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Evaluation of Global Conformation of Polydialkylsilane Using Correlation between Persistence Length and Excitonic Absorption

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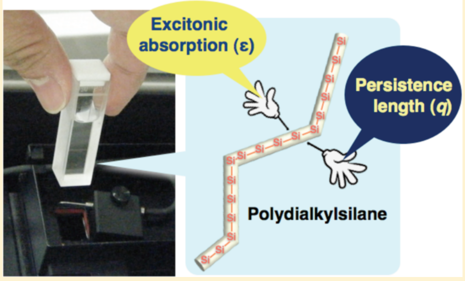
Supporting Information



ABSTRACT: An empirical relationship between persistence length (q) and molar absorptivity (ε) of poly(dialkylsilane)s (PSis) was developed. Here the q value was estimated by a touched-bead wormlike-chain model with the relationship between the intrinsic viscosity and the molecular weight, which were obtained from a size exclusion chromatography equipped with a viscometer. The resulting $\varepsilon - q$ plot showed an apparent saturation curve, which could be formulated as $\varepsilon = 10^5/(2.16 + 21.3q^{-1.23})$ with a high correlation coefficient, $r = 0.99$. Furthermore, using this empirical $\varepsilon - q$ relational equation, changes in the q value of the PSis among thermochromism with (i) abrupt transition, (ii) gradual transition, and (iii) nontransition were estimated. (i) Abrupt type of thermochromism: poly(n-decylmethylsilane) exhibited an UV absorption band at 308 nm above transition temperature (T_c). This band drastically decreased in the relatively narrow range of transition temperature (ca. −35 to −50 °C), accompanied by an appearance of a new UV absorption band at λ_{max}: 334 nm. In this case, the q value above T_c at 308 nm and below T_c at λ_{max}: 334 nm was nearly identical, at ca. 1.5 nm. (ii) Gradual type of thermochromism: poly(n-hexyl-n-propylsilane) showed a gradual bathochromic shift from λ_{max}: 320 to 350 nm in the relatively wide range of trandition temperature between −20 and −55 °C, involving conformation change from 7_3 helix to all-trans. Here the q value for the all-trans conformation with 5 nm increased approximately twice than that for the 7_3 helix conformation. (iii) Nontransition type: poly(n-hexylmethylsilane) showed a bathochromic shift of ca. 11 nm in the ranges of observation temperature (+25 to −80 °C) without an apparent transition. Here the q values were gradually and contiuously increased from ca. 1.2 to 1.4 nm. These results allowed to estimate the q value of PSis under various conditions, leading to a novel approach of investigation of the conformation-dependent chromic behavior of PSis, such as thermochromism, solvatochromism, piezochromism, and electrochromism.

INTRODUCTION

Poly(dialkylsilane)s (PSis) can be regarded as quasi-one-dimensional (Q1D) materials with delocalized σ-conjugated electrons along the Si main chain.[1] Their unique optical/electronic properties have been rationalized by quantum confinement effects of these σ-conjugated electrons both theoretically[2] and experimentally.[3] Because of their one-dimensional direct band gap nature, PSis exhibit UV absorption around 300−380 nm, depending on the global and local conformation of their main chains. Typically, when PSis adopt the conformations of the deviant (dihedral angle, φ: 150°), transoid (φ: 165°), and anti (φ: 180°), the wavelength of maximum absorption (λ_{max}) of the UV absorption bands appear to be ca. 320, 355, and 370 nm, respectively.[4] This unique UV absorption behavior depending on the conformation has been extensively studied in terms of a chromophoric segmental model, where the individual segments are loosely, electronically coupled, but which communicate through rapid energy migration[3b,5] Here the conformation-dependent UV absorption has been utilized as a "chromophoric indicator for global conformations" of PSis under any conditions, as far as UV measurement is available.[6]

On the other hand, the global conformation of PSis in a dilute solution, such as stiff, semiflexible, and random-coiled chains, can be estimated by the viscosity index, α, through the Mark−Houwink−Sakurada (MHS) equation $[\eta] = kM^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, k a constant, and M molecular weight, respectively.[7] In a previous paper, Fujiki reported an empirical relationship among the main-chain peak intensities per silicon repeat unit, ε (Si repeat unit)$^{-1}$ dm^3 cm^{-1}, α, and the full width at half-maximum (fwhm) in the PSis with a variety of combinations of alkyl side chains in tetrahydrofuran (THF) at 30 °C.[8] Consequently, the value of ε increases exponentially as a function of the value of α, whereas the value of fwhm decreases as a function of α. Here the correlation between ε, α, and fwhm allows estimation of the global conformation of PSis under various conditions, such as cast film, solution, and bulk solid. Although this study is an important step toward exploiting the universal correlation between the main chain conformation and the electronic structure

