

Melt Copolymerization Reactions between 1,3-Bis(diethylamino)tetramethyldisiloxane and Aryldiol Derivatives

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Melt copolymerization reactions of bis(diethylamino)tetramethyldisiloxane with several aryldiols were carried out to afford poly(carbotetramethyldisiloxane)s containing fluorescent aromatic chromophore groups in the polymer main chain: poly{oxy(4,4'-biphenylene)oxytetramethyldisiloxane}, poly{oxy(1,4-phenylene)oxytetramethyldisiloxane}, poly[oxy{(4,4'-isopropylidene)diphenylene}oxytetramethyldisiloxane], poly[oxy{(4,4'-hexafluoroisopropylidene)diphenylene}oxytetramethyldisiloxane], poly{oxy(2,6-naphthalene)oxytetramethyldisiloxane}, poly[oxy{4,4'-(9-fluorenylidene)diphenylene}oxytetramethyldisiloxane], poly{oxy(flourene-9,9-dimethylene)oxytetramethyldisiloxane}, and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxytetramethyldisiloxane]. These materials are soluble in common organic solvents such as CHCl₃ and THF. The FTIR spectra of all the polymers exhibit the characteristic Si-O-C stretching frequencies at 1021-1082 cm⁻¹. In the THF solution, the polymeric materials show strong maximum absorption peaks at 215-311 nm, with strong maximum excitation peaks at 250-310 nm, and strong maximum fluorescence emission bands at 310-360 nm. TGA thermograms indicate that most of the polymers are stable up to 200 °C with a weight loss of less than 10% in nitrogen.

Key Words : Polycarbodisiloxanes, Aryldiols, Absorption, Excitation, Fluorescence, Thermal stability

Introduction

Organosilicon polymeric materials bearing π -conjugated groups have attracted considerable interest because of their potential applications as photonic, electronic, ionic conductive, and ceramic materials.¹⁻³ Fluorescent organosilicon polymers have also been of great interest for use in electroluminescence materials.⁴ For example, polysiloxanes containing fluorophores such as pyrene or carbazole in the polymer side chain were synthesized by hydrosilation reactions of poly(methylhydrosiloxane) with vinyl- or allyl-functionalized pyrene or carbazole in the presence of a Pt catalyst in toluene at around 70 °C.⁵ Fluorescent polysiloxanes bearing a fluorescent group such as anthryl, fluorenyl, naphthyl, quinoline, or quinaldyl along the polymer side chain were synthesized by dehydrogenative coupling reactions of the poly(methylhydrosiloxane) with fluorescent alcohols or phenols.⁶ Interestingly, the linear copolymers of silarylene-siloxane-diacetylene exhibit elastomeric properties with thermal stabilities in air at high temperatures of up to 330 °C.⁷ The temperature dependence of the steady-state fluorescence of linear poly(methylphenylsiloxane) in a dilute solution at temperatures below -50 °C was investigated using fluorescence spectroscopy and the ¹H NMR spectra to explain its photophysical properties.⁸

Ladder-like oligo(*p*-phenylenevinylene)s with silicon and carbon bridges composed of an annelated π -conjugated skeleton were also prepared by intramolecular cyclization reactions of 2,5-bis(silyl)-1,4-diethynylbenzene derivatives, and the obtained polymers were found to be intensely fluorescent in the visible region with emission colors varying from

blue to green to yellow.⁹ End-capped silole dendrimers on an ethenyl-phenyl carbosilane periphery have also been found to exhibit green to greenish-blue fluorescence, showing their potential applications as electroluminescent materials.¹⁰ However, the photoelectronic properties such as the absorption, excitation, and fluorescence emission of polycarbodisiloxanes containing aromatic fluorophores along the polymer main chain have seldom been reported.¹¹

Polymers containing polysiloxane segments and other organic backbones are of interest in the production of a new type of hybrid polymers,¹² which are expected to possess novel properties with adjustable characteristics such as the glass transition temperature and thermal stability. For example, a new type of polymerization involving the polycondensation reaction of dihydrosilanes with dialkoxysilanes was reported at or below room temperature in the presence of very low levels of B(C₆F₅)₃ to yield hybrid polysiloxanes with the elimination of hydrocarbon as a byproduct.¹³ The condensation of a dichlorosilane with a silanediol in the presence of triethylamine was reported to readily yield alternating cyclotetrasiloxanes.^{14,15} 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 weight.¹⁶

We examined the syntheses and, in particular, the electronic and thermal properties of oligomers containing the π -conjugated moiety C=C-B-C=C and an organosilacyclic group along the polymer backbone by polyaddition reactions of 1,1-diethynyl-1-silacyclopent-3-enes with borane derivatives.^{17,18} We also reported the syntheses, as well as the photoelectronic and thermal properties, of polycarbo-

silanes containing diethynyl and organosilane groups such as poly(1,1-diethynyl-1-silacyclopent-3-enes and -1-silacyclobutane) and poly(diethynyldialkyl and -diarylsilane)s by oxidative coupling reactions of diethynyl organosilane monomers.^{19,20} We previously reported 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.^{21,22}

Recently, we reported the melt copolymerizations of bis(diethylamino)methyloctylsilane with several aryldiols to yield poly(carbomethyloctylsiloxane)s containing a fluorescent aromatic chromophore group in the main chain.²³ With these results in mind, we extended our study to the preparation and photoelectronic properties of fluorescent poly(carbotetramethylsiloxane) materials containing an aromatic chromophore group in the main chain.

