

Synthesis and Photoelectronic Properties of Thermally Stable Poly[oxy(2,7-fluoren-9-onenylene)oxy(diorganosilylene)]s

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Melt copolymerization reactions of several bis(diethylamino)silane derivatives, bis(diethylamino)methylphenylsilane, bis(diethylamino)methyloctylsilane, 1,2-bis(diethylamino)tetramethyldisilane, and 1,3-bis(diethylamino)tetramethyldisiloxane, with 2,7-dihydroxyfluoren-9-one were carried out to yield poly[oxy(2,7-fluoren-9-onenylene)oxy(diorganosilylene)]s bearing the fluoren-9-one fluorescent aromatic group in the polymer main chain: poly[oxy(2,7-fluoren-9-onenylene)oxy(methylphenylsilylene)], poly[oxy(2,7-fluoren-9-onenylene)oxy(methyloctylsilylene)], poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisilylene)], and poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisiloxanylene)]. These polymeric materials are soluble in common organic solvents such as CHCl_3 and THF. FTIR spectra of all the materials reveal characteristic Si-O-C stretching frequencies at $1012\text{--}1018\text{ cm}^{-1}$. In the THF solution, the prepared materials show strong maximum absorption peaks at 258–270 nm, strong maximum excitation peaks at 260–280 nm, and strong maximum fluorescence emission bands at 310–420 nm. TGA thermograms suggest that most of the polymers are essentially stable to 200 °C without any weight loss and up to 300 °C with only a weight loss of less than 5% in nitrogen.

Key Words : Poly[oxy(2,7-fluoren-9-onenylene)oxy(diorganosilylene)]s, Absorption, Excitation, Fluorescence, Thermal stability

Introduction

Polyconjugated organosilicon materials have attracted considerable attention owing to their potential applications to photonic, electronic, ionic conductive, and ceramic materials.^{1–4} Fluorescent organosilicon polymers containing a polyconjugated system have also been of great interest for the use in plastic electronic devices such as field-effect transistors (FETs), light-emitting diodes (LEDs) or photovoltaic cells.^{5,6} For example, polysiloxanes containing pyrene or carbazole in the polymer side chain have been prepared by hydrosilation reactions of poly(methylhydrosiloxane) with vinyl- or allyl-functionalized pyrene or carbazole.⁷ Fluorescent polysiloxanes bearing a fluorescent group such as an anthryl, fluorenyl, naphthyl, quinoline, or quinaldyl group along the side chain have been synthesized by dehydrogenative coupling reactions of fluorescent alcohols or phenols with poly(methylhydrosiloxane) using coupling catalysts.⁸ The silylene-siloxane-diacetylene linear copolymers exhibit elastomeric properties with thermal stabilities up to high temperatures of 330 °C in air.⁹

The intramolecular cyclization reactions of 2,5-bis(silyl)-1,4-diethynylbenzene derivatives were reported to produce ladder-like oligo(*p*-phenylenevinylene)s with silicon and carbon bridges consisting of an annelated π -conjugated framework, and the obtained materials were intensely fluorescent in the visible region with various emission colors from blue to green to yellow.¹⁰

A new polymerization process for the preparation of polysiloxane copolymers is of great interest for the production of

a new type of hybrid polymers,¹¹ that are expected to possess novel properties including adjustable glass transition temperatures or thermal stabilities. For example, a new type of polymerization, the polycondensation reaction of dihydrosilanes with dialkoxysilanes, was reported at or below ambient temperature in the presence of catalytic amounts of tris(pentafluorophenyl)borane and can produce a wide variety of siloxane copolymers with an easily removable hydrocarbon byproduct.¹² The condensation of a dichlorosilane with a silanediol in the presence of triethylamine was reported to readily yield alternating cyclotetrasiloxanes.^{13,14} The interfacial polymerization of a dichlorosilane in an organic solvent such as octane and a diol in 2,5-hexanedione was reported to produce poly[alkyl(aryl)oxysilanes] with low molecular weights.¹⁵