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of PSis, these data may not be suitable for quantitative discussions on the stiffness of chain-like polymers, because the MHS equation is only applicable over a limited molecular weight range.[9]

As a more reliable approach to quantitatively define the global conformation, the worm-like chain[9a,10] has been proposed. In these models, degree of stiffness was expressed as a persistence length (q), which is a better parameter than α to depict the global nature of chain-like polymers in dilute solutions.[11] Experimentally, one of the facile but reliable methods to determine the q value is a size exclusion chromatography (SEC) measurement equipped with a viscometer. Indeed, the q values of several PSis have been successfully determined.[12] Here we expected that if the global conformation of PSis could be interrelated to an electronic structure in terms of q and ε, an inherent correlation among the global conformation, electronic structure, and actual optical characteristics could be disclosed in considerably detail.

In this paper, we first developed a clear correlation between q and ε of the PSis by combinational analysis with an SEC equipped with a viscometer and an ordinary UV spectroscopy. The obtained q-ε relational expression was successfully applied for quantitative evaluation of q values of PSis with thermochromic behaviors with abrupt-, gradual-, and nontransition in dilute solutions.

■ EXPERIMENTAL SECTION

PSis used in this study were prepared by a sodium-mediated Wurtz reductive coupling of dichlorodialkylsilanes in refluxing toluene.[1,6,13] The resulting samples were precipitated with careful successive additions of 2-propanol, ethanol, and methanol, which provided the PSis with relatively narrow molecular weight distribution. Molecular properties of the PSis, such as weight-averaged molecular weight (M_w), polydispersity index (PDI), and α were evaluated by an SEC with a universal calibration (eluent: tetrahydrofuran, THF, flow rate: 1.0 mL min^{-1}, and column temperature: 30 °C, column: TSKgel GMHHR-M (Tosoh Bioscience, Japan) (300 mm in length, 7.8 mm in diameter, two columns were connected in series with a guard column). Both refractive index and viscosity were recorded on a Viscotek chromatograph using a Triple Detector Array 302 in series (Viscotek, Houston, TX). The obtained viscosity data were analyzed by the touched-bead, wormlike-chain model with excluded volume[9a,14] to estimate the persistence length (q) and the bead diameter (d_B) assuming the contour length (h = 0.2 nm) per residue and the excluded volume strength (B = 1.7 nm) for a previously investigated PSi, that is, poly{n-hexyl-[(S)-3-methylpentyl]silane}.[11a,15] Here λ^{-1} equals twice the value of q. In order to clarify the uncertainty in λ^{-1}'s, we also estimated the q values when B = 0.5 nm (see Figure S1, Supporting Information). Temperature-dependent UV spectra of PSis were recorded using a *JASCO* V-570 spectrophotometer equipped with a cryostat (UNISOKU, Japan) for working in a temperature range between +25 and −80 °C. Molecular length (L_m) was estimated by the product of the repeat length of Si−Si (0.196 nm) with a 7-residue 3-turn (7_3) helix and the averaged Si repeating number.[16]

■ RESULTS AND DISCUSSION

Sample Preparation and Characterization. Chemical structures for the PSis used in this study are summarized in Figure 1. In this study, the PSis were divided into four categories by chemical structures of alkyl side chains on the Si main chain; (I) PSi**1a**−**1e** with methyl and an n-alkyl group, (II) PSi**2a**−**2c** with two n-alkyl groups, (III) PSi**3a**−**3f** with an n-alkyl and branched alkyl group, and (IV) PSi**4a** with 3,3,3-trifluoropropyl and an n-alkyl group. Here, it should be noted that both the ε value and thermochromic behavior of PSis are significantly affected by L_m[17] and PDI,[18] as well as the main chain's stiffness. Therefore, we carefully chose the PSi's fractions with the similar ranges of L_m between 15 and 200 nm, to avoid complexity in the quantitative evaluation (Table 1).

