

## Synthesis and Properties of Poly[oxy(arylene)oxy(tetramethyldisilylene)]s via Melt Copolymerization Reaction

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We carried out the melt copolymerization reactions of 1,2-bis(diethylamino)tetramethyldisilane with several aryldiols such as, 4,4'-biphenol, 4,4'-isopropylidenediphenol, 9*H*-fluoren-9,9-dimethanol, and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) to afford poly[oxy(arylene)oxy(tetramethyldisilylene)]s containing fluorescent aromatic chromophore groups in the polymer main chain: poly[oxy(4,4'-biphenylene)oxy(tetramethyldisilylene)], poly[oxy{(4,4'-isopropylidene) diphenylene}oxy(tetramethyldisilylene)], poly[oxy(9*H*-fluorene-9,9-dimethylene)oxy(tetramethyldisilylene)], and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxy(tetramethyldisilylene)]. These prepared materials are soluble in common organic solvents such as CHCl<sub>3</sub> and THF. The obtained polymers were characterized by several spectroscopic methods such as <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR. Further, FTIR spectra of all the polymers exhibited characteristic Si–O stretching frequencies at 1014–1087 cm<sup>-1</sup>. These polymeric materials in THF showed strong maximum absorption peaks at 268–281 nm, strong maximum excitation peaks at 263–291 nm, and strong maximum fluorescence emission bands at 314–362 nm due to the presence of tetramethyldisilylene and several arylene chromophores in the polymer main chain. TGA thermograms indicated that most of the polymers were stable up to 200 °C with a weight loss of 3–16% in nitrogen.

**Key Words :** Poly[oxy(arylene)oxy(tetramethyldisilylene)]s, Absorption, Excitation, Fluorescence, Thermal stability

### Introduction

Organosilicon polymeric materials containing arylene derivatives with  $\pi$ -conjugated groups have received considerable interest due to their potential applications as photonic and electronic materials.<sup>1–3</sup> Polyconjugated systems of fluorescent organic polymers have also received great interest because of their use in electronic devices such as light-emitting diodes (LEDs) and photovoltaic cells.<sup>4,5</sup> For instance, fluorescent organosilicon polymers, *i.e.*, polysiloxanes bearing 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 Pt catalyst.<sup>6</sup> Fluorescent polysiloxanes, containing fluorescent groups such as anthryl, fluorenyl, naphthyl, quinoline, or quinaldyl along the polymer side chain, were synthesized by dehydrogenative coupling reactions of fluorescent alcohols or phenols with poly(methylhydrosiloxane).<sup>7</sup>

Fluorescent poly(aryleneethynylene)s carrying silole and tetraphenylethene luminogens along the polymer main chain were synthesized by Sonogashira cross-coupling reaction of terminal alkynes with aryl halides.<sup>8</sup> Interestingly, the linear copolymers of silarylene–siloxane–diacetylene demonstrated elastomeric properties with thermal stabilities at high temperature up to 330 °C in air.<sup>9</sup> The temperature dependence of the steady-state fluorescence of linear poly(methylphenylsiloxane) in a dilute solution at temperatures below –50 °C was investigated to explain their photophysical properties,

using fluorescence spectroscopy and <sup>1</sup>H NMR spectra.<sup>10</sup>

Ladder-type oligo(*p*-phenylenevinylene)s with silicon and carbon bridges and annelated  $\pi$ -conjugated skeletons were also prepared by intramolecular cyclization of 2,5-bis(silyl)-1,4-diethynylbenzene derivatives. The obtained polymers were intensely fluorescent in the visible region with the emission colors varying from blue to green to yellow.<sup>11</sup> End-capped silole dendrimers on an ethenyl-phenyl carbosilane periphery also exhibited a green to greenish-blue fluorescence, which showed their versatility and potential use as electroluminescent materials.<sup>12</sup>

However, photoelectronic properties such as absorption, excitation and fluorescence emission of poly[oxy(arylene)oxy(tetramethyldisilylene)]s containing aromatic arylene fluorophores along the polymer main chain have seldom been reported.<sup>13,14</sup>

