the θ state were evaluated to be 42.5 and 19.9, respectively.

For PDBS, *n*-hexane was used as the solvent for the SLS measurements, and the θ temperature was determined as 19.1 °C. The C_∞ value of the unperturbed PDBS chain was evaluated to be 42.3. From the C_∞ values thus obtained, the polysilane chains were shown to be considerably extended and rigid in comparison with ordinary carbon backbone polymers.

The conformational characteristics of the three polysilanes were discussed by reference to UV spectra observed from their θ solutions and solid states. It can be concluded that the unperturbed PDBS and PDHS chains have almost the same backbone conformations.

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