

Synthesis and Properties of Polysiloxanes Possessing 9,9-Diarylfluorene Structure in the Main Chain

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Polysiloxanes possessing 9,9-diarylfluorene moieties (F-PSiOs **3**) were synthesized in 83–91% yield by the polycondensation of 9,9-bis(hydroxyaryl or hydroxyethoxyphenyl)fluorenes with Ph_2SiCl_2 in the presence of pyridine. F-PSiOs with higher molecular weight (M_n 19000–32000, M_w 32000–75000) were obtained, when less polar solvents such as toluene and CCl_4 were used as the polymerization solvent. The F-PSiOs showed good solubility toward various organic solvents, high 5% weight loss temperature (T_{d5} : 443–544 °C), and lower glass transition temperature (T_g : 100–171 °C) under nitrogen atmosphere rather than 9,9-diarylfluorene-based polymers reported. On the other hand, no melting point (T_m) was observed owing to the amorphous nature of F-PSiOs. Dynamic viscoelasticity of F-PSiO film was also measured to evaluate the thermal behavior. The transmittance of F-PSiOs in the film state (thickness: 62–70 μm) reached over 90% in the visible region. The F-PSiOs exhibited remarkably high refractive index values in a range of 1.64–1.66 at 589 nm in addition to sufficiently low birefringence values, probably due to the *cardo* structure of the fluorene moiety placed in the main chain.
KEY WORDS: *Cardo* Structure / Polysiloxane / Refractive Index / Birefringence / Solubility / Thermal Stability / Processability /

9,9-Diarylfluorene-based transparent resins are an intriguing class of polymers owing to their high refractive index^{1–6} and low birefringence.^{7–12} The optical properties were originated from many aromatic rings of the 9,9-diarylfluorene moiety as so-called “*cardo* structure,” in which each aromatic ring occupies different planes. In addition, such polymers exhibit other characteristic properties including fine dispersing ability for inorganic fillers,^{13,14} good solubility toward organic solvents,¹⁵ high thermal stability,^{16–19} and so on.^{20–24} Although several studies directed toward optical use of 9,9-diarylfluorene-based high performance polymers have been reported, the polymers often suffer from low heat-processability due to the high glass transition temperature (T_g).^{16–19} As a potential solution to this issue, we postulated that the siloxane linkage in the main chain would serve as an effective linker, because polysiloxanes generally exhibit low T_g in addition to high thermal stability.^{25–27} While Nakamura *et al.* first reported the synthesis of polysiloxanes possessing 9,9-diarylfluorene structure by the elaborations with dianilindiphenylsilane,²⁷ there remains ample opportunities directed toward simple polymerization protocols for polysiloxanes and the optical applications.

Herein, we describe the synthesis of polysiloxanes (F-PSiOs) bearing 9,9-diarylfluorene moieties in the main chain by the polycondensation of 9,9-diarylfluorene derivatives (Figure 1) and commercially available Ph_2SiCl_2 . Several typical optical properties such as transparency, refractive index, and birefringence of the F-PSiOs are also evaluated in addition to the thermal properties and solubility.

EXPERIMENTAL

Materials and Methods

9,9-Bis(4-hydroxy-3-methylphenyl)fluorene (**1a**), 9,9-bis(4-hydroxyphenyl)fluorene (**1b**), and 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene (**1c**) (provided by Osaka Gas Co., Ltd.) were used after drying *in vacuo* at 100 °C for 5 h. All solvents were dried over freshly activated molecular sieves 4A. Commercially available materials and solvents including Ph_2SiCl_2 (Wako Pure Chemical Industries, Ltd.) were used without further purification.

¹H (400 MHz) and ²⁹Si (79.3 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using CDCl_3 as the solvent and tetramethylsilane as the internal standard. Molecular weight and its distribution were measured by gel permeation chromatography (GPC) on a JASCO Gulliver system equipped with two consecutive liner polystyrene gel columns (TOSOH TSKgel G2000HXL and GMHXL) at 30 °C, eluted with CHCl_3 at a flow rate of 0.85 mL/min, and calibrated using polystyrene standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Thermogravimetry (TG) was performed on a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under N_2 atmosphere (flow rate of 50 mL/min) to determine decomposition temperature T_{d5} at which 5% weight loss was observed. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under N_2 atmosphere (flow rate of 50 mL/min) to determine glass transition temperature T_g . Dynamic mechanical properties of polymer film were evaluated in a temperature