A new synthetic process for making polymers containing siloxane segments and conjugated organic backbones is of great interest for the production of a new type of hybrid polymers.<sup>15</sup> These are expected to possess novel characteristics with adjustable mechanical properties such as glass transition temperature and thermal stability. For instance, a new type of polymerization involving the polycondensation of dihydrosilanes with dialkoxysilanes was reported at or below room temperature in the presence of catalytic amounts of tris(pentafluorophenyl)borane to produce a wide variety of hybrid polysiloxanes with elimination of a hydrocarbon as a byproduct.<sup>16</sup> The condensation of a dichlorosilane with a silanediol in the presence of triethylamine was reported to

readily yield alternating cyclotetrasiloxanes, which then might be ring-opened to produce linear polysiloxanes.<sup>17,18</sup> The interfacial polymerization reaction of a dichlorosilane in an organic solvent such as octane and a diol in 2,5-hexanedione was reported to afford poly[alkyl(aryl)oxysilane]s with low molecular weights.<sup>19</sup>

Recently, we examined the melt copolymerizations of bis(diethylamino)methyloctylsilane and 1,3-bis(diethylamino)-tetramethyldisiloxane with several fluorescent aryldiols such as biphenylene, naphthalene, and fluorenylidene derivatives to yield poly(carbomethyloctylsiloxane)s and poly(carbotetramethyldisiloxane)s, respectively, that contain fluorescent aromatic chromophores in the main chain.<sup>20,21</sup> We had previously reported the preparation and excited-state energy dynamics of polycarbosilanes and polycarbogermans containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne in the polymer backbone.<sup>22,23</sup>

Very recently, we also reported the melt copolymerization of several bis(diethylamino)silane derivatives with 2,7-dihydroxyfluorene-9-one to yield poly[oxy(2,7-fluorene-9-onenylene)oxy(diorganosilylene)]s that contain fluorene-9-one as a fluorescent aromatic chromophore group in the main chain.<sup>24</sup> With these results, we have extended our study to the preparation and photoelectronic properties of fluorescent poly[oxy(arylene)oxy(tetramethyldisilane)]s materials containing several aromatic fluorophore groups in the main chain.

In this work, we report the melt copolymerizations of bis(diethylamino)tetramethyldisilane (**2**) with several aryldiols such as 4,4'-biphenol (**3a**), 4,4'-isopropylidenediphenol (**3b**), 9*H*-fluorene-9,9-dimethanol (**3c**), and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3d**) to afford poly[oxy(arylene)oxy(tetramethyldisilylene)]s **4a-d**, respectively, that contain a fluorescent aromatic chromophore group in the main chain: poly[oxy(4,4'-biphenylene)oxy(tetramethyldisilylene)] (**4a**), poly[oxy{(4,4'-isopropylidene)diphenylene}oxy(tetramethyldisilylene)] (**4b**), poly[oxy(9*H*-fluorene-9,9-dimethylene)oxy(tetramethyldisilylene)] (**4c**), and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxy(tetramethyldisilylene)] (**4d**). The polymers **4a-d** contained tetramethyldisilylene and several arylene groups, such as biphenylene, isopropylidenediphenylene, fluorenedimethylene, and fluorenylidenephenoxyethylene, along the polymer main chain, and the aromatic chromophores were different from the previously reported results.<sup>20-24</sup> The objective of these melt copolymerizations was to synthesize the copolymers of poly[oxy(arylene)oxy(tetramethyldisilylene)]s with high molecular weights. The synthesized materials were characterized by several spectrophotometric methods such as <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR in the solution state, and by using

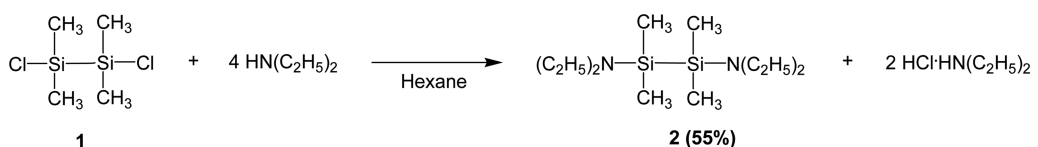
FTIR as well as elemental analysis. We will focus our investigation on the photoelectronic and thermal properties of the synthesized polymers **4a-d**, using absorption, excitation, and fluorescence emission spectrophotometers in the solution state and by performing thermogravimetric analysis (TGA).