We have reported the synthesis of oligomers containing the π -conjugated moiety $\text{C}=\text{C}-\text{B}-\text{C}=\text{C}$ and an organosilacyclic group along the polymer backbone by polyaddition reactions of 1,1-diethynyl-1-silacyclopent-3-enes with borane derivatives, as well as, notably, their electronic and thermal properties.^{16,17} We have also reported the synthesis of polycarbosilanes containing diethynyl and organosilane groups, such as poly(1,1-diethynyl-1-silacyclopent-3-ene), poly(1,1-diethynyl-1-1-silacyclobutane), poly(diethynyldialkylsilane)s, and poly(diethynyldiarylsilane)s by oxidative coupling reactions of diethynyl organosilane monomers, along with their photoelectronic and thermal properties.^{18,19} We previously examined the preparation and excited-state energy dynamics of polycarbosilanes as well as polycarbogermanes containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne in

the polymer backbone.^{20,21}

Fluorene-containing organic polymers, for example, polyfluorene and fluorenone-alkylthiophene copolymer, have been reported recently, along with their applications.²²⁻²⁵ Polysiloxanes containing a phenolic derivative of curcumin that exhibits anti-oxidant activity along the main chain have been also reported.²⁶

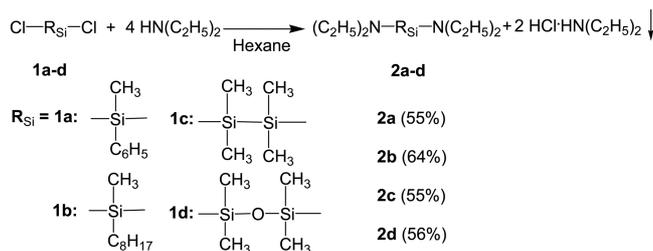
Recently, we have reported the melt copolymerizations of bis(diethylamino)methyloctylsilane and 1,3-bis(diethylamino)tetramethyldisiloxane with several fluorescent aromatic aryldiol chromophores to yield poly(carbomethyloctylsiloxane)s and poly(carbotetramethyldisiloxane)s, respectively.^{27,28}

However, the thermal and photoelectronic properties such as absorption, excitation, and fluorescence emission of polysiloxane copolymers containing the fluorene-9-one group in the backbone have seldom been reported. On the basis of our previous results, we have decided to continue our study on the preparation and properties of poly[oxy(2,7-fluorene-9-onenylene)oxy(diorganosilylene)] materials containing an aromatic chromophore, the fluorene-9-one group, in the main chain.

Here, we describe the melt copolymerizations of the bis(diethylamino)silane derivatives **2a-d**, bis(diethylamino)methylphenylsilane (**2a**), bis(diethylamino)methyloctylsilane (**2b**), 1,2-bis(diethylamino)tetramethyldisilane (**2c**), and 1,3-bis(diethylamino)tetramethyldisiloxane (**2d**), with 2,7-dihydroxyfluorene-9-one (**3**) to yield the poly[oxy(2,7-fluorene-9-onenylene)oxy(diorganosilylene)]s **4a-d**, poly[oxy(2,7-fluorene-9-onenylene)oxy(methylphenylsilylene)] (**4a**), poly[oxy(2,7-fluorene-9-onenylene)oxy(methyloctylsilylene)] (**4b**), poly[oxy(2,7-fluorene-9-onenylene)oxy(tetramethyldisilylene)] (**4c**), and poly[oxy(2,7-fluorene-9-onenylene)oxy(tetramethyldisiloxanylene)] (**4d**), respectively, which each contain fluorene-9-one as a fluorescent aromatic chromophore group in the main chain. The goal of these melt copolymerization was to synthesize linear poly(carbosiloxane)s with high molecular weights. We tried to carry out the melt copolymerization process for the bis(diethylamino)silane derivatives **2a-d** with the 2,7-dihydroxyfluorene-9-one diol (**3**). The materials produced were characterized by FTIR and ¹H, ¹³C, and ²⁹Si NMR spectrophotometry in the solution state as well as by elemental analysis. These prepared poly(carbosiloxane)s include the fluorescent aromatic fluorene-9-one group along the main chain. We will focus on examining the photoelectronic and thermal properties of the prepared polymers **4a-d** using absorption, excitation, and fluorescence emission spectrophotometers in the solution state as well as thermogravimetric analysis (TGA).

Results and Discussion

Synthesis of Monomers and Polymers. The condensation reactions of dimethyldichlorosilane and dimethyldiethoxysilane with aliphatic diols to yield only cyclic dimethyl(alkylenedioxy)silanes have been investigated pre-