Here, we report the melt copolymerizations of bis(diethylamino)tetramethylsiloxane (**2**) with several aryldiols such as 4,4'-biphenol (**3a**), hydroquinone (**3b**), 4,4'-isopropylidenediphenol (**3c**), 4,4'-hexafluoroisopropylidenediphenol (**3d**), 2,6-dihydroxynaphthalene (**3e**), 4,4'-(9-fluorenylidene)-diphenol (**3f**), 9H-fluoren-9,9-dimethanol (**3g**), and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3h**) to yield poly(carbotetramethylsiloxane)s **4a-h** containing a fluorescent aromatic chromophore group in the main chain, such as poly{oxy(4,4'-biphenylene)oxytetramethylsiloxane} (**4a**), poly{oxy(1,4-phenylene)oxytetramethylsiloxane} (**4b**), poly[oxy{(4,4'-isopropylidene)diphenylene}oxytetramethylsiloxane] (**4c**), poly[oxy{(4,4'-hexafluoroisopropylidene)diphenylene}oxytetramethylsiloxane] (**4d**), poly{oxy(2,6-naphthalene)oxytetramethylsiloxane} (**4e**), poly[oxy{4,4'-(9-fluorenylidene)diphenylene}oxytetramethylsiloxane] (**4f**), poly{oxy(flourene-9,9-dimethylene)oxytetramethylsiloxane} (**4g**), and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxytetramethylsiloxane] (**4h**), respectively. In order to synthesize linear poly(carbotetramethylsiloxane)s with high molecular weights, we attempted to carry out the melt copolymerization of **2** with several aryldiols. The materials produced were characterized using FTIR, ¹H, ¹³C, and ²⁹Si NMR spectroscopies in the solution state, as well as elemental analyses. These poly(carbotetramethylsiloxane)s include fluorescent aromatic groups along the main chain. We will focus on our investigation of the photoelectronic and thermal properties of the prepared polymers, **4a-h**, using absorption, excitation, and fluorescence emission spectrophotometries, as well as thermogravimetric analyses (TGA).

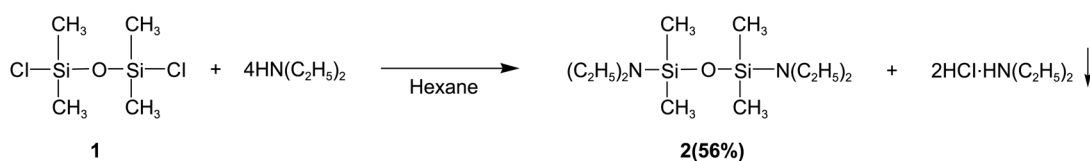
Results and Discussion

Synthesis of Monomers and Polymers. The condensation of aliphatic diols with dimethyldichlorosilane in solution has been reported to give only cyclodioxysilanes.²⁴ The solution polycondensation of 1,2-dichlorotetramethylsiloxane with resorcinol in *N*-methyl-2-pyrrolidone or toluene has been reported to yield polysiloxanes with low molecular weight.²⁵ For the preparation of poly(carbotetramethylsiloxane)s with high molecular weight we decided to use bis(diethylamino)tetramethylsiloxane (**2**) as a comonomer in order to carry out melt copolymerization. The monomer **2** was readily prepared by the reaction of dichlorotetramethylsiloxane (**1**) with 4 equivalents of diethylamine under an argon atmosphere in a moderate yield (Scheme 1).