## Results and Discussion

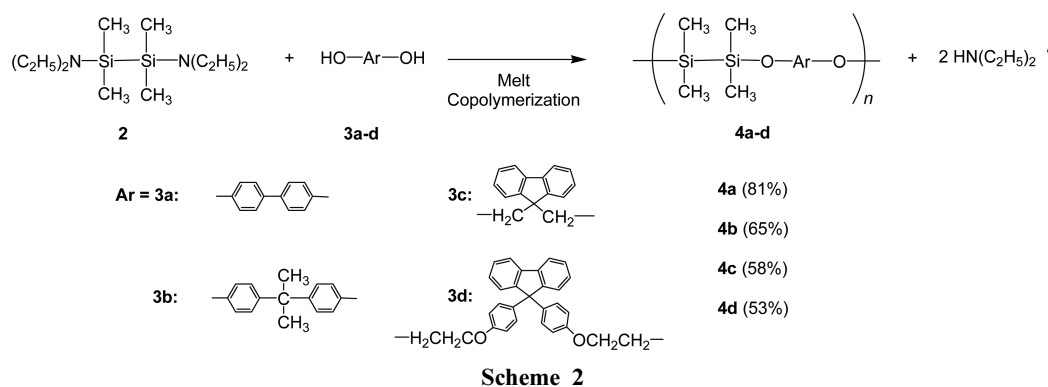
**Synthesis of Monomers and Polymers.** The condensation reaction of dichlorodimethylsilane or diethoxydimethylsilane with aliphatic diols has been reported to afford only cyclic dimethyl(alkylenedioxy)silanes.<sup>25</sup> The polycondensation reaction of 1,2-dichlorotetramethyldisilane with resorcinol has been reported to yield polysiloxanes with low molecular weights.<sup>26</sup> For the preparation of poly[oxy(arylene)oxy(disilylene)]s with high molecular weights, we decided to carry out the melt copolymerization reactions of 1,2-bis(diethylamino)tetramethyldisilane **2** with several flexible aryldiols such as 4,4'-biphenol **3a**, 4,4'-isopropylidenediphenol **3b**, 9*H*-fluorene-9,9-dimethanol **3c**, and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) **3d** as co-monomers. The monomer **2** was readily prepared in moderate yield by the reaction of dichlorotetramethyldisilane (**1**) with four equivalents of diethylamine under an argon atmosphere (Scheme 1).<sup>24</sup>

The monomer **2** was characterized using several spectroscopic methods. The <sup>1</sup>H NMR spectrum of **2** clearly showed triplet and quartet resonances at 0.95 and 2.79 ppm, respectively, which could be attributed to the ethyl group bonded to nitrogen. In the <sup>13</sup>C NMR spectrum of **2**, two carbon peaks of the ethyl group bonded to the nitrogen were observed at 16.09 and 41.09 ppm.<sup>27</sup> In the <sup>29</sup>Si NMR spectrum of **2**, the silicon resonance was observed at 0.66 ppm.<sup>28</sup> We also confirmed the molecular ion peak at the *m/z* of 260 in the mass spectrum of **2**. This data suggested that the diethylamination reaction of the starting material **1**, namely, the substitution reaction of two chlorine atoms with diethylamino groups, using four equivalents of diethylamine was completed under the given reaction condition.

Melt copolymerization reactions of bis(diethylamino)silanes or diaminosilanes with bisphenols to yield poly(oxyaryleneoxysilane)s were investigated previously.<sup>29,30</sup> We also recently reported the melt copolymerizations of bis(diethylamino)silane and bis(diethylamino)disiloxane with several aryldiols.<sup>20,21,24</sup> We had tried copolymerization reactions between 1,2-bis(diethylamino)tetramethyldisilane **2** carrying the functionality of diethylamine group and several diol derivatives, by using a previously reported method.<sup>20,21,24</sup> The melt copolymerizations of **2** with various diol deriva-



Scheme 1



tives **3a-d**, which are more flexible than the previously reported 2,7-dihydroxyfluorene-9-one,<sup>24</sup> produced poly[oxy(arylene)oxy(tetramethyldisilylene)]s **4a-d**, containing aromatic as well as tetramethyldisilylene groups in the polymer main chain (Scheme 2).