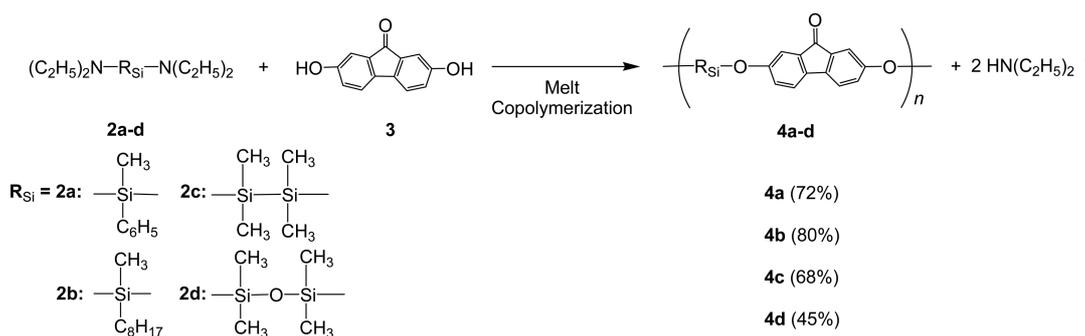
Scheme 1

viously.²⁹ The polycondensation of 1,2-dichlorotetramethyldisilane with resorcinol in *N*-methyl-2-pyrrolidone or toluene was reported to yield polysiloxanes with low molecular weights.³⁰ For the preparation of poly(carbosiloxane)s with high molecular weights, we decided to use the bis(diethylamino)silane derivatives **2a-d**, bis(diethylamino)methylphenylsilane (**2a**), bis(diethylamino)methyloctylsilane (**2b**), 1,2-bis(diethylamino)tetramethyldisilane (**2c**), and 1,3-bis(diethylamino)tetramethyldisiloxane (**2d**), as co-monomers in order to carry out melt copolymerization. The monomers **2a-d** were readily prepared by the reaction of dichlorosilane derivatives **1a-d**, respectively, with four equivalents of diethylamine under an argon atmosphere with moderate yield (Scheme 1).

The monomers **2a-d** were characterized using several spectroscopic methods, including NMR, IR, and mass spectroscopy. ¹H NMR spectra of **2a-d** clearly revealed triplet resonances at 1.06, 0.98, 0.95, and 0.98 ppm and quartet resonances at 2.96, 2.81, 2.79, and 2.82 ppm, which could be ascribed to the ethyl group bonded to nitrogen.³¹ This suggests that the diethylamination reaction of the starting material **1**, the substitution reaction of two chlorine atoms with diethylamino groups, was complete under our reaction conditions using four equivalents of diethylamine. In the ¹³C NMR spectra of **2a-d**, two carbon peaks of the ethyl group bonded to the nitrogen were also observed between 15.0 and 41.09 ppm.³¹ In the ²⁹Si NMR spectra of **2a-d**, the silicon resonances were observed at -30.74, -4.71, 0.66, and -13.54 ppm, respectively.³² We also confirmed all of the molecular ion peaks in each of the mass spectra of **2a-d**.

The melt copolymerization reaction between 1,2-bis(diethylamino)disilane and bisphenol has been reported to yield poly(oxyaryleneoxydisilane).^{30,33} We also very recently reported the melt copolymerization of several aryldiols with bis(diethylamino)methyloctylsilane.^{26,27} We attempted the copolymerization reactions of bis(diethylamino)silane derivatives **2a-d** as novel monomers with unique functionalities according to the previously reported method.³⁰ The melt copolymerizations of **2a-d** with 2,7-dihydroxyfluorene-9-one (**3**) have been carried out to produce the poly[oxy(flourene-9-onenylene)oxy(organosilylene)]s **4a-d**, which contain fluorene-9-one and organosilyl groups in the polymer main chain (Scheme 2).

The prepared poly[oxy(flourene-9-onenylene)oxy(diorganosilylene)]s **4a-d** are dark brownish powders or very viscous liquids and are soluble in common organic solvents such as CHCl₃ and THF. Polymer **4b** is also soluble in dimethyl-



Scheme 2

formamide (DMF) and toluene. However, polymers **4a**, **4c**, and **4d** are only very slightly soluble in toluene and DMF. We determined the molecular weights of polymers **4a-d** using gel permeation chromatography (GPC) in THF as an eluent. The observed weight average molecular weights (M_w) of materials **4a-d** were in the range of 832–12,884 with polydispersities of 1.02–1.09 (Table 1), suggesting that the obtained hybrids **4a-d** are oligomeric materials with low molecular weights. This can be explained by considering the rigidity of the aromatic fluoren-9-one diol used as comonomer **3** as well as the 1,2- or 1,3-bis(diethyl)amino functionalities of comonomers **2c** and **2d**. We characterized the resulting polymers **4a-d** by using several spectroscopic methods such as ^1H , ^{13}C , and ^{29}Si NMR and FTIR spectroscopy as well as by measuring optical properties such as absorption, excitation, and fluorescence emission in THF solution. Some selected spectral properties of the polymers **4a-d** are listed in Table 1.