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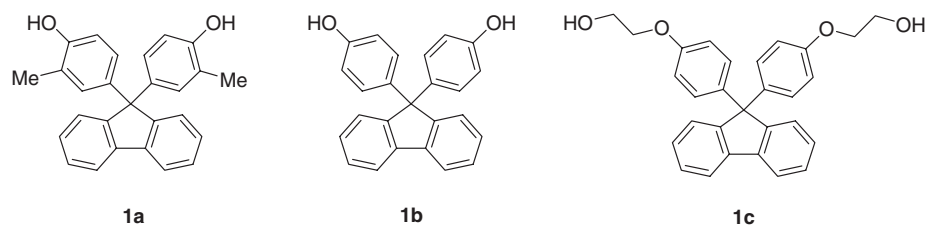


Figure 1. Chemical structures of 9,9-diarylfluorene diol monomers used in this work.

range from room temperature to 115 °C by using an IT-DVA200s (ITK Co., Ltd, Japan). The measurement was conducted in the oscillatory tensile mode at a frequency of 10 Hz and a heating rate of 5 °C/min. The dimension of a rectangular specimen was 4.8 mm in width and 600 μm in thickness and the distance between clamps was 1.5 cm, respectively. Transmittance of polymer films was evaluated by a UV-visible spectrophotometer (UV-550, JASCO) with the scanning range from 300 nm to 800 nm. Refractive indices of polymers were measured with an Abbe refractometer (DR-M2/1550, ATAGO Co., Ltd). Birefringences of the film were evaluated by taking the picture of the film placed between two cross axes polarizing films. Retardations were measured by polarized optical microscopy (OPTIPHOTO-POL, Nikon Co., Ltd) under the cross-Nicols (546 nm).

Typical Experimental Procedure for the Reaction of 9,9-Bis(4-hydroxyphenyl)fluorene (1b) and Ph₂SiCl₂ (2).²⁸ To a mixture of 9,9-bis(4-hydroxyphenyl) fluorene (**1b**, 7.74 g, 22.1 mmol) and pyridine (5.0 mL, 62 mmol) in toluene (14 mL) was added dropwise a solution of Ph₂SiCl₂ (**2**, 5.59 g, 22.1 mmol) in toluene (6 mL) at room temperature under an argon atmosphere. After stirring at 40 °C for 8 h, the mixture was cooled to room temperature, and diluted with toluene to precipitate pyridinium hydrochloride, which was filtered off. The filtrate was washed with 7.7% aqueous pyridine, and then poured into MeOH. The precipitates formed were collected by filtration, and the solid product was dried *in vacuo* at room temperature for 1 d to give F-PsSiO **3b** (9.73 g, 83%) as a white solid; M_n 21000, M_w 40000, MWD 1.9; T_g 166 °C, T_{d5} 544 °C; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.65 (d, 4H, $J = 7.4$ Hz), 7.61 (d, 2H, $J = 7.6$ Hz), 7.36 (t, 2H, $J = 7.6$ Hz), 7.27 (t, 4H, $J = 7.4$ Hz), 7.19 (t, 2H, $J = 7.4$ Hz), 7.15 (d, 2H, $J = 7.6$ Hz), 7.07 (t, 2H, $J = 7.6$ Hz), 6.82 (d, 4H, $J = 8.2$ Hz), 6.64 (d, 4H, $J = 8.2$ Hz) ppm; ²⁹Si NMR (79.3 MHz, CDCl₃, 298 K) δ -39.1 ppm; IR (neat) 3033, 1604, 1504, 1447, 1429, 1241, 1173, 1125, 1015, 915, 826, 737, 718, 697, 630 cm⁻¹.

F-PsSiO 3a. A white solid (91%); M_n 19000, M_w 32000, MWD 1.7; T_g 171 °C, T_{d5} 528 °C; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.8–7.5 (m, 6H), 7.5–6.9 (m, 12H), 6.85 (s, 2H), 6.57 (s, 4H), 2.03 (s, 6H) ppm; ²⁹Si NMR (79.3 MHz, CDCl₃, 298 K) δ -38.3 ppm; IR (neat) 3049, 2919, 1604, 1590, 1497, 1447, 1429, 1254, 1125, 943, 809, 741, 717, 698, 647 cm⁻¹.