The synthesized polymers **4a-d** were brownish or yellowish powders and were soluble in common organic solvents such as  $\text{CHCl}_3$  and THF. We determined molecular weights of **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 5,396 to 9,099 with polydispersities of 1.20 to 1.40 (Table 1), indicating that **4a-d** were oligomeric. This phenomenon of the low molecular weights of materials **4a-d** may be explained by considering the rigidity of aromatic diols used as the comonomer. However, the molecular weights of **4a-d** were much higher than the weight-average molecular weights (827-832) of the reported previously poly[oxy(flouren-9-onylene)oxy(organodisilylene)]s containing fluorene-9-one,<sup>24</sup> and this might be ascribed to the flexibility of comonomers **3a-d** being higher than that of fluorene-9-one.

We characterized the polymers **4a-d** using several spectroscopic methods. Some selected spectral properties of the polymers **4a-d** are listed in Table 1.

FTIR spectra of all the polymers **4a-d** indicated the

characteristic Si-O stretching frequencies at 1014, 1087, 1037, and 1022  $\text{cm}^{-1}$ , respectively, suggesting that Si-O bonds were newly formed during the copolymerization reactions.<sup>27,31</sup> The  $^{29}\text{Si}$  NMR spectra of the polymers **4a-d** in  $\text{CDCl}_3$  solution showed major singlet resonance peaks at -12.57, -12.97, -11.20, and 0.52 ppm, respectively. This indicated that the silicon atoms in the polymer main chain have the structural environment  $(\text{R}_2\text{SiO})_x$ ,<sup>28</sup> and structures consistent with the backbone shown in Scheme 2.

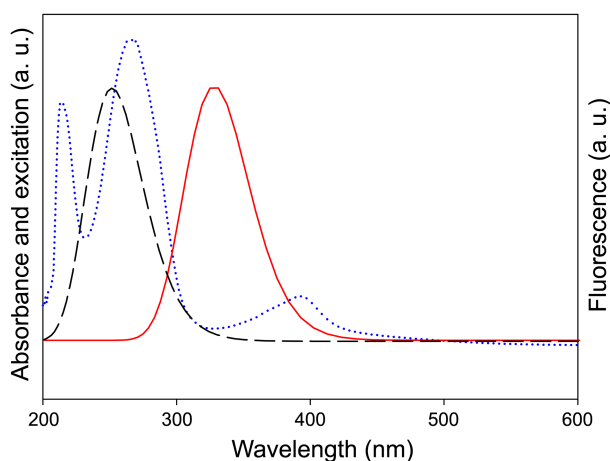
**Properties of Polymers.** We investigated absorption, excitation, and fluorescence emission spectra of the polymers **4a-d** in THF solution. A typical absorption spectrum of the polymer **4a** in THF is shown in Figure 1 as a dotted line. The maximum absorption band for **4a** was observed at 268 nm, and the band extended from 232 to 323 nm with a molar absorptivity of  $8.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ . The absorption spectra of **4b-d** reveal strong absorption peaks at  $\lambda_{\text{max}}$  ranging from 268 to 281 nm. These strong absorption bands in the UV-Vis spectra of **4a-d** may be attributed to the tetramethyldisilylene as well as several arylene chromophore groups such as biphenylene, isopropylidenediphenylene, fluorenedimethylene, and fluorenylidene-phenoxyethylene along the polymer backbone.<sup>5</sup>

The excitation spectrum for **4a** at the detection wavelength of 362 nm showed a strong excitation peak at the  $\lambda_{\text{ex, max}}$  of

