# Synthesis and Properties of Polymers Containing Silphenylene Moiety via Catalytic Cross-Dehydrocoupling Polymerization of 1,4-Bis(dimethylsilyl)benzene

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ABSTRACT: The catalytic cross-dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water, ammonia, disilanol, aliphatic and aromatic diols, and dicarboxylic acids was successfully conducted under mild conditions to afford silphenylene-containing polycarbosilazane, polycarbosiloxanes, poly(silyl ether)s, and poly(silyl ester)s. This efficient novel route allowed accessing various silphenylene-containing polymers with well-defined structures which were verified by NMR, IR, and SEC analyses. The influence of the structures of the constitutional units between silphenylene groups on the transition temperatures, crystallization behavior, thermal stability, solubility, and degradability of these polymers was also systematically investigated.

## Introduction

Silarylene-containing polymers, which exhibit a wide range of physical properties depending on their composition and structure, have received considerable academic and commercial interests over the past 30 years.[1−3] One of the prominent properties of silarylene-containing polymers is their excellent thermal stability. For instance, silarylene−siloxane polymers with the combination of aromatic groups and siloxane groups in the main chain are very excellent high-temperature elastomers with low $T_g$'s and high decomposition temperatures.[1,4−11] Most of the methods employed for the synthesis of silarylene−siloxane polymers up until now are the self-polycondensation of arylenedisilanols or the copolycondensation of arylenedisilanols with other bifunctional compounds.[4−11] However, the preparation of arylenedisilanols requires many tedious procedures,[4] and no industrially feasible synthetic pathway to the arylenedisilanols has yet been found.[1f] This obstacle still stands in the way of the commercialization of these useful polymers although they were first prepared in the laboratory as early as the 1960s.[4,5]

In our preliminary reports, the construction of the Si−O linkage by catalytic cross-dehydrocoupling reaction of organosilanes with water or diols was utilized for the first time in the synthesis of Si−O-containing polymers under mild conditions.[12,13] It was found that the easily accessible 1,4-bis(dimethylsilyl)benzene (BDSB) could react with water in the presence of a catalytic amount of transition metal (Pd, Pt, Rh, etc.) compounds at room temperature to afford high molecular weight poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] (**I**) with $H_2$ as the only byproduct.[12] Here we extend this method to the polymerization of BDSB with other labile-hydrogen-containing compounds, such as ammonia, disilanol, aliphatic and aromatic diols, and dicarboxylic acids, to prepare a series of silphenylene-containing polymers, including polycarbosilazane, polycarbosiloxanes, poly(silyl ether)s, and poly(silyl ester)s. The Si−O (Si−O−Si or Si−O−C) and Si−N linkages could modify the chemical and physical properties of polymers and render some useful functionality, such as excellent low-temperature properties (low $T_g$'s),[1a,e] chemo- and biological degradability,[14−16] and so on. Thus, the coexistence of silphenylene units and Si−O or Si−N linkages in polymer main chains is preferable to afford new functional materials.

## Experimental Section

**Measurements.** The 500 MHz $^1$H, 75.3 MHz $^{13}$C, and 79.6 MHz $^{29}$Si NMR spectra were recorded in $CDCl_3$ on a Varian 500 MHz Unity INOVA, 300 MHz Gemini 2000, and 400 Unity INOVA spectrometer, respectively. $^{29}$Si NMR spectra were obtained on samples with chromium(III) acetylacetonate (0.05 M) as a relaxation agent. The chemical shifts are given in ppm relative to internal $CHCl_3$ ($\delta$ 7.26, $^1$H), $CDCl_3$ ($\delta$ 77.00, $^{13}$C), and external tetramethylsilane (TMS) ($\delta$ 0.00, $^{29}$Si). IR spectra were obtained on a JASCO VALOR-III spectrophotometer. Size exclusion chromatography (SEC) analysis was performed on a JASCO HPLC with the combination of Shodex KF-803L (exclusion limit: $M_n = 7 \times 10^4$, polystyrene) and KF-804 (exclusion limit: $M_n = 4 \times 10^5$, polystyrene) columns at 40 °C using tetrahydrofuran (THF) as an eluent. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed on a Seiko SSC/5200H instrument at a heating rate of 10 °C/min (DSC) and 5 °C/min (TGA) under a nitrogen atmosphere (50 mL/min), respectively. A Nikon Microphoto-FXA polarizing microscope with a Mettler FP82HT hot stage was used to observe the crystalline textures of polymers.

