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Structural Modification of Living Polymers: Synthesis of Helical Block Copolymers from a Single Monomer via Palladium-Mediated Aromatizing Polymerization of 1,2-Diisocyanobenzenes

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ABSTRACT: New optically active helical block copolymers were synthesized by palladium-mediated living sequential copolymerization of 4,5-bis[(*tert*-butyldimethylsilyloxy)ethoxymethyl]-3,6-dimethyl-1,2-diisocyanobenzene followed by deprotection of the polymer side chains and subsequent structural modification without quenching the living site of the polymer.

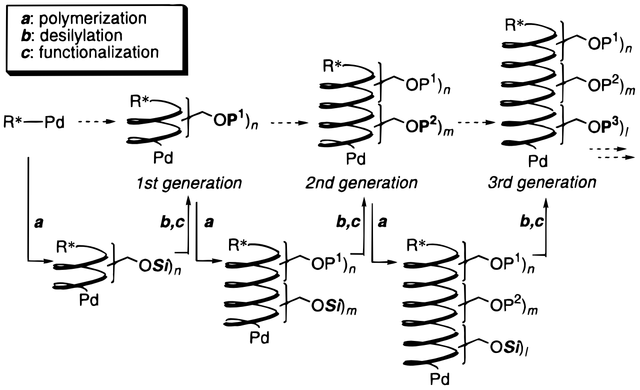
Introduction

Living polymerization is a highly attractive strategy for the synthesis of block copolymers bearing a desired functional group in each block with controlled chain length. Such block copolymers with well-regulated structures are expected to serve as functional materials.[1] Block copolymers are generally synthesized by stepwise addition of a functionalized monomer to a living polymerization system. Since the growing species for living polymerizations are generally vulnerable toward moisture and air, it may be difficult to add monomer and/or reagents without killing the chain ends.

We have developed a palladium-mediated living polymerization of 1,2-diisocyanobenzene derivatives to give helical poly(2,3-quinoxaline)s with a living palladium(II) terminus.[2,3] The living terminus is stable to some chemical operations in air. Use of an enantiomerically pure binaphthylpalladium(II) initiator (**2**) in the living polymerization leads to helical poly(quinoxaline-2,3-diyl)s with a single screw sense.[4−6]

Herein, we report the novel synthesis of new block copolymers by controlled extension of the polymer chain followed by modification of the side chains without quenching the living chain end. As outlined in Scheme 1, the new block copolymer synthesis involves the polymerization of diisocyanobenzene **1** (shown in Scheme 2) in the presence of the optically active organopalladium(II) complex **2** (step ***a***), desilylation of the resulting living polymer (step ***b***), followed by functionalization of the hydroxy groups on the side chains (step ***c***) to give the first-generation polymer. The palladium terminus survived the chemical operations and remained reactive for further polymerization. The second- and third-generation polymers were prepared by repetition of steps ***a***−***c***.

Scheme 1. Synthesis of Block Copolymers via Molecular Modification of Living Polymers



Results and Discussion

The synthesis of the block copolymers starting from a single 1,2-diisocyanobenzene monomer **1** bearing TBDMS-protected side chains was initiated by a enantiopure binaphthylpalladium(II) complex, **2**, in THF at room temperature (Scheme 2). After complete monomer consumption, the reaction mixture provided helical bis(dimethylphenylphosphine)(oligoquinoxalinyl)palladium(II) iodide, **3** (M_n = 3360, M_w/M_n = 1.23), whose ^{31}P NMR exhibited two singlets at −14.5 and −15.4 ppm. Next, the selective deprotection of the TBDMS groups on **3** was examined (Table 1). An attempt to deprotect the silyl group of **3** with tetrabutylammonium fluoride (TBAF) in THF gave quinoxaline oligomers, whose ^{31}P NMR showed two singlets at 43 and 34 ppm (entry 1). However, the resulting oligomers did not initiate polymerization of **1**, indicating that the palladium termini have deteriorated. The deprotection of **3** was also successful with 1% hydrochloric acid in THF,[7] with about 70% of the palladium termini remaining in **3** (entry 2). The ^{31}P NMR shows two sets of two singlets at −10.1 and −11.7 ppm and at −14.2 and −15.2 ppm in nearly a 1:2 to 1:3 ratio, which varied with the reaction time.

The selective deprotection of the silyl groups of **3** by pyridinium *p*-toluenesulfonate (PPTS),[8] which exhibited two singlets at −14.2 and −15.2 ppm in the ^{31}P NMR spectra, did not go to completion after 12 h at room temperature (entry 3). Treatment of **3** with BF_3OEt_2 in CH_2Cl_2 at 0 °C for 2 h was the best procedure for the selective deprotection (entry 4).[9] The desilylated oligo(quinoxaline-2,3-diyl)s (**4**) thus obtained quantitatively kept the living palladium termini on the polymer chains, showing only two singlets at −14.2 and −15.1 ppm in the ^{31}P NMR spectrum.