**Table 1.** Selected Properties of the Poly[oxy(arylene)oxy(tetramethyldisilylene)]s **4a-d**

Polymer	$M_w/M_n^a$ (PDI)	$^{29}\text{Si}$ NMR <sup>b</sup> $\delta$ (ppm)	IR <sup>c</sup> $\nu(\text{Si-O})$ ( $\text{cm}^{-1}$ )	Absorption <sup>d</sup> $\lambda_{\text{abs, max}}$ ( $\epsilon$ ) ( $\text{nm} (\text{M}^{-1}\text{cm}^{-1})$ )	Excitation <sup>e</sup> $\lambda_{\text{ex, max}}$ (nm)	Fluorescence <sup>f</sup> $\lambda_{\text{em, max}}$ (nm)	Fluorescence FWHM <sup>g</sup> (nm)	TGA <sup>h</sup>
<b>4a</b>	7,968/6,640 (1.20)	-12.57	1014	268 ( $8.4 \times 10^3$ ) 393 ( $1.4 \times 10^3$ )	263	362	54	51
<b>4b</b>	5,396/4,151 (1.30)	-12.97	1087	281 ( $6.8 \times 10^3$ ) 288 ( $5.7 \times 10^3$ )	268	314	60	08
<b>4c</b>	5,569/3,978 (1.40)	-11.20	1037	268 ( $2.1 \times 10^4$ ) 288 ( $8.7 \times 10^3$ ) 299 ( $9.7 \times 10^3$ )	270	314	31	41
<b>4d</b>	9,099/7,583 (1.20)	0.52	1022	272 ( $3.5 \times 10^4$ ) 299 ( $8.0 \times 10^3$ ) 311 ( $1.3 \times 10^4$ )	291	333	50	88

<sup>a</sup>Determined by GPC in THF relative to polystyrene standards.  $M_w/M_n$  = Polydispersity index (PDI). <sup>b</sup>In  $\text{CDCl}_3$ . <sup>c</sup>In KBr. <sup>d</sup>In THF solution. <sup>e</sup>Detection wavelengths at 362, 314, 314, and 333 nm in THF solution for **4a-d**, respectively. <sup>f</sup>Excitation wavelengths at 263, 268, 270, and 291 nm in THF solution for **4a-d**, respectively. <sup>g</sup>FWHM = Full width at half maximum. <sup>h</sup>% Weight remaining at 300 °C under nitrogen.

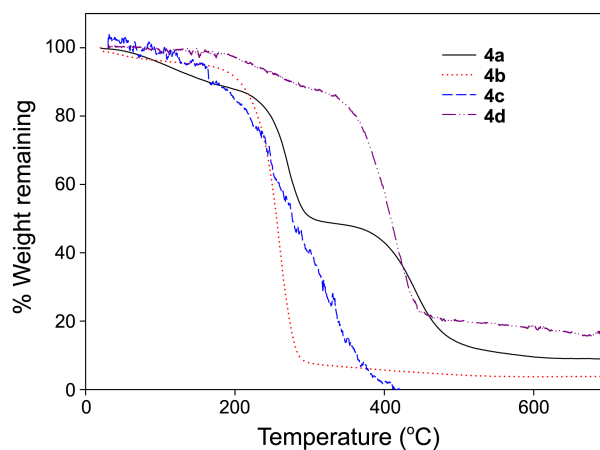


**Figure 1.** Absorbance (dotted line,  $\lambda_{\text{max}} = 268$  nm), excitation (dashed line,  $\lambda_{\text{det}} = 362$  nm) and fluorescence emission (solid line,  $\lambda_{\text{ex}} = 263$  nm) spectra of the polymer **4a** in the THF solution.

263 nm (Table 1). A typical excitation spectrum of the polymer **4a** in THF solution is shown in Figure 1 as a dashed line. The excitation spectra of **4b-d** at the detection wavelength of 314, 314, and 333 nm also exhibited strong excitation peaks at the  $\lambda_{\text{ex, max}}$  of 268, 270, and 291 nm, respectively (Table 1). These strong excitation bands in the excitation spectra of the polymers **4a-d** may be attributed to the tetramethyldisilene and several arylene chromophore groups along the polymer backbone.<sup>5</sup>

The fluorescence emission spectrum for **4a** at the excitation wavelength of 263 nm in THF solution revealed a strong emission peak at the  $\lambda_{\text{em, max}}$  of 362 nm (Table 1). A typical fluorescence spectrum of the polymer **4a** in the THF solution is exhibited in Figure 1 as a solid line. The fluorescence spectra of **4b-d** at the excitation wavelength of 268, 270, and 291 nm showed strong emission peaks at the  $\lambda_{\text{em, max}}$  of 314, 314, and 333 nm, respectively (Table 1). These strong emission bands in the fluorescence spectra of the polymers may be attributed to the fluorophore of arylene groups along the polymer backbone.<sup>5</sup> As shown in Table 1, the fluorescence-emission full width at half maximum (FWHM) values of the materials **4a-d** were also observed at 54, 60, 31, and 50 nm, respectively. Both excitation and fluorescence emission spectra of the polymers indicated that the prepared materials **4a-d** have fluorophores such as the tetramethyldisilylene and several arylene chromophore groups along the polymer main chains.<sup>5</sup> An ultrafast time-resolved kinetic study may be required in order to further investigate the electronic conjugation properties of the obtained materials.