**Materials.** 1,4-Bis(dimethylsilyl)benzene (BDSB) was obtained from Shin-Etsu Chemical and distilled from calcium hydride (>99.0% (HPLC)). Ammonia solution (0.5 M in 1,4-dioxane) was purchased from Aldrich Chemical and used as received. Ethylene glycol (>99.0%) and 1,3-propanediol (>97.0%) were purchased from Wako Pure Chemical and distilled from calcium hydride. Diphenylsilanediol (>99.0%, Shin-Etsu Chemical), catechol (>99.0%, Kanto Chemical), hydroquinone (>99.0%, Tokyo Chemical), adipic acid (>99.5%, Wako Pure Chemical), and terephthalic acid (>99.0%, Tokyo Chemical) were dried at room temperature under a reduced pressure prior to use. The tris(dibenzylideneacetone)dipalladium(0)−chloroform adduct ($Pd_2(dba)_3$·$CHCl_3$) and palladium on activated carbon (10 wt %) were purchased from Aldrich Chemical. Tetrahydrofuran (THF) used as a polymerization solvent was dried before use by fluxing over a sodium−benzophenone solution under a dry argon atmosphere, followed by distillation.

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**Polymerization.** All reactions were conducted under nitrogen. The polymerization procedure and the characterization of polymers **I** and **IV** were described in the previous reports.[12,13]

**Polymer II.** BDSB (1.94 g, 0.01 mol) was allowed to react with ammonia (20 mL, 0.5 M 1,4-dioxane solution) in a 10 mL flask in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, $2.5 \times 10^{-5}$ mol) at room temperature for 72 h. The byproduct $H_2$ was released to a balloon attached to the flask. Removing the catalyst from the product by a Florisil column with $CHCl_3$ and precipitating the concentrated polymer solution to cold methanol (0 °C) gave a white solid material (0.65 g, 31.6%). SEC: $M_n = 8500$, $M_w/M_n = 1.44$. $^1$H NMR: $\delta$ 0.29 (s, 12 H, SiC*H*$_3$), 0.62 (s, 1H, −N*H*−), 7.56 (s, −*p*-C$_6$*H*$_4$−). $^{13}$C NMR: $\delta$ 1.02 (Si*C*H$_3$), 132.68, 142.05 (−*p*-*C*$_6$H$_4$−). $^{29}$Si NMR: $\delta$ − 3.8 (−*p*-C$_6$H$_4$−*Si*(CH$_3$)$_2$NH−). IR (neat): $\nu$ 3346 (N−H), 3047−2899, 1380, 1252, 1180, 1135, 1063, 932, 825, 788 cm$^{-1}$. DSC: $T_g$ − 10.5 °C, $T_k$ (crystallization temperature) = 36.7 °C, $T_m$ = 92.5 °C.

**Polymer III**. Following the similar procedure, the polymerization of BDSB (0.972 g, 0.005 mol) with diphenylsilanediol (1.08 g, 0.005 mol) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (13 mg, $1.3 \times 10^{-5}$ mol) in THF (2 mL) at 50 °C gave a colorless viscous liquid material (1.40 g, 68.0%). SEC: $M_n = 7700$, $M_w/M_n = 1.55$. $^1$H NMR: $\delta$ 0.27 (s, 12 H, SiC*H*$_3$), 7.21−7.33, 7.44, 7.49−7.53. $^{13}$C NMR: $\delta$ 0.58 (Si*C*H$_3$), 127.68, 129.87, 132.38, 134.35, 135.96, 140.37. $^{29}$Si NMR: $\delta$ −0.1 (−*p*-C$_6$H$_4$−*Si*(CH$_3$)$_2$O−), −46.0 (−O*Si*(Ph)$_2$O−). IR (neat): $\nu$ 3137−2900, 1592, 1429, 1381, 1255, 1120, 1062, 818, 780, 743, 700 cm$^{-1}$. DSC: $T_g$ − 3.3 °C.

**Polymer V**. BDSB (0.972 g, 0.005 mol) was allowed to react with 1,3-propanediol (0.381 g, 0.005 mol) in the presence of 10% Pd/C (27 mg, $2.5 \times 10^{-5}$ mol Pd) in THF (1 mL) at room temperature. After the rapid evolution of hydrogen almost ceased (about 30 min), the temperature was raised to 50 °C and maintained for 3 h. Similar workup procedure gave a colorless viscous liquid product (1.16 g, yield 87.0%). SEC: $M_n$ = 12 400, $M_w/M_n = 1.83$. $^1$H NMR: $\delta$ 0.34 (s, 12 H, SiC*H*$_3$), 1.74 (pent, 2H, OCH$_2$C*H*$_2$CH$_2$O, *J* 6.3 Hz), 3.68 (t, 4H, OC*H*$_2$-CH$_2$C*H*$_2$O, *J* 6.3 Hz), 7.55 (s, 4 H, −*p*-C$_6$*H*$_4$−). $^{13}$C NMR: $\delta$ −1.98 (Si*C*H$_3$), 35.31 (OCH$_2$*C*H$_2$CH$_2$O), 59.62 (O*C*H$_2$CH$_2$*C*H$_2$O), 132.82, 139.44 (aromatic carbons). $^{29}$Si NMR: $\delta$ 7.2 (−*p*-C$_6$H$_4$−*Si*(CH$_3$)$_2$O−). IR (neat): $\nu$ 3050−2871, 1253, 1086, 977, 844, 821, 777, 659 cm$^{-1}$. DSC: $T_g$ − 43.7 °C.