FTIR spectra of the polymers **4a-d** show the characteristic Si-O-C stretching frequencies at 1015, 1017, 1012, and 1018 cm^{-1} , respectively, indicating that Si-O-C bonds are newly formed in the copolymerization reactions.^{31,34} The FTIR spectra of materials **4a-d** exhibit the characteristic C=O stretching frequencies at 1712, 1713, 1715, and 1719 cm^{-1} , respectively, suggesting that the O=C functional group of fluoren-9-one is contained along the polymer backbone after the copolymerization reaction.^{31,34} We note, in particular, that the solid-state ^{29}Si CP-MAS NMR spectra of the polymers **4a-d** show major singlet resonance peaks at -33.75 , -13.52 , -22.21 , and -22.37 ppm, respectively, indicating that the silicon atoms in the polymer main chain have the structural environment $(\text{R}_2\text{SiO})_x$,³² and suggesting structures

consistent with the backbone structures shown in Scheme 2.

Properties of Polymers. We examined absorption, excitation, and fluorescence emission spectra of the polymers in THF solution. A typical absorption spectrum of polymer **4a** in THF is shown in Figure 1 as a dashed line. The maximum absorption band for **4a** is observed at 258 nm, and the band extends from 232 to 310 nm with a molar absorptivity of $4.3 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$. The absorption spectra of **4b-d** exhibit strong absorption peaks at λ_{max} values ranging from 258 to 270 nm. These strong absorption bands in the UV-vis spectra of **4a-d** may be attributed to the aryl or fluoren-9-one groups along the polymer backbone.⁶ In the case of **4b**, in particular, the maximum absorption peak was red-shifted from 258 nm to 270 nm, while the maximum excitation peak was shifted from 260 nm to 280 nm, when compared with the spectrum of **4a**. As shown in Table 1, the fluorescence FWHM (full width at half maximum) values of 171 nm and 150 nm of polymers **4a** and **4c**, respectively, are much larger than the 55 nm value of polymer **4b**. This phenomenon may be due in part to the intra- and/or inter-molecular nonpolar interactions of octyl groups in **4b**, which do not occur in **4a**. The discrepancy between the maximum absorption (258 nm) and excitation (280 nm) bands in polymer **4d** may be ascribed to the energy change of the Si-O-Si bond, considering the 90 nm fluorescence FWHM in polymer **4d**.

The excitation spectrum for **4a** at the detection wavelength of 420 nm shows a strong excitation peak at a $\lambda_{\text{ex,max}}$ value of 260 nm (Table 1). A typical excitation spectrum of the polymer **4a** in THF solution is shown in Figure 1 as a solid line. The excitation spectra of **4b-d** at the detection wavelengths of 310, 410, and 420 nm also exhibit strong excitation peaks at $\lambda_{\text{ex,max}}$ values of 280, 270, and 280 nm,

Table 1. Selected Properties of Poly[oxy(2,7-fluoren-9-onenylene)oxy(diorganosilylene)]s **4a-d**

Polymer	M_w/M_n^a (PDI)	^{29}Si NMR ^b δ (ppm)	IR ^c $\nu_{\text{(Si-O-C)}}$ (cm^{-1})	Absorption ^d $\lambda_{\text{abs,max}}$ (ϵ) (nm ($\text{cm}^{-1}\text{M}^{-1}$))	Excitation ^e $\lambda_{\text{ex,max}}$ (nm)	Fluorescence ^f $\lambda_{\text{em,max}}$ (nm)	Fluorescence FWHM ^g (nm)	TGA ^h
4a	12,884/12,388 (1.04)	-33.57	1015	258 (4.3×10^4)	260	420	171	89
4b	3,321/3,256 (1.02)	-13.52	1017	270 (3.1×10^3)	280	310	55	63
4c	827/759 (1.09)	-22.21	1012	266 (5.7×10^4)	270	410	150	82
4d	832/763 (1.09)	-22.37	1018	258 (5.8×10^4)	280	420	90	89

^aDetermined by GPC in THF relative to polystyrene standards. M_w/M_n = Polydispersity index (PDI). ^bIn CDCl_3 . ^cIn KBr. ^dIn THF solution. ^eDetection wavelengths at 420, 310, 410, and 420 nm in THF solution for **4a-d**, respectively. ^fExcitation wavelengths at 260, 280, 270, and 280 nm in THF solution for **4a-d**, respectively. ^gFWHM = Full width at half maximum. ^hPercent weight remaining at 500 °C in nitrogen.

