Synthesis of Poly(quinoxaline-2,3-diyl)s with Alkoxy Side Chains by Aromatizing Polymerization of 4,5-Dialkoxy-Substituted 1,2-Diisocyanobenzenes

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Keywords

Poly(quinoxaline-2,3-diyl)s, living polymerization, alkoxy side chain, thermal properties

Abstract

Poly(quinoxaline-2,3-diyl)s bearing alkoxy pendants was synthesized by living polymerization of 4,5-dialkoxy-3,6-dimethyl-1,2-diisocyanobenzenes, which were easily accessible from 3,6-dimethylcatechol, using organonickel complexes as initiators. Thermal properties of the obtained polymers were fully determined by TGA and DSC, exhibiting strong dependence on their side chains.

Introduction

Much interest has focused on rigid-rod polymers having fully aromatic backbone, such as poly(phenylene)s, poly(thiophene)s, and poly(pyridine)s.[1] Because of their unique electronic, optical, chemical, and thermal properties, the polymers are regarded as promising candidate for electroluminescent,[2] nonlinear-optical,[3] ion-conducting,[4] and liquid-crystalline[5] materials. It is highly important to explore new aromatic polymers with development of new polymerization reactions. Current efforts are being made to utilize transition-metal catalysts in polymerization,[6] aiming at exploration of new polymer scaffolds with fine control of molecular weight and molecular weight distribution.[7]

We have developed a living polymerization of 1,2-diisocyanobenzene derivatives with transition metal initiators.[8] The polymerization gives rigid aromatic polymers, poly(quinoxaline-2,3-diyl)s, with narrow dispersities. Because of steric hindrance of the two substituents at the 5- and 8-positions of the quinoxaline rings, the poly(quinoxaline)s form rigid helical structure.[9] Quite recently, we have reported that single-handed helical poly(quinoxaline- 2,3-diyl) bearing metal-binding sites serves as a highly efficient chiral ligand for palladium-catalyzed asymmetric hydrosilylation.[10] To explore intriguing structure and functions of poly(quinoxaline-2,3-diyl)s, it seems to be highly important to expand the scope of the polymerization reaction. In particular, variation for the 4,5-substituent of diisocyanobenzene, which are located at the surrounding of the polymer backbone and determine the properties of polymers, is critically important. We have so far used alkoxymethyl groups as substituents at 4 and 5 positions. We expected that introduction of alkoxy groups directly to the quinoxaline rings would change the properties of polymers, and also make the synthesis of polymer much easier. Although

Reggelin and co-workers reported the synthesis of poly(quinoxaline)s having alkoxy groups at the 6- and 7-positions of the quinoxaline ring,[11] the synthesis is limited to 5,8-dibromo- and 5,8-pyridyl-substituted derivatives, of which properties and applicability have not been explored at all in contrast to the 5,8-dialkyl derivatives. Furthermore, all the polymerizations were carried out using organopalladium initiators, whose activity has recently been recognized to be much lower than the corresponding organonickel initiators in the polymerization of 6,7-dialkoxymethyl substituted 1,2-diisocyanobenzenes. It seems to be important to see if the organonickel complex serves as superior initiators even with 1,2-diisocyanobenzenes bearing alkoxy groups at the 6,7-positions. We herein report the nickel-mediated synthesis of poly(quinoxaline)s bearing alkoxy pendants and their thermal properties in comparison with poly(quinoxaline)s previously reported. We also report on the formation of non-racemic helical polyquinoxalines using a chiral organonickel initiator.

Results and Discussion

Synthesis of new monomers **1a–e**, which carry methyl groups at 3-and 6-positions and alkoxy groups at 4-and 5-positions of the benzene rings, is shown in Scheme 1. We adopted 3,6-dimethylcathecol as a starting compound, which can be prepared in multi-gram quantities from inexpensive catechol, morpholine, and paraformaldehyde.[12] In the first step, various side chains were introduced onto the catechol oxygen atoms through a Williamson ether synthesis. Thus obtained compounds **3a–e** were treated with fuming nitric acid in acetic acid to yield dinitrobenzene derivatives **4a–e**. The nitro groups were reduced quantitatively in the presence of palladium on carbon under hydrogen atmosphere to amino groups, which were then formylated with an excess amount of

acetic formic anhydride to obtain diformamide. Diisocyanobenzenes **1a–d** were finally

obtained after dehydration with phosphoryl chloride in the presence of triethylamine. All

monomers were stored under dry nitrogen atmosphere at −20 °C to avoid gradual

decomposition. Monomer **1a** showed a good crystallinity, affording single crystals by

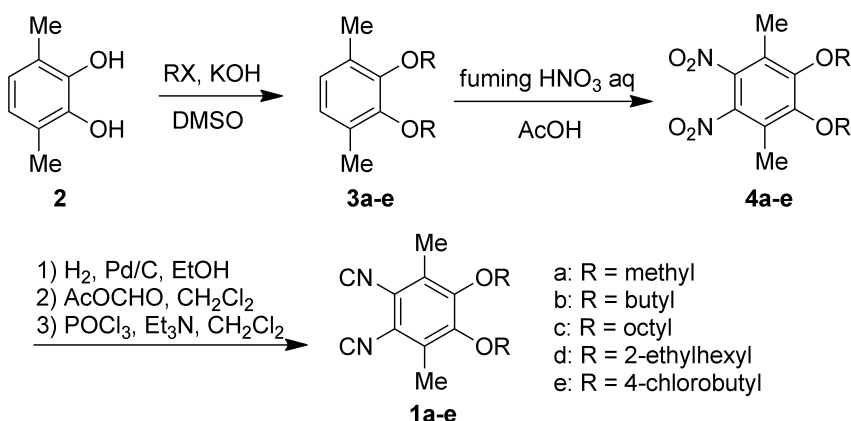recrystallization from hot hexane.

