methods (SHELXS-97) and refined against all F^2 using SHELXL-97) with non hydrogen atoms anisotropic and hydrogen atoms in riding mode. a) Crystallographic data for **1** at 173(2) K: ($C_{39}H_{52}LiN_4Si_2Y$, $M_r = 728.88$) crystal dimensions $0.4 \times 0.4 \times 0.3$ mm^3: triclinic, space group $P\bar{1}$ (no. 2), $a = 11.2801(6)$, $b = 12.5170(8)$, $c = 14.0742(9)$ Å, $\alpha = 106.916(3)$, $\beta = 92.003(4)$, $\gamma = 93.380(3)^\circ$, $V = 1895.1(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.28$ Mg m^{-3}, $\mu = 1.63$ mm^{-1}. Of 12364 reflections measured ($3.75 < \theta < 24.10^\circ$), 5977 were independent ($R_{int} = 0.051$). $wR2 = 0.093$ (all data), $R1 = 0.045$ (for 4962 reflections with $I > 2\sigma(I)$), 436 parameters, GOF = 1.049. b) Crystallographic data for **2** at 173(2) K: ($C_{32}H_{44}CuN_4Si_2Y$, $M_r = 693.34$) crystal dimensions $0.1 \times 0.1 \times 0.1$ mm^3: orthorhombic, space group *Pbcn* (no. 60), $a = 11.9268(5)$, $b = 17.0281(6)$, $c = 16.0764(7)$ Å, $V = 3265(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.41$ Mg m^{-3}, $\mu = 2.52$ mm^{-1}. Of 15424 reflections measured ($3.84 < \theta < 25.01^\circ$), 2872 were independent ($R_{int} = 0.079$). The molecule lies on a twofold rotation axis. $wR2 = 0.098$ (all data), $R1 = 0.041$ (for 1907 reflections with $I > 2\sigma(I)$), 188 parameters, GOF = 1.025. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168596 and CCDC-168597 for **1** and **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Helical Chiral Polyisocyanides Possessing Porphyrin Pendants: Determination of Helicity by Exciton-Coupled Circular Dichroism**

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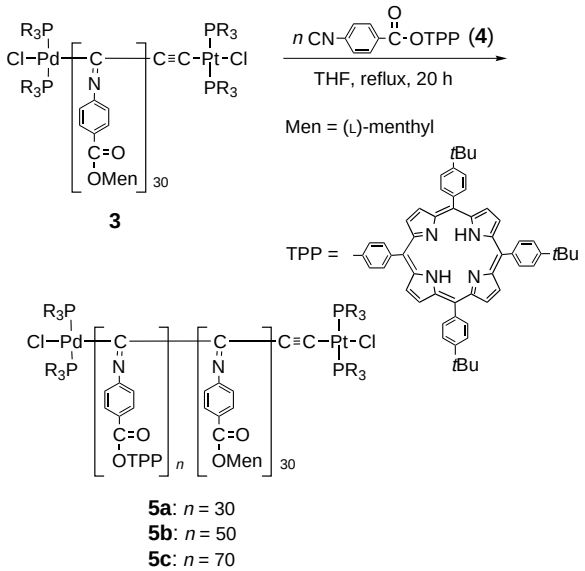
There has been considerable interest in helical chiral polymers because of their unique functions that are applicable to a wide range of scientific disciplines, such as molecular recognition and asymmetric syntheses.[1] Although the helical structure is often found in biopolymers, only a limited number of artificial polymers that maintain a stable helical conformation in solution have so far been reported. Polyisocyanide with bulky substituents is a representative example of such helical polymers.[2] In recent years, interesting studies on the selective syntheses of single-handed helical polyisocyanides using chiral monomers, chiral initiators, and chiral additives have been reported.[3–6] Many problems associated with helical polymers, however, still remain to be solved. One such problem is the determination of the helical sense. Although theoretical circular dichroism (CD) calculations provide useful information on the helical sense, experimental determination of the helical sense is quite rare.[7, 8] We previously developed a living polymerization of aryl isocyanides by the use of a Pd/Pt μ-ethynediyl complex (**1**) as an initiator.[9] This living polymerization system is applicable to aryl isocyanides bearing various kinds of substituents, and poly(aryl isocyanide)s with porphyrin pendants in their side chains have been prepared.[10] Herein we present a novel method of determining the helical sense of poly(aryl isocyanide)s that is based on exciton-coupled CD of the porphyrin Soret band.

It is well-known that the CD sign arising from exciton coupling is a useful probe for the assignment of the absolute configuration of chiral organic molecules.[11] Porphyrin derivatives are one of the best candidates since they exhibit a sharp and intense absorption band (the Soret band) at around 420 nm.[12] Thus, we started our study from the preparation of helical chiral poly(aryl isocyanide)s having porphyrin pendants. Since we had already shown that helical chiral poly(aryl isocyanide)s are selectively synthesized by block copolymerization between chiral and achiral isocyanides[13], aryl isocyanide (**4**), which has a tetraphenylporphyrin derivative linked through an ester group,[10] was polymerized using a helical chiral initiator (**3**; $M_n = 7000$, $M_w/M_n = 1.12$, $\Delta\varepsilon_{364} = 9.60$ dm^3 cm^{-1} mol^{-1}) prepared from complex **1** and 30 equivalents of the chiral isocyanide (**2a**) with a (L)-menthyl group.