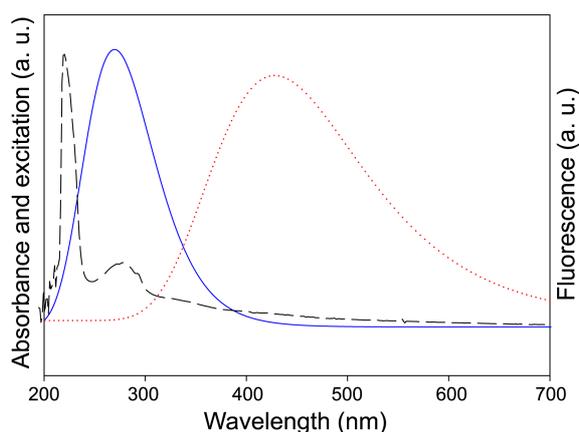


Figure 1. Absorbance (dashed line), excitation (solid line), and fluorescence (dotted line) spectra of polymer **4a** in THF solution.

respectively (Table 1). These strong excitation bands in the excitation spectra of polymers **4a-d** may be attributed to the aryl or fluoren-9-one groups along the polymer backbone.⁶ In the case of **4b**, in particular, the maximum emission peak was shifted from 420 nm to 310 nm when compared with the spectrum of **4a**. This phenomenon may be also due to the intra- and/or inter-molecular nonpolar interactions of octyl groups in **4b**, which do not occur in **4a**.

The fluorescence emission spectrum for **4a** at the excitation wavelength of 260 nm in THF solution exhibited a strong emission peak at a $\lambda_{em,max}$ value of 420 nm (Table 1). A typical fluorescence spectrum of polymer **4a** in THF solution is shown in Figure 1 as a dotted line. The fluorescence spectra of polymers **4b-d** at the excitation wavelength of 280, 270, and 280 nm show strong emission peaks at $\lambda_{em,max}$ values of 310, 410, and 420 nm, respectively (Table 1). These strong emission bands in the fluorescence spectra of the polymers may be ascribed to the fluorophores of the aryl or fluoren-9-one groups along the polymer backbones.⁶ Both the excitation and fluorescence emission spectra of the polymers imply that the polycarbosiloxanes **4a-d** have chromophores containing the fluoren-9-one functional group along the main polymer chains.⁶ Ultrafast time-resolved kinetic study may be required in order to further investigate the electronic conjugation properties of the prepared materials.

The thermal stabilities of polycarbosiloxanes **4a-d** in nitrogen atmosphere were evaluated using TGA with a heating rate of 10 °C/min (Figure 2). Polymers **4a-d** were found to be stable up to 200 °C without any loss of the initial weight in nitrogen. The weight losses of polymers **4a-d** occurred upon heating to 300 °C. A small weight loss of 1%-5% of the initial weight occurred between 200 and 300 °C. An additional weight loss of 8%-28% of the initial weight occurred between 300 and 500 °C. When **4a-d** were heated up to 500 °C, 11%-37% of the initial weight of each of the polymers was lost, and approximately 63%-89% of the initial polymer weight remained.

As shown in Figure 2 and Table 1, most of the prepared polymers, **4a-d**, were more stable up to 300 °C than the polycarbosiloxanes previously prepared by melt copoly-

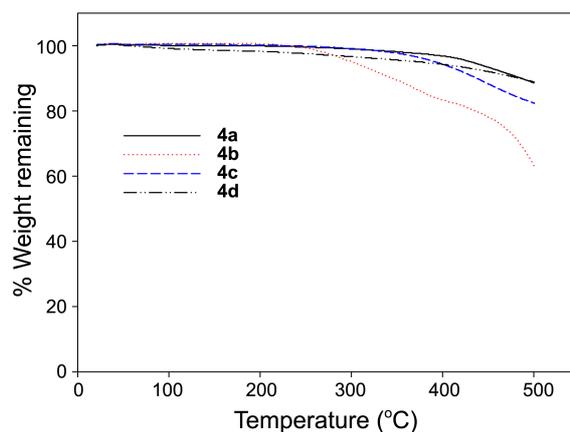


Figure 2. TGA thermograms of polymers **4a-d** in nitrogen.

merization, with a weight loss of less than 5% in nitrogen,^{27,28} and approximately 63-89% of the initial polymer weights remained at 500 °C in nitrogen.

