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Thermochromism and solvatochromism of non-ionic polar polysilanes

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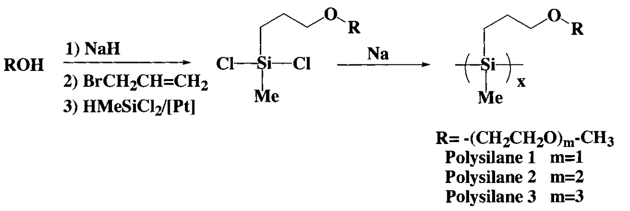
Abstract

Polar polysilanes bearing ethereal side groups [$\{CH_3\text{–}Si\text{–}(CH_2)_m\text{–}O\text{–}(CH_2CH_2O)_n\text{–}CH_3\}_x$, $m = 3\text{–}5$ and $n = 0\text{–}3$}] were prepared and were found to be soluble in a wide range of polar solvents. UV spectroscopic behavior is highly dependent on the nature of the solvents used but no simple relationship between λ_{max} and specific solvent parameter is found. Small molar absorbance ($\varepsilon < 10\,000$/Si–Si bond) suggests that water-soluble polysilanes take highly entangled form in water. Solvatochromic redshift is induced by THF in aqueous solution of water-soluble polysilanes. This solvatochromism is ascribed to disentanglement the non-polar main chain by non-polar solvent. Another type of solvatochromic shift is also caused by $(CF_3)_2CHOH$ (HFIP) in non-polar solvent (benzene, CH_2Cl_2) or even in $(CH_3)_2CHOH$ solution, where higher HFIP concentration brings about longer wavelength absorption. This type of solvatochromism is originated by strong hydrogen bond formation between the ethereal side groups and HFIP. Because non-dissociative nature of HFIP-concerned hydrogen bonding, increased bulkiness of the side moieties brings about disentanglement. Polysilanes **1**–**5**, though having long side chains, show thermochromism of continuous spectral shift on cooling. The same λ_{max} value in thermochromism and solvatochromism indicates that nearly the same degree of disentanglement is caused by HFIP and thermally. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thermochromism; Solvatochromism; Polar polysilanes

1. Introduction

Polyorganosilanes are known to have unusual electronic and optical properties which arise from the delocalized sigma electrons along their backbones [1]. They have been recognized as a new advanced material having a possible potential application for a photo-resist [2], a non-linear optical material [3], a radical reaction initiator [4], an electron-luminescence material [5] and so on. Strong absorption in the UV region is one of the most interesting physical properties among the diverse properties that delocalized sigma electrons along a silicon backbone show. Degree of silicon catenation and dihedral angle of silicon chains are the principal factors to determine the UV characteristics of polysilanes [1,6]. Because of the flexible nature of an Si–Si single bond, the backbone conformation is sensitive to external circumstances and thus results in various chromotropisms [1,6]. Thermochromism [7] and piezochromism [8] are among the most well known and have been studied extensively in conjunction with structure of polysilanes. Here, side chains on the silicon backbone are known to play the important role on determining the type of chromotropism. However, simple alkyl or aryl groups



Scheme 1. Synthetic route for polysilanes **1**–**3**.

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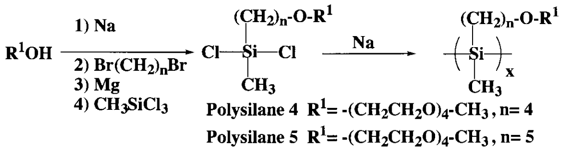

Scheme 2. Synthetic route for polysilanes **4** and **5**.

Table 1
Yields, molecular weights, and solubilities [a] of polar polysilanes

Polysilane	*n*-Hexane	Toluene	THF	MeOH	H_2O
1	X	○	○	△	X
2	X	○	○	○	△
3	△	○	○	○	○
4	X	○	○	○	○
5	X	○	○	○	○

[a] ○, soluble; △, partially soluble; X, insoluble.