F-PsSiO 3c. A white solid (85%); M_n 32000, M_w 75000, MWD 2.3; T_g 100 °C, T_{d5} 443 °C; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.68 (d, 2H, $J = 7.4$ Hz), 7.62 (d, 4H, $J = 7.4$ Hz), 7.4–7.1 (m, 12H), 7.03 (d, 4H, $J = 8.7$ Hz), 6.65 (d, 4H, $J = 8.7$ Hz),

4.04 (t, 4H, $J = 4.8$ Hz), 3.96 (t, 4H, $J = 4.8$ Hz) ppm; IR (neat) 3068, 2933, 2876, 1607, 1507, 1448, 1429, 1373, 1290, 1250, 1179, 1125, 1064, 971, 916, 823, 745, 718, 701, 667 cm⁻¹.

Film Preparation. Polymer films of the F-PsSiOs for the evaluation of refractive index and birefringence were prepared by a spincoating method using the toluene solutions of the corresponding polymers at room temperature. The films for the evaluation of transmittance were prepared by a casting method using the toluene solutions of the corresponding polymers at room temperature.

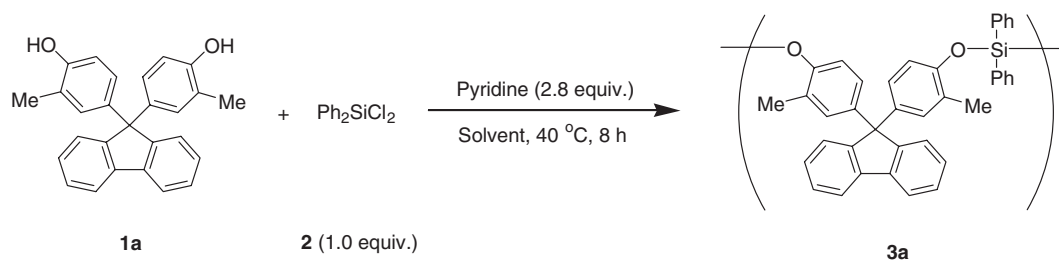
RESULTS AND DISCUSSION

Synthesis and Structure of F-PsSiOs

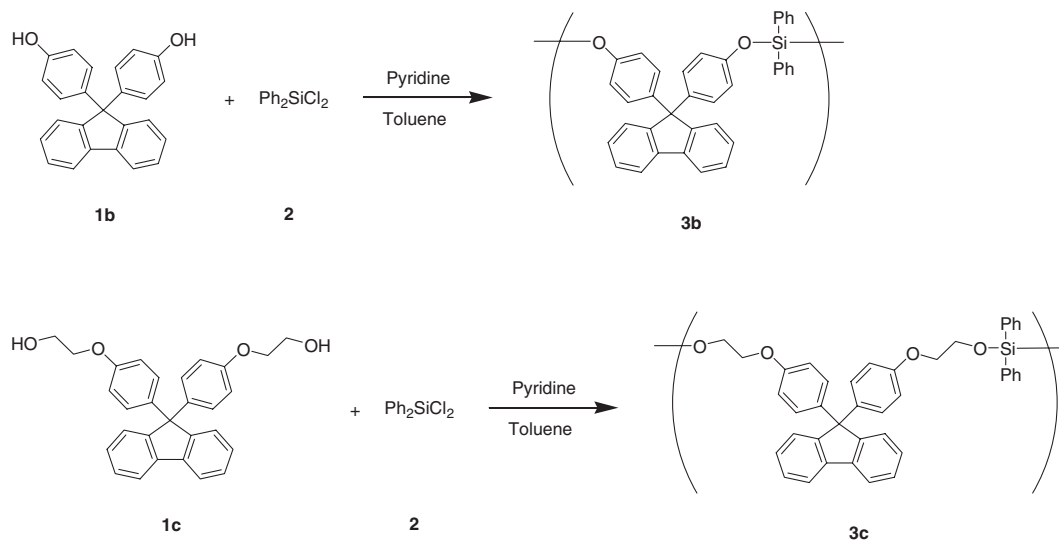
Since we previously used 9,9-bis(4-hydroxy-3-methylphenyl)fluorene (**1a**) for the preparation of high performance poly(ether-ketone)s with excellent optical properties,¹² we have first examined **1a** as the diol monomer for the preparation of F-PsSiOs. Polycondensation reactions of **1a** (11.0 mmol) with commercially available dichlorodialkylsilanes (11.0 mmol) in the presence of pyridine (30 mmol) were conducted in various solvents (1.1 M). After the initial unfruitful attempts utilizing Me₂SiCl₂, we found that the preparation of stable polysiloxane was achieved by using Ph₂SiCl₂ (**2**) probably owing to the more acid-resistant Si–O linkage (Scheme 1).