Scheme 1

Figure 1

ORTEP drawing of monomer **1a**. Displacement ellipsoids are drawn at the 50%

probability level and H atoms are shown as small spheres of arbitrary radii. Selected

distances (Å) and angles (°) related with isocyano groups are as follows; C1-N1:

1.165(3), N1-C5: 1.397(3), C2-N2: 1.161(3), N2-C6: 1.394(3), C13-N3: 1.166(4), N3-

C17: 1.403(3), C14-N4: 1.163(3), N4-C18: 1.395(3), C1-N1-C5: 178.3(3), C2-N2-C6:

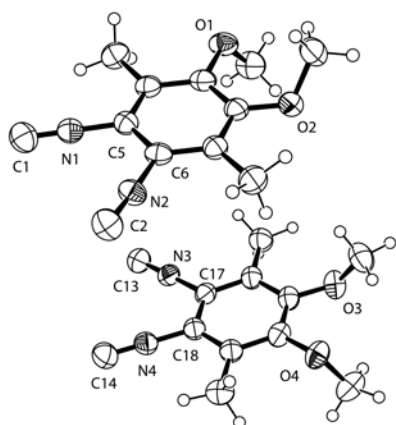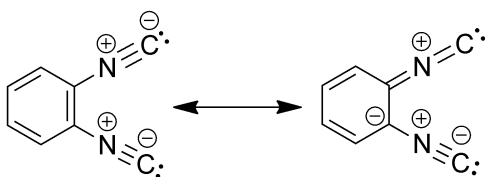176.8(3), C13-N3-C17: 179.1(3), C14-N4-C18: 179.9(3).

Figure 2

Plausible resonance structures of diisocyanobenzene.

ORTEP drawing of monomer **1a** is shown in Figure 1. Two independent molecules are observed in an asymmetric unit, although they are almost structurally identical. Selected geometric parameters related with the isocyano groups are summarized in Figure 1. The $N \equiv C$ bond distances (1.163–1.166 Å) are slightly longer than those found in aromatic monoisocyanides (1.153–1.163 Å).[13] It is known that the distance of $N \equiv C$ bonds in monoisocyanobenzene derivatives is not strongly influenced by the electronic density of the aromatic ring (*p*-isocyanoaniline: 1.158 Å,[14] pentafluorophenyl isocyanide: 1.159 Å[15]) or a methyl group at the ortho position (2,4,6-trimethylphenyl isocyanide: 1.158 Å[13]). The elongation of the $N \equiv C$ bond may arise from appreciable contributions of a resonance structure containing $C=N^+=C$ form, which reduces the $N \equiv C$ bond order

(Figure 2). This assumption is supported by shortening of the bond distance between the isocyano nitrogen and aromatic carbon atom (1.394–1.403 Å in **1a** vs. 1.407 Å in trimethylphenyl isocyanide). Infrared spectroscopic study was also carried out on monomer **1a**, which showed a sharp absorption peak at 2117 cm^{-1} originated from a stretching vibration of N≡C bond. All other monomers **1b–e** also exhibited similar absorption peaks in the range of 2116 to 2118 cm^{-1}. These values are significantly smaller than that of aromatic monoisocyanides (2130–2140 cm^{-1})[16] indicating that the N≡C bond was stretched in diisocyanobenzenes reported here. It should be noted here that the C≡N bond distance in 3,6-bis(4-methylphenyl)-1,2-diisocyanobenzene is reported to be 1.147 Å,[11] which is significantly shorter than ordinary monoisocyanides, although we can provide no clear explanation to the critical difference between them.

Table 1

Polymerization of diisocyanobenzene derivatives with alkoxy chains in the presence of an organonickel or organopalladium initiator [a]
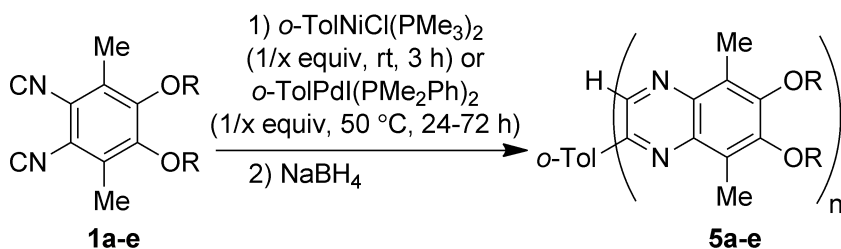
entry	monomer (R)	x	Polymer [b] (yield/%)	M_n [c]	M_w/M_n [c]
1	**1a** (Me)	100	**5a** (-[d])	-[d]	-[d]
2	**1b** (Bu)	100	**5b** (96)	3.26×10^4	1.14

3	**1c** (Oct)	100	**5c** (88)	2.77×10^4	1.30
4	**1d** (2-EtHexyl)	100	**5d** (88)	3.69×10^4	1.74
5	**1e** ((CH$_2$)$_4$Cl)	100	**5e** (97)	2.72×10^4	1.13
6	**1b** (Bu)	40	**5b^{40}** (92)	1.19×10^4	1.08
7	**1b** (Bu)	60	**5b^{60}** (91)	1.99×10^4	1.09
8	**1b** (Bu)	80	**5b^{80}** (95)	2.85×10^4	1.16
9[e, f]	**1b** (Bu)	100	**5b** (81)	2.30×10^4	1.50
10[e, g]	**1c** (Oct)	100	**5c** (79)	3.41×10^4	1.62

[a] *o*-TolNiCl(PMe$_3$)$_2$ was used as an initiator unless otherwise noted.