**Polymer VI**. A similar procedure to the preparation of **III** using catechol (0.55 g, 0.005 mol) in place of diphenyldisilanediol gave a colorless viscous liquid material (0.88 g, 58.4%). SEC: $M_n$ = 4900, $M_w/M_n = 1.26$. $^1$H NMR: $\delta$ 0.46 (s, 12 H, SiC*H*$_3$), 6.73 (br, 4H, −O−*o*-C$_6$*H*$_4$−O−), 7.65 (s, −Si(CH$_3$)$_2$−*p*-C$_6$*H*$_4$−Si(CH$_3$)$_2$−). $^{13}$C NMR: $\delta$ −1.24 (Si*C*H$_3$), 121.02, 121.91, 132.91, 139.34, 146.39. $^{29}$Si NMR: $\delta$ 9.0 (−*p*-C$_6$H$_4$−*Si*(CH$_3$)$_2$O−). IR (neat): $\nu$ 3052−2901, 1592, 1505, 1451, 1278, 1255, 1221, 1138, 1109, 1040, 936, 905, 782, 751 cm$^{-1}$. DSC: $T_g$ 2.7 °C.

**Polymer VIII**. The similar procedure to the preparation of **V** using adipic acid (0.73 g, 0.005 mol) instead of 1,3-propanediol gave a white solid material (without precipitation to methanol) (1.70 g, 100%). SEC: $M_n$ = 4400, $M_w/M_n = 1.79$. $^1$H NMR: $\delta$ 0.54 (s, 12 H, SiC*H*$_3$), 1.61 (br, 4H, OCOCH$_2$C*H*$_2$C*H*$_2$-CH$_2$COO), 2.34 (br, 4H, OCOC*H*$_2$CH$_2$CH$_2$C*H*$_2$COO), 7.63 (s, −*p*-C$_6$*H*$_4$−). $^{13}$C NMR: $\delta$ −1.83 (Si*C*H$_3$), 24.17 (OCO*C*H$_2$CH$_2$-CH$_2$*C*H$_2$COO), 35.37 (OCOCH$_2$*C*H$_2$CH$_2$CH$_2$COO), 132.97, 137.84 (−*p*-*C*$_6$H$_4$−), 173.96 (O*C*OCH$_2$CH$_2$CH$_2$CH$_2$*C*OO). $^{29}$Si NMR: $\delta$ 11.8 (−*p*-C$_6$H$_4$−*Si*(CH$_3$)$_2$O−). IR (neat): $\nu$ 3056−2877, 1717, 1382, 1257, 1176, 1139, 1050, 924, 825, 796 cm$^{-1}$. DSC: $T_g$ = −14.2 °C, $T_k$ 65.6, $T_m$ 93.2 °C.

**Methanolysis.** To a 10 mL flask were added the polymer (20 mg) and THF (2 mL). After the polymer dissolved completely, methanol (0.5 mL) was added to the solution. A small amount of the solution was taken for SEC analysis after stirring for a certain time.

## Results and Discussion

The conditions and results of polymerization and the structures of polymers **I**−**IX** are shown in Table 1 and Scheme 1. $Pd_2(dba)_3$ is an excellent catalyst for the polymerization of BDSB with water to give a high molecular weight polymer ($M_n$ = 16 300) at room temperature in a short time (2 h) (polymer **I** in Table 1), showing a high catalytic activity for both the hydrolysis of Si−H and the SiOSi formation steps.[12] Several attempts made by other research groups to prepare polysilazanes by the dehydrocoupling reaction of organosilanes with ammonia or amines in the presence of $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$, or dimethyltitanocene ($Cp_2TiMe_2$) resulted in the formation of rather low molecular weight products ($M_n$ < 3000).[14] In our case, when an ammonia solution in 1,4-dioxane (0.5 M) was used to polymerize with BSDB in the presence of $Pd_2(dba)_3$ at room temperature, a polymer **II** with a relatively higher molecular weight ($M_n$ = 7100) in 76.1% yield (confirmed by the SEC curve of the reaction mixture) was formed after reacting for 72 h. It seems that the catalyst $Pd_2(dba)_3$ and/or the organosilane BDSB used here may be favorable for this polymerization. The rather long time required in this reaction is considered due to the much lower concentration of the monomers and the catalyst than those in the preparation of polymer **I**. When the solution of polymer **II** (upon removing the catalysts by a Florisil column) was precipitated into chilled methanol (0 °C), only 31% yield of **II** with $M_n$ = 8500 was obtained. Since the $M_n$ at peak top of the SEC curve decreased from 10 200 (before precipitation) to 9440 (after precipitation), the low isolated yield was mainly caused by the partial decomposition of **II** in methanol (also confirmed by the following methanolysis experiment) rather than the fractional separation.