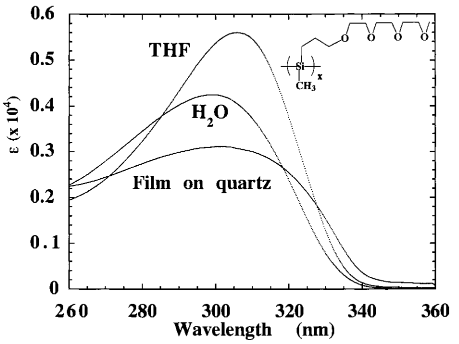

Fig. 1. UV spectra of polysilane **3** in various states.

are commonly adopted as the side chains and, thus, they show limited types of interaction with their environment. Thermochromic behavior of non-polar polysilanes is explained as the result of dispersion interaction of delocalized sigma electrons with surrounding polarizable medium including side groups or by co-operative transition from one ordered form to other [9]. When functional groups such as polar side groups are introduced on silicon chains, extra function and interaction can be added to sigma conjugation. Several polysilanes with polar side chains including quarterly ammonium [10], end-hydroxyl group [11], and ether groups [12] have been reported so far. These polysilanes have mostly been utilized to prepare LB films at water | air interface. Miller [13] reported that polysilanes having *p*-alkoxyphenyl side moieties showed solvent dependent UV spectral behavior. On the other hand, oligo(ethyleneglycol) groups have been recognized as nonionic parts to induce polar interactions with ionic species. Phosphazenec [14] and siloxane polymers [15] bearing this side groups were synthesized recently and showed the expected polar characteristics. Similarly, several polysilanes bearing ethereal side groups were recently synthesized [16,17] and were found that these polymers showed unusual polar characteristics. We have, thus, studied the solvent dependent UV spectroscopic behavior of these polar polysilanes by comparing thermochromic behavior.

2. Results and discussion

2.1. Synthesis of polar polysilanes

Polar polysilanes **1**–**5** having ethereal side groups were prepared by reactions depicted in Schemes 1 and 2. Monomers for polysilanes **1**–**3** were prepared by hydrosilylation reactions of the corresponding allyl ether with methyldichlorosilane. Those for polysilane **4** and **5** were prepared by Grignard reactions with corresponding alkyltrichlorosilane. Yields, molecular weights, and solubilities in representative solvents are summarized in Table 1. Polysilanes **2**–**5** having more than two oxygen atoms in the ethereal side group are highly polar and are soluble in methanol or even in water. Therefore, the ordinary procedure to isolate and/or fractionate polysilanes was inapplicable to polysilanes **2**–**5**. Sodium chloride, after the reaction was quenched with methanol and then water, was firstly removed by dialysis using a cellulose acetate film. Repeated fractionations from dibutyl ether gave polysilanes **2**–**5** with mono-modal pattern in GPC and good polydispersity. Polysilanes **1**–**5** have more than 50 silicon atoms in their main chains and thus are suitable for studying as polymeric materials.

2.2. UV spectral characteristics of water-soluble polysilanes

Polysilane **3** gives clear aqueous solution and is also soluble in various polar solvents. Thus, we have studied UV spectral behavior of polysilane **3** as a representative material. Fig. 1 shows UV spectra of polysilane **3** in various states. Polysilane **3** gives broad absorption in solid state and in aqueous solution compared with that in THF. Because THF and water are freely miscible each other, we have examined UV spectral behavior of polysilane **3** in the mixed solution and found new solvatochromism as shown in Fig. 2. Redshift is induced as THF concentration is increased. This suggests that polysilane **3** takes more extended form in THF than in aqueous solution, and vise versa [18]. Because of non-polar nature, the silicon main-chain must take more extended form in non-polar solvent than in polar solvent but takes shrunk form in water. The highly polar side groups behave oppositely.

Since polysilane **3** was expected to have more polar interaction s with polar species, spectral behavior was further studied in aqueous solution. No spectral shift

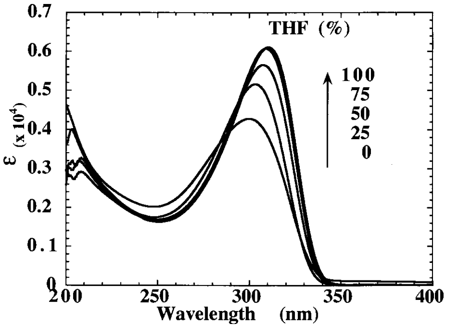

Fig. 2. Solvatochromism of polysilane **3** in THF–H_2O system.