[b] All polymers named without superscripts are 100mer. Other polymers are named with superscripts which refer to their degree of polymerization (40, 60, and 80).

[c] Determined by GPC calibrated with polystyrene standards.

[d] The yield and the molecular weight were not determined due to its low solubility.

[e] *o*-TolPdI(PMe$_2$Ph)$_2$ was used as an initiator instead of *o*-TolNiCl(PMe$_3$)$_2$. Reaction temperature was set at 50 °C

[f] Reaction time was extended to 24 h.

[g] Reaction time was extended to 72 h.

Polymerizations of monomers **1a–e** were carried out in the presence of an organonickel initiator. After mixing a THF solution of monomer **1a** and a solution of nickel complex in THF, the solution immediately turned turbid with formation of insoluble beige precipitates. The methoxy group may be too short to dissolve the polyquinoxaline. In the polymerization of monomer **1b** having butoxy groups, the solubility of the formed polymer was much improved, and the reaction mixture remained homogeneous until the end of the polymerization. The polymer **5b** was obtained in almost quantitative yield with narrow molecular weight distribution (M_w/M_n = 1.14). This suggests that the polymerization proceeded in a living fashion as previously reported.[9j] Polymerization of
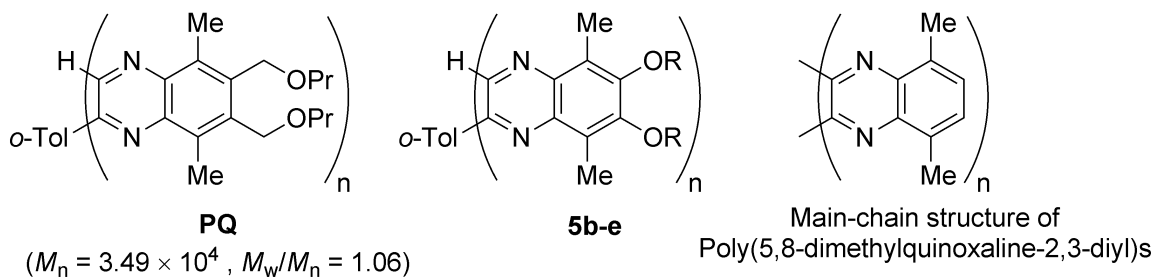
monomer **1c** having *n*-octyloxy groups gave the corresponding polymer **5c** with relatively broad molecular weight distribution. Monomer **1d** with 2-ethylhexyloxy groups resulted in further broadening of molecular weight distribution, probably because of steric hindrance of the bulky side chains. Polymerization of monomer **1e** having chloroalkyl side chains, which would be utilized for introduction of functional groups after polymerization, successfully proceeded without causing any side reactions associated with the presence of the $C(sp^3)$-Cl bond. In entries 2 and 6–8, polymerizations of monomer **1b** with varied monomer/initiator ratios were examined. As the monomer/initiator ratio increased in the range of 40–100, molecular weights of the obtained polymers were proportionally increased with good PDIs, ranging between 1.08-1.16. Polymerizations of monomers **1b** and **1c** were also carried out in the presence of an organopalladium complex instead of the organonickel initiator (entries 9 and 10). The palladium initiator required longer reaction time than the organonickel initiator. To achieve full conversion of monomers **1b** and **1c**, it took 24 h and 72 h, respectively, even at elevated reaction temperature (50 °C). Moreover, these polymerizations resulted in broader molecular weight distributions (M_w/M_n = 1.50 and 1.62), suggesting that the nickel initiator is more suitable for polymerizations of this type of diisocyanobenzene monomers.

Polymers **5b–e** showed good solubilities in common organic solvents such as THF, chloroform, dichloromethane, and toluene. Polymer **5c** and **5d** were soluble even in non-polar hydrocarbons such as *n*-hexane and cyclohexane. On the other hand, these polymers were insoluble in polar solvents such as acetone, methanol, ethanol, and 2-propanol. The solubilities depended not only on the structures of the side chains but also on their

molecular weight. For instance, polymer **5b⁴⁰** and **5b⁶⁰** were soluble in hexane, while polymer **5b⁸⁰** and **5b** were insoluble.

Table 2

Thermal properties of polymers **PQ** and **5b–e**.

	PQ	**5b-e**	Main-chain structure of
	($M_n = 3.49 \times 10^4$, $M_w/M_n = 1.06$)		Poly(5,8-dimethylquinoxaline-2,3-diyl)s

Polymer (R)	$T_{5\%}{}^a$ (°C)	Residue at 500 °C (%)	Content of main chain (%)	$T_m{}^b$ (°C)
PQ	354.7	56.3	52.0	-^{c}
5b (Bu)	350.7	56.2	52.0	161.6, 176.5
5c (Oct)	325.6	43.6	37.9	50.3, 116.4
5d (2-EtHexyl)	348.7	42.4	37.9	149.6, 170.9
5e ((CH$_2$)$_4$Cl)	329.7	49.0	42.3	160.9, 182.7

^{a} Temperature for 5% weight loss as determined by TGA, 10 °C/min.

^{b} Melting temperatures as determined by DSC, 10 °C/min.

^{c} Small exothermic peak was observed at 175.3 °C.