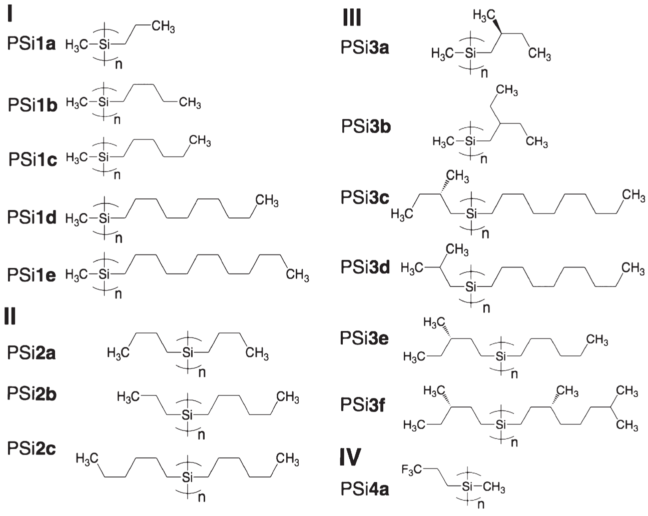

Figure 1. Chemical structures of poly(dialkylsilane)s used in this study. (I) poly(methyl-n-alkylsilane)s (PSi**1a**−**1c**) [PSi**1a**, poly(methyl-n-propylsilane); PSi**1b**, poly(methyl-n-pentylsilane); PSi**1c**, poly(n-hexylmethylsilane); PSi**1d**, poly(n-decylmethylsilane); and PSi**1e**, poly(n-dodecylmethylsilane)], (II) poly(n-alkylsilane)s (PSi**2a**−**2c**) [PSi**2a**, poly(di-n-butylsilane); PSi**2b**, poly(n-hexyl-n-propylsilane); and PSi**2c**, poly(di-n-hexylsilane)], (III) poly(branched alkyl-n-alkylsilane)s (PSi**3a**−**3e**) [PSi**3a**, poly(methyl-(S)-2-methylbutylsilane); PSi**3b**, poly(2-ethylbutylmethylsilane); PSi**3c**, poly(n-decyl-(S)-2-methylbutylsilane); PSi**3d**, poly(n-decylisobutylsilane); PSi**3e**, poly(n-hexyl-(S)-2-methylbutylsilane); and PSi**3f**, poly((R)-3,7-dimethyloctyl-(S)-2-methylbutylsilane)], (IV) poly(alkyl-3,3,3-trifluoropropylsilane) (PSi**4a**) [PSi**4a**, poly(methyl-3,3,3-trifluoropropylsilane)].

Correlation between Molar Absorptivity and Persistence Length. All ε and λ_{max} data for the PSis are summarized in Table 2. Here the ε values were calculated using the Lambert−Beer law. UV spectra of PSis with marked difference in q values (PSi**1a**, 1.3 nm; PSi**2c**, 2.4 nm; PSi**3d**, 50 nm) are shown in Figure 2. As a result, the UV absorption band of the PSis became intense with an increase in the q values, reflecting that global conformation of the PSis changed from random-coil to rod-like nature in THF solution, similar to those observed previously.[21] This result prompted us to clarify the relationship between global conformation and electronic structure in terms of q and ε, respectively.

To further clarify the relationship between global conformation and electronic structure of the PSis, the relationship among ε, λ_{max}, and q were investigated (Figure 3). Consequently, in the region below 10 nm of the q value, we could not find an apparent relationship between λ_{max} and ε, due to an existence of several local minima of rotation barrier energy of the Si main chain (blue filled circle in Figure 3). This result indicates that the flexible PSis with shorter q value can adopt a variety of conformations by subtle structural changes in alkyl side chains appended to the Si main chain. On the other hand, the PSis with relatively longer q values between 50 and 80 nm showed λ_{max} at ca. 320 nm only, originating from the PSis with 7_3 helix conformation.

Although an apparent relationship between ε and λ_{max} was not found, ε exhibited a clear saturation curve with increase in q,

Table 1. Sample Data for PSis[a]

sample	$M_w/10^{4b}$	PDI[c]	L_m/nm[d]	α	q/nm	d_B/nm	M_L/nm^{-1}	B
PSi**1a**	8.0	1.6	114	0.66	1.3	0.95	421.05	0.5
PSi**1b**	4.4	2.2	34	0.74	1.5	0.95	561.5	0.8
PSi**1c**	6.0	1.5	61	0.66	1.2	1	631.5	0.5
PSi**1d**	12	2.2	58	0.69	0.9	1.3	911.95	1.7
PSi**1e**	11	2.1	48	0.61	1.2	1.23	1052	0.5
PSi**2a**	35	2.7	179	0.73	2.3	1.15	701.55	0.6
PSi**2b**	15	2.2	85	0.66	1.4	1.9	800	1.7
PSi**2c**	5.8	1.7	34	0.86	2.4	1.04	982	1.0
PSi**3a**	3.3	1.8	31	0.68	1.3	0.97	561	0.5
PSi**3d**	1.7	1.6	16	0.63	1.4	1.05	631.5	0.5
PSi**3c**	7.3	1.1	54		70 (isooctane, 25 °C)[19]			
PSi**3d**	20	2.0	87	1.27	50	1.1	1122.35	1.0
PSi**3e**					5.0 (isooctane, 45 °C)[11a]			
					6.1 (isooctane, 25 °C)[11a]			
					7.7 (isooctane, 5 °C)[11a]			
					11.9 (isooctane, −15 °C)[11a]			
PSi**3f**					103 (isooctane, 25 °C)[20]			
PSi**4a**	5.1	1.8	40	0.62	1.0	0.73	691	0.5

[a] SEC conditions: temperature, 30 °C; solvent, tetrahydrofuran (THF). [b] M_w: weight-averaged molecular weight. [c] PDI: polydispersity index (M_w/M_n). [d] L_m: molecular length. [e] M_L: molar mass per unit contour length of the chain.