The thermal stabilities of poly[oxy(arylene)oxy(tetramethyldisilylene)]s **4a-d** in a nitrogen atmosphere were evaluated by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min (Figure 2). Polymers **4a-d** were stable up to 200 °C with only 3-16% weight loss of the initial weight in nitrogen. Weight loss of polymers **4a-d** occurred rapidly upon heating above 200 °C. Rapid weight loss of 78-87% of the initial weight occurred between 200 and 600 °C. Addi-



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

tionally, weight loss of 1-3% occurred between 600 and 700 °C. Particularly, polymer **4c** decomposed completely under nitrogen at 420 °C. When **4a-d** were heated up to 700 °C, 85-100% of the initial polymer weight was lost, and char yield of about 0-15% was observed.

Most of the prepared polymers **4a-d** were stable up to 200 °C with a weight loss of 3-16% under nitrogen and about 3-58% of the initial polymer weights remained at 400 °C under nitrogen as shown in Figure 2 and Table 1.

## Conclusion

We successfully prepared poly[oxy(arylene)oxy(tetramethyldisilylene)]s containing fluorescent aromatic groups in the main chain, such as, poly[oxy(4,4'-biphenylene)oxy(tetramethyldisilylene)] (**4a**), poly[oxy{(4,4'-isopropylidene)diphenylene}oxy(tetramethyldisilylene)] (**4b**), poly[oxy(9*H*-fluoren-9,9-dimethylene)oxy(tetramethyldisilylene)] (**4c**), and poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)}oxy(tetramethyldisilylene)] (**4d**) using the melt copolymerizations of 1,2-bis(diethylamino)tetramethyldisilane with several aryldiols like 4,4'-biphenol (**3a**), 4,4'-isopropylidenediphenol (**3b**), 9*H*-fluoren-9,9-dimethanol (**3c**), and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3d**), respectively. The prepared materials were soluble in common organic solvents such as  $\text{CHCl}_3$  and THF. These materials were characterized using various spectroscopic methods in the solution states. Further, the FTIR spectra of all the polymeric materials showed that the characteristic Si-O stretching frequencies at 1014-1087  $\text{cm}^{-1}$ . The polymers in the THF solution exhibited strong maximum absorption bands at 268-281 nm, strong maximum excitation peaks at 263-291 nm, and strong maximum emission bands at 314-362 nm due to tetramethyldisilylene and several arylene groups, such as biphenylene, isopropylidenediphenylene, fluorenedimethylene, and fluorenylidene-phenoxyethylene, along the polymer main chain. All the absorption, excitation, and emission spectra suggested that the prepared poly[oxy(arylene)oxy(tetramethyldisilylene)]s contained the aromatic arylene chromophore groups in the polymer main chain.

According to TGA most of these materials were stable up to 200 °C with a weight loss of 3-16% under nitrogen.

### Experimental Section

**General Procedures.** All chemicals were purchased from Sigma-Aldrich Chemicals Inc. All glasswares were assembled, and then flame-dried while being swept 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.<sup>32</sup> All the other reagents were used as received. Reactions were monitored using a Hewlett Packard 5890II analytical GLC equipped with HP-1 capillary column (0.53 mm × 30 m) coated with cross-linked methyl silicon gum and flame ionization detector (FID). The column was deactivated immediately before use by injection of 10 μL of hexamethyldisilazane. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si nuclear magnetic resonance (NMR) spectroscopy were performed on a Bruker ARX-400 or a Bruker DRX Avance 400 MHz FT-NMR spectrometers or a Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Daegu Center of the Korea Basic Science Institute using CDCl<sub>3</sub> as solvent. Chemical shifts were measured using tetramethylsilane as an internal standard or the residual proton signal of the solvent as standard. IR spectra were recorded on a Shimadzu IR 430 spectrophotometer or a Bruker IFS-48 FT-IR spectrophotometer. Low-resolution mass spectra were recorded on a Hewlett Packard 5890II gas chromatography equipped with a Hewlett Packard 5971A mass-selective detector by EI ionization at 70 eV. UV-Vis absorption spectra were obtained on a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were recorded on a Spex Fluorolog-3-11 fluorescence spectrophotometer. 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 used was THF at a flow rate of 1.0 mL/min. Calibration was done with a series of monodisperse polystyrene standards with  $M_p = 580, 3250, 10100, \text{ and } 28500$  whose  $M_w/M_n$  were less than 1.2. Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature was increased at the heating rate of 10 °C/min from room temperature to 900 °C with nitrogen flow rate of 20 mL/min. Elemental analyses were performed using a Fisons EA 1108 element analyzer.