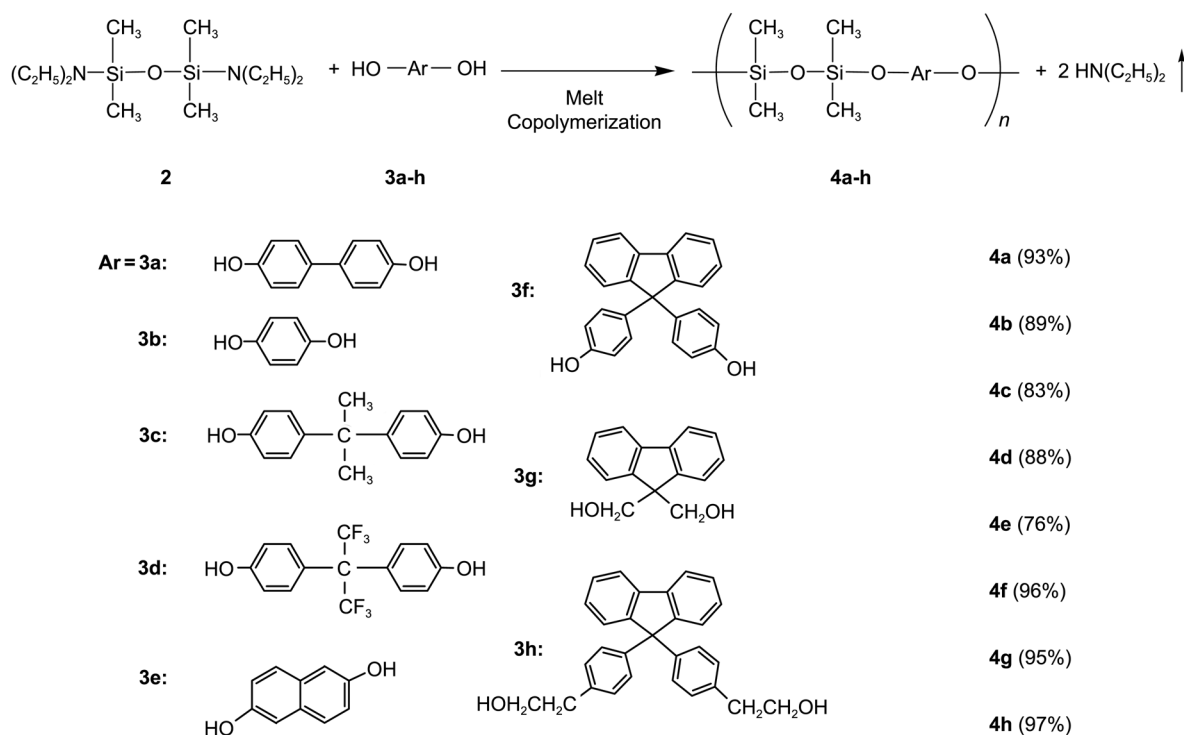
The monomer **2** was characterized using several spectroscopic methods such as NMR, IR, and mass spectroscopies. The ¹H NMR spectrum of **2** clearly exhibited triplet resonance at 0.98 ppm and quartet resonance at 2.82 ppm, which could be ascribed to the ethyl group bonded to nitrogen. This suggests 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 4 equivalents of diethylamine. In the ¹³C NMR spectrum of **2**, two carbon peaks of the ethyl group bonded to the nitrogen were observed at 15.52 and 39.41 ppm.²⁶ In the ²⁹Si NMR spectrum of **2**, the silicon resonance was observed at -13.54 ppm.²⁷ We confirmed the molecular ion peak at the *m/z* of 276 in the mass spectrum of **2**.

A melt copolymerization reaction between 1,2-bis(diethylamino)disilane and bisphenol has been reported to yield poly(oxyaryleneoxydisilane).^{25,28} We also recently reported the melt copolymerizations of several aryldiols with bis(diethylamino)methyloctylsilane.²³ We attempted a copolymerization reaction by utilizing the functionalities of 1,3-bis(diethylamino)tetramethylsiloxane **2** as a novel monomer according to the previously reported method.²⁵ The melt copolymerizations of **2** with various diol derivatives, **3a-h**, were carried out to afford poly(oxyaryleneoxydisiloxane)s, **4a-h**, containing aromatic and organosilyl groups in the polymer main chain (Scheme 2).

The prepared poly(oxyaryleneoxydisiloxane)s, **4a-h**, were dark brownish powders or very viscous liquids soluble in common organic solvents such as CHCl₃ and THF. We determined the molecular weights of polymers **4a-h** using gel permeation chromatography (GPC) in THF as an eluent. The weight average molecular weights (*M_w*) of materials



Scheme 1



Scheme 2

4a-h were found to be in the range of 1,064-13,070 with polydispersities of 1.04-2.08 (Table 1), suggesting that the obtained hybrids, **4a-h**, were oligomeric materials with low molecular weights. This seems to be explained by considering the rigidity of the aromatic diols used as the comonomer. We characterized the resulting polymers, **4a-h**, using several spectroscopic methods such as the ^1H , ^{13}C , ^{29}Si NMR, and FTIR spectra, as well as by measuring the optical properties such as the absorption, excitation, and fluorescence emission spectra in the THF solution. Some of the selected spectral properties of polymers **4a-h** are listed in Table 1.