Thermal properties of alkoxy-substituted polymers **5b–e** were summarized in Table 2. Propoxymethyl-substituted **PQ** was also subjected to the measurement for comparison with polymers **5b–e**. They generally showed high thermal stability with high decomposition temperatures (5% weight loss measured by thermogravimetric analysis, TGA, 10 °C/min, dry nitrogen atmosphere) higher than 300 °C. Polymer **PQ** and **5b**

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exhibited almost the same decomposition temperatures around 350 °C. On the other hand, polymers **5c–e** having longer side chain showed lower decomposition temperatures. These results suggest that the thermal degradation occurred mainly at the side chains. Weights of TGA residues at 500 °C correspond roughly to the weight of their main-chains, being consistent with our assumption that the thermal weight loss is due to the cleavage of the side chains.

To analyze more detailed thermal properties, differential scanning calorimetry (DSC) studies were carried out for these polymers. In order to avoid an influence of thermal histories of the polymers, all samples were heated to 200 °C (10 °C/min), held at that temperature for 5 min, and then cooled to 40 °C (10 °C/min) just before measurements. Measurements were repeated twice and it was confirmed that the first scan was in complete agreement with the second scan. Although polymers **PQ** and **5b** showed comparable thermal stability in the TGA measurements, a significant difference between these polymers was observed in the DSC analyses. Polymer **PQ** had no endothermic peaks during heating and showed a small exothermic peak at 175.3 °C, which might arise from polymer crystallization. By contrast, polymer **5b** showed a clear melting peak at 161.6 °C and a weak endothermic peak at 176.5 °C. This difference should be originated from higher flexibilities of butoxy groups in polymer **5b** than propoxymethyl groups in polymer **PQ**. Polymer **5c** with longer alkoxy chain exhibited a lower melting point at 50.3 °C. Polymer **5d** bearing branched side chains showed a higher melting temperature compared to polymer **5c** with weak endothermic peaks at 149.6 °C and 170.9 °C. Introduction of chlorine groups to side chains also influenced their thermal properties. A weak endothermic peak at 160.9 °C and a strong peak at 182.7 °C were observed for **5e**.

Noteworthy, all the polymers showed multiple melting points, which indicate liquid crystalline transition. Further investigations about liquid crystalline properties of newly synthesized polymers are currently underway.
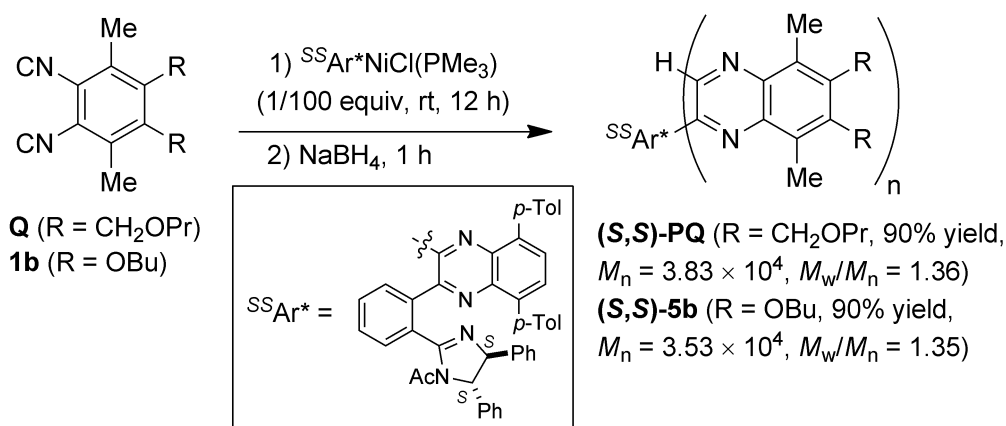
Scheme 2

Q (R = CH₂OPr)
1b (R = OBu)

1) ^{SS}Ar*NiCl(PMe₃)
(1/100 equiv, rt, 12 h)

2) NaBH₄, 1 h

(S,S)-PQ (R = CH₂OPr, 90% yield, $M_n = 3.83 \times 10^4$, $M_w/M_n = 1.36$)
(S,S)-5b (R = OBu, 90% yield, $M_n = 3.53 \times 10^4$, $M_w/M_n = 1.35$)

Figure 3

UV-visible absorption spectra of **(S,S)-PQ** (solid line, 9.25×10^{-5} mol/dm³) and **(S,S)-5b** (dotted line, 9.59×10^{-5} mol/dm³) in chloroform.
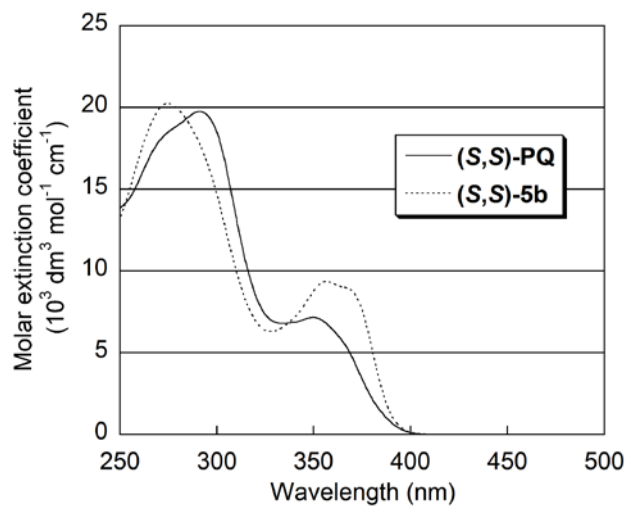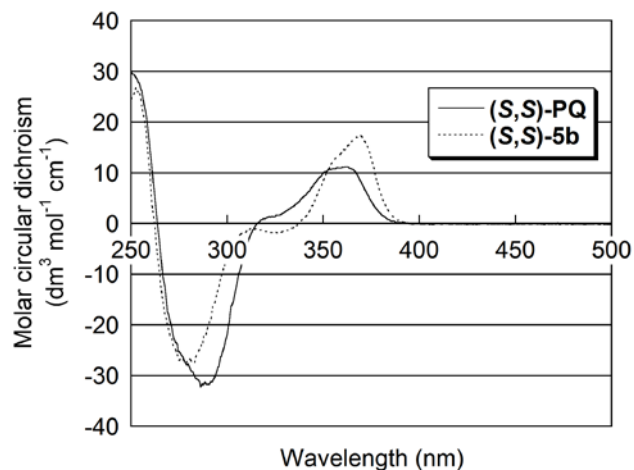
Figure 4

CD spectra of **(S,S)-PQ** (solid line, 9.25×10^{-5} mol/dm^3) and **(S,S)-5b** (dotted line, 9.59×10^{-5} mol/dm^3) in chloroform.