The reaction of BDSB with diphenylsilanediol in the presence of $Pd_2(dba)_3$ was too slow to produce a polymer at room temperature, confirming that the reactivity of the −SiOH group in diphenylsilanediol is much lower than that of −SiOH in −Me$_2$Si−*p*-C$_6$H$_4$−SiMe$_2$OH. Raising the temperature to 50 °C could accelerate this reaction and afforded a polymer **III** with $M_n$ = 7700 in 68.0% yield after 18 h.

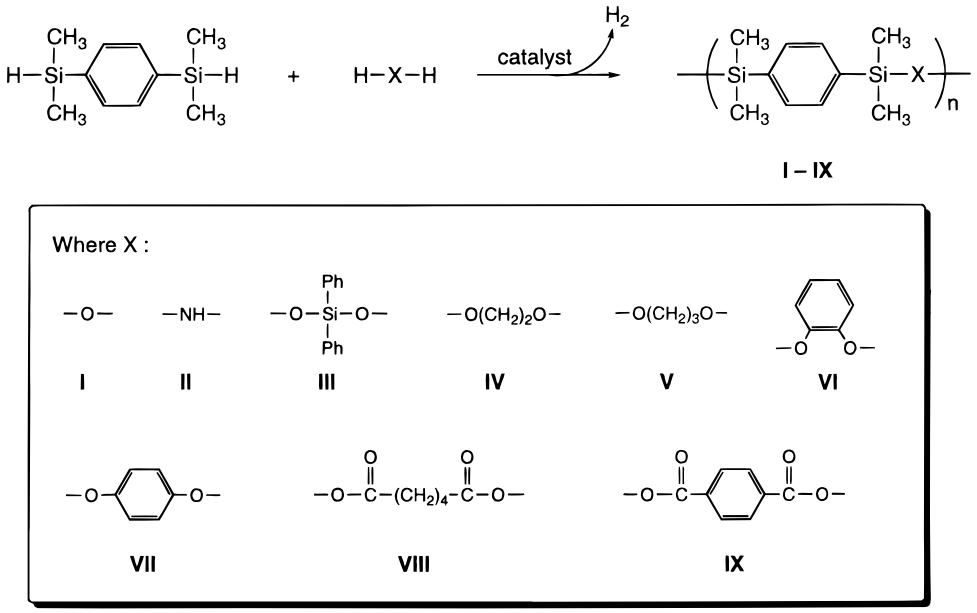
The $Pd_2(dba)_3$ was not a proper catalyst for the polymerization of BDSB with aliphatic diols such as ethylene glycol and 1,3-propanediol, and rather low molecular weight poly(silyl ether)s **IV** and **V** were obtained ($M_n$ = 1000−3000). The reason is not completely clear but is tentatively considered due to the removal of the ligand of $Pd_2(dba)_3$ during the polymerization that leads to the congestion of naked palladium particles.[13] On the other hand, 10% Pd/C was an efficient catalyst to afford higher molecular weight **IV**

**Table 1. Syntheses of Polymers I−IX by Cross-Dehydrocoupling Polymerization**[a]

| polymer | time, h | yield, %[b] | $M_n$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|
| **I** | 2 | 89.0 | 16300 | 2.19 |
| **II** | 72 | 31.6 (76.1)[c] | 8500 (7100) | 1.44 (1.96) |
| **III** | 6 | 68.0 | 7700 | 1.55 |
| **IV** | 3 | 73.1 | 9400 | 1.59 |
| **V** | 3 | 87.0 | 12400 | 1.83 |
| **VI** | 4 | 58.4 | 4900 | 1.26 |
| **VII** | 4 | *d* | | |
| **VIII** | 20 | ∼100 | 4400 | 1.79 |
| **IX** | 5 | *d* | | |

[a] Polymerization conditions: [catalyst]/[silane] = $5 \times 10^{-3}$, catalysts: $Pd_2(dba)_3{\cdot}CHCl_3$ (**I**−**III**, **VI,** and **VII**) and 10% Pd/C (**IV**, **V**, **VIII**, and **IX**), solvent: THF (except for **II**: 1,4-dioxane), temperature: 50 °C (except for **I** and **II**: room temperature). [b] Isolated yields. [c] Estimated by SEC with polystyrene standards after (before) reprecipitation. [d] Insoluble.