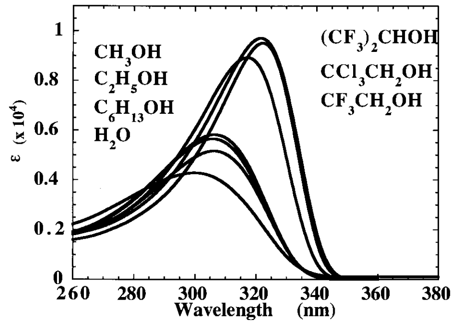

Fig. 3. UV spectra of polysilane **3** in alcoholic solvents.

was induced either by change of H^+ or Li^+ ion concentration, suggesting that polysilane **3** does not form any stable ionic complexes in aqueous solution. Blue shift (ca. 5 nm) was, however, induced when europium chloride was added to aqueous solution of polysilane **3**. This indicates that complex formation with Eu^{3+} results in more shrunk form for polysilane **3**.

UV spectral data of polysilane **3** are summarized in Table 2 together with several solvent parameters. λ_{max} value ranges from 299 to 322 nm and ε/Si–Si from 4280 to 9520. No simple relationship between UV spectral data and any solvent parameters was found. It is, however, noticeable that halogenated solvents give longer λ_{max} than others. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) shows amongst the most remarkable feature to give λ_{max} at long wavelength. ε in HFIP is almost the same value with that of poly(methylphenylsilane) or poly(methylhexylsilane) in hexane, indicating that polysilane **3** takes similarly extended chain structure. Since this is out of expectation from the result in Fig. 2, different mechanism from simple polar–non-polar interaction as in Fig. 1 must be attributed to induce the unusual spectral shift. Since HFIP is known to make strong hydrogen bonding with ethereal oxygen atoms [19], polysilane **3** forms strong hydrogen bonding with HFIP at the ethereal side groups as shown by H-NMR (vide infra). Other hydrogen bonding donors are expected to induce similar spectral shift. Fig. 3 depicts the effect of hydroxyl group on UV spectral behavior of polysilane **3**. It is obvious that halogenated alcohols induce red-shift more effectively than ordinary alcohols, and HFIP is confirmed to be the strongest

Table 2
UV data for $\{CH_3O–(CH_2CH_2O)_3–(CH_2)_3–Si–CH_3\}_n$ and solvent parameters

Solvent	λ_{max} (nm)	ε (O.D.) [a]	ε [b]	I_s (eV) [c]	n [d]	$(n^2-1)/(n^2-2)I_{av}$ [e]
H_2O	299.6	4280	72.39	12.59	1.33250	1.435
THF	310.4	6110	7.58	9.54	1.40496	0.989
MeOH	306.2	5820	32.7	10.85	1.32652	0.859
CH_3CH_2OH	305.6	5660	24.55	10.48	1.35941	0.923
p-Dioxane	309.4	6050	2.209	9.13	1.42025	1.002
CH_3CN	306.2	5950	37.5	12.22	1.31416	0.868
AcOAm	305.5	6950	4.75	10.01	1.4028	1.005
Diglyme	307.4	5700		9.70	1.4043	0.995
$CHCl_3$	315.8	6440	4.806	11.42	1.4293	1.197
$CH_3CONHCH_3$	305.2	5090	191.3	8.90	1.4286	1.340
$BuNH_2$	308.4	5690	4.88	8.71	1.3987	0.939
o-$C_6H_4Cl_2$	314.9	5550	9.93	9.07	1.54911	1.256
Et_2O	304.8	5640	4.335	9.53	1.34954	0.868
Toluene	311.4	5530	2.379	8.822	1.49413	1.136
Ethyl oxalate	304.2	5550	1.8		1.41023	
$C_6H_{13}OH$	306.2	5160	13.3		1.4161	
$(CF_3)_2CHOH$	322.4	9520			1.2765	
CF_3CH_2OH	317	8930				
DMSO	304.2	4730	46.68		1.4773	
Propylene carbonate	304.8	4670			1.4210	

[a] Molar absorbance per Si–Si bond.
[b] Dielectric constant.
[c] Ionization potential.
[d] Refractive index.
[e] Schweizer's solvent constant.

solvent to induce the red-shift among all solvents examined.