Finally we examined the synthesis of non-racemic polyquinoxalines using a chiral organonickel initiator, which has been successful in inducing helical chirality to alkoxymethyl-substituted polymer **(S,S)-PQ**. Monomer **1b** was polymerized in the presence of a chiral organonickel complex. The polymerization proceeded at room temperature, affording **(S,S)-5b** in good yield (90%) with narrow dispersity ($M_w/M_n = 1.35$). The polymer was showed UV-vis and CD spectra whose intensities can be well comparable to that of **(S,S)-PQ** (80% screw-sense excess). Although we haven't determined the g value for 100% single-handed structure for the alkoxy-substituted polyquinoxalines, we could assume that that the level of helix induction is quite comparable to that for **(S,S)-PQ**.

Conclusion

In summary, we have established the facile synthetic route to *o*-diisocyanobenzene derivatives bearing alkoxy groups on the quinoxaline rings. Crystal structure of 1,2-diisocyano-4,5-dimethoxy-3,6-dimethylbenzene **1a** revealed significantly longer isocyano C-N bond distance than that of monoisocyanobenzenes. Polymerizations of these diisocyanobenzene monomers proceeded in a living fashion in the presence of an ArNiCl(PMe$_3$)$_2$ complex as an initiator. The solubilities of the polymers obtained here were strongly dependent on their side chains and the degree of polymerization. The yielded polymers **5b–e** and the previously reported polymer **PQ**, which has di(propoxymethyl) side chains, showed similar decomposition temperatures higher than 300 °C. In contrast, in DSC measurement, polyquinoxalines bearing alkoxy side chains exhibited clear endothermic peaks, which were not observed for polymer **PQ**. A chiral organonickel initiator was used as an initiator for the polymerization of 1,2-diisocyanobenzens, affording non-racemic polyquinoxaline bearing alkoxy side chains in good yield with narrow dispersity. Polymerization of 1,2-diisocyanobenzenes bearing other functional alkoxy side chains, introduction of optically active side chains, and study on liquid crystalline properties of poly(quinoxaline)s are now being undertaken in this laboratory.

Experimental

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-VX 400, 400-MR or JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows:

chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were obtained using a Shimadzu FTIR-8400 FT-IR spectrometer on NaCl plates or in KBr pressed pellets. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus EVO II TG-DTA TG8120 at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was recorded using Rigaku Thermo Plus EVO II DSC8230 at a heating rate of 10 °C/min under nitrogen. The GPC analysis was carried out with TSKgel G4000H$_{HR}$ (CHCl$_3$, polystyrene standards). Preparative GPC was performed on JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series (CHCl$_3$). X-ray diffractions were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated MoKα radiation diffractometer with imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR[17]. The analysis was carried out with direct methods (SHELX-97[18] and SIR92[19]) using Yadokari-XG.[20] The program ORTEP3[21] was used to generate the X-ray structural diagrams. UV spectra were recorded on a JASCO V-500 spectrometer. CD spectra were recorded on a JASCO J-750 spectrometer. THF was dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Compound **2** (3,6-dimethylcatechol),[12] acetic formic anhydride,[22] o-TolNiCl(PMe$_3$)$_2$,[23] monomer **Q**,[9b] ^{SS}Ar*NiCl(PMe$_3$),[9j] and (η^3-allyl)(η^5-cyclopentadianyl)palladium(II)[24] were prepared according to the reported procedures. Dimethyl sulfoxide (DMSO), triethylamine and phosphoryl chloride (POCl$_3$) were distilled, degassed, and stored under nitrogen. Other

chemical reagents were purchased from the commercial sources and were used without further purification.

Typical Procedure for the Synthesis of Monomer 1 via 2, 3, and 4

Synthesis of 3b: To a mixture of **2** (1.00 g, 7.24 mmol), potassium hydroxide (3.25 g, 57.9 mmol), and 1-bromobutane (3.1 mL, 3.97 g, 29.0 mmol) was added DMSO (14.5 mL) at room temperature. The mixture was stirred at room temperature for 2 h. Water (100 mL) was added to the reaction mixture, and then organic materials were extracted with hexane (100 mL × 2). The combined organic layer was washed with water (100 mL × 3) and then brine (100 mL). The organic extract was dried over Na_2SO_4, filtered, concentrated, and dried under reduced pressure to give **3b** as a colorless liquid, which required no further purification (1.78 g, 98% yield). ^1H NMR (CDCl$_3$) δ 6.79 (s, 2H), 3.93 (t, J = 6.8 Hz, 4H), 2.22 (s, 6H), 1.78–1.71 (m, 4H), 1.56-1.46 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 150.7, 129.8, 125.1, 72.6, 32.6, 19.4, 15.9, 14.0; IR (neat) 2958, 2872, 1492, 1464, 1426, 1379, 1279, 1215, 1161, 1080, 1029, 973, 841, 799 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{26}O_2$ (M$^+$): 250.1927, found: 250.1933.