The FTIR spectra of all of the polymers, **4a-h**, show the characteristic Si-O-C stretching frequencies at 1047, 1030, 1034, 1027, 1021, 1082, 1032, and 1023 cm^{-1} , respectively, indicating that Si-O-C bonds are formed through the copolymerization reactions.^{26,29} In particular, the ^{29}Si NMR spectra of polymers **4a-h** show that the major singlet resonance peaks appear at -12.20, -13.52, -13.21, -13.58, -21.62, -13.53, -10.75, and -12.39 ppm, respectively, indicating that the silicon atoms in the polymer main chain have the structural environment $(\text{R}_2\text{SiO})_x$ ²⁷ and suggesting consistence with the backbone structures shown in Scheme 2.

Properties of Polymers. We studied the absorption and excitation, as well as the fluorescence emission, spectra of the polymers in the THF solution. The typical absorption spectrum of polymer **4a** in THF is indicated in Figure 1 by a dotted line. The maximum absorption band for **4a** is observed at 262 nm with a band of 232-310 nm and molar absorptivity of $5.1 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$. The absorption spectra of **4b-h** exhibit strong absorption peaks at λ_{max} ranging from

215 to 311 nm. These strong absorption bands in the UV-vis spectra of **4a-h** may be attributed to the aryl groups along the polymer backbone.⁴

The excitation spectrum for **4a** at the detection wavelength of 360 nm shows a strong excitation peak at the $\lambda_{\text{ex, max}}$ of 310 nm (Table 1). A typical excitation spectrum for polymer **4a** in the THF solution is indicated in Figure 1 by a dashed line. The excitation spectra of **4b-h** at the detection wavelength of 330, 328, 310, 383, 310, 320, and 320 nm also exhibit strong excitation peaks at $\lambda_{\text{ex, max}}$ of 310, 310, 280, 250, 270, 260, and 277 nm, respectively (Table 1). These strong excitation bands in the excitation spectra of polymers **4a-h** may be attributed to the aryl groups along the polymer backbone.⁴ The maximum excitation wavelength of **4d** is longer than those of the other polycarbosiloxanes, **4a-c** and **4e**, probably because of the presence of naphthalene groups along the polymer main chain.

The fluorescence emission spectrum for **4a** at the excitation wavelength of 310 nm in the THF solution revealed a strong emission peak at the $\lambda_{\text{em, max}}$ of 360 nm (Table 1). A typical fluorescence spectrum of polymer **4a** in the THF solution is indicated in Figure 1 by a solid line. The fluorescence spectra of **4b-h** at the excitation wavelengths of 310, 310, 280, 250, 270, 260, and 277 nm show strong emission peaks at the $\lambda_{\text{em, max}}$ of 330, 328, 310, 383, 310, 320 and 320 nm, respectively (Table 1). These strong emission bands in the fluorescence spectra of the polymers may be ascribed to the fluorophore of the aryl groups along the polymer backbone.⁴ Both the excitation and fluorescence emission spectra of the polymers imply that polycarbosiloxanes **4a-h** have chromophores containing the aryl functional

Table 1. Selected Properties of Poly(carbotetramethyldisiloxane)s **4a-h**

| 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) ($\text{nm} (\text{cm}^{-1}\text{M}^{-1})$) | Excitation ^e $\lambda_{\text{ex,max}}$ (nm) | Fluorescence ^f $\lambda_{\text{em,max}}$ (nm) | TGA ^g |
|-----------|------------------------|---|---|--|---|---|------------------|
| 4a | 13,070/6,284 (2.08) | -12.20 | 1047 | 262 (5.1×10^4) | 310 | 360 | 59 |
| 4b | 4,581/3,636 (1.26) | -13.52 | 1030 | 297 (6.2×10^3) | 310 | 330 | 13 |
| 4c | 1,064/1,023 (1.04) | -13.21 | 1034 | 299 (3.8×10^3) 310 (4.3×10^3) | 310 | 328 | 44 |
| 4d | 11,725/6,550 (1.79) | -13.58 | 1027 | 275 (5.4×10^3) 282 (4.8×10^3) | 280 | 310 | 06 |
| 4e | 11,785/5,863 (2.01) | -21.62 | 1021 | 231 (8.3×10^3) | 250 | 383 | 34 |
| 4f | 5,656/3,347 (1.69) | -13.53 | 1026 | 215 (2.7×10^4) 231 (2.9×10^4) 281 (9.9×10^3) | 270 | 310 | 22 |
| 4g | 2,813/2,164 (1.30) | -10.75 | 1032 | 216 (7.7×10^4) 235 (7.1×10^4) 273 (3.0×10^4) | 260 | 320 | 37 |
| 4h | 3,520/2,514 (1.40) | -12.39 | 1023 | 235 (4.8×10^4) 273 (2.0×10^4) 311 (9.1×10^3) | 277 | 320 | 33 |

^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 360, 330, 328, 310, 383, 310, 320, and 320 nm in THF solution for **4a-h**, respectively. ^fExcitation wavelengths at 310, 310, 310, 280, 250, 270, 260, and 277 nm in THF solution for **4a-h**, respectively. ^g% Weight remaining at 500 °C in nitrogen.