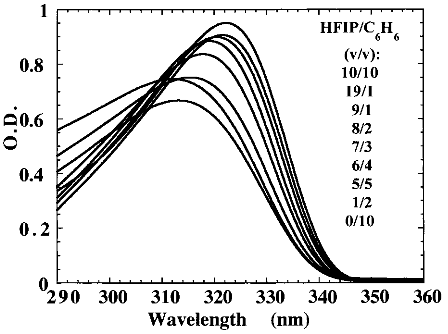

Fig. 4. Solvatochromism of polysilane **3** in HFIP–benzene.

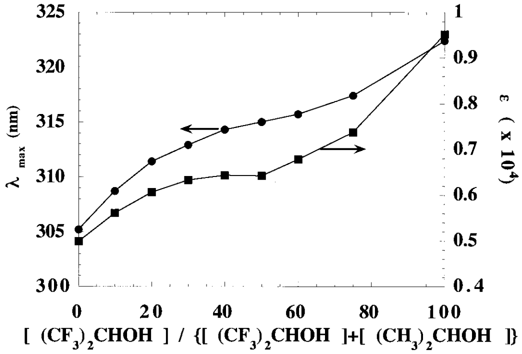

Fig. 5. Solvatochromic shift and absorbance change of polysilane **3** in HFIP–IPA.

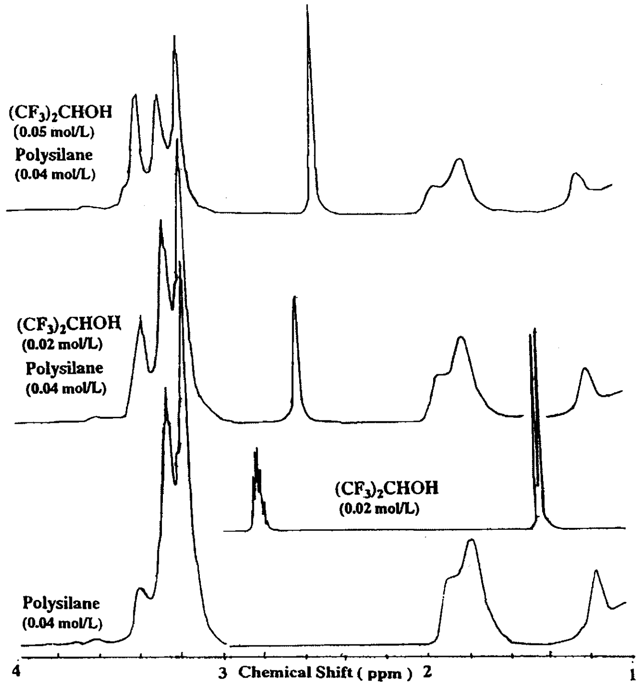

Fig. 6. ^{1}H-NMR spectra of polysilane **3** in C_6D_6.

To obtain more insight of the effect of HFIP on inducing the red-shift, we have measured UV spectra of polysilane **3** in benzene and dichloromethane. As shown in Fig. 4, HFIP is found to induce continuous solvatochromic spectral shift in benzene. Similar feature is also seen in CH_2Cl_2. Furthermore, HFIP is found to induce solvatochromism even in alcoholic solution; Fig. 5 shows solvatochromism of polysilane **3** in 2-propanol-HFIP system. This suggests that HFIP forms hydrogen bonding more effectively with ethereal oxygen than hydroxyl oxygen in alcohol groups. THF, known to make distillable complex with HFIP, quenches this solvatochromism when added into an HFIP-containing benzene solution. Polysilanes **1**, **2**, **4**, and **5** behave similarly towards HFIP-induced solvatochromism and shows λ_{max} around 322–324 nm in HFIP.