The deprotected polymer **4** with the two hydroxy side chains per repeat unit was functionalized with three

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Scheme 2. Synthesis of the First- and Second-Generation Block Copolymers; $n,m \approx 10$

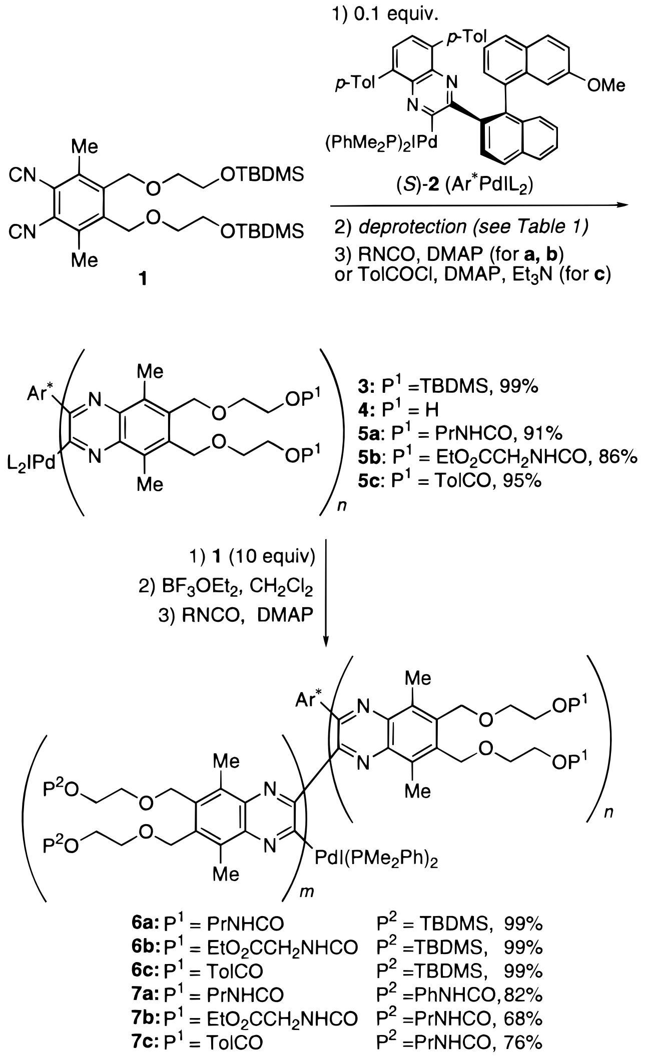


Table 1. Synthesis of 4 by Deprotection of the TBDMS Group of 3

entry	conditions	conversion/%[a]	activity/%[b]
1	TBAF, THF, rt, 2 h	100	0
2	1% HCl(aq), EtOH, THF, rt, 2 h	100	70
3	PPTS, EtOH, rt, 12 h	82	nd[c]
4	BF_3OEt_2, CH_2Cl_2, 0 °C, 2 h	100	>95

[a] Determined by ^{1}H NMR. [b] Percent living palladium termini after the desilylation. [c] Not determined.

different electrophiles (Scheme 2). Reaction of **4** with a large excess of propyl isocyanate (10 equiv/hydroxy group) in the presence of 4-(dimethylamino)pyridine (DMAP) (5 equiv) in benzene afforded the new *N*-propylcarbamate functionalized polymer **5a** in high yield (91%) after isolation with preparative GPC. Functionalization of **4** with ethyl isocyanatoacetate was also successful in producing polymer **5b** with carboester groups on the side chains of the polymer. In addition to the isocyanates, acid chlorides worked well. For example, reaction of **4** with *p*-toluoyl chloride (2.5 equiv) in the presence of Et_3N (2.5 equiv) and DMAP (0.25 equiv) afforded the acylated polymer **5c** in 95% yield. In each case, the complete introduction of the functionalities to the free hydroxy groups was unambiguously confirmed by both ^{1}H and ^{13}C NMR.

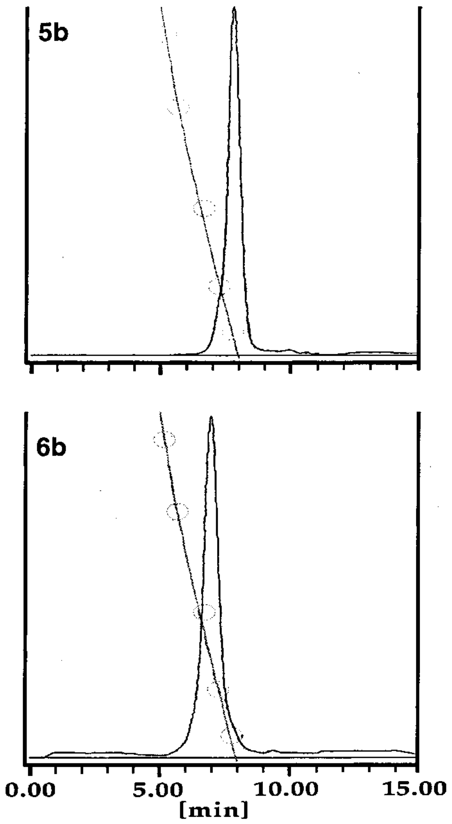
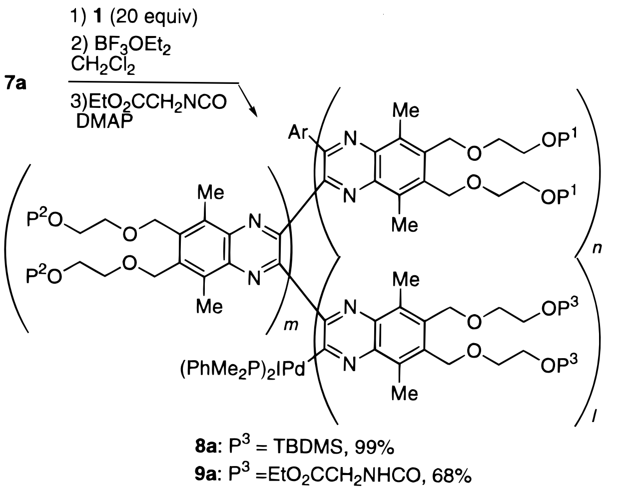


Figure 1. GPC traces of polymer **5b** and **6b**.