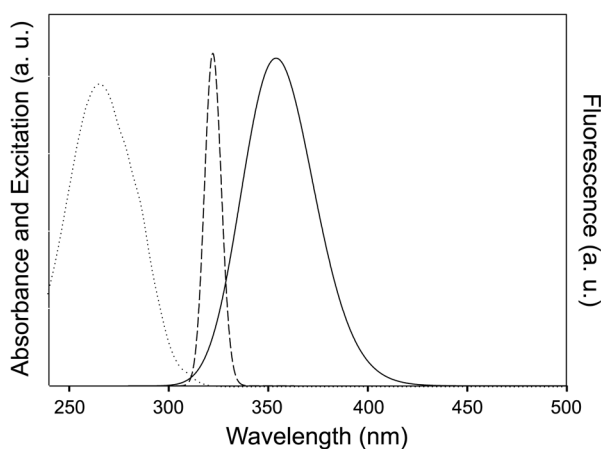


Figure 1. Absorbance (dotted line, $\lambda_{\text{max}} = 262$ nm), excitation (dashed line, $\lambda_{\text{det}} = 360$ nm), and fluorescence (solid line, $\lambda_{\text{ex}} = 310$ nm) spectra of polymer **4a** in THF solution.

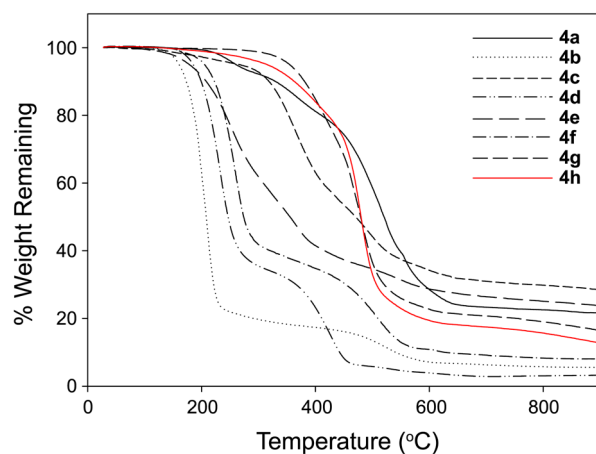


Figure 2. TGA thermograms of polymers **4a-h** in nitrogen.

groups along the polymer main chains.⁴ An ultrafast time-resolved kinetic study may be required to further investigate the electronic conjugation properties of the prepared materials.

The thermal stabilities of polycarbotetramethyldisiloxanes **4a-h** in nitrogen atmosphere were evaluated using a thermogravimetric analysis (TGA) with a heating rate of 10 °C/min (Figure 2). Polymers **4a** and **4c-h** were found to be stable up to 200 °C with a loss of less than 10% of the initial weight in nitrogen, while polymer **4b** lost 37% of its initial weight under nitrogen. The weight losses for polymers **4a-h** occurred rapidly upon heating above 200 °C. A rapid weight loss of 56-86% of the initial weight occurred between 200

and 600 °C. Additionally, a weight loss of 1-6% of the initial weight occurred between 600 and 800 °C. When **4a-h** were heated to 900 °C, 71-94% of the initial weight of each polymers was lost, and char yields of approximately 6-29% were observed.

Most of the prepared polymers, **4a-h**, were stable up to 200 °C, with weight losses of less than 10% in nitrogen, while approximately 6-59% of the initial polymer weights remained at 500 °C in nitrogen, as shown in Figure 2 and Table 1.