**Scheme 1**




and **V** ($M_n$ = 9400 and 12 400, respectively) at an elevated temperature (50 °C) in 3 h. In the case of the reaction of BDSB with catechol, however, 10% Pd/C showed low activity. Instead, a polymeric product **VI** with $M_n$ = 4900 in 58.1% yield was obtained by using $Pd_2(dba)_3$ at 50 °C after 4 h. When hydroquinone was used under similar conditions, the product **VII** became insoluble in THF when the $M_n$ became higher than 1600 (traced by SEC), and the final product might be a mixture of oligomers having $M_n$ slightly higher than 1600. The IR spectrum revealed the presence of unreacted Si−H and −OH groups. The resulting solid **VII** was neither soluble in chloroform, acetone, DMF, etc. The poor solubility of **VII** was considered due to the poor polymer−solvent interaction originating from the structural nature of **VII** (e.g., the symmetry and rigidity of the −O(*p*-$C_6H_4$)O− group).

Poly(silyl ester)s containing −Si−OCO− linkages, as a new class of degradable polymers with variable and predictable degradation behavior, have a potential application for controlled drug release systems.[15,16] These polymers were only successfully approached by transsilylation reactions between α,ω-bis(trimethylsilyl) esters and α,ω-dichlorosilanes.[15] This method, however, required prolonged reaction times (10−14 days).[15] As shown in Table 1, the cross-dehydrocoupling polymerization of BDSB with adipic acid could afford a poly(silyl ester) **VIII** ($M_n$ = 4400) under a mild condition (50 °C, 20 h), demonstrating that this is an efficient alternative route to poly(silyl ester)s. **VIII** is labile to water and therefore was purified by passing through a Florisil column with anhydrous $CHCl_3$ to remove the catalyst and without further purification. An aromatic dicarboxylic acid, terephthalic acid, was also used to react with BDSB under the same conditions. However, the product **IX** did not dissolve in common solvents probably due to a similar reason described for **VII**.

The structures of polymers **I**−**VI** and **VIII** were determined by $^1H$, $^{13}C$, and $^{29}Si$ NMR and IR spectroscopies. Besides a major peak at −3.4 ppm, polymer **II** showed a minor signal at −1.2 ppm in the $^{29}Si$ NMR spectrum, which could be assigned to the Si−O−Si linkages (also confirmed by $^1H$ and $^{13}C$ NMR spectra).

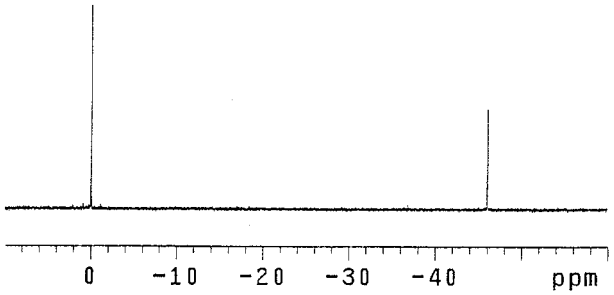



**Figure 1.** $^{29}Si$ NMR spectrum of polymer **III**.

The formation of the small amount of Si−O−Si bonds was considered caused by the reaction of the trace water comprised in the ammonia solution with BDSB[12] rather than by the precipitation procedure, since polymer **II** obtained without precipitation into methanol also contained the same amount of Si−O−Si linkages. The NMR assignments of other polymers clearly indicated that they have very regular structures identical to those shown in Scheme 1, suggesting that there are few side reactions occurring in the polymerization reactions. For instance, polymer **III** prepared in this work showed only two peaks at −0.1 and −46.0 ppm in the $^{29}Si$ NMR spectrum (Figure 1), which are assignable to two types of silicon atoms, −*p*-$C_6H_4$−*Si*$Me_2$O− and −O*Si*$(Ph)_2$O−, respectively. While the polymer prepared by other methods was reported to present numerous minor peaks besides two major peaks at −0.1 and −46.0 ppm, which was considered to result from some side reactions.[1c] The cross-dehydrocoupling polymerization introduced here is very clean, by which one could tailor various silphenylene-containing polymers with well-defined structures.