Scheme 3. Synthesis of the Third-Generation Block Copolymers; $(n,m,l) = (10,10,20)$



Polymers **5a**–**c** completely retained their living palladium termini, and addition of 10 equiv of monomer **1** to **5** provided the "second-generation" block copolymer **6a**–**c** (Scheme 2). No "dead" first-generation polymers were found in any of the crude reaction mixtures, as exemplified by the GPC traces of **5b** and **6b** (Figure 1). Treatment of **6a**–**c** with BF_3OEt_2 followed by that with isocyanates under the reaction conditions produced new second-generation block copolymers **7a**–**c** with different functionalities on the side chains of each block.

Similarly, third-generation block copolymer **8a** was synthesized by polymerization of **1** with **7a** (Scheme 3). Deprotection of the TBDMS groups of **8a** with BF_3OEt_2 followed by treatment with ethyl isocyanatoacetate produced block copolymer **9a** in 68% yield. It possesses three different urethane groups (PrNHCO–,

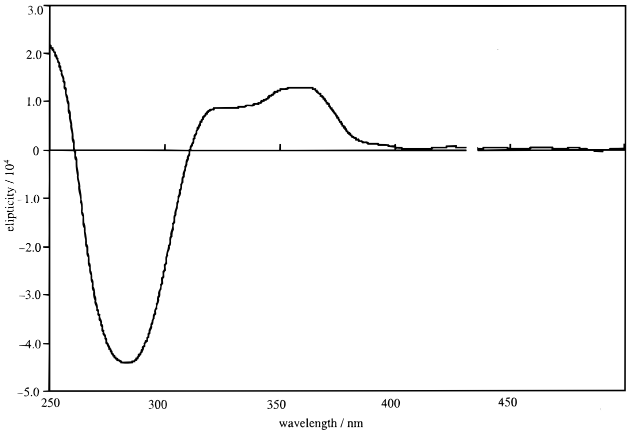


Figure 2. CD spectrum of **9a**.

PhNHCO−, EtO_2CCH_2NHCO-) on their side chains.[10] Polymer **9a** exhibited a CD spectrum characteristic of the helical polyquinoxalines reported so far (Figure 2).

This new approach for preparing block copolymers with structural modification of the living polymers is versatile and can be used to synthesize new functional materials.

Experimental Section

General. All reactions using palladium complexes were carried out under a dry nitrogen or argon atmosphere. Solvents were distilled from the indicated drying agents under argon: THF (Na/benzophenone), CH_2Cl_2 (CaH_2), Et_3N (CaH_2), and benzene ($LiAlH_4$). The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 2000 equipped with a 7.0 T magnet (300 MHz for ^1H NMR). The GPC analysis was carried out with TSK-GEL G3000HHR column (exclusion limit M_w 60 000, $CHCl_3$, polystyrene standard, flow rate 1 mL/min, temperature 20 °C, detection UV 254 nm). Preparative GPC was performed with JAI LC-908 equipped with JAIGEL-2H and -2.5H columns (20 mm diameter × 600 mm length) in a series ($CHCl_3$).

4,5-Bis[2-(*tert*-butyldimethylsiloxy)ethoxymethyl]-1,2-diisocyano-3,6-dimethylbenzene (**1**)[5] and (*S*)-bis(dimethylphenylphosphine)iodo[3-(7′-methoxy[1,1′-binaphthalen]-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinyl]palladium (**2**)[6] were prepared according to the reported procedures.

Propyl isocyanate (Aldrich, 99%), *p*-toluoyl chloride (Wako, 98%), and TBAF (1 M in THF, Aldrich) were used as purchased. Phenyl isocyanate (Nacalai, 98%), ethyl isocyanatoacetate (Aldrich, 95%), and BF_3OEt_2 (Wako) were distilled before use.

A listing summarizing results of GPC analyses of the polymers and the conditions for polymerization is given as Table 2.

General Procedure for Polymerization, Deprotection, and Functionalization. *Step **a** (polymerization).* A solution of **1** in THF was added to a solution of **2**, **5**, or **7** in THF under argon. The mixture was stirred for 18−48 h at room temperature; the solvent was removed in vacuo to give the corresponding silyl-protected polymers.

*Step **b** (deprotection).* BF_3OEt_2 (4 equiv/TBDMS group) was added dropwise to a solution of the silyl-protected polymers in CH_2Cl_2 over 5 min at 0 °C. After stirring for 2 h at 0 °C, ice water was added. The solvent was evaporated in vacuo. The residue was washed with water and Et_2O several times and dissolved in EtOH. Filtration followed by evaporation of the filtrate gave deprotected polymers.