Conclusion

We have successfully prepared four poly[oxy(2,7-fluoren-9-onenylene)oxy(diorganosilylene)]s containing the fluorescent fluoren-9-one group in the main chain, poly[oxy(2,7-fluoren-9-onenylene)oxy(methylphenylsilylene)] (**4a**), poly[oxy(2,7-fluoren-9-onenylene)oxy(methyloctylsilylene)] (**4b**), poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisilylene)] (**4c**), and poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisiloxanylene)] (**4d**), by the melt copolymerization of the bis(diethylamino)silane derivatives **2a-d**, bis(diethylamino)methylphenylsilane (**2a**), bis(diethylamino)methyloctylsilane (**2b**), 1,2-bis(diethylamino)tetramethyldisilane (**2c**), and 1,3-bis(diethylamino)tetramethyldisiloxane (**2d**), respectively, with 2,7-dihydroxyfluoren-9-one (**3**). The prepared materials are soluble in common organic solvents such as CHCl_3 and THF. The polymers were characterized using several spectroscopic methods in solution or in a solid state. In particular, FTIR spectra of all the polymeric materials show that the characteristic Si-O-C stretching frequencies appear at 1012-1018 cm^{-1} . In THF solution, the materials show strong maximum absorption bands at 258-270 nm, strong maximum excitation peaks at 260-280 nm, and strong maximum emission bands at 310-420 nm. All the absorption, excitation, and emission spectra suggest that the obtained poly[oxy(flouren-9-onenylene)oxy(diorganosilylene)]s contain the fluoren-9-one chromophore in the polymer main chain. TGA suggested that most of these polymers were essentially stable to 200 °C without any weight loss and up to 300 °C with only weight loss of less than 5% in nitrogen, particularly.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich Chemicals Inc. All glassware was assembled and then flame-dried while being flushed with argon. All

solvents were purified prior to use according to standard literature methods: *n*-hexane was distilled from sodium benzophenone ketyl and diethylamine was distilled from potassium hydroxide.³⁵ Other reagents and chemicals were used as received. Reactions were monitored by a Hewlett Packard 5890II analytical GLC equipped with an HP-1 capillary column (0.53 mm × 30 m) coated with cross-linked methyl silicon gum and a flame ionization detector (FID). The column was deactivated immediately before use by injection of 10 μL of hexamethyldisilazane. ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a Bruker ARX-400, Bruker DRX Avance 400 MHz FT-NMR, or Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Daegu Center of the Korea Basic Science Institute using CDCl₃ as solvent or in the solid-state for magic-angle spinning nuclear magnetic resonance (MAS NMR). Chemical shifts were measured using tetramethylsilane as an internal standard or the residual proton signal of the solvent as a standard. IR spectra were recorded by a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FT-IR spectrometer. Gel permeation chromatography (GPC) analyses were performed on a Waters 1525 pump with a Breeze software system, a Waters Styragel HR 3 column, and a refractive index detector at 40 °C. The eluent was THF at a flow rate of 1.0 mL/min. Calibration was done with a series of monodisperse polystyrene standards with *M_p* = 580, 3250, 10100, and 28500 whose *M_w*/*M_n* are less than 1.2. UV-vis absorption spectra were obtained on a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were taken on a Spex Fluorolog-3-11 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature was increased at a heating rate of 10 °C/min from room temperature to 500 °C with a nitrogen flow rate of 20 mL/min. Elemental analyses were performed using a Fisons EA 1108 elemental analyzer.

Bis(diethylamino)methylphenylsilane (2a), bis(diethylamino)methyloctylsilane (2b), 1,2-bis(diethylamino)tetramethyldisilane (2c), and 1,3-bis(diethylamino)tetramethyldisiloxane (2d) were prepared following the reported method.^{27,28,30} **2a**: ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 0.39 (s, 3H), 1.06 (t, *J* = 7 Hz, 12H), 2.96 (q, *J* = 7 Hz, 8H), 7.40–7.66 (m, 5H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) –2.20, 15.0, 39.2, 127.4, 128.6, 134.5, 139.6. ²⁹Si-NMR (99 MHz, CDCl₃): δ (ppm) –30.74. IR (KBr disk): ν 3067, 2963, 2863 (ν_{C-H}), 1342, 1253, 1203 (ν_{Si-C}), 1173, 1107, 1057 (ν_{C-N}), 928 (ν_{Si-N}), 787, 722 cm⁻¹. MS *m/z* (% relative intensity): 264 (3, M⁺), 249 (2, M⁺-CH₃), 235 (2), 219 (2), 192 (4, M⁺-NEt₂), 178 (2), 164 (3), 150 (6), 131 (2), 120 (3, M⁺-2(NEt₂)), 105 (6), 95 (3), 72 (8), 58 (16), 44 (100, Si-CH₄⁺), 28 (77). **2b**: ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 0.04 (s, 3H), 0.56–1.30 (m, 17H), 0.98 (t, *J* = 7.2 Hz, 12H), 2.81 (q, *J* = 7.2 Hz, 8H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) –3.15, 14.13, 15.15, 15.50, 22.74, 23.76, 29.37, 29.42, 32.01, 33.92, 39.16. ²⁹Si-NMR (99 MHz, CDCl₃): δ (ppm) –4.71. IR (KBr disk): ν 2961, 2924, 2854, 1465, 1372, 1251, 1204,