Synthesis of 4b: To fuming nitric acid (11.0 mL) was added dropwise an acetic acid (5.0 mL) solution of **3b** (8.06 g, 29.0 mmol) at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h. Water (100 mL) was added to the reaction mixture, and organic materials were extracted with Et$_2$O (100 mL). The combined organic layer was washed with water (100 mL) then washed with NaOH aq (5 N, 100 mL × 2). The organic layer was washed with water (100 mL × 3) then brine (100 mL). The organic extract was dried over MgSO$_4$, filtered, and concentrated under reduced

pressure. The crude product was subjected to silica gel chromatography (hexane/AcOEt=95/5), giving **4b** (5.99 g, 56% yield). ^{1}H NMR (CDCl$_3$) δ 3.99 (t, J = 6.4 Hz, 4H), 2.28 (s, 6H), 1.80–1.73 (m, 4H), 1.56–1.45 (m, 4H), 0.99 (t, J = 7.4 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 153.0, 140.3, 125.8, 73.7, 32.2, 19.2, 13.8, 11.8; IR (neat) 2959, 2938, 2877, 1539, 1468, 1356, 1284, 1247, 1093, 1059, 1017, 939, 831, 788, 757 cm^{-1}. HRMS (EI) m/z calcd for C$_{16}$H$_{24}$N$_2$O$_6$ (M$^+$): 340.1629, found: 340.1630.

Synthesis of 1b: A mixture of **4b** (5.99 g, 17.6 mmol) and 10 wt% Pd/C (1.87 g, 1.76 mmol) in EtOH (17.6 mL) was stirred for 14.5 h under H$_2$ atmosphere. The mixture was filtered through a pad of Celite. The Celite pad was washed with EtOH (50 mL), and the filtrate was concentrated and dried under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (88.0 mL), and acetic formic anhydride (12.4 g, 140.9 mmol) was added to the solution. After stirring at room temperature for 20 h, removal of volatiles under reduced pressure gave a diformate compound as a white powder (5.02 g). The diformate (2.00 g, 5.94 mmol) was suspended in CH$_2$Cl$_2$ (89 mL) and Et$_3$N (8.3 mL), and POCl$_3$ (1.66 mL, 2.73 g, 17.8 mmol) was added at 0 °C to the suspension. After stirring for 1 h at 0 °C, the reaction mixture was washed with saturated NaHCO$_3$ (50 mL × 2). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane to hexane/CH$_2$Cl$_2$=50/50) to give **1b** as pale yellow liquid (1.47 g, 70%). ^{1}H NMR (CDCl$_3$) δ 3.93 (t, J = 6.8 Hz, 4H), 2.33 (s, 6H), 1.77–1.70 (m, 4H), 1.53–1.44 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 171.6, 151.7, 128.7, 119.9, 73.4, 32.2, 19.2, 13.9, 12.7; IR (neat) 2960, 2934, 2874, 2116, 1575, 1456, 1380, 1337, 1271, 1095, 1050, 946, 917, 739 cm^{-1}; HRMS (EI) m/z calcd for C$_{18}$H$_{24}$N$_2$O$_2$ (M$^+$): 300.1832, found: 300.1837.

Other diisocyanobenzenes **1a**, **1c**, **1d**, and **1e** were prepared according to the procedure for **1b**.

1a: yield = 73%. ^{1}H NMR (CDCl$_3$) δ 3.84 (6H, s), 2.34 (6H, s); ^{13}C NMR (CDCl$_3$) δ 171.9, 152.2, 128.6, 100.6, 60.6, 12.5; IR (KBr) 3004, 2948, 2117, 1577, 1462, 1406, 1339, 1275, 1095, 1047, 979, 963, 906, 817, 771 cm^{-1}; HRMS (EI) m/z calcd for C$_{12}$H$_{12}$N$_2$O$_2$ (M$^+$): 216.0893, found: 216.0899.

1c: yield = 80%. ^{1}H NMR (CDCl$_3$) δ 3.92 (t, J = 6.8 Hz, 4H), 2.33 (s, 6H), 1.78−1.71 (m, 4H), 1.49–1.39 (m, 4H), 1.33–1.18 (m, 18H), 0.89 (t, J = 7.0 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 171.6, 151.7, 128.7, 119.9, 73.7, 31.8, 30.4, 30.2, 29.4, 29.2, 26.0, 22.6, 14.1, 12.7. IR (neat) 2956, 2927, 2855, 2116, 1456, 1379, 1338, 1269, 1095, 1049, 963, 919, 722 cm^{-1}; HRMS (EI) m/z calcd for C$_{26}$H$_{40}$N$_2$O$_2$ (M$^+$): 412.3084, found: 412.3083.

1d: yield = 75%. ^{1}H NMR (CDCl$_3$) δ 3.82-3.75 (m, 4H), 2.33 (s, 6H), 1.78−1.72 (m, 2H), 1.59–1.23 (m, 16H), 0.96–0.88 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 171.6, 151.9, 128.6, 119.9, 40.5, 30.2, 29.1, 23.6, 23.0, 14.1, 12.7, 11.1; IR (neat) 2960, 2931, 2873, 2858, 2116, 1700, 1457, 1380, 1338, 1295, 1269, 1169, 1113, 1094, 1048, 962, 811 cm^{-1}; HRMS (EI) m/z calcd for C$_{26}$H$_{40}$N$_2$NaO$_2$ ([M+Na]$^+$): 435.2982, found: 435.2978.