*Step **c** (functionalization).* Isocyanate (10 equiv/hydroxy group) was added to a solution of the deprotected polymer and DMAP (5 equiv/hydroxy group) at room temperature. The mixture was stirred for 48 h, and then water was added. Organic materials were extracted with $CHCl_3$. The solution was dried over sodium sulfate and evaporated in vacuo. The residue was purified by preparative GPC for complete removal of the reagents used in excess to give functionalized polymer.

Synthesis of 3 (Scheme 2). A solution of **1** (100 mg, 1.9×10^{-1} mmol) in THF (20 mL) was added to a solution of **2** (20.7 mg, 1.9×10^{-2} mmol) in THF (5 mL) at room temperature. The mixture was stirred for 18 h; the solvent was removed in vacuo to give **3** (120 mg, 99%). **3**: ^1H NMR ($CDCl_3$) δ −0.1−0.2 (br m, 12*n*H, $SiCH_3$), 0.7−1.0 (br m, 18*n*H, $C(CH_3)_3$), 1.8−2.6 (br m, 6*n*H, $ArCH_3$), 3.4−3.9 (br m, 8*n*H, OCH_2CH_2O), 4.4−5.0 (br m, 4*n*H, $ArCH_2O$), 6.4−7.0 (m, 14 H), 7.2−8.0 (m, 19 H), 8.1−8.4 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −5.3, 12.0, 18.4, 25.9, 62.3, 67.6, 72.4, 135.3, 136.3, 138.8, 152.1 (weak signals corresponding to the binaphthyl, di-*p*-tolylquinoxalinyl, and dimethylphenylphosphine moieties were detected at 125−140 ppm); ^{31}P NMR ($CDCl_3$) δ −14.4(s), −15.3(s); IR (KBr) 1256, 1140, 1098 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 4 (Scheme 2). BF_3OEt_2 (190 μL, 1.50 mmol) was added dropwise over 5 min to a solution of oligomer **3** (120 mg) in CH_2Cl_2 (10 mL) at 0 °C. After stirring for 2 h at 0 °C, ice water was added. The solvents were evaporated in vacuo. The residue was washed with water and Et_2O several times and dissolved in EtOH. Filtration followed by evaporation of the filtrate gave **4** (77 mg, 99%). **4**: ^1H NMR ($CDCl_3$) δ 1.6−2.6 (br m, 6*n*H, $ArCH_3$), 3.3−3.9 (br m, 8*n*H, OCH_2CH_2O), 4.4−5.0 (br m, 4*n*H, $ArCH_2O$), 6.5−7.0 (m, 14 H), 7.2−8.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 12.0, 61.4, 67.6, 72.2, 136.0, 136.8, 139.0, 152.1 (weak signals corresponding to the binaphthyl, di-*p*-tolylquinoxalinyl, and dimethylphenylphosphine moieties were detected at 125−140 ppm); ^{31}P NMR ($CDCl_3$) δ −14.2(s), −15.1(s); IR (KBr) 3420, 1104 cm^{-1}.

Determination of the "Polymerization Activity" of the Polymers Obtained by the Deprotection of the Silyl Groups of 3 (Table 1). The polymer obtained by deprotection of the TBDMS groups of **3** under the condition indicated in Table 1 was reacted with propyl isocyanate (10 equiv) and DMAP (5 equiv) according to the procedure for the synthesis of **5a** (see below). The resulting propylcarbamate functionalized polymer (13 mg) was reacted with **1** (36 mg, ca. 30 equiv) in THF at room temperature for 24 h. Then, GPC analysis was carried out for each polymerization mixture.

(1) Entry 1: Polymer prepared via the deprotection with TBAF promoted no further polymerization.

(2) Entry 2: The GPC analysis of the polymer obtained via the deprotection with aqueous HCl showed two peaks corresponding to the "dead" polymer and living polymer (M_n = 1659 and 13 850) in a ratio of 8/92. From the ratio, approximately 4.0 mg (0.08 × (13 mg + 36 mg)) out of 13 mg of the polymer obtained by the deprotection with aqueous HCl was inactive for further polymerization. Accordingly, the activity of the polymer is estimated to be 70% ((13 − 4)/13).

(3) Entry 4: Polymers obtained via the deprotection with BF_3OEt_2 showed only one peak ($M_n = 1.36 \times 10^4$, M_w/M_n = 1.64) in the GPC analysis, being indicative of intactness of the active palladium termini.