Various solvents were used as polymerization solvents. The results are summarized in Table I. It turned out that toluene and CCl₄ used as the suitable less polar solvents (entries 5 and 6) gave a highly viscous mixture including the corresponding polysiloxane **3a** (M_n 7900–8000, M_w 14000–15000) and pyridinium hydrochloride as precipitates. Meanwhile, the polycondensation in polar solvents such as THF and CH₂Cl₂ afforded lower molecular weight polysiloxane **3a** (M_n 4700–5300, M_w 7500–9000; entries 1 and 2) than those in less polar solvents. After considerable experimental work, polysiloxane **3a** with relatively high molecular weight (M_n 19000, M_w 32000, MWD 1.7) enough to evaluate the optical properties was obtained by the polymerization in CCl₄ at 80 °C for 18 h (entry 7).

Considering the moderate reactivity of **1a**, we planned to exploit both 9,9-bis(4-hydroxyphenyl)fluorene **1b** without the methyl substituents at the *ortho* position to the phenolic OH group and 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene **1c** as the alcoholic monomer, which could hopefully serve as the more reactive monomers owing to the less steric hindrance.



Scheme 1.



Scheme 2.

Table I. Effect of solvent on the polycondensation of bisphenol **1a** and Ph_2SiCl_2 **2**^a

Entry	Solvent	Yield ^b / %	M_n^c	M_w^c	MWD^c
1	THF	86	4700	7500	1.6
2	CH_2Cl_2	84	5300	9000	1.7
3	CHCl_3	78	4500	7200	1.6
4	$\text{ClCH}_2\text{CH}_2\text{Cl}$	80	6800	12000	1.8
5	CCl_4	83	8000	14000	1.8
6	Toluene	81	7900	15000	1.9
7 ^d	CCl_4	91	19000	32000	1.7

^aA mixture of **1a** (11.0 mmol) and **2** (11.0 mmol) was heated in the presence of pyridine (30 mmol) in toluene (10 mL) at 40 °C for 8 h. ^bYield of MeOH-insoluble part. ^cEstimated by GPC using polystyrene standards (eluent: CHCl_3). ^dThe reaction was performed at 80 °C for 18 h.

Since the use of CCl_4 as a solvent gave a good result in the synthesis of **3a**, we examined the use of less polar solvents such as toluene in place of CCl_4 from a viewpoint of green chemistry (Scheme 2). Relationship between polymer molecular weight and reaction time in the polycondensation to **3b** and **3c** was evaluated at 40 °C and 100 °C. The results are shown in Figure 2. During the polymerization, the molecular weights of **3b** and **3c** initially increased but then decreased except for the polymerization of **1c** at 40 °C. These results suggest that both the formation and the cleavage of Si–O bond of the polymer

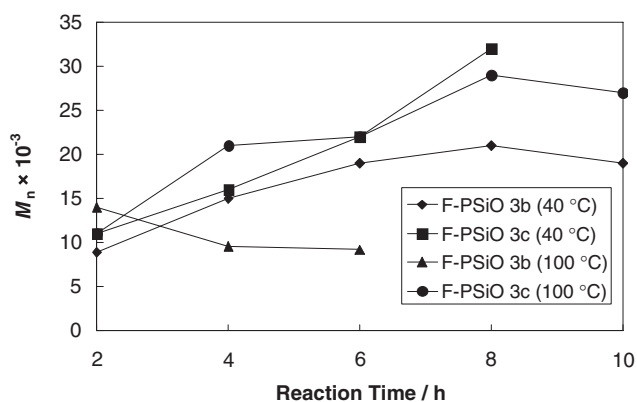


Figure 2. Effect of reaction temperature and time on the molecular weight of F-PSiOs **3b** and **3c** in the polymerization in toluene (1.1 M) in the presence of pyridine (2.8 equiv.).

chain proceed competitively. To clarify the degradation process, the reduction in polymer molecular weight by additive was examined using F-PSiO **3b** (M_n 16000) (Table II). Treatment of **3b** with either pyridine in toluene and pyridinium hydrochloride in THF resulted in the considerable decrease in molecular weight due to the cleavage of Si–O bond, undoubtedly by nucleophilic attack of pyridine or chloride anion at the