DSC results of polymers **I**−**VI** and **VIII** are shown in Table 2. As the constitutional unit (X group) between silphenylenes was varied from −O− (**I**) to −O$(CH_2)_2$O− (**IV**) and −O$(CH_2)_3$O− (**V**), the glass transition temperature ($T_g$) decreased markedly from −19.1 °C (**I**) to −38.0 °C (**IV**) and −43.7 °C (**V**), respectively. On the other hand, introducing −OSi$(Ph)_2$O− (**III**) and −O(*o*-$C_6H_4$)O− (**VI**) groups increased the $T_g$ to − 3.3 and 2.7 °C, respectively, indicating that incorporating aromatic

**Table 2. DSC and TGA Data of Polymers**[a]

| | I | II | III | IV | V | VI | VIII |
|---|---|---|---|---|---|---|---|
| $T_g$ | −19.1 (−17)[c] | −10.5 | −3.3 (−4)[c] | −38.0 | −43.7 | 2.7 | −14.2 |
| $T_k$[b] | 34.0 | 37.6 | | | | | 65.6 |
| $T_m$ | 123.5 (148)[c] | 92.5 | | | | | 93.3 |
| $T_{d(onset)}$ | 475.4 | 480.0 | 469.0 | 376.9 | 374.4 | 400.0 | 326.0 |
| char yield, % (600 °C) | 28.3 | 31.0 | 64.9 | 2.8 | 2.8 | 11.1 | 6.7 |

[a] DSC: second heating (10 °C/min) in air (**I**, **III**−**VI**) and under nitrogen flow (50 mL/min) (**II** and **VIII**); TGA: 5 °C/min under nitrogen flow (50 mL/min). [b] $T_k$: crystallization temperature. [c] Data in parentheses were adopted from ref 17 ($T_g$ = − 25 °C and $T_m$ = 152 °C were also reported for polymer **I**).