Table 2. Characterization of UV Spectral Data for PSis[a] Used in This Study

sample	$\varepsilon/10^3$	λ_{max}
PSi**1a**	5.8	307
PSi**1b**	5.6	306
PSi**1c**	6.8	306
PSi**1d**	5.8	307
PSi**1e**	5.7	308
PSi**2a**	9.1	316
PSi**2b**	8.2	318
PSi**2c**	9.1	317
PSi**3a**	6.2	296
PSi**3b**	5.2	296
PSi**3c**	52 (isooctane, 25 °C)	323 (isooctane, 25 °C)
PSi**3d**	43	321
PSi**3e**	15.5 (isooctane, 45 °C)[21]	320 (isooctane, 45 °C)[21]
	22.2 (isooctane, 25 °C)[21]	320 (isooctane, 25 °C)[21]
	27.7 (isooctane, 5 °C)[21]	320 (isooctane, 5 °C)[21]
	36.8 (isooctane, −15 °C)[21]	319 (isooctane, −15 °C)[21]
PSi**3f**	48 (isooctane, 25 °C)[20]	323 (isooctane, 25 °C)[20]
PSi**4a**	3.0	290

[a] UV measurement conditions: for PSi**1a**–**3b, 3d, 4a**, temperature, 30 °C; solvent, THF; for PSi**3c, e, f**; solvent, isooctane.

regardless of their conformations. The obtained plot was successfully fitted to the following equation with a correlation coefficient, $r = 0.99$ (red solid line in Figure 3);

$$\varepsilon = \frac{10^5}{2.16 + 21.3q^{-1.23}} \qquad (1)$$

This empirical equation allows us to estimate the q values of PSis from the ε value.

Here it is worth considering the UV absorption of the PSis from a viewpoint of electronic structure. As mentioned above, PSis can be regarded as quasi-one-dimensional semiconductors. Unlike bulk semiconducting materials, optical absorption in PSis produces photogenerated hole–electron pairs, so-called "excitons", even at room temperature. Indeed, notable features of the excitons in the Q1D systems have been elucidated with PSis from both experimental and theoretical aspects.[22] Through a number of sophisticated studies, it is now widely accepted that the exciton in PSis consists of a strongly bound excition that exhibits a character intermediate between Frenckel and Wannier excitons.[5] Here the PSi's main chains are assumed to be complete periodic systems with rigid lattices, where the excitons travel along the Si main chain. Furthermore, the coherent length of the PSi's exciton was estimated to be over 20–30 Si atoms of the main chain within lifetime,[22b] which is roughly calculated to be ca. 4–6 nm, if the projection length of Si–Si bond equal to that of 7_3 helix conformation (0.196 nm). Here the values of ε and q are closely associated with the structural segment length and excitonic coherent length, respectively. Thus, in the region of several nm in q, the ε value increased almost linearly with an increase in q. This is most likely because exciton's coherent length is restricted by the kink between the structural segments. However, when the q value is sufficiently longer than the inherent coherent length within lifetime, the exciton is no longer able to occupy the single segment. Therefore, the ε values would exhibit a saturation curve with an increase in the q value.

Quantitative Evaluation of PSi's Conformation in Thermochromism. One of the most unique physical phenomena of PSis is thermochromism, which has been observed under various conditions; such as dilute solution, cast film, and even isolated

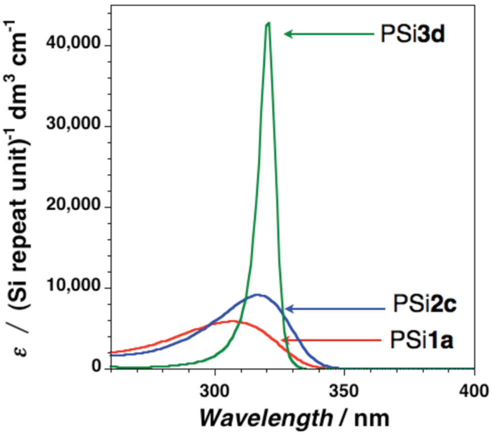

Figure 2. UV spectra of PSis with varying persistence length (q): PSi**1a**, q = 1.3 nm (red solid line); PSi**2c**, q = 2.4 nm (blue solid line); and PSi**3d**, q = 50 nm (green solid line).