Synthesis of 5a (Scheme 2). Propyl isocyanate (350 μL, 3.76 mmol) was added to a benzene (30 mL) solution of **4** (77 mg) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (230 mg, 1.88 mmol) at room temperature. The mixture was stirred for 2 days, and then water (2 mL) was added. Organic materials were extracted with $CHCl_3$. The solution was dried over sodium sulfate and evaporated in vacuo. The residue was purified by preparative GPC ($CHCl_3$) to give **5a** (99 mg, 91%). **5a**: ^1H NMR ($CDCl_3$) δ 0.6−1.1 (br m, 6*n*H, $CH_2CH_2CH_3$), 1.2−1.7 (br m, 4*n*H, $CH_2CH_2CH_3$), 2.0−2.7 (br m, 6*n*H, $ArCH_3$), 2.8−3.4 (br m, 4*n*H, $CH_2CH_2CH_3$), 3.5−4.0 (br m, 4*n*H, OCH_2-CH_2OCONH), 4.0−4.4 (br m, 4*n*H, OCH_2CH_2OCONH), 4.4−4.9 (br m, 4*n*H, $ArCH_2O$), 5.2−5.8 (br s, 2*n*H, OCON*H*), 6.4−7.0 (m, 14H), 7.2−8.6 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 11.1, 12.0, 23.0, 42.6, 63.9, 67.1, 69.1, 136.1, 136.4, 139.0, 152.0, 156.7 (weak signals corresponding to the binaphthyl, di-*p*-tolylquinoxalinyl, and dimethylphenylphosphine moieties were detected at 125−140 ppm); ^{31}P NMR ($CDCl_3$) δ −14.2(s), −15.0(s); IR (KBr) 3352, 1708, 1266, 1104 cm^{-1}. See Table 2 for the result of GPC analysis.

Table 2. Summary of Polymer Preparation

polymer	M_n[a]	M_w/M_n[a]	theor mol wt	yield/%	polymerization [M]/[I][b]	polymerization time/h
first generation						
3	3.36×10^3	1.23	6.43×10^3	99	10	18
5a	1.36×10^3	1.94	5.85×10^3	91		
5b	2.18×10^3	1.17	6.73×10^3	86		
5c	2.44×10^3	1.58	6.51×10^3	95		
second generation						
6a	2.35×10^3	1.96	1.12×10^4	99	10	18
6b	4.75×10^3	1.29	1.21×10^4	99	10	18
6c	4.14×10^3	1.36	1.18×10^4	99	10	18
7a	2.43×10^3	2.73	1.13×10^4	82		
7b	2.60×10^3	2.05	1.15×10^4	68		
7c	2.21×10^3	2.83	1.13×10^4	76		
third generation						
8a	8.64×10^3	2.84	1.66×10^4	99	20	18
9a	3.95×10^3	2.07	1.69×10^4	68		
9a′[c]	1.18×10^4	1.65	2.24×10^4			

[a] Determined by GPC (polystyrene standard). [b] Molar ratios of **1** to palladium complexes used in the polymerization. [c] Polymer obtained from **9a** by complete deprotection of the carbamate group followed by full protection with TBDMSOTf. See ref 10.

Synthesis of 5b (Scheme 2). According to a procedure similar to that for the synthesis of **5a**, **5b** (42 mg, 86%) was synthesized from **4** (30 mg) and ethyl isocyanatoacetate (220 μL, 1.98 mmol) in the presence of DMAP (120 mg, 0.99 mmol). **5b**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.8−1.3 (br m, 6*n*H, $\mathrm{OCH_2C}H_3$), 1.8−2.6 (br m, 6*n*H, $\mathrm{ArC}H_3$), 3.3−3.9 (br m, 4*n*H, $\mathrm{OC}H_2\mathrm{CH_2OCONH}$), 3.9−4.4 (br m, 8*n*H, $\mathrm{OCH_2C}H_2\mathrm{OCONH}$ and $\mathrm{OC}H_2\mathrm{CH_3}$), 4.4−5.0 (br m, 8*n*H, $\mathrm{ArC}H_2\mathrm{O}$ and $\mathrm{NHC}H_2\mathrm{CO}$), 5.76 (br s, 2*n*H, OCON*H*), 6.4−7.0 (m, 14H), 7.0−8.0 (m, 19H), 8.0−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.9, 14.1, 42.6, 61.3, 64.5, 67.2, 69.1, 135.6, 136.3, 138.8, 151.9, 156.7, 170.2 (weak signals corresponding to the binaphthyl, di-*p*-tolylquinoxalinyl, and dimethylphenylphosphine moieties were detected at 125−140 ppm); IR (KBr) 3416, 1732, 1218 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 5c (Scheme 2). *p*-Toluoyl chloride (65 μL, 0.49 mmol) was added to a THF (8 mL) solution of **4** (30 mg), DMAP (6.0 mg, 0.05 mmol), and $\mathrm{Et_3N}$ (70 μL, 0.49 mmol) at room temperature. After stirring for 2 days, water (2 mL) was added to the mixture. Organic materials were extracted with $\mathrm{CHCl_3}$. The extract was dried over sodium sulfate and evaporated in vacuo. The residue was purified by preparative GPC ($\mathrm{CHCl_3}$) to give **5c** (45 mg, 95%). **5c**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.0−2.4 (br m, 12*n*H, $\mathrm{ArC}H_3$), 3.4−3.8 (br m, 4*n*H, $\mathrm{OC}H_2\mathrm{CH_2OCO}$), 4.0−5.0 (br m, 8*n*H, $\mathrm{ArC}H_2\mathrm{O}$ and $\mathrm{OCH_2C}H_2\mathrm{OCO}$), 6.4−6.8 (m, 14H), 6.8−7.2 (br m, 4*n*H, $H^{3,5}$ of tolyl group), 7.2−7.6 (m, 14H), 7.6−8.0 (br m, 4*n*H, $H^{2,6}$ of tolyl group), 8.0−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 12.1, 21.3, 63.6, 67.4, 68.8, 127.2, 129.1, 129.6, 135.1, 136.3, 138.9, 143.8, 151.1, 166.5 (weak signals corresponding to the binaphthyl, di-*p*-tolylquinoxalinyl, and dimethylphenylphosphine moieties were detected at 125−140 ppm); IR (KBr) 1720, 1276, 1098 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 6a−c (Scheme 2). According to a procedure similar to that for the synthesis of **3**, **6a−c** (99%) was synthesized from **5a−c**.