**1,2-Bis(diethylamino)tetramethyldisilane (2).**<sup>24</sup> 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 coated magnetic stirring bar. The flask was charged with diethylamine (33.4 g, 0.460 mol) and hexane (150 mL) under an argon atmosphere. The mixture was placed in an ice bath. Dichlorotetramethyldisilane **1** (18.7 g, 0.100 mol) was added dropwise over a period of 1 h to the well-stirred and cooled reaction mixture by using an addition funnel. 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. To the white semi-solid reaction mixture was added *n*-hexane (50 mL), filtered to remove the solid diethylamine hydrochloride salt, and the volatile solvent removed by simple distillation. The crude product was purified by fractional distillation under reduced pressure to give **2**, 13.7 g (55.0%); bp 50.0 °C/0.75 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.102 (s, 12H), 0.95 (t, *J* = 8 Hz, 12H), 2.79 (q, *J* = 8 Hz, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 0.46, 16.09, 41.09. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, δ): 0.66. IR (KBr disk)  $\tilde{\nu}_{\text{max}}$ : 2865, 2957 (ν<sub>C-H</sub>), 1243 (ν<sub>Si-C</sub>), 1033 (ν<sub>C-N</sub>), 926 (ν<sub>Si-N</sub>), 786, 686 cm<sup>-1</sup>. GC-MS *m/z* (% relative intensity) 260 (33, M<sup>+</sup>), 245 (13, M<sup>+</sup>-CH<sub>3</sub>), 202 (21), 187 (19), 130 (100, M<sup>+</sup>-SiMe<sub>2</sub>-NEt<sub>2</sub>), 116 (46), 101 (13), 86 (15), 58 (24).

**Poly[oxy(4,4'-biphenylene)oxy(tetramethyldisilylene)] (4a).** A 50 mL round bottomed flask was equipped with a heating mantle, a reflux condenser with an inert gas inlet, and a Teflon coated magnetic stirring bar. The flask was charged with **2** (2.60 g, 10.0 mmol) and 4,4'-biphenol (**3a**) (1.86 g, 10.0 mmol) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 12 h, at 200 °C for 10 h, and then finally at 260 °C for 2 h under an argon atmosphere. The reaction mixture was then allowed to cool to room temperature. The crude polymeric material obtained was dissolved in a minimum amount of THF and precipitated by addition of methanol. The precipitate was separated using a centrifuge, dried at room temperature, and then, subjected to reduced pressure. The polymeric product **4a** thus obtained was a brown solid that was almost soluble in common organic solvents such as THF and CHCl<sub>3</sub>. In this way, 2.42 g, 81.0% yield, of **4a** was prepared. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.23 (s, 12H), 6.77-6.89 (m, 4H), 7.41-8.22 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 2.80, 116.8, 128.8, 133.7, 157.9. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, δ): -12.57. IR (KBr disk)  $\tilde{\nu}_{\text{max}}$ : 3036 (ν<sub>C-H</sub>), 2949 (ν<sub>C-H</sub>), 1612, 1239 (ν<sub>Si-C</sub>), 1014 (ν<sub>Si-O</sub>), 816, 758 cm<sup>-1</sup>. UV-Vis (THF) λ<sub>max</sub>, nm (ε): 268 (8.4 × 10<sup>3</sup>), 393 (1.4 × 10<sup>3</sup>). Anal. Calcd for (C<sub>16</sub>H<sub>20</sub>Si<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 63.9; H, 6.7. Found: C, 63.1; H, 6.6.