Treatment of **4** with **3** in refluxing THF for 20 h resulted in the quantitative formation of block copolymers (**5a**–**5c**) with a narrow polydispersity index (Scheme 1). The CD spectra of



5a: $n = 30$
5b: $n = 50$
5c: $n = 70$

Scheme 1.

the resulting polymers **5a**–**5c** exhibited a Cotton effect at 364 nm, which is characteristic of helical chiral polyisocyanides and assignable to the n–π^* transition of the imino chromophore.[2] The $\Delta\varepsilon_{364}$ values of **5a**–**5c** are smaller than that of the helical chiral initiator **3**, but almost constant and

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independent of the degree of polymerization (Table 1). Chiroptical properties of helical chiral poly(aryl isocyanide)s are strongly affected by substituents on the aromatic ring, while a decrease in the $\Delta\varepsilon_{364}$ values with an increase in the degree of polymerization indicates that the helical sense of the

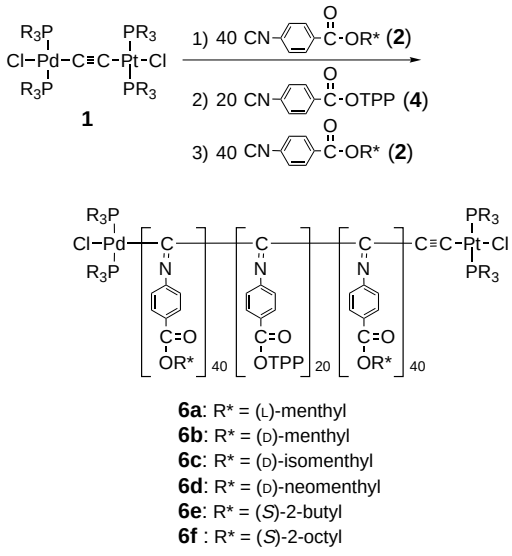
Table 1. Polymerization of porphyrin isocyanide **4** by chiral oligomer complex **3**.

polymer	n	M_n[a]	M_w/M_n[a]	$\Delta\varepsilon_{364}$ [$dm^3 cm^{-1}$][b]
5a	30	10300	1.16	5.40
5b	50	15300	1.16	5.29
5c	70	19000	1.15	5.68

[a] Determined by gel-permeation chromatography using polystyrene standards. [b] In $CHCl_3$ at room temperature.

block copolymers is not well-controlled by the helical chiral initiator **3**.[13] In the present case, the constant values of $\Delta\varepsilon_{364}$, independent of the degree of polymerization, clearly show that porphyrin isocyanide **4** was polymerized with a high helical-sense selectivity to give block copolymer **5** having a predominantly single-handed helical structure. It is noteworthy that the polymer block composed of **4**, which possesses *para* substituents on the porphyrin ring forms a stable helical structure, whereas the analogous polymer block with cyclohexyloxycarbonyl pendants does not maintain a helical conformation as a result of insufficient steric bulkiness. An intense Cotton effect with exciton coupling arising from the Soret band was observed in the CD spectra of **5a**–**5c**. However, uncertainty remains in determining the helical sense of the main chain on the basis of the CD sign since the chain end of the polymer, in which the porphyrin chromophore is also situated, would be relatively flexible.[13]

Thus, we have designed a triblock copolymer (**6**), in which porphyrin units line up as pendant groups only in the central part of the main chain, thus keeping a rigid helical conformation. This triblock polymer was prepared by successive polymerization of chiral and achiral monomers **2** and **4** (Scheme 2). Figure 1 shows the electronic absorption and the



6a: R* = (L)-menthyl
6b: R* = (D)-menthyl
6c: R* = (D)-isomenthyl
6d: R* = (D)-neomenthyl
6e: R* = (*S*)-2-butyl
6f : R* = (*S*)-2-octyl

Scheme 2.

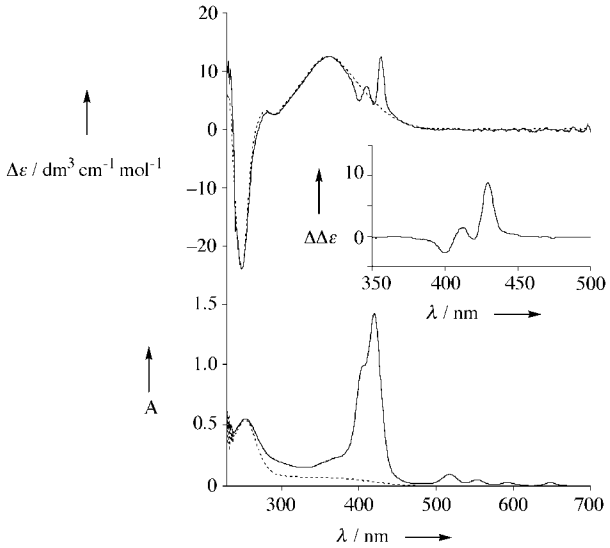
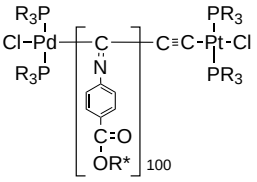


Figure 1. Electronic and CD spectra of triblock copolymer **6a** and homopolymer **7a** in $CHCl_3$ at room temperature (——: **6a**, - - - -: **7a**). The inset indicates the substraction of the CD spectrum in the Soret band region ($\Delta\Delta\varepsilon = \Delta\varepsilon$(**6a**) $- \Delta\varepsilon$(**7a**)).

CD spectra of **6a** in chloroform along with those of homopolymer **7a** prepared from **2a**. Homopolymer **7a** has a weak broad absorption band between 300 and 500 nm in



7a: R* = (L)-menthyl
7b: R* = (D)-menthyl
7c: R* = (D)-isomenthyl
7d: R* = (D)-neomenthyl
7e: R