6a: ^{1}H NMR ($\mathrm{CDCl_3}$) δ −0.1−0.2 (br m, 12*m*H, $\mathrm{SiC}H_3$), 0.6−1.0 (br m, 6*n*H+18*m*H, $\mathrm{CH_2CH_2C}H_3$ and $\mathrm{C(C}H_3)_3$), 1.3−1.6 (br m, 4*n*H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.28 (br s, 6*n*H+6*m*H, $\mathrm{ArC}H_3$), 2.6−3.1 (br m, 4*n*H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$) 3.4−3.9 (br m, 4*n*H+8*m*H, $\mathrm{OC}H_2\mathrm{CH_2OCONH}$ and $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OSi}$), 4.14 (br s, 4*n*H, $\mathrm{OCH_2C}H_2\mathrm{OCONH}$), 4.60 (br s, 4*n*H+4*m*H, $\mathrm{ArC}H_2\mathrm{O}$), 6.5−7.0 (m, 14H), 7.2−8.0 (m, 19H), 8.1−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −5.3, 11.1, 12.0, 18.2, 23.0, 25.9, 42.6, 62.3, 63.8, 67.5, 69.2, 72.5, 135.7, 136.2, 138.8, 152.1, 156.6; ^{31}P NMR ($\mathrm{CDCl_3}$) δ −14.4(s), −15.4(s); IR (KBr) 3350, 1720, 1256, 1104 cm^{-1}. See Table 2 for the result of GPC analysis.

6b: ^{1}H NMR ($\mathrm{CDCl_3}$) δ −0.1−0.2 (br m, 12*m*H, $\mathrm{SiC}H_3$), 0.8−1.0 (br m, 18*m*H, $\mathrm{C(C}H_3)_3$), 1.1−1.3 (br m, 6*n*H, $\mathrm{OCH_2C}H_3$), 2.28 (br s, 6*n*H+6*m*H, $\mathrm{ArC}H_3$), 3.59 (br s, 4*m*H, $\mathrm{OCH_2C}H_2\mathrm{OSi}$), 3.73 (br s, 4*n*H+4*m*H, $\mathrm{OC}H_2\mathrm{CH_2OCONH}$ and $\mathrm{OC}H_2\mathrm{CH_2OSi}$) 4.10 (br s, 4*n*H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.15 (br s, 4*n*H, $\mathrm{OCH_2C}H_2\mathrm{OCONH}$), 4.4−5.0 (br m, 8*n*H+4*m*H, $\mathrm{NHC}H_2\mathrm{CO}$ and $\mathrm{ArC}H_2\mathrm{O}$), 6.5−7.0 (m, 14H), 7.2−8.0 (m, 19H), 8.1−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −5.3, 12.0, 14.1, 18.2, 25.9, 42.6, 61.2, 62.3, 64.4, 67.7, 69.2, 72.4, 135.9, 136.3, 138.9, 152.2, 156.7, 170.2; ^{31}P NMR ($\mathrm{CDCl_3}$) δ −14.4(s), −15.4(s); IR (KBr) 1728, 1218 cm^{-1}. See Table 2 for the result of GPC analysis.

6c: ^{1}H NMR ($\mathrm{CDCl_3}$) δ −0.2−0.1 (br m, 12*m*H, $\mathrm{SiC}H_3$), 0.6−1.0 (br m, 18*m*H, $\mathrm{C(C}H_3)_3$), 1.9−2.5 (br m, 12*n*H+6*m*H, $\mathrm{ArC}H_3$), 3.3−3.9 (br m, 4*n*H+8*m*H, $\mathrm{OC}H_2\mathrm{CH_2OCO}$ and $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OSi}$), 4.1−4.4 (br m, 4*n*H, $\mathrm{OCH_2C}H_2\mathrm{OCO}$), 4.4−5.0 (br m, 4*n*H+4*m*H, $\mathrm{ArC}H_2\mathrm{O}$), 6.5−6.8 (m, 14H), 6.98 (br s, 4*n*H, $H^{3,5}$ of tolyl group), 7.2−8.0 (m, 19H), 7.79 (br s, 4*n*H, $H^{2,6}$ of tolyl group), 8.1−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −5.3, 12.1, 18.3, 21.4, 25.9, 62.3, 63.7, 67.4, 68.7, 72.4, 127.3, 129.1, 129.6, 135.5, 136.7, 138.9, 143.7, 152.0, 166.6; ^{31}P NMR ($\mathrm{CDCl_3}$) δ −14.4(s), −15.4(s); IR (KBr) 1722, 1218 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 7a (Scheme 2). According to a procedure similar to that for the synthesis of **5a**, **7a** (156 mg, 82%) was synthesized from **6a** (150 mg) and phenyl isocyanate (409 μL, 3.76 mmol) in the presence of DMAP (230 mg, 1.88 mmol).