1e: yield = 67%. ^{1}H NMR (CDCl$_3$) δ 3.96 (t, J = 6.2 Hz, 4H), 3.62 (t, J = 6.0 Hz, 4H), 2.34 (s, 6H) 2.03-1.93 (8H, m); ^{13}C NMR (CDCl$_3$) δ 172.0, 151.4, 128.7, 120.2, 72.9, 44.5, 29.2, 27.6, 12.8; IR (neat) 2958, 2876, 2118, 1570, 1444, 1384, 1337, 1269, 1098, 1050, 967, 933, 726, 682, 652 cm^{-1}; HRMS (EI) m/z calcd for C$_{18}$H$_{22}$Cl$_2$N$_2$O$_2$ (M$^+$): 368.1053, found: 368.1057.

o-**TolPdI(PMe₂Ph)₂**: To a solution of (η^3-allyl)(η^5-cyclopentadianyl)palladium(II) (0.213 g, 1.00 mmol) in THF (10 mL) was added dimethylphenylphosphine (0.415 g, 3.00 mmol) at −78 °C. After 15 min at −78 °C, 2-iodotoluene (0.196 g, 0.90 mmol) was added, and the mixture was heated at 50 °C. After 3 h, all volatiles were removed under vacuum, and the residue was subjected to silica gel column chromatography (Hexane/AcOEt = 90/10), giving *o*-TolPdI(PMe₂Ph)₂ as a white powder (0.261 g, 48%). ^{1}H NMR (CDCl₃) δ 7.56−7.50 (4H, m) 7.37−7.29 (6H, m) 6.86−6.76 (3H, m) 6.76−6.69 (1H, m) 2.10 (3H, s) 1.62 (6H, t, J = 3.4 Hz) 1.43 (6H, t, J = 3.4 Hz); ^{31}P NMR (CDCl₃) δ −10.33; IR (KBr) 3043, 2980, 2959, 2907, 2895, 2365, 1572, 1558, 1485, 1456, 1433, 1420, 1373, 1308, 1296, 1281, 1188, 1101, 1070, 1043, 1028, 1013, 999, 947, 903, 847, 739, 714, 690, 679, 644, 611 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{29}IP_2Pd$ (M+Na$^+$): 622.9716, found: 622.9702.

Polymerization of monomer 1a: A THF solution of *o*-TolNiCl(PMe₃)₂ (37.3 mmol/L, 124.0 µL, 4.6 µmol) was added to a solution of **1a** (0.100 g, 0.463 mmol) in THF (13.8 mL) with vigorous stirring. The reaction mixture immediately turned turbid with formation of insoluble beige precipitates. After 3 h, monomer **1a** was completely disappeared. The obtained precipitates were not soluble in any common solvents.

Polymer 5b: A THF solution of *o*-TolNiCl(PMe₃)₂ (37.3 mmol/L, 76.7 µL, 2.9 µmol) was added to a solution of **1b** (85.9 mg, 0.286 mmol) in THF (8.5 mL) with vigorous stirring. After 3 h, NaBH₄ (10.8 mg, 0.286 mmol) was added to the reaction mixture and stirred for 1 h. Water (20 mL) and CH₂Cl₂ (50 mL) was added, and organic materials were extracted with CH₂Cl₂. The organic layer was collected and dried over Na₂SO₄. The

crude material obtained by evaporation of solvent was purified by preparative GPC, giving polymer **5b** as a beige solid (82.8 mg, 96% yield). ^{1}H NMR (CDCl$_3$) δ 4.00 (2H, br s), 3.85 (2H, br s), 2.17 (6H, br s), 1.74 (4H, br s), 1.51-1.45 (4H, m), 0.96 (6H, t, J = 7.2 Hz). GPC (CHCl$_3$, g/mol): M_n = 3.26 × 10^4, M_w/M_n = 1.14.

Other polymers **5c−e**, **5b^{40}**, **5b^{60}**, **5b^{80}**, and **PQ** were prepared according to the procedure for polymer **5b**. (*S,S*)-**PQ** and (*S,S*)-**5b** were prepared according to the procedure for polymer **5b** using ^{SS}Ar*NiCl(PMe$_3$) as an initiator.

Polymer 5c: yield = 88%. ^{1}H NMR (CDCl$_3$) δ 4.03 (2H, br s), 3.82 (2H, br s), 2.19 (6H, br s), 1.79 (4H, br s), 1.44 (4H, br s), 1.27 (16H, br s), 0.90−0.84 (6H, m); GPC (CHCl$_3$, g/mol): M_n = 2.77 × 10^4, M_w/M_n = 1.30.

Polymer 5d: yield = 88%. ^{1}H NMR (CDCl$_3$) δ 3.75 (4H, br s), 2.13 (6H, br s), 1.70-1.20 (18H, m), 0.84 (12H, br s); GPC (CHCl$_3$, g/mol): M_n = 3.69 × 10^4, M_w/M_n = 1.74.

Polymer 5e: yield = 97%. ^{1}H NMR (CDCl$_3$) δ 3.97 (2H, br s), 3.90 (2H, br s), 3.60 (4H, br s), 2.17 (6H, br s), 1.94 (8H, br s); GPC (CHCl$_3$, g/mol): M_n = 2.72 × 10^4, M_w/M_n = 1.33.

Polymer 5b^{40}: yield = 92%. ^{1}H NMR (CDCl$_3$) δ 4.00 (2H, br s), 3.84 (2H, br s), 2.50-1.90 (6H, m), 1.90−1.62 (4H, m), 1.57−1.32 (4H, m), 1.07−0.84 (6H, m), small peaks originated from end-group were observed in 9.95 and 7.84−7.12 ppm; GPC (CHCl$_3$, g/mol): M_n = 1.19 × 10^4, M_w/M_n = 1.08.