H-NMR shows that hydroxyl proton of HFIP appears as a doublet at 1.43 ppm in C_6D_6 (Fig. 6), supporting non-dissociative characteristics. It loses coupling with the methine proton and shows downfield shift to 2.62 ppm when polysilane **3** is added into the C_6D_6 solution. Methine proton of HFIP also shows downfield shift to around 3.0–3.4 ppm where the signal become indistinguishable with $-OCH_2$-moieties. Three signals of CH_2–O– groups of polysilane **3** at 3.0–3.4 ppm change their intensity ratio. Other signals (0–2 ppm) of polysilane **3** stay unchanged by mixing with HFIP. Therefore, HFIP makes strong hydrogen bonding with the ethereal oxygen atoms in polar polysilanes, suggesting that no direct interaction takes place with the main chain. Therefore, hydrogen bonding with HFIP must increase bulkiness of the side groups which makes the main chain more disentangled form.

2.3. Comparison of thermochromism and solvatochromism

Thermochromic behavior is known to be controlled from continuous to discontinuous by adjusting the balance of alkyl side groups in poly(dialkylsilane)s, $(R–Si–R')_n$ [1,6]. In general, large size difference in the side chain length, such as in poly(hexylmethysilane) [20], induces continuous spectral shift in solution while two long alkyl side chains, such as in polydihexylsilane, brings about discontinuous spectral shift. However, this widely accepted generalization is overthrown recently by the fact that poly(hexylmethylsilane) in solid state shows discontinuous thermochromic shift on cooling, though polybutylmethylsilane and polypentylmethylsilane show continuous spectral shift [21]. Therefore, chromotropism of polysilanes is very sensitive to the subtle change of environment as well as the balance of the side chains. The ethereal side chains of polysilanes **1**–**5** are longer than hexyl group and it is interesting to examine the type of their thermochromic behaviors. We can also compare the effect of driving forces on thermochromism and solvatochromism in polar polysilanes.

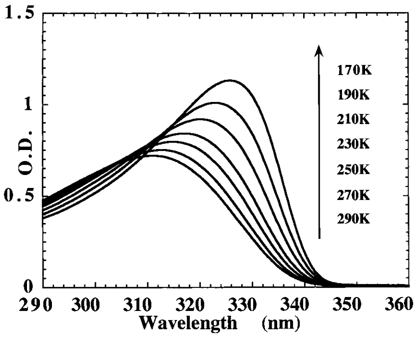

Fig. 7. Thermochromism of polysilane **3** in THF.

Thermochromic behavior of these polar polysilanes in ethanol and THF has been studied. Polysilanes **1**–**3**, having three methylene chain between silicon atom and the ethereal oxygen atom, show continuous redshift on cooling and λ_{max} are 322 nm at 180 K (Fig. 7). In spite of their having longer methylene chains on silicon atoms, polysilanes **4** and **5** show only continuous thermochromic spectral shift giving λ_{max} around 322–324 nm at 180 K in THF, ethanol, and dichloromethane. No solvent dependence was so far found in thermochromic behavior of these polar polysilanes. The long ethereal side moieties of polysilanes **1**–**5** must be too flexible and entangled, which restrict further conformational change. Therefore, there is no room to induce drastic conformational change resulting in discontinuous spectral shift to polysilanes **1**–**5**. The λ_{max} value (322–324 nm) at low temperature and in HFIP is almost the same value with λ_{max} value of polydialkylsilanes at room temperature in solution. Thus, polysilanes **1**–**5** must have still very irregular form even their most disentangled shapes.