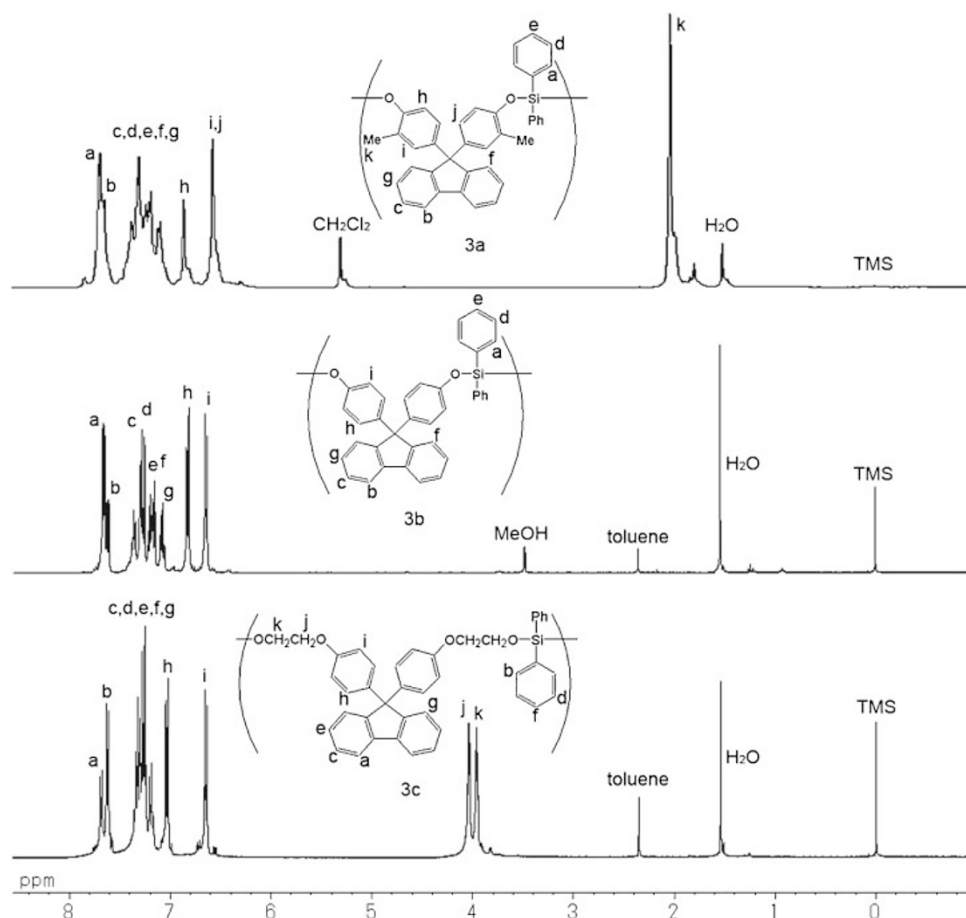


Figure 3. ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of F-PSiOs **3a**, **3b** and **3c**.

Table II. Effect of additive on the reduction of polymer molecular weight^a

Entry	Additive	Solvent	Temp./ $^{\circ}\text{C}$	M_n^b
1	—	toluene	100	14000
2	pyridine	toluene	100	2400
3	pyridinium hydrochloride	toluene	100	13000
4	pyridinium hydrochloride	THF	50	4300

^aA mixture of F-PSiO **3b** (M_n 16000, 1.06 g) and an additive (pyridine (0.25 mL) or pyridinium hydrochloride (690 mg)) was heated in a solvent (10 mL) for 12 h. ^bGPC data based on the polystyrene standards (eluent: CHCl_3).

silicon atom (entries 2 and 4). On the other hand, the reduction in polymer molecular weight by the addition of pyridinium hydrochloride in toluene was sluggish probably owing to the low solubility of pyridinium hydrochloride toward toluene (entry 3). The results suggest that the use of less polar solvents such as toluene and CCl_4 controls the reduction in polymer molecular weight in the synthesis of F-PSiOs. Although the polymerization of **1b** at 0°C afforded a remarkably highly viscous mixture, the polymer molecular weight was low (**3b**: M_n 2800, M_w 4800), because of the low solubility behavior of the polymer to toluene at 0°C . After considerable experimental work based on the knowledge thus obtained, we decided the optimal condition to obtain polysiloxanes **3b** (M_n 21000, M_w

40000, MWD 1.9) and **3c** (M_n 32000, M_w 75000, MWD 2.3) suitable for the film preparation. Namely, the polymerizations were conducted in toluene at 40°C for 8 h, contrary to extremely elevated temperature (220°C) in the case of dianilinosilane system.²⁷