7a: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.4−1.0 (br m, 6*n*H, $\mathrm{CH_2CH_2C}H_3$), 1.0−1.6 (br m, 4*n*H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.36 (br s, 6*n*H+6*m*H, $\mathrm{ArC}H_3$), 2.7−3.1 (br m, 4*n*H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.65 (br s, 4*n*H+4*m*H, $\mathrm{OC}H_2\mathrm{CH_2OCONH}$), 4.20 (br s, 4*n*H+4*m*H, $\mathrm{OCH_2C}H_2\mathrm{OCONH}$), 4.61 (br s, 4*n*H+4*m*H, $\mathrm{ArC}H_2\mathrm{O}$), 6.5−6.8 (m, 14H), 6.8−7.8 (br s, 10*m*H, $\mathrm{C_6}H_5$), 7.2−8.0 (m, 19H), 8.1−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.1, 12.2, 23.0, 42.7, 63.8, 64.4, 67.3, 69.0, 69.3, 119.1, 123.4, 128.9, 135.8, 136.4, 138.1, 138.9, 152.0, 154.1, 156.7; IR (KBr) 3384, 1724, 1706 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 7b (Scheme 2). According to a procedure similar to that for the synthesis of **5a**, **7b** (49 mg, 68%) was synthesized from **6b** (61 mg) and propyl isocyanate (120 μL, 1.25 mmol) in the presence of DMAP (76 mg, 0.63 mmol). **7b**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.87 (br s, 6*m*H, $\mathrm{CH_2CH_2C}H_3$), 1.21 (br s, 6*n*H, $\mathrm{OCH_2C}H_3$), 1.41 (br s, 4*m*H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.28 (br s, 6*n*H+6*m*H, $\mathrm{ArC}H_3$), 2.95 (br s, 4*m*H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.4−3.9 (br m, 4*n*H+4*m*H, $\mathrm{OC}H_2\mathrm{CH_2OCONH}$), 3.9−4.4 (br m, 8*n*H+4*m*H, $\mathrm{OC}H_2\mathrm{CH_3}$ and $\mathrm{OCH_2C}H_2\mathrm{OCONH}$), 4.4−5.0 (br s, 8*n*H+4*m*H, $\mathrm{NHC}H_2\mathrm{CO}$ and $\mathrm{ArC}H_2\mathrm{O}$), 6.5−7.0 (m, 14H), 7.2−8.0 (m, 19H), 8.1−8.4 (m, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.2, 12.0, 14.1, 23.0, 42.6, 61.2, 63.7, 67.3, 69.3, 135.4, 136.4, 138.9, 152.0, 156.7, 170.3; IR (KBr) 3448, 1748, 1726 cm^{-1}. See Table 2 for the result of GPC analysis.

Synthesis of 7c (Scheme 2). According to a procedure similar to that for the synthesis of **5a**, **7c** (59 mg, 76%) was synthesized from **6c** (68 mg) and propyl isocyanate (129 μL, 1.38 mmol) in the presence of DMAP (84.3 mg, 0.69 mmol). **7c**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.6−1.0 (br m, 6*m*H, $\mathrm{CH_2CH_2C}H_3$), 1.2−1.7 (br m, 4*m*H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.9−2.6 (br m, 12*n*H+6*m*H, $\mathrm{ArC}H_3$), 2.8−3.3 (br m, 4*m*H), 3.64 (br s, 4*n*H+4*m*H, $\mathrm{OC}H_2$-

$\mathrm{CH_2OCO}$), 4.27 (br s, $4n\mathrm{H}+4m\mathrm{H}$, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OCO}$), 4.58 (br s, $4n\mathrm{H}+4m\mathrm{H}$, $\mathrm{ArC}\mathit{H}_2\mathrm{O}$), 6.5−6.8 (m, 14H), 6.99 (br s, $4n\mathrm{H}$, $H^{3,5}$ of tolyl group), 7.2−7.6 (m, 19H), 7.77 (br s, $4n\mathrm{H}$, $H^{2,6}$ of tolyl group)8.1−8.4 (m, 1H); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$) δ 11.1, 12.0, 21.4, 23.0, 42.6, 63.7, 67.4, 68.8, 127.2, 129.1, 129.6, 135.9, 136.3, 138.9, 143.7, 152.0, 156.7, 166.4; IR (KBr) 1718, 1218 $\mathrm{cm^{-1}}$. See Table 2 for the result of GPC analysis.

Synthesis of 8a (Scheme 3). According to a procedure similar to that for the synthesis of **3**, **8a** (97 mg, 100%) was synthesized from **7a** (50 mg) and **1** (47 mg, 0.089 mmol). **8a**: $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 0.03 (br s, $12l\mathrm{H}$, $\mathrm{SiC}\mathit{H}_3$), 0.65 (br s, $6n\mathrm{H}$, $\mathrm{CH_2CH_2C}\mathit{H}_3$), 0.87 (br s, $18l\mathrm{H}$, $\mathrm{C(C}\mathit{H}_3)_3$), 1.2−1.6 (br s, $4n\mathrm{H}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 2.32 (br s, $6n\mathrm{H}+6m\mathrm{H}+6l\mathrm{H}$, $\mathrm{ArC}\mathit{H}_3$), 2.6−3.2 (br s, $4n\mathrm{H}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 3.62 (br s, $4l\mathrm{H}$, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OSi}$), 3.76 (br s, $4n\mathrm{H}+4m\mathrm{H}+4l\mathrm{H}$, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OCONH}$ and $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OSi}$), 4.21 (br s, $4n\mathrm{H}+4m\mathrm{H}$, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OCONH}$), 4.61 (br s, $4n\mathrm{H}+4m\mathrm{H}+4l\mathrm{H}$, $\mathrm{ArC}\mathit{H}_2\mathrm{O}$), 6.8−8.0 (br m, $10m\mathrm{H}$, $\mathrm{C_6}\mathit{H}_5$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$) δ −5.3, 10.9, 12.0, 18.2, 22.9, 25.9, 42.6, 62.3, 63.8, 64.4, 67.5, 68.7, 72.4, 119.2, 123.4, 128.8, 135.4, 136.3, 138.0, 138.9, 152.1, 154.1, 156.8. No signals were observable by $^{31}\mathrm{P}$ NMR ($\mathrm{CDCl_3}$). See Table 2 for the result of GPC analysis.