3. Experimental

3.1. Materials

Methyldichlorosilane was obtained from Shin-etsu Chemical Co Ltd. and was used after distillation from K_2CO_3. Sodium, sodium hydride, magnesium, and potassium carbonate were obtained from Wako Pure Chemical Co. Ltd. 2-Methoxyethanol, (2-methoxyethoxy)ethoxy]ethanol (or 4,7,10-trioxaundecanol), [2-(2-methoxyethoxy)ethoxy]ethanol (or 4,7,10,13-tetraoxatetradecanol), toluene, THF, dibutyl ether, diethyl ether, 2-propanol (IPA), pentyl acetate, 2-fluoroethanol, trifluoroacetic acid, 2,2,2-trifluoroethanol, triethylamine, and diethylamine were obtained from Wako Pure Chemical Co Ltd. and used after distillation. Solvents for UV measurements (toluene, THF, ethanol, methanol, acetonitrile, DMSO, DMF, dioxane, chloroform, dichloromethane, benzene) were Spectrograde and obtained from Dojin Chemical Co. Ltd. Platinum divinyltetramethyldisiloxane complex (Karstead's Catalyst) as hydrosilylation catalyst and hexafluoro-2-propanol (HFIP) were obtained from Toshiba Silicone Co. Ltd. and Central Glass Co. Ltd., respectively.

3.2. Synthesis of monomers

The synthetic route of polysilane **1** is depicted in Scheme 1. The starting dichlorosilane was synthesized according to Wang et al. [22].

Reaction of 4,7,10,13-tetraoxatetradecanol (84.1 g, 0.5 mol) with NaH (40.0 g, 1.0 mol) in THF (200 ml) under argon atmosphere afforded the corresponding alcoholate which was reacted with allyl bromide to yield allyl derivatives. Unreacted NaH was quenched with water and the product was extracted with diethyl ether (200 ml). The ether layer was washed with water three times and then distillation under reduced pressure gave allyl 4,7,10,13-tetraoxatetradecyl ether (b.p.: 125–126°C/6 torr, yield: 78%).

Hydrosilylation reaction of the allyl ether (60.9 g, 0.3 mol) with methyldichlorosilane (52.2 g, 0.45 mol) by use of Karstead's catalyst was carried out under argon atmosphere at reflux temperature for 4 h. Vacuum distillation gave [4,7,10,13-tetraoxatetradecyl]methyldichlorosilane (b.p.: 120–121°C/0.1 torr, yield: 78%). H-NMR ($CDCl_3$): δ 3.46–3.64 (14H, OCH_2–), 3.35 (3H, OCH_3), 1.76 (2H, Si–CH_2–CH_2–CH_2–), 1.15 (2H, Si–CH_2–), 0.76 (3H,Si–CH_3).

Homologous monomers were similarly prepared from the corresponding alcohols. (4,7,10-Trioxaundecanyl)methyldichlorosilane: b.p.: 123°C/2 torr, yield: 77%). H-NMR ($CDCl_3$): δ 3.44–3.6 (10H, OCH_2–), 3.35 (3H, OCH_3), 1.76 (2H, Si–CH_2–CH_2–CH_2–), 1.16 (2H, Si–CH_2–), 0.76 (3H, Si–CH_3).

(4,7-Dioxaoctyl)methyldichlorosilane: b.p.: 121°C/10 torr, yield: 77%). H-NMR ($CDCl_3$): δ 3.44–3.55 (6H, OCH_2–), 3.35 (3H, OCH_3), 1.77 (2H, Si–CH_2–CH_2–CH_2–), 1.15 (2H, Si–CH_2–), 0.75 (3H,Si–CH_3).

Monomers for polysilanes **4** (and **5**) was prepared as follows: Williamson reaction of the corresponding alcohol (168.2 g, 1.0 mol) with sodium (11.5 g, 0.5 mol) in THF at 60–70°C for 24 h was carried out and 1,4-dibrimobutane (216 g, 1.0 mol) was added into the mixture at room temperature. After filtering off the resultant salt, desired product was extracted with diethyl ether, washed with water. Vacuum distillation gave the corresponding 4-bromobutyl ether in 39% yield (b.p.: 112–115°C/0.15 torr). Grignard reagent obtained from the 4-bromobutyl ether was reacted with methyltrichlorosilane to give [5,8,11,14-tetraoxapentadecyl]methyldichlorosilane (b.p.: 133–141°C/0.1 tor, yield: 9.7). H-NMR ($CDCl_3$): δ 3.29–3.50 (14H, OCH_2–), 3.22 (3H, OCH_3), 1.43–1.52 (4H, Si–CH_2–CH_2–CH_2–CH_2–), 0.99 (2H, Si–CH$_2$–), 0.63 (3H,Si–CH$_3$). ^{13}C-NMR (CDCl$_3$): 72.2, 71.5, 70.9, 70.8, 70.4, 59.2, 32.5, 21.7, 19.5, 5.4 ppm. ^{29}Si-NMR(CDCl$_3$): δ 32.7 ppm.