Figures 3 and 4 show ^1H NMR and ^{29}Si NMR spectra of F-PSiOs **3**. In the ^1H NMR spectra, all aromatic signals of **3** appeared sharply, which suggested a low degree of disorderness in polymer structure (Figure 3). In ^{29}Si NMR spectra, the sharp signal appeared around -40 ppm was assignable to that of Si atom of $\text{Ph}_2\text{Si}(\text{OAr})_2$, whereas signals corresponding to neither Ph_2SiCl_2 nor $\text{Ph}_2\text{SiCl}(\text{OAr})$ was observed (Figure 4). IR spectral data also supported the polysiloxane structure; a medium absorption band at 1429 cm^{-1} and a strong band at 1125 cm^{-1} corresponding to Si–C linkage in addition to strong broad absorptions at $1100\text{--}1000\text{ cm}^{-1}$ and $1300\text{--}1200\text{ cm}^{-1}$ for Si–O linkage.²⁸

Properties of F-PSiOs

Thermal and optical properties of **3a** (M_n 19000, M_w 32000, MWD 1.7), **3b** (M_n 21000, M_w 40000, MWD 1.9), and **3c** (M_n 32000, M_w 75000, MWD 2.3) were examined. The F-PSiO films for the measurement were prepared by casting from a toluene solution (film thickness: 62–70 μm).

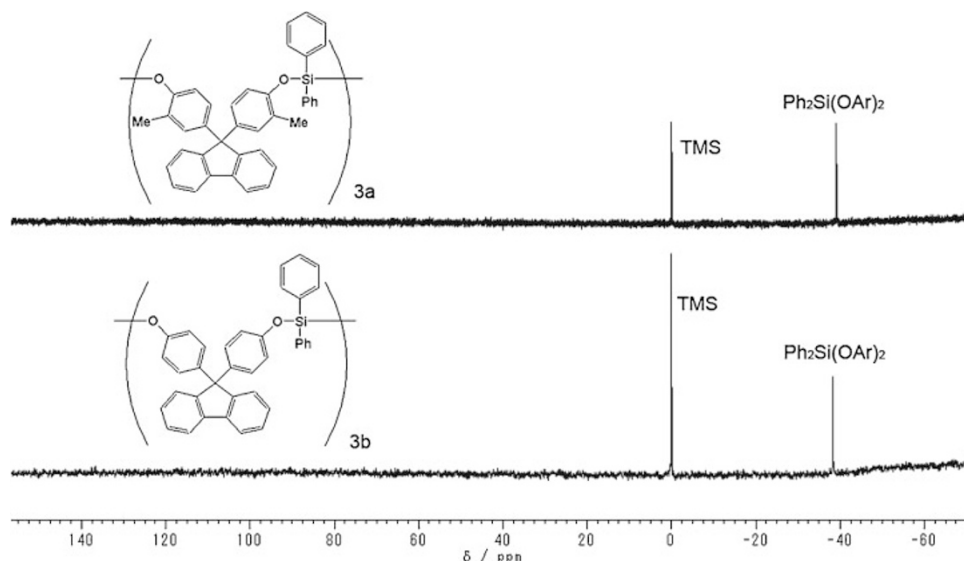


Figure 4. ^{29}Si NMR spectra (79.3 MHz, CDCl_3 , 298 K) of F-PSiOs **3a** and **3b**.

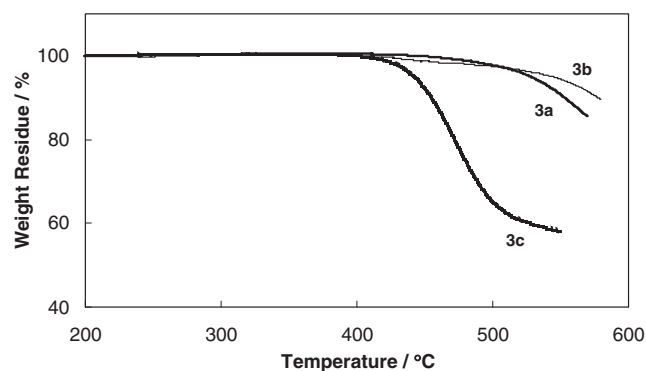


Figure 5. TGA results of F-PSiOs, measured at a heating rate $10^\circ\text{C}/\text{min}$ in N_2 atmosphere.