Synthesis of 9a (Scheme 3). According to a procedure similar to that for the synthesis of **5a**, **9a** (68 mg, 68%) was synthesized from **8a** (65 mg) and ethyl isocyanatoacetate (200 μL, 1.78 mmol) in the presence of DMAP (109 mg, 0.89 mmol). **9a**: $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 0.66 (br s, $6n\mathrm{H}$, $\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.0−1.3 (br m, $6l\mathrm{H}$, $\mathrm{OCH_2C}\mathit{H}_3$), 1.3−1.6 (br s, $4n\mathrm{H}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 2.38 (br s, $6n\mathrm{H}+6m\mathrm{H}+6l\mathrm{H}$, $\mathrm{ArC}\mathit{H}_3$), 2.8−3.2 (br s, $4n\mathrm{H}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 3.70 (br s, $4n\mathrm{H}+4m\mathrm{H}+4l\mathrm{H}$, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OCONH}$), 4.02 (br s, $4l\mathrm{H}$, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 4.15 (br s, $4n\mathrm{H}+4m\mathrm{H}+4l\mathrm{H}$, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OCONH}$), 4.48 (br s, $4l\mathrm{H}$, $\mathrm{NHC}\mathit{H}_2\mathrm{CO}$), 4.61 (br s, $4n\mathrm{H}+4m\mathrm{H}+4l\mathrm{H}$, $\mathrm{ArC}\mathit{H}_2\mathrm{O}$), 5.99 (br s, $2n\mathrm{H}+2m\mathrm{H}+2l\mathrm{H}$, $\mathrm{OCON}\mathit{H}$), 6.8−8.0 (br m, $10m\mathrm{H}$, $\mathrm{C_6}\mathit{H}_5$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$) δ 11.7, 12.1, 14.1, 22.9, 42.6, 61.3, 64.1, 67.2, 69.2, 119.2. 123.5, 128.9, 135.7, 136.3, 138.1, 139.0, 152.3, 154.0, 156.8, 170.3; IR (KBr) 3416, 1726 $\mathrm{cm^{-1}}$. See Table 2 for the result of GPC analysis.

Determination of the Molecular Weight of 9a.[10] KOH (200 mg) and hydrazine monohydrate (1 mL) was added to a suspension of **9a** (60 mg) in EtOH (10 mL) at room temperature. The mixture was stirred under reflux for 10 h. The solvent was evaporated in vacuo. The residue was washed with water and $\mathrm{CHCl_3}$ several times and then dissolved in EtOH. After filtration, the filtrate was evaporated to give deprotected polymer (25 mg). A portion of the deprotected polymer (15 mg) was dissolved in $\mathrm{CH_2Cl_2}$ (2 mL). 2,6-Lutidine (68 μL, 0.45 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (100 μL, 0.86 mmol) were added at 0 °C. The mixture was allowed to warm to room temperature while stirring. After being stirred for 36 h, water (50 mL) was added to the mixture. Extractive workup with $\mathrm{CHCl_3}$ followed by preparative GPC gave poly(quinoxaline-2,3-diyl) (**9a′**) fully protected by TBDMS groups (4.2 mg). See Table 2 for the result of GPC analysis.

References and Notes

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(10) The GPC analysis of the copolymers functionalized by the carbamate groups exhibited a much smaller M_n value and a much larger $M_\mathrm{w}/M_\mathrm{n}$ value than those fully protected by TBDMS groups. For instance, the GPC analysis of **9a** indicated an M_n value of 3.95×10^3 and an $M_\mathrm{w}/M_\mathrm{n}$ value of 2.07, which were remarkably different from the values obtained for the corresponding polymer whose side chains were protected by TBDMS groups ($\mathrm{P^1 = P^2 = P^3 =}$ TBDMS, $M_\mathrm{n} = 1.08 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 1.25$ for the 40-mer).[4b] However, M_n and $M_\mathrm{w}/M_\mathrm{n}$ of poly(quinoxaline)s having TBDMS side chains, which were prepared from **9a** by hydrolysis of the carbamate groups on the polymer side chains ($\mathrm{H_2NNH_2/KOH/EtOH}$) followed by the treatment with TBDMSOTf/2,6-lutidine, were nearly the same as those of the corresponding poly(quinoxaline)s directly prepared from **1a**, suggesting that no degradation of the polymer main chain took place during the structural modification of the living polymer.

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