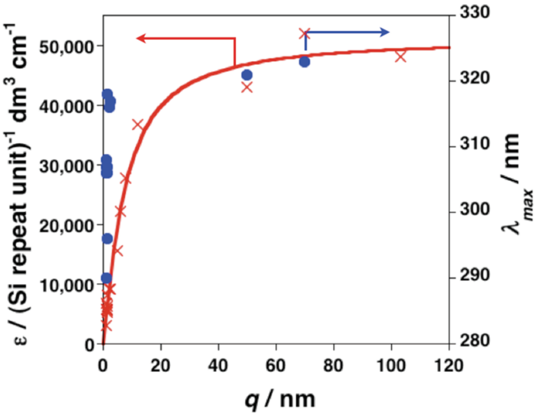

Figure 3. Molar absorptivity (ε) (red crosses) and absorption maximum ($\lambda_{\max}$) (blue filled circles) of PSis as a function of persistence length (q).

single chain tethered on the substrates.[23] Depending on their alkyl side chains, the thermochromism of the PSis involves either gradual or abrupt bathocromic shift in the $\lambda_{\max}$ with decrease in temperature.[24] Although considerable efforts have been devoted to disclosing the nature of the thermochromic transition,[25] the detailed mechanism remains controversial. Among various arguments on the origin of thermochromism,[26] Sanji proposed a statistical model for the cooperative thermochromism of the PSis.[27] In this model, two basic assumptions were made for the theoretical treatment of the cooperative nature of the conformational transition. (i) The thermochromism originates from conformational transition between two ordered states; namely all-trans- and helix-ordered conformation, not order−disorder transition. (ii) The ordered helix form is transformed to a statistical mixture of trans and gauche units at high temperature, which is based on the experimental fact that the radius of gyration of the helix-rod like form decreases with increasing temperature. According to the model, transition-type thermochromism is observable only when the conformation stabilization energies of the ordered sequences are large. Here the free energy of stabilization of the ordered sequences has been estimated by the intensity of absorption maxima. Considering that the q value can be directly estimated with the $\varepsilon-q$ equation, we expected that if the changes in stiffness of the PSi in the thermochromic transition could be estimated by the q value, an inherent transition manner of the thermochromism of the PSis could become more clearly understandable while scattering and viscosity measurements are mostly infeasible at such low temperatures. Therefore, here we applied the $\varepsilon-q$ equation to evaluate the q value in the vicinity of thermochromic shift.

To quantitatively evaluate changes in stiffness of PSis during thermochromic transition, we specifically chose PSi**1d**, PSi**2b**, and PSi**1c**, as a model to exhibit an abrupt, gradual, and nontransition type of thermochromism, respectively (Figure 4).[27,28] Although PSi**1d**, PSi**2b**, and PSi**1c** exhibited a bathochromic shift with decrease in temperature, significant difference was observed in the transition manner. Here we categorized the stiffness-dependent thermochromic transitions into (i) abrupt, (ii) gradual, and (iii) nontransition types.

(i) Abrupt type: in the case of PSi**1d**, the UV band at 308 nm decreased with decrease in temperature. Simultaneously, a new UV band appeared at 334 nm with an isosbestic point at ca. 325 nm (Figure 4a). This type of thermochromic transition is often seen in the PSis with symmetrical long alkyl side chains; such as poly(di-*n*-hexylsilane) (PDHS).[29] The origin of the thermochromism of the PSis has been long thought to be order−disorder change of the main chain. However, Sanji suggested that this could be regarded as a transition between two ordered states, namely, all-trans to 7_3-helix conformation, based on the sophisticated kinetic analysis of the conformational transition of PDHS.[29] According to this argument, UV band at 308 and 334 nm of PSi**1d** was assigned to be 7_3 helix and all trans form, respectively. Changes in molar absorption at 308 nm (7_3 helix) and 334 nm (all-trans), and changes in the q value are shown as a function of temperature in Figure 5a. Above T_c, PSis with 7_3 helix at 308 nm had 1.5 nm in the q value. The q value at 308 nm drastically decreased at T_c between −35 and −50 °C, following the shortness of the q value near 0.5 nm. On the other hand, the q value at 334 nm drastically increased in response to the transition, and eventually reached the similar q value at 308 nm above T_c. This result suggests that apparent main chain stiffness remains unchanged in the vicinity of the bathochromic shift, whereas the main chain conformation drastically transformed from 7_3 helix to all-trans conformation.

(ii) Gradual type of thermochromic shift: PSi**2b** showed a gradual bathochromic shift from 320 to 350 nm, accompanied by a significant increase in the absorption intensity with decrease in temperature (Figure 4b).[24] Here the q values increased nearly twice from 2 to 5 nm with a relatively wide range of transition temperature between +25 °C and −80 °C, suggesting that rod−coil transition occurred during the gradual thermochromic transition (Figure 5b).