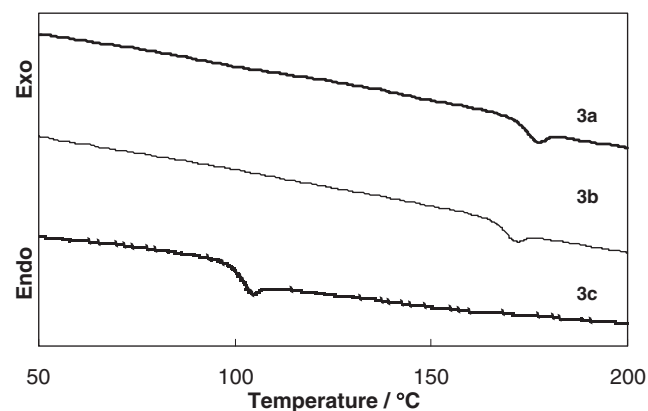


Figure 6. DSC results of F-PSiOs, measured at a heating rate $10^\circ\text{C}/\text{min}$ in N_2 atmosphere.

Thermal Property

The thermal properties were evaluated by TGA and DSC (Figures 5 and 6). The decomposition temperatures (T_{d5}) were very high; 528°C (**3a**), 544°C (**3b**), and 443°C (**3c**), which clearly depended on the structure of the siloxane linkage of the polymers. The high thermal stability probably comes from the strong Si–O covalent bond: bond energy of Si–O is 368 kJ/mol, while that of C–O is 336 kJ/mol. On the other hand, no melting point (T_m) was observed in this case, clearly suggesting the amorphous nature of the F-PSiOs. T_g s of the F-PSiOs were sufficiently low as expected according to the literature:²⁷ 171°C (**3a**), 166°C (**3b**), and 100°C (**3c**), unambiguously due to the flexible siloxane main chain structure. The low T_g for **3c** also suggests that T_g of the F-PSiO was controlled easily by controlling the structure of the spacer between the diarylfluorene and the siloxane moieties.

Dynamic Viscoelasticity of F-PSiO Film

Dynamic mechanical properties of F-PSiO **3c** film was evaluated in a temperature range from room temperature to

115°C . Figure 7 shows the temperature dependence of the dynamic viscoelastic properties such as tensile storage modulus E' and $\tan \delta$. The results suggested that the plateau region in E' appeared until 80°C , while the peak top of the $\tan \delta$ curve was 94°C , mostly corresponding to the T_g of F-PSiO **3c** evaluated by DSC.

Solubility

The solubility toward various organic solvents was evaluated. The results are summarized in Table III. All three polymers **3** were highly soluble in typical organic solvents such as toluene, CHCl_3 , and THF, even though they consist mostly of aromatics. The unusually high solubility observed here presumably comes from the special structure of 9,9-diarylfluorene moieties, so-called “cardo structure” and the flexible Si–O linkage in the main chain, as mentioned above.¹⁵ The high solubility along with the good thermal properties of the F-PSiOs seems to enhance their processability.

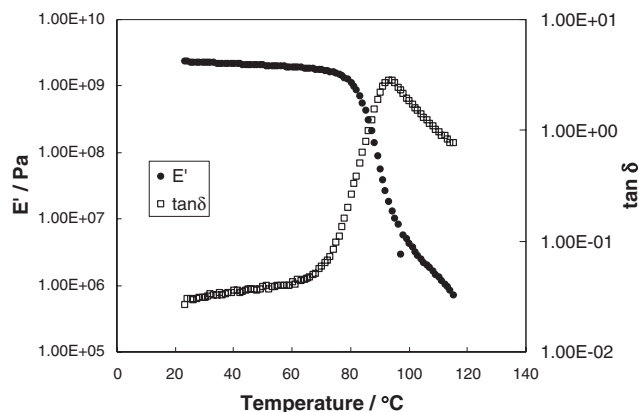


Figure 7. Viscoelastic property of F-PSiO **3c** in a range from room temperature to 115 °C.

Table III. Solubility behavior of F-PSiOs to organic solvents^a

F-PSiO	CHCl ₃	THF	toluene	acetone	MeCN	MeOH	hexane
3a	++	++	++	+	-	+	-
3b	++	++	++	-	-	-	-
3c	++	++	++	-	-	-	-

^aF-PSiO (100 mg) was added to a solvent (1 mL) and stirred at room temperature. ++, soluble; +, partially soluble; -, insoluble.