5-Bromopentyl ether was similarly prepared from 1,5-dibromopentane to give the 4-bromopentyl ether (b.p.: 125–130°C/0.2, yield: 36%) and Grignard reaction with methyltrichlorosilane gave [6,9,12,15-Tetraoxahexadecyl]methyldichlorosilane (b.p.: 135–140°C/0.1 torr, yield: 16%). H-NMR (CDCl$_3$): δ 3.45–3.68 (14H, OCH$_2$–), 3.39 (3H, OCH$_3$), 1.39–1.61 (6H, Si–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 1.12 (2H, Si–CH$_2$–), 0.77 (3H,Si–CH$_3$). ^{13}C-NMR (CDCl$_3$): 72.2, 71.5, 71.1, 70.9, 70.4, 59.2, 32.2, 21.0, 18.0, 5.5 ppm. ^{29}Si NMR (CDCl$_3$): δ 32.75 ppm.

3.3. Polymerization

Representative polymerization procedure for polar polysilanes **2**–**6** is described. To a 0.5 l four necked round bottom flask equipped with a pressure equilibrated dropping funnel which was connected to an argon inlet, a stirring rod, a condenser, a thermometer were placed toluene (50 ml) and sodium (2.2 g, 0.01 atom). After sodium was finely dispersed at reflux temperature, [4,7,10,13-tetraoxatetradecyl]methyldichlorosilane (13.9 g, 0.0435 mol) was introduced quickly into the flask through the dropping funnel. Several minutes took for initiation of the polymerization reaction, which was detected by the characteristic blue coloration of the reaction system. After refluxing for 2 h and then cooled to room temperature by use of an ice bath, 40 ml of ethanol and 100 ml of water were added to quench the reaction. Organic layer was extracted by 160 ml of toluene and evaporation gave pasty material. To remove residual NaCl, the resultant crude material was dissolved in water and subjected to dialysis using a cellulose acetate membrane for one week. Evaporation of water gave oily material which was dissolved in toluene and insoluble materials were filtered off. The oily product obtained after evaporation of toluene layer was subjected to repeated precipitation from dibutyl ether. Centrifugation and subsequent vacuum drying at 70°C yielded a colorless, pasty polymer (1.46 g, 7.2%). GPC: $M_w/M_n = 21\,000/12\,000$. ^{1}H-NMR (C$_6Cl_3$): δ 3.60–3.68 (12H, OCH$_2$–), 3.47 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 3.24 (3H, OCH$_3$), 1.94 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 1.20 (2H, Si–CH$_2$–), 0.65 (3H, Si–CH$_3$). ^{13}C-NMR (C$_6Cl_3$): δ 73.9, 71.8, 70.5, 70.3, 70.1, 58.0, 26.3, 10.0, 4.9 ppm. ^{29}Si-NMR (C$_6$Cl$_3$): δ -32.1 ppm. $T_g = 193$ K.

Polysilane **4**: (yield; 6.8%). GPC: $M_w/M_n = 36\,000/14\,000$. $T_g = 193$ K. ^{1}H-NMR (C$_6$Cl$_3$): δ 3.54–3.60 (12H, OCH$_2$–), 3.42 (2H, Si–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 3.20 (3H, OCH$_3$), 1.75 (4H, Si–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 1.15 (2H, Si–CH$_2$–), 0.62 (3H,Si–CH$_3$). ^{13}C-NMR (C$_6$Cl$_3$)): δ 71.7, 71.0, 70.4, 70.2, 70.0, 58.0, 34.2, 23.3, 14.7, 4.4 ppm. ^{29}Si NMR (C$_6$Cl$_3$): δ -31.7 ppm.