Conclusion

We successfully prepared poly(carbotetramethyldisiloxane)s

containing fluorescent aromatic groups in the main chain: poly{oxy(4,4'-biphenylene)oxytetramethyldisiloxane} (**4a**), poly{oxy(1,4-phenylene)oxytetramethyldisiloxane} (**4b**), poly[oxy{(4,4'-isopropylidene)diphenylene}oxytetramethyldisiloxane] (**4c**), poly[oxy{(4,4'-hexafluoroisopropylidene)diphenylene}oxytetramethyldisiloxane] (**4d**), poly{oxy(2,6-naphthalene)oxytetramethyldisiloxane} (**4e**), poly[oxy{4,4'-(9-fluorenylidene)diphenylene}oxytetramethyldisiloxane] (**4f**), poly{oxy(fluorene-9,9-dimethyl-ene)oxytetramethyldisiloxane} (**4g**), and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxytetramethyldisiloxane] (**4h**) by the melt copolymerizations of bis(diethylamino)tetramethyldisiloxane with several aryldiol, namely 4,4'-biphenol (**3a**), hydroquinone (**3b**), 4,4'-isopropylidenediphenol (**3c**), 4,4'-hexafluoroisopropylidenediphenol (**3d**), 2,6-dihydroxynaphthalene (**3e**), 4,4'-(9-fluorenylidene)diphenol (**3f**), 9H-fluorene-9,9-dimethanol (**3g**), and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3h**), respectively. The prepared materials were found to be soluble in common organic solvents such as CHCl_3 and THF. The polymers were characterized using several spectroscopic methods in the solution states. In particular, the FTIR spectra of all the polymeric materials showed that the characteristic Si-O-C stretching frequencies appeared at 1021-1082 cm^{-1} . In the THF solution, the materials showed strong maximum absorption bands at 215-311 nm, strong maximum excitation peaks at 250-310 nm, and strong maximum emission bands at 310-360 nm. All of the absorption, excitation, and emission spectra suggested that the obtained poly(carbotetramethyldisiloxane)s contained the aromatic chromophore groups in the polymer main chain. TGA suggested that most of these polymers were stable up to 200 °C with weight losses of less than 10% in nitrogen.

Experimental Section

General Procedures. All of the chemicals were purchased from Aldrich Chemicals Inc. All of the glassware was assembled and then flame-dried while being swept with argon. All of the solvents were purified prior to use according to standard literature methods: *n*-hexane was distilled from sodium benzophenone ketyl and diethylamine from potassium hydroxide.³⁰ The reactions were monitored using a Hewlett Packard 5890II analytical GLC equipped with an HP-1 capillary column (0.53 mm \times 30 m) coated with cross-linked methyl silicon gum and a flame ionization detector (FID). The column was deactivated immediately before use by the injection of 10 μL of hexamethyldisilazane. ^1H , ^{13}C , and ^{29}Si nuclear magnetic resonance (NMR) spectroscopies were performed on a Bruker ARX-400 or a Bruker DRX Avance 400 MHz FT-NMR spectrometer or a Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Daegu Center of the Korea Basic Science Institute using CDCl_3 as a solvent. The 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 using a Shimadzu IR 430 spectrometer or a Bruker IFS-48

FT-IR spectrometer. Low-resolution mass spectra were recorded by GC/MS, using a Hewlett Packard 5890II gas chromatography equipped with a Hewlett Packard 5971A mass selective detector by EI ionization at 70 eV. Gel permeation chromatography (GPC) analyses were performed on a Waters 1525 pump and Breeze software system with a Waters Styragel HR 3 column and refractive index detector at 40 °C. The eluent was THF at a flow rate of 1.0 mL/min. Calibration was performed using a series of monodispersed polystyrene standards: M_p 580, 3250, 10100, and 28500, which had M_w/M_n values of less than 1.2. UV-vis absorption spectra were obtained on a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were obtained using a Spex Fluorolog-3-11 fluorescence spectrophotometer. The 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 900 °C with a nitrogen flow rate of 20 mL/min. Elemental analyses were performed using a Fisons EA 1108 elemental analyzer.