(iii) Nontransition type: The UV band of PSi**1c** undergoes a continuous bathochromic shift from 307 to 318 nm with decrease in temperature during an operation temperature between +25 and −72 °C (Figure 4c). Only small changes were observed in the absorption intensity and the caluculated q values changed from 1.2 to 1.4 nm, suggesting that no apparent conformational transition occurred (Figure 5c).

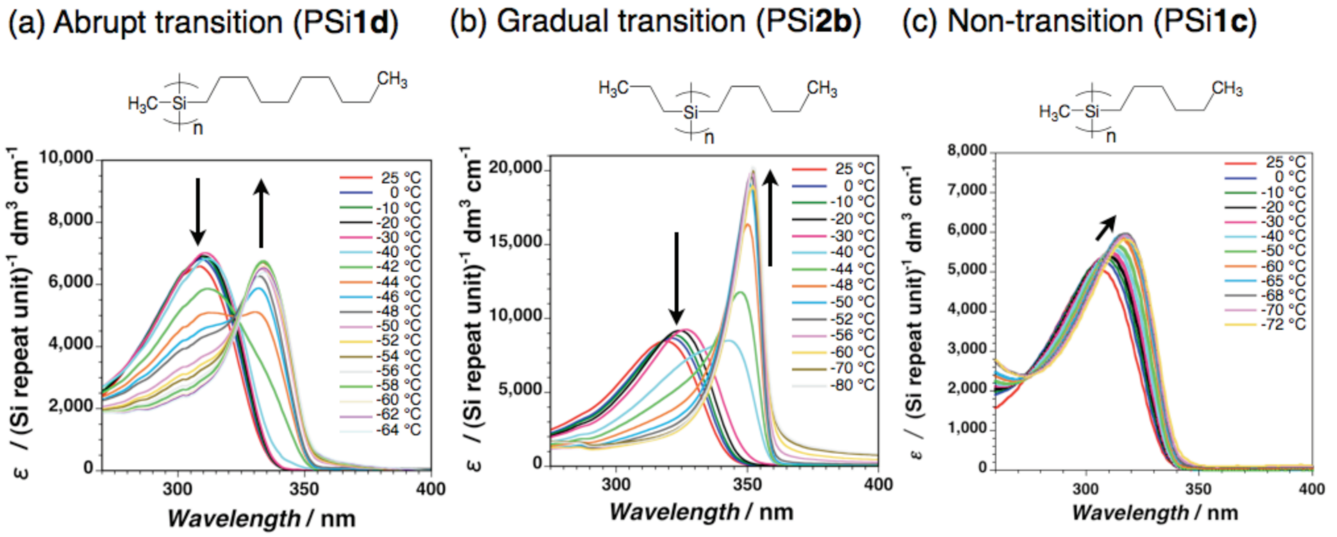

Figure 4. Temperature-dependent UV absorption spectra of (a) PSi**1d**, (b) PSi**2b**, and (c) PSi**1c**. Concentrations of PSis were adjusted to 4.0×10^{-5} M in THF. Observation temperature is indicated in the plots.