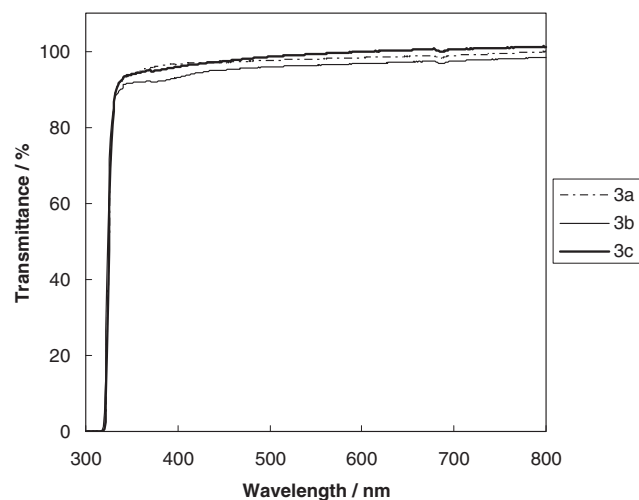


Figure 8. Transmittance of **3** in film state measured by UV-vis spectrometer (film thickness: 62–70 μm).

Transparency

The transmittance of the all films reached *ca.* 90% over 340 nm, and gradually increased with increase of wavelength in the visible light region (Figure 8). The high transparency of the F-PSiOs probably results from their amorphous nature owing to the *cardo* structure of the 9,9-diarylfluorene moiety, and is consistent with the largely decreased interchromophore interaction in or within the polymer chain.

Refractive Index

The refractive indices of the F-PSiOs were measured using their thin films which were obtained by the spincoating method

Table IV. Refractive index of F-PSiOs **3**^a

F-PSiO	Refractive Index	
	589 nm	656 nm
3a	1.65	1.64
3b	1.64	—
3c	1.66	1.66

^aRefractive indices of the polymer samples were measured by an Abbe refractometer (film thickness: 440–460 μm).

Table V. Degree of retardation of F-PSiOs **3**^a

F-PSiO	Degree of Retardation/nm	
	undrawn	drawn ^b
3a	0.0	—
3b	0.0	—
3c	0.0	0.0

^aRetardation was measured by a polarized optical microscopy under the cross Nicols with the light wavelength of 546 nm. ^bThe film was drawn at 100–120 °C. Drawn ratio was 2.0.

using toluene solutions of the polymers at room temperature. The results are summarized in Table IV. The refractive index values were sufficiently high as polymer consisting only of C, H, and O atoms: 1.65 (**3a**), 1.64 (**3b**) and 1.66 (**3c**) at a typical wavelength of 589 nm. The high refractive index values of the F-PSiOs are certainly attributable to the polynuclear aromatic main chain consisting of both the 9,9-diarylfluorene and the diphenylsilyl moieties. Meanwhile, it can be concluded that the flexible alkyl chain as the spacer moiety of **3c** enables the dense packing of polymer chains resulting in the high refractive index.

Birefringence

The birefringence of the F-PSiOs **3** was evaluated using both the drawn and undrawn films. Degree of retardation of visible light at 546 nm in the F-PSiOs was 0.0 nm in both drawn and undrawn states (Table V). Very low or zero birefringence observed is attributed to the *cardo* structure of the 9,9-diarylfluorene moiety in the main chain as mentioned previously.^{7–12} The fluorene moiety and the two phenyl groups at the C9-position of the fluorene group occupy different planes and are crossed at the precise angle that renders the structure most stable. Placing the aromatic rings on the different planes might disturb their one-directional folding, and thereby the optical anisotropy of the F-PSiOs disappears.

SUMMARY

This paper has disclosed the simple polycondensation of diphenolic or alcoholic 9,9-diarylfluorene derivatives with Ph₂SiCl₂ and the characteristic properties of the resulting polymers (F-PSiOs **3a–3c**). The F-PSiOs showed their relatively high *T*_{d5}, low *T*_g, and high solubility, which seems to enhance their processability. The transparent films of the F-PSiOs exhibited remarkably high refractive index values in a

range of 1.64–1.66, whereas they showed zero birefringence. These characteristic optical properties of the F-PSiOs come mainly from the *cardo* structure of the 9,9-diarylf luorene skeleton in the main chain.^{1–12} Thus, the F-PSiOs can unambiguously be regarded as a promising advanced material that may be applied to a variety of fields including optical material fields.

Electronic Supporting Information Available: Experimental Details, Figures S1, S2 and S3. These materials are available via the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>

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28. See, Supporting Information.