1175, 1023, 927, 789 cm⁻¹. MS *m/z* (% relative intensity): 302 (1.3), 301 (5.2), 300 (21, M⁺), 285 (20, M⁺-CH₃), 271 (12, M⁺-CH₃CH₂), 187 (84, M⁺-C₈H₁₇), 115 (100, M⁺-C₈H₁₇-NEt₂). **2c**: ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 0.102 (s, 12H), 0.95 (t, *J* = 8 Hz, 12H), 2.79 (q, *J* = 8 Hz, 8H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 0.46, 16.09, 41.09. ²⁹Si-NMR (99 MHz, CDCl₃): δ (ppm) 0.66. IR (KBr disk): ν 2865, 2957 (ν_{C-H}), 1243 (ν_{Si-C}), 1033 (ν_{C-N}), 926 (ν_{Si-N}), 786, 686 cm⁻¹. MS *m/z* (% relative intensity): 260 (33, M⁺), 245 (13, M⁺-CH₃), 202 (21), 187 (19), 130 (100, M⁺-SiMe₂-NEt₂), 116 (46), 101 (13), 86 (15), 58 (24). **2d**: ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 0.05 (s, 12H), 0.98 (t, *J* = 8 Hz, 12H), 2.82 (q, *J* = 8 Hz, 8H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) –0.43, 15.52, 39.41. ²⁹Si-NMR (99 MHz, CDCl₃): δ (ppm) –13.54. IR (KBr disk): ν 2963, 2930, 2865 (ν_{C-H}), 1206 (ν_{Si-C}), 1059 (ν_{C-N}), 1023 (ν_{Si-O}), 928 (ν_{Si-N}) cm⁻¹. MS *m/z* (% relative intensity): 278 (3), 277 (7), 276 (28, M⁺), 261 (5, M⁺-CH₃), 206 (8), 205 (19), 204 (96, M⁺-NEt₂), 203 (18), 202 (40), 192 (8), 191 (17), 190 (100, M⁺-NEt₂-CH₂), 189 (13), 188 (67), 176 (16), 175 (16), 174 (88), 160 (9), 134 (10), 133 (68), 123 (14), 119 (16), 95 (6), 58 (2).

Poly[oxy(2,7-fluoren-9-onenylene)oxy(methylphenylsilylene)] (4a). A 50-mL round bottomed flask was equipped with a heating mantle, a reflux condenser with an inert gas inlet, and a Teflon-covered magnetic stirring bar. The flask was charged with **2a** (39.7 mg, 150 μmol) and 2,7-dihydroxyfluoren-9-one (**3**) (32.1 mg, 150 μmol) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 12 h, at 200 °C for 3 h, and finally at 260 °C for 20 h under an argon atmosphere. The reaction mixture was then allowed to cool to room temperature. The crude polymeric material was dissolved with a minimum amount of THF and precipitated by addition of methanol. After being separated by centrifuge, dried at room temperature, and then put under reduced pressure, the polymeric product **4a** was obtained as a blackish solid that was almost soluble in the usual organic solvents such as THF and CHCl₃. In this way, 35.0 mg, a 72.0% yield, of **4a** was prepared. ¹H-NMR (400 MHz, THF-*d*₈): δ (ppm) 0.10 (s, 3H), 7.10–7.38 (m, 11H). ¹³C-NMR (150 MHz, CP-MAS): δ (ppm) 0.13, 128.21 (br), 133.73 (br), 153.08. ²⁹Si-NMR (119 MHz, CP-MAS): δ (ppm) –33.57. IR (KBr disk): ν 3062 (ν_{C-H}), 2965 (ν_{C-H}), 1712 (ν_{C=O}), 1587, 1432, 1259 (ν_{Si-C}), 1124, 1015 (ν_{Si-O}), 769, 724, 692 cm⁻¹. UV-vis (THF): λ_{max} nm (ε): 258 (4.3 × 10⁴ M⁻¹cm⁻¹). Elem. Anal. Calcd for (C₂₀H₁₄SiO₃)_n: C, 72.70; H, 4.27. Found: C, 71.43; H, 4.71.