Polymer 5b^{60}: yield = 91%. ^{1}H NMR (CDCl$_3$) δ 4.00 (2H, br s), 3.84 (2H, br s), 2.18 (6H, br s), 1.90−1.62 (4H, m), 1.60−1.30 (4H, m), 0.96 (6H, t, J = 7.2 Hz), small peaks

originated from end-group were observed in 9.95 and 7.84−7.10 ppm; GPC (CHCl$_3$, g/mol): $M_n = 1.99 \times 10^4$, $M_w/M_n = 1.09$.

Polymer 5b[80]: yield = 95%. ^{1}H NMR (CDCl$_3$) δ 4.01 (2H, br s), 3.85 (2H, br s), 2.18 (6H, br s), 1.75 (4H, br s), 1.60−1.30 (4H, m), 0.96 (6H, t, J = 7.2 Hz). small peaks originated from end-group were observed in 9.95 and 7.84−7.12 ppm; GPC (CHCl$_3$, g/mol): $M_n = 2.85 \times 10^4$, $M_w/M_n = 1.16$.

Polymer PQ: yield = 93%. ^{1}H NMR (CDCl$_3$) δ 4.66 (2H, br s), 4.57 (2H, br s), 3.46 (2H, br s), 2.35 (6H, br s), 1.85−1.56 (4H, m), 0.90 (6H, t, J = 7.0 Hz). small peaks originated from end-group were observed in 10.06 and 7.87−7.09 ppm; GPC (CHCl$_3$, g/mol): $M_n = 3.49 \times 10^4$, $M_w/M_n = 1.06$.

Polymer (S,S)-PQ: yield = 90%. ^{1}H NMR (CDCl$_3$) δ 4.66 (2H, br s), 4.56 (2H, br s), 3.47 (2H, br s), 2.35 (6H, br s), 1.59 (4H, br m), 0.90 (6H, t, J = 7.0 Hz). small peaks originated from end-group were observed in 10.06 and 7.72−6.54 ppm; GPC (CHCl$_3$, g/mol): $M_n = 3.83 \times 10^4$, $M_w/M_n = 1.36$.

Polymer (S,S)-5b: yield = 90%. ^{1}H NMR (CDCl$_3$) δ 4.00 (2H, br s), 3.84 (2H, br s), 2.17 (6H, br s), 1.75 (4H, br s), 1.60−1.30 (4H, m), 0.96 (6H, t, J = 7.2 Hz). small peaks originated from end-group were observed in 9.95 and 8.06−6.55 ppm; GPC (CHCl$_3$, g/mol): $M_n = 3.53 \times 10^4$, $M_w/M_n = 1.35$.

5b obtained by palladium-initiated polymerization: A THF solution of *o*-TolPdI(PMe$_2$Ph)$_2$ (41.4 mmol/L, 40.3 µL, 1.7 µmol) was added to a solution of **1b** (50.0 mg, 0.166 mmol) in THF (4.9 mL) with vigorous stirring. After stirring at 50 °C for 24 h,

NaBH$_4$ (6.3 mg, 0.242 mmol) was added to the reaction mixture, and the reaction mixture was stirred for 12 h. Water (20 mL) and CH$_2$Cl$_2$ (20 mL) were added, and organic materials were extracted. After the organic layer was collected by using a phase separation filter and dried over Na$_2$SO$_4$, solvents were removed under reduced pressure. The crude product was purified by preparative GPC, giving polymer **5b** as a beige solid (40.6 mg, 81% yield). ^{1}H NMR (CDCl$_3$) δ 4.00 (2H, br s), 3.85 (2H, br s), 2.18 (6H, br s), 1.75 (4H, br s), 1.54−1.46 (4H, m), 0.96 (6H, t, J = 7.2 Hz); GPC (CHCl$_3$, g/mol): M_n = 2.30 × 10^4, M_w/M_n = 1.50.

5c obtained by palladium-initiated polymerization: By the same procedure as that used for polymerization of **1b**, **1c** (50.0 mg, 0.121 mmol) was polymerized at 50 °C for 72 h in THF (2.8 mL) with a THF solution of o-TolPdI(PMe$_2$Ph)$_2$ (41.4 mmol/L, 29.3 μL, 1.2 μmol), giving **5c** in 79% yield. ^{1}H NMR (CDCl$_3$) δ 4.04 (2H, br s), 3.84 (2H, br s), 2.18 (6H, br s), 1.80 (4H, br s), 1.44 (4H, br s), 1.27 (16H, br s), 0.98−0.74 (6H, m); GPC (CHCl$_3$, g/mol): M_n = 3.41 × 10^4, M_w/M_n = 1.62.

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Graphical Abstract

A facile synthesis of poly(quinoxaline-2,3-diyl)s bearing alkoxy side chains was established by using 4,5-dialkoxy-3,6-dimethyl-1,2-diisocyanobenzenes as monomers, which were easily accessible from 3,6-dimethylcatechol. The DSC traces of poly(quinoxaline)s were significantly dependant on their side chains, although all polymers showed similar decomposition temperatures higher than 300 °C from TGA measurement.
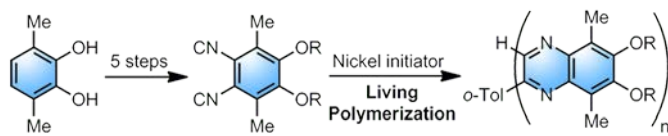
Poly(6,7-alkoxy-quinoxaline-2,3-diyl)s
Easily accessible, Soluble in common solvents,
and Thermally stable