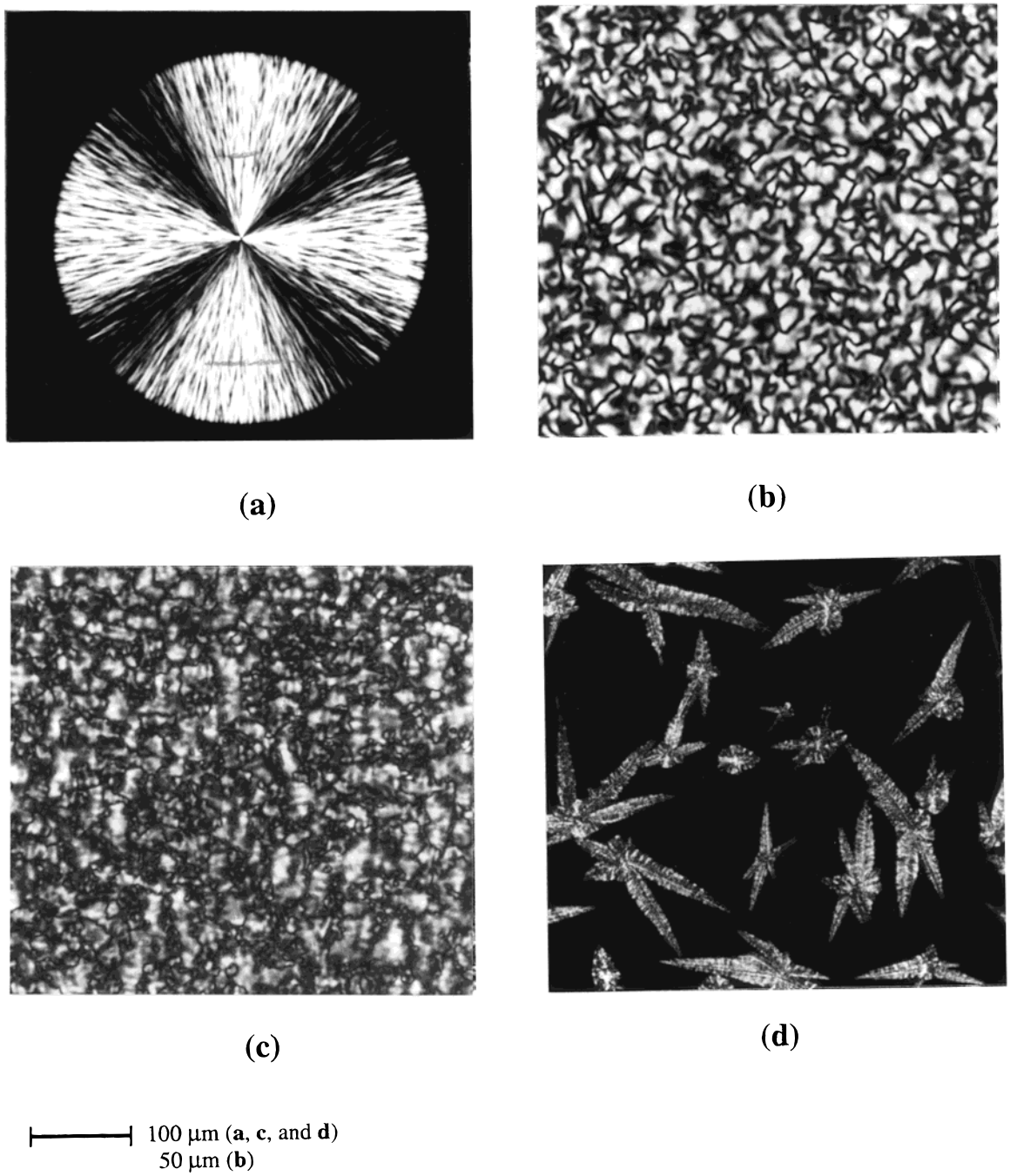



**Figure 2.** Crystalline textures of (a) **I** (80 °C, 10 min), (b) **II** (50 °C, 30 min), (c) **IV** (30 °C, 3 h), and (d) **VIII** (50 °C, 30 min) crystallized by cooling from 160 °C at a rate of 10 °C/min in air (**I** and **IV**) or under a dry nitrogen flow (50 mL/min) (**II** and **VIII**).

groups in both side chain or main chain increased the barrier of the longitudinal motion of the polymer chains, while polycarbosilazane **II** with X = −NH− and poly(silyl ester) **VIII** with X = −OCO$(CH_2)_4$COO− showed similar or a little higher $T_g$'s (−10.5 and −14.2 °C, respectively) than that of **I**. In addition to a glass transition temperature, polymers **I**, **II**, and **VIII** also exhibited a melting point $T_m$ (123.5 (**I**), 92.5 (**II**), and 93.2 °C (**VIII**)) and a crystallization temperature $T_k$ (34.0 (**I**), 37.6 (**II**), and 65.5 °C (**VIII**)), while polymers **IV**−**VI** showed no other thermal transitions except for a $T_g$ on their DSC curves.