Poly[oxy(2,7-fluoren-9-onenylene)oxy(methyloctylsilylene)] (4b) was prepared in a manner similar to that used for the synthesis of **4a**, from **2b** (34.0 mg, 150 μmol) and 2,7-dihydroxyfluoren-9-one (**3**) (32.1 mg, 150 μmol). Polymeric material **4b** was obtained in 80.0% yield, 33.0 mg, as a brownish viscous liquid and was soluble in common organic solvents such as THF, CHCl₃, toluene, and DMF. ¹H-NMR (400 MHz, THF-*d*₈): δ (ppm) 0.12 (s, 3H), 0.59–1.30 (m, 17H), 7.26–7.60 (m, 6H). ¹³C-NMR (150 MHz, CP-MAS): δ (ppm) 0.04 (br), 111–137 (br), 158.83, 193.53.

^{29}Si -NMR (119 MHz, CP-MAS): δ (ppm) -13.52 . IR (KBr disk): ν 3042, 2949 ($\nu_{\text{C-H}}$), 2821, 2853, 1713 ($\nu_{\text{C=O}}$), 1647, 1459, 1269 ($\nu_{\text{Si-C}}$), 1017 ($\nu_{\text{Si-O}}$), 794 cm^{-1} . UV-vis (THF): λ_{max} nm (ϵ): 270 ($3.1 \times 10^3\text{ M}^{-1}\text{cm}^{-1}$). Elem. Anal. Calcd for $(\text{C}_{22}\text{H}_{26}\text{SiO}_3)_n$: C, 72.09; H, 7.15. Found: C, 71.95; H, 7.12.

Poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisilylene)] (4c) was prepared in a manner similar to that used for the synthesis of **4a**, from **2c** (38.0 mg, 150 μmol) and 2,7-dihydroxyfluoren-9-one (**3**) (32.1 mg, 150 μmol). Polymeric material **4c** was obtained in 68.0% yield, 29.0 mg, as a blackish solid and was soluble in common organic solvents such as THF and CHCl_3 . ^1H -NMR (400 MHz, THF- d_6): δ (ppm) 0.09 (s, 12H), 6.71-7.05 (m, 6H). ^{13}C -NMR (150 MHz, CP-MAS): δ (ppm) 1.65, 100-140 (br), 153.75. ^{29}Si -NMR (119 MHz, CP-MAS): δ (ppm) -22.21 . IR (KBr disk): ν 3034, 2963 ($\nu_{\text{C-H}}$), 2910, 1715 ($\nu_{\text{C=O}}$), 1613, 1510, 1360, 1253 ($\nu_{\text{Si-C}}$), 1012 ($\nu_{\text{Si-O}}$), 838, 800, 694 cm^{-1} . UV-vis (THF): λ_{max} nm (ϵ): 266 ($5.7 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$). Elem. Anal. Calcd for $(\text{C}_{17}\text{H}_{18}\text{Si}_2\text{O}_3)_n$: C, 62.54; H, 5.56. Found: C, 63.59; H, 5.34.

Poly[oxy(2,7-fluoren-9-onenylene)oxy(tetramethyldisiloxanylene)] (4d) was prepared in a manner similar to used that for the synthesis of **4a**, from **2d** (42.0 mg, 150 μmol) and 2,7-dihydroxyfluoren-9-one (**3**) (32.1 mg, 150 μmol). Polymeric material **4d** was obtained in 45.0% yield, 24.0 mg, as a blackish solid and was soluble in common organic solvents such as THF and CHCl_3 . ^1H -NMR (400 MHz, THF- d_6): δ (ppm) 0.26 (s, 12H), 6.11-6.60 (m, 6H). ^{13}C -NMR (150 MHz, CP-MAS): δ (ppm) 0.58, 102, 130-140 (br). ^{29}Si -NMR (119 MHz, CP-MAS): δ (ppm) -22.37 . IR (KBr disk): ν 3043, 2964 ($\nu_{\text{C-H}}$), 2911, 1719 ($\nu_{\text{C=O}}$), 1658, 1608, 1462, 1260 ($\nu_{\text{Si-C}}$), 1018 ($\nu_{\text{Si-O}}$), 797 cm^{-1} . UV-vis (THF): λ_{max} nm (ϵ): 258 ($5.8 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$). Elem. Anal. Calcd for $(\text{C}_{17}\text{H}_{18}\text{Si}_2\text{O}_4)_n$: C, 59.62; H, 5.30. Found: C, 58.41; H, 5.47.

The excitation and fluorescence emission spectra in THF solution as well as TGA thermograms for polymers **4a-d** are described in Results and Discussion.

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