**Poly[oxy{(4,4'-isopropylidene)diphenylene}oxy(tetramethyldisilylene)] (4b)** was prepared in a manner similar to that used for the synthesis of **4a**, using **2** (1.56 g, 6.00 mmol) and 4,4'-isopropylidenediphenol (**3b**) (1.34 g, 6.00 mmol). Polymeric material **4b** was obtained in 1.33 g, 65.0% yield, as a yellow solid and was soluble in common organic solvents such as THF and CHCl<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.03 (s, 12H), 1.58 (s, 6H), 6.70-6.72 (m, 4H), 7.03-7.05 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): -0.4, 30.6, 41.9, 114.4, 127.5, 142.8, 153.1. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, δ): -12.97. IR (KBr disk)  $\tilde{\nu}_{\text{max}}$ : 3059 (ν<sub>C-H</sub>), 2970 (ν<sub>C-H</sub>), 1583, 1429, 1211 (ν<sub>Si-C</sub>), 1087 (ν<sub>Si-O</sub>), 809 cm<sup>-1</sup>. UV-Vis (THF) λ<sub>max</sub>, nm (ε): 281 (6.8 × 10<sup>3</sup>), 288 (5.7 × 10<sup>3</sup>). Anal. Calcd for (C<sub>19</sub>H<sub>26</sub>Si<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 66.6; H, 7.6. Found: C, 66.1; H, 7.5.

**Poly[oxy(9H-fluoren-9,9-dimethylene)oxy(tetramethyldisilylene)] (4c)** was prepared in a manner similar to that used for the synthesis of **4a**, using **2** (1.56 g, 6.00 mmol) and 9H-fluoren-9,9-dimethanol (**3c**) (1.37 g, 6.00 mmol). Poly-

meric material **4c** was obtained in 1.29 g, 58.0% yield, as a brown solid and was soluble in common organic solvents such as THF and CHCl<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.01-0.20 (s, 12H), 3.70-4.00 (m, 4H), 7.30-7.79 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): -1.48, 0.88, 56.53, 57.25, 66.81, 119.73, 120.09, 124.52, 124.87, 126.49, 126.94, 127.24, 127.76, 140.64, 140.89, 145.66, 146.07. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, δ): -11.20. IR (KBr disk)  $\tilde{\nu}_{\max}$ : 3035 (ν<sub>C-H</sub>), 2928 (ν<sub>C-H</sub>), 1245 (ν<sub>Si-C</sub>), 1037 (ν<sub>Si-O</sub>), 858, 800, 759, 734 cm<sup>-1</sup>; UV-Vis (THF) λ<sub>max</sub>, nm (ε): 268 (2.1 × 10<sup>4</sup>), 288 (8.7 × 10<sup>3</sup>), 299 (9.7 × 10<sup>3</sup>). Anal. Calcd for (C<sub>19</sub>H<sub>24</sub>Si<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 67.0; H, 7.1. Found: C, 66.7; H, 7.2.

**Poly[oxy{4,4'-(9-fluorenylidene)bis(2-phenoxyethylene)-oxy(tetramethyldisilylene)}] (4d)** was prepared in a manner similar to that used for the synthesis of **4a**, using **2** (1.56 g, 6.00 mmol) and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol) (**3d**) (2.64 g, 6.00 mmol). Polymeric material **4d** was obtained in 2.03 g, 53.0% yield, as a brown solid and was soluble in common organic solvents such as THF and CHCl<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.02-1.58 (s, 12H), 3.92-4.03 (m, 8H), 6.75-7.13 (m, 8H), 7.34-7.53 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 1.12, 11.27, 21.20, 29.51, 61.37, 64.01, 68.94, 113.98, 119.92, 125.85, 127.26, 127.60, 129.10, 139.82, 151.52, 157.20. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, δ): 0.52. IR (KBr disk):  $\tilde{\nu}_{\max}$  3067 (ν<sub>C-H</sub>), 2960 (ν<sub>C-H</sub>), 1258 (ν<sub>Si-C</sub>), 1022 (ν<sub>Si-O</sub>), 858, 795, 682 cm<sup>-1</sup>. UV-Vis (THF) λ<sub>max</sub>, nm (ε): 272 (3.5 × 10<sup>4</sup>), 299 (8.0 × 10<sup>3</sup>), 311 (1.3 × 10<sup>4</sup>). Anal. Calcd for (C<sub>33</sub>H<sub>36</sub>Si<sub>2</sub>O<sub>4</sub>)<sub>n</sub>: C, 71.6; H, 6.5. Found: C, 71.1; H, 6.4.

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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