1,3-Bis(diethylamino)tetramethyldisiloxane (2). A 500 mL three-necked, round bottomed flask was equipped with a reflux condenser, a pressure equalizing addition funnel with an inert gas inlet, and a Teflon covered magnetic stirring bar. The flask was charged with diethylamine (33.4 g, 0.460 mol) and hexane (150 mL) under argon atmosphere. The mixture was placed in an ice bath. Dichlorotetramethyldisiloxane **1** (20.0 g, 0.100 mol) was placed in the addition funnel and added dropwise over a period of 1 h to the well stirred and cooled reaction mixture. After the addition was completed, the ice bath was replaced by a heating mantle. The reaction mixture was well stirred at room temperature for an additional 12 h and then at 100 °C for 2 h. The reaction was monitored by GLC. The white semi-solid reaction mixture was added to *n*-hexane (50 mL), filtered to remove the solid diethylamine hydrochloride salt, and the volatile solvent was removed by simple distillation. The crude product was purified by fractional distillation under a reduced pressure to give **2**, 15.7 g (56.0%); bp 67 °C/4.1 mmHg; ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 0.05 (s, 12H), 0.98 (t, $J = 8$ Hz, 12H), 2.82 (q, $J = 8$ Hz, 8H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) -0.43, 15.52, 39.41; ^{29}Si -NMR (99 MHz, CDCl_3): δ (ppm) -13.54; IR (KBr disk) ν (cm^{-1}): 2963, 2930, 2865 ($\nu_{\text{C-H}}$), 1206 ($\nu_{\text{Si-C}}$), 1059 ($\nu_{\text{C-N}}$), 1023 ($\nu_{\text{Si-O}}$), 928 ($\nu_{\text{Si-N}}$) cm^{-1} ; MS m/z (relative intensity): 278 (3), 277 (7), 276 (M^+ , 28), 261 ($M^+ - \text{CH}_3$, 5), 206 (8), 205 (19), 204 ($M^+ - \text{NEt}_2$, 96), 203 (18), 202 (40), 192 (8), 191 (17), 190 ($M^+ - \text{NEt}_2 - \text{CH}_2$, 100), 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(4,4'-biphenylene)oxytetramethyldisiloxane} (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 **2** (2.78 g, 10.0 mmol) and 4,4'-biphenol (**3a**) (1.86 g, 10.0 mmol) under argon atmosphere. The reaction mixture was stirred at 130 °C for 12 h, at 200 °C for 10 h, and finally at 260 °C for 2 h under 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 with the addition of methanol. After being separated using a centrifuge, dried at room temperature, and then put under a reduced pressure, polymeric product **4a** was obtained as a brownish solid, which was almost soluble in typical organic solvents such as THF and CHCl_3 . In this manner, a 2.94 g, 93.0% yield of **4a** was prepared. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.10–0.28 (s, 12H), 6.90–6.95 (m, 4H), 7.38–7.40 (m, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) –0.5, 115.5, 120.1, 127.7, 153.4; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –12.20; IR (KBr disk) ν (cm^{-1}): 3034 ($\nu_{\text{C-H}}$), 2962 ($\nu_{\text{C-H}}$), 1495, 1249 ($\nu_{\text{Si-C}}$), 1047 ($\nu_{\text{Si-O}}$), 916, 798 cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 262 ($5.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{16}\text{H}_{20}\text{Si}_2\text{O}_3)_n$: C, 60.8; H, 6.4. Found: C, 60.2; H, 6.6.

Poly{oxy(1,4-phenylene)oxytetramethyldisiloxane} (4b) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and hydroquinone (**3b**) (1.10 g, 10.0 mmol). Polymeric material **4b**, 2.14 g, 89.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.05–0.20 (s, 12H), 6.65–6.77 (m, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) –0.6, 0.9, 115.9, 120.4, 120.6, 148.8; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –13.52; IR (KBr disk) ν (cm^{-1}): 3039 ($\nu_{\text{C-H}}$), 2963 ($\nu_{\text{C-H}}$), 1507, 1467, 1258 ($\nu_{\text{Si-C}}$), 1235, 1214, 1030 ($\nu_{\text{Si-O}}$), 797 cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 297 ($6.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{10}\text{H}_{16}\text{Si}_2\text{O}_3)_n$: C, 50.0; H, 6.7. Found: C, 52.6; H, 6.5.

Poly[oxy{(4,4'-isopropylidene)diphenylene}oxytetramethyldisiloxane] (4c) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 4,4'-isopropylidenediphenol (**3c**) (2.28 g, 10.0 mmol). Polymeric material **4c**, 2.96 g, 83.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.06–0.34 (s, 12H), 1.62 (s, 6H), 6.72–6.74 (d, $J = 8.8$ Hz, 4H), 7.08–7.10 (d, $J = 8.8$ Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 2.0, 31.0, 41.7, 114.7, 127.6, 143.3, 153.2; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –13.21; IR (KBr disk) ν (cm^{-1}): 3059 ($\nu_{\text{C-H}}$), 2960 ($\nu_{\text{C-H}}$), 1503, 1442, 1258 ($\nu_{\text{Si-C}}$), 1034 ($\nu_{\text{Si-O}}$), 802, 507, 492 cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 299 ($3.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), 310 ($4.3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{19}\text{H}_{26}\text{Si}_2\text{O}_3)_n$: C, 63.7; H, 7.3. Found: C, 67.5; H, 6.3.

Poly[oxy{(4,4'-hexafluoroisopropylidene)diphenylene}oxytetramethyldisiloxane] (4d) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 4,4'-hexafluoroisopropylidenediphenol (**3d**) (3.36 g, 10.0 mmol). Polymeric material **4d**, 4.09 g, 88.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.06–0.26 (s, 12H), 6.80–6.83 (m, 4H), 7.24–7.26 (m, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) –0.5, 1.0, 29.7, 63.2, 63.5, 63.7, 114.9, 125.6, 131.7, 155.9; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –13.58; IR (KBr disk) ν (cm^{-1}): 3049 ($\nu_{\text{C-H}}$), 2963 ($\nu_{\text{C-H}}$), 1612, 1513,

1248 ($\nu_{\text{Si-C}}$), 1207, 1170, 1084 ($\nu_{\text{C-F}}$), 1027 ($\nu_{\text{Si-O}}$), 800, 491 cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 275 ($5.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), 282 ($4.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{19}\text{H}_{20}\text{F}_6\text{Si}_2\text{O}_3)_n$: C, 49.0; H, 4.3. Found: C, 49.5; H, 3.8.