Polysilane **5**: (yield; 4.9%). GPC: $M_w/M_n = 36\,000/14\,000$. $T_g = 194$ K. ^{1}H-NMR (C$_6$Cl$_3$): δ 3.50–3.60 (12H, OCH$_2$–), 3.41 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 3.19 (3H, OCH$_3$), 1.80–1.58 (6H, Si–CH$_2$CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 1.15 (2H, Si–CH$_2$–), 0.59 (3H, Si–CH$_3$). ^{13}C-NMR (C$_6$Cl$_3$)): δ 71.7, 71.0, 70.4, 70.2, 70.0, 58.0, 30.7, 29.5, 27.0, 14.9, 4.5 ppm. ^{29}Si NMR (C$_6$Cl$_3$): δ -31.7 ppm.

Polysilane **2**: (yield; 9.7%). GPC: $M_w/M_n = 19\,000/12\,000$. $T_g = 193$ K. ^{1}H-NMR (C$_6$Cl$_3$): δ 3.60–3.68 (8H, OCH$_2$–), 3.47 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 3.23 (3H, OCH$_3$), 1.95 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 1.20 (2H, Si–CH$_2$–), 0.59 (3H,Si–CH$_3$). ^{13}C-NMR (C$_6$Cl$_3$): δ 74.0, 71.8, 70.5, 70.4, 70.1, 58.1, 27.0, 10.6, 4.3 ppm. ^{29}Si NMR (C$_6$Cl$_3$): δ -31.6 ppm.

In the cases of polysilane **1**, toluene layer involving crude product was separated from water layer by a separating funnel. The toluene layer was washed with water several times to remove ionic species. After evaporation of toluene, the residual crude material is dissolved in defined amount of toluene and then was subjected to fractionation with methanol to give polysilane **1** (yield; 9.7%). (1.46 g, 7.2%). GPC: $M_w/M_n = 21\,000/12\,000$. $T_g = 193$ K. ^{1}H-NMR (C$_6$Cl$_3$): ^{1}H-NMR (CDCl$_3$): δ 3.60–3.68 (12H, OCH$_2$–), 3.47 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 3.24 (3H, OCH3), 1.94 (2H, Si–CH$_2$–CH$_2$–CH$_2$–), 1.20 (2H, Si–CH$_2$–), 0.65 (3H,Si–CH$_3$). ^{13}C-NMR (C$_6$Cl$_3$): $\delta = 73.9$, 71.8, 70.5, 70.3, 70.1, 58.0, 26.3, 10.0, 4.9 ppm. ^{29}Si-NMR (C$_6$Cl$_3$): $\delta = 32.1$ ppm.

3.4. Instruments and measurement

IR spectra of polysilanes were measured as neat films on KBr plate by a Horiba FT-210 Spectrophotometer. NMR spectra were obtained in DCCl$_3$ or C$_6$D$_6$ solutions with a Varian Unity 300 Spectrometer (300 MHz for H and 75.5 MHz for C). Mass spectra were obtained by a Shimadzu QP-5000 Mass Spectrometer. Thermal analysis (DSC) was performed by a Rigaku TAS 200. Molecular weight was obtained by gel permeation chromatography (GPC) using a set of Waters Ultrastyragel columns of 10^3, 10^4, 10^5, 10^6 referring to polystyrene standards. THF (0.8 ml min^{-1}) was employed as the eluent using a Toyo Soda HCL-800D pump. Yanaco M-315 SpectroMonitor (measured at 254 nm) was used to monitor the chromatogram.

UV spectra were measured with a Shimadzu UV-PC 3100 Spectrophotometer by dissolving polysilanes in a solvent (ca. 1.54×10^{-3} mol l^{-1}) at ambient temperature. Variable temperature spectra were obtained by use of an Oxford 39498 type Cryostat with an ITC 502 temperature controller. Fluorescence spectra were obtained by a Shimadzu FP-1600 spectrophotometer.

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