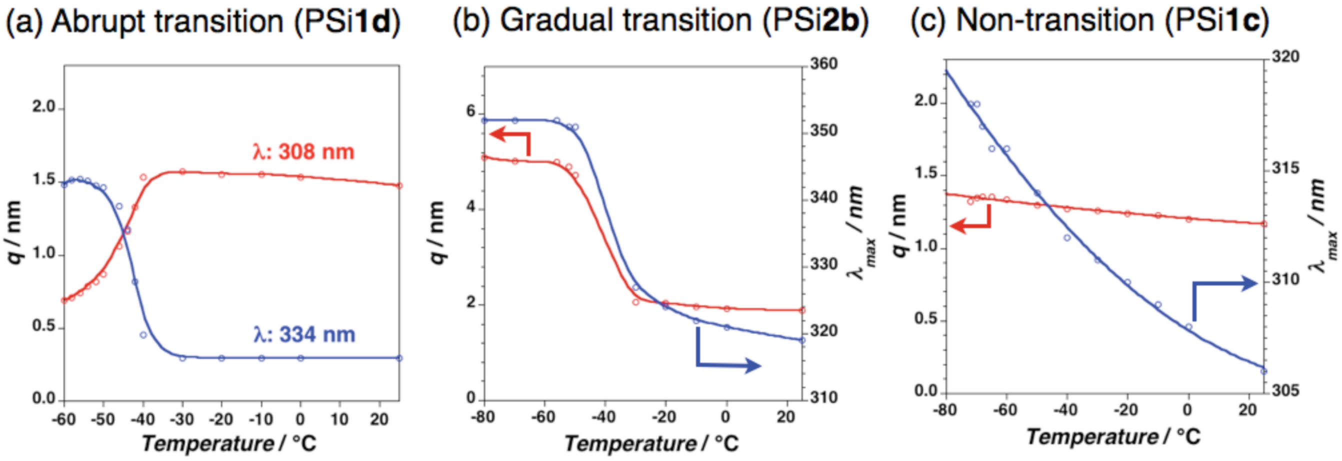

Figure 5. (a) Changes in persistence length of PSi**1d** at 308 nm (red) and 334 nm (blue) in wavelength as a function of temperature. (b) Changes in persistence length (red) and λ_{max} (blue) of PSi**2b** as a function of temperature. (c) Changes in persistence length (red) and λ_{max} (blue) of PSi**1c** as a function of temperature.

■ CONCLUSION

We have demonstrated that persistence length and molar absorptivity of the PSis exhibits a clear correlation. The empirical ε-q equation enabled us to estimate the q value in various conditions by using ordinary UV spectroscopy, which was successfully applied to the quantitative evaluation of global conformation changes during abrupt, gradual, and nontransition type of thermochromism. This result should greatly contribute to further investigations on the structural origins of a variety of conformation-dependent chromic behavior of PSis; such as thermochromism,[1] solvatochromism,[30] piezochromism,[31] and electrochromism.[32]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Viscosity data along with the wormlike chain fit. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (b) West, R. *J. Organomet. Chem.* **1986**, *300*, 327–346.

(2) (a) Mintmire, J. W. *Phys. Rev. B* **1989**, *39*, 13350–13357. (b) Parascandolo, G.; Cantele, G.; Ninno, D.; Iadonisi, G. *Phys. Rev. B* **2003**, *68*, 245318. (c) Takeda, K.; Matsumoto, N.; Fukuchi, M. *Phys. Rev. B* **1984**, *30*, 5871–5876. (d) Takeda, K.; Shiraishi, K. *Phys. Rev. B* **1989**, *39*, 11028–11037. (e) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186–8190.

(3) (a) Tilgner, A.; Trommsdorff, H. P.; Zeigler, J. M.; Hochstrasser, R. M. *J. Chem. Phys.* **1992**, *96*, 781–796. (b) Tachibana, H.; Kishida, H.; Tokura, Y. *Appl. Phys. Lett.* **2000**, *77*, 2443–2445. (c) Hasegawa, T.; Iwasa, Y.; Sunamura, H.; Koda, T.; Tokura, Y.; Tachibana, H.; Matsumoto, M.; Abe, S. *Phys. Rev. Lett.* **1992**, *69*, 668–671.

(4) (a) Tsuji, H.; Michl, J.; Tamao, K. *J. Organomet. Chem.* **2003**, *685*, 9–14. (b) Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821–823.(c) West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons, Ltd: Chichester, U.K., 2001; Vol. 3, p 541−563.

(5) (a) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438–7439. (b) Hasegawa, T.; Iwasa, Y.; Koda, T.; Kishida, H.; Tokura, Y.; Wada, S.; Tashiro, H.; Tachibana, H.; Matsumoto, M. *Phys. Rev. B* **1996**, *54*, 11365–11374. (c) Shimizu, M.; Suto, S.; Goto, T.; Watanabe, A.; Matsuda, M. *Phys. Rev. B* **1998**, *58*, 5032–5042.

(6) Naito, M.; Fujiki, M. *Soft Matter* **2008**, *4*, 211–223.

(7) (a) Cotts, P. M.; Ferline, S.; Dagli, G.; Pearson, D. S. *Macromolecules* **1991**, *24*, 6730–6735. (b) Cotts, P. M. *Macromolecules* **1994**, *27*, 2899–2903.

(8) Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7424–7425.

(9) (a) Yamakawa, H. *Helical wormlike chains in polymer solutions*; Springer: Berlin, 1997. (b) Norisuye, T. *Prog. Polym. Sci.* **1993**, *18*, 543–584.

(10) Kratky, O.; Porod, G. *Recl. Trav. Chim.Pays-Bas* **1949**, *68*, 1106–1122.

(11) (a) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 4519–4525. (b) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Terakawa, I.; Sato, T. *Macromolecules* **2001**, *34*, 2682–2685.

(12) Naito, M.; Nakamura, M.; Terao, K.; Kawabe, T.; Fujiki, M. *Macromolecules* **2010**, *43*, 7919–7923.

(13) (a) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563. (b) Koe, J. *Polym. Int.* **2009**, *58*, 255–260.

(14) (a) Shimada, J.; Yamakawa, H. *J. Chem. Phys.* **1986**, *85*, 591–600. (b) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566–1572.

(15) See ref 11a for the viscosity−radius expansion factor.