Poly{oxy(2,6-naphthalene)oxytetramethyldisiloxane} (4e) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 2,6-dihydroxynaphthalene (**3e**) (1.60 g, 10.0 mmol). Polymeric material **4e**, 2.20 g, 76.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.04–0.26 (s, 12H), 6.71–7.61 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 1.3, 109.7, 119.3, 128.0, 130.5, 154.2; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –21.62; IR (KBr disk) ν (cm^{-1}): 3051 ($\nu_{\text{C-H}}$), 2962 ($\nu_{\text{C-H}}$), 1259 ($\nu_{\text{Si-C}}$), 1021 ($\nu_{\text{Si-O}}$), 767, 515 cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 231 ($8.3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{14}\text{H}_{18}\text{Si}_2\text{O}_3)_n$: C, 58.0; H, 6.2. Found: C, 60.7; H, 5.9.

Poly[oxy{4,4'-(9-fluorenylidene)diphenylene}oxytetramethyldisiloxane] (4f) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 4,4'-(9-fluorenylidene)diphenol (**3f**) (3.50 g, 10.0 mmol). Polymeric material **4f**, 4.60 g, 96.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.05–0.23 (s, 12H), 6.71–6.80 (m, 8H), 7.06–7.10 (m, 8H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) –0.4, 0.9, 31.0, 114.6, 114.7, 119.1, 119.2, 127.6, 127.9, 143.3, 143.9, 152.1, 153.2; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –13.55; IR (KBr disk) ν (cm^{-1}): 3032 ($\nu_{\text{C-H}}$), 2964 ($\nu_{\text{C-H}}$), 1256 ($\nu_{\text{Si-C}}$), 1082 ($\nu_{\text{Si-O}}$) cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 215 ($2.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 231 ($2.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 281 ($9.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{29}\text{H}_{28}\text{Si}_2\text{O}_3)_n$: C, 72.4; H, 5.9. Found: C, 75.1; H, 6.3.

Poly{oxy(flourene-9,9-dimethylene)oxytetramethyldisiloxane} (4g) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 9H-fluorene-9,9-dimethanol (**3g**) (2.26 g, 10.0 mmol). Polymeric material **4g**, 2.15 g, 95.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.05–0.20 (s, 12H), 3.94–4.06 (s, 4H), 6.76–7.77 (m, 8H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) –0.9, 1.1, 61.5, 64.2, 69.1, 114.1, 120.2, 127.4, 127.7, 129.1, 138.6, 139.9, 151.7, 157.3; $^{29}\text{Si-NMR}$ (99 MHz, CDCl_3): δ (ppm) –10.75; IR (KBr disk) ν (cm^{-1}): 3035 ($\nu_{\text{C-H}}$), 2928 ($\nu_{\text{C-H}}$), 1245 ($\nu_{\text{Si-C}}$), 1032 ($\nu_{\text{Si-O}}$) cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 216 ($7.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 235 ($7.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 273 ($3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{19}\text{H}_{24}\text{Si}_2\text{O}_3)_n$: C, 64.0; H, 6.8. Found: C, 67.9; H, 6.4.

Poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxytetramethyldisiloxane] (4h) was prepared in a manner similar to that for the synthesis of **4a**, using **2** (2.78 g, 10.0 mmol) and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3h**) (4.40 g, 10.0 mmol). Polymeric material **4h**, 5.51 g, 97.0%, was obtained as a brownish solid that was soluble in typical organic solvents such as THF and CHCl_3 . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 0.07–0.22 (s, 12H), 3.78–4.02

(s, 8H), 6.76-6.82 (m, 4H), 7.14-7.19 (m, 4H), 7.27-7.44 (m, 6H), 7.77-7.80 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) -3.0, -1.0, 1.0, 25.5, 61.3, 64.1, 67.9, 68.8, 114.0, 120.1, 125.9, 127.2, 127.6, 129.0, 138.0, 139.8, 151.6, 157.2; ^{29}Si -NMR (99 MHz, CDCl_3): δ (ppm) -12.39; IR (KBr disk) ν (cm^{-1}): 3067 ($\nu_{\text{C-H}}$), 2960 ($\nu_{\text{C-H}}$), 1258 ($\nu_{\text{Si-C}}$), 1023 ($\nu_{\text{Si-O}}$) cm^{-1} ; UV-vis (THF) λ_{max} nm (ϵ): 235 ($4.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 273 ($2.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 311 ($9.1 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Elem. Anal. Calcd for $(\text{C}_{33}\text{H}_{36}\text{Si}_2\text{O}_3)_n$: C, 69.7; H, 6.4. Found: C, 65.9; H, 6.2.

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

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