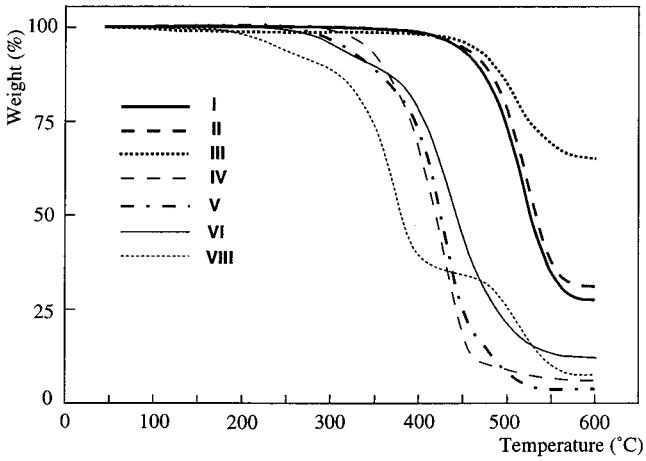



**Figure 3.** TGA of polymers **I**−**VI** and **VIII** at a heating rate of 5 °C/min under a nitrogen flow (50 mL/min).

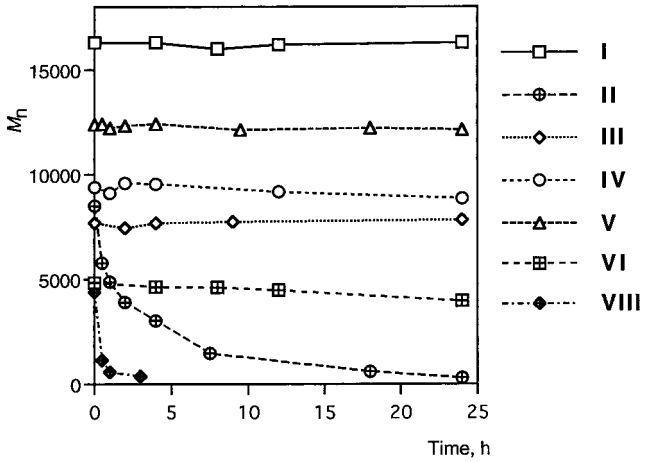



**Figure 4.** Degradation behavior of polymers in a THF−methanol mixture (80/20, v/v) at room temperature.

Poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] (**I**) was reported to easily form a spherulite texture from melt.[1b] A well-developed spherulite texture was also observed for polymer **I** prepared in this work (Figure 2a), indicating its very regular structure. Polycarbosilazane **II** has a very similar main chain structure to polymer **I**. The thermal transitions exhibited on their DSC curves are also very similar. Unexpectedly, the crystalline texture of **II** was not a spherulite, but a liquid crystalline-like texture (Figure 2b). The differences in the bond angles and/or the mobility between Si−O−Si in polymer **I** and Si−NH−Si in polymer **II** may account for this observation. Polymer **VIII** exhibited a dendrite texture as shown in Figure 2d. Interestingly, polymer **IV** showed a crystalline texture after cooling from melt (Figure 2c), although neither a melting point nor a crystallization temperature was observed on its DSC curve. The structure of this crystalline texture is still not clear but is tentatively considered to be a liquid crystal, since its main-chain structure, which contains a rigid silphenylene group and a flexible $-OCH_2CH_2O-$ moiety, may tend to form a liquid crystal. Polymers **III**, **V**, and **VI** are amorphous, showing no crystalline textures.

The influence of the structure of X groups on the thermal stability of polymers was studied by thermogravimetric analysis (TGA), and the results are represented in Figure 3 and Table 2. Polymer **I**, a well-known thermally stable polymer, showed an onset decomposition temperature at 475 °C and a residue of 28.3% at 600 °C under our conditions (at a heating rate of 5 °C/min in nitrogen). As the X groups were changed to $-NH-$ (**II**) and $-OSi(Ph)_2O-$ (**III**), no obvious changes were observed in their onset decomposition temperatures ($T_d$ = 480 (**II**) and 469 °C (**III**), respectively), while the char yield of **III** was remarkably increased (64.9%) compared to that of **I**. On the other hand, incorporating $-O(CH_2)_2O-$ (**IV**), $-O(CH_2)_3O-$ (**V**), $-O(o\text{-}C_6H_4)O-$ (**VI**), and $-OCO(CH_2)_4COO-$ (**VIII**) groups into the main chain greatly decreased the thermal stability of these polymers, confirming that the Si−O−C linkages are much less stable than the Si−O−Si linkages. Poly(silyl ester) **VIII** showed the worst thermal stability among all polymers investigated here. The TGA scan of **VIII** exhibits a multistep weight loss profile, indicating that several decomposition pathways occurred.

The solubility of these polymers was tested in several common organic solvents.[18] Polymer **I** dissolves in chloroform, THF, and toluene but is insoluble in other solvents investigated. Polysilazane **II** is soluble or partially soluble in most solvents except hexane and methanol, while polycarbosiloxane **III** and poly(silyl ether)s **IV**, **V**, and **VI** are soluble in most of organic solvents except for methanol. Poly(silyl ester) **VIII** showed poorer solubility, which is only soluble in chloroform and THF.

The degradability of polymers in methanol was examined in a THF−methanol mixture (80/20 (v/v)) at room temperature. The change of the molecular weight of polymers was monitored by SEC. As shown in Figure 4, polymers **I** and **III** are very stable to methanol, showing no change in molecular weight after being stirred for 24 h in the THF−MeOH mixture. It was reported that poly(silyl ether)s with primary carbons bonded to oxygen undergo rapid methanolysis at room temperature, while those with secondary carbons bonded to oxygen are considerably more resistant to methanolysis.[19,20] However, in our case, both poly(silyl ether) **IV** or **V** with primary carbons and **VI** with secondary carbons in Si−O−C are quite stable to methanol, showing almost no decreases in $M_n$ after 24 h. The rigid structure of $-SiMe_2-p\text{-}C_6H_4-SiMe_2-$ in these poly(silyl ether)s may contribute to their stability. On the other hand, polycarbosilazane **II** is unstable to methanol. The $M_n$ of polymer **II** decreased gradually from 8500 to 300 after 24 h. Poly(silyl ester) **VIII** is very sensitive to methanol, which $M_n$ decreased rapidly from 4400 to 1200 in 15 min and to 380 in 3 h.

## Conclusion

The catalytic cross-dehydrocoupling polymerization of BDSB with labile-hydrogen-containing compounds, water, ammonia, disilanol, aliphatic and aromatic diols, and dicarboxylic acids provided a convenient route to a class of known and new silphenylene-containing polymers, such as polycarbosilazane, polycarbosiloxanes, poly(silyl ether)s, and poly(silyl ester)s under very mild conditions. The structural analysis of these polymers proved that almost no side reactions occurred in the polymerization, which allowed tailoring polymers with well-defined structures. The thermal properties, crystalline textures, solubility in common organic solvents, and the stability to methanol were greatly influenced by the constitutional units, X groups, between two silphenylene groups. Highly thermally stable (**I**−**III**), low-$T_g$ (**IV** and **V**), liquid crystalline (**II** and **IV**), and degrad-

able (**II** and **VIII**) polymers were obtained by changing the X groups.

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