(16) (a) Okoshi, K.; Kamee, H.; Suzaki, G.; Tokita, M.; Fujiki, M.; Watanabe, J. *Macromolecules* **2002**, *35*, 4556–4559. (b) Okoshi, K.; Watanabe, J. *Macromolecules* **2010**, *43*, 5177–5179. (c) Oka, H.; Suzaki, G.; Edo, S.; Suzuki, A.; Tokita, M.; Watanabe, J. *Macromolecules* **2008**, *41*, 7783–7786.

(17) Fujiki, M. *Appl. Phys. Lett.* **1994**, *65*, 3251–3253.

(18) Schreiber, M.; Abe, S. *Synth. Met.* **1993**, *55*, 50–55.

(19) Natsume, T.; Wu, L. B.; Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Macromolecules* **2001**, *34*, 7899–7904.

(20) Teramoto, A.; Terao, K.; Terao, Y.; Nakamura, N.; Sato, T.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 12303–12310.

(21) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 6519–6525.

(22) (a) Tachibana, H.; Matsumoto, M.; Tokura, Y.; Moritomo, Y.; Yamaguchi, A.; Koshihara, S.; Miller, R. D.; Abe, S. *Phys. Rev. B* **1993**, *47*, 4363–4371. (b) Thorne, J. R. G.; Williams, S. A.; Hochstrasser, R. M.; Fagan, P. J. *Chem. Phys.* **1991**, *157*, 401–408. (c) Allan, G.; Delerue, C.; Lannoo, M. *Phys. Rev. B* **1993**, *48*, 7951–7959.

(23) Furukawa, K.; Ebata, K.; Ichikawa, D.; Matsumoto, N. *Macromolecules* **2003**, *36*, 7681–7688.

(24) Yuan, C. H.; West, R. *Macromolecules* **1994**, *27*, 629–630.

(25) (a) Gahimer, T.; Welsh, W. J. *Polymer* **1996**, *37*, 1815–1823. (b) Welsh, W. *Adv. Polym. Tech.* **1993**, *12*, 379–388. (c) Schweizer, K. S. *Chem. Phys. Lett.* **1986**, *125*, 118–122. (d) Schweizer, K. S. *J. Chem. Phys.* **1986**, *85*, 1176–1183. (e) Schweizer, K. S. *J. Chem. Phys.* **1986**, *85*, 1156–1175. (f) Schweizer, K. S. *Synth. Met.* **1989**, *28*, 565–572.

(26) As a theoretical approach to explain the thermochromism of conjugated polymers, commonly accepted persuasive model is Schweizer's theory, which was originally proposed for that of conjugated polymers, such as polyenes. According to the theory, the thermochromism of the conjugated polymers can arise from the dispersion interaction of delocalized electrons along the polymer backbone with the surrounding polarizable medium, such as solvent in dilute solutions or appended side chains on the main chain in solid state. The transition between the ordered and disordered conformations is controlled by a competition between the dispersion interaction for fully conjugated chain segments, V_D, and the rotational defect energy, ϵ. Here the ratio V_D/ϵ determines the type of thermochromic behavior, leading to either gradual shifts or an abrupt transition. In the case of low values of V_D/ϵ, so-called "weak coupling", a continuous, gradual red shift of the absorption band may take place as the temperature is decreased, due to the gradual reduction of nonplanar defects with cooling. With high values of V_D/ϵ, so-called "strong coupling", an abrupt order−disorder transition is triggered, in which the polymer chain becomes straightened, producing long fully conjugated segment. Although several relevant works have been reported to support the proposal, polarization of the delocalized electrons by the solvent molecules may not be the fundamental energetic reason for the transition because PSis with extended trans form sometime cause precipitation in the vicinity of the transition temperature.

(27) Sanji, T.; Sakamoto, K.; Sakurai, H.; Ono, K. *Macromolecules* **1999**, *32*, 3788–3794.

(28) Thermochromic behaviors of PSi**1d** in a cast film, and PSi**2b** and PSi**1c** in hexane solutions were originally reported in refs 24 and 27, respectively. In order to unify measurement conditions, we scrupulously reevaluated the thermochromic behaviors of these PSis in THF solution, especially, in the vicinity of the thermochromic transition points.

(29) Sanji, T.; Sakamoto, K.; Sakurai, H. *Chem. Lett.* **1998**, *27*, 255–256.

(30) Oka, K.; Fujiue, N.; Dohmaru, T.; Yuan, C.-H.; West, R. *J. Am. Chem. Soc.* **1997**, *119*, 4074–4075.

(31) Song, K.; Kuzmany, H.; Wallraff, G. M.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1990**, *23*, 3870–3872.

(32) Fujino, M.; Hisaki, T.; Matsumoto, N. *Macromolecules* **1995**, *28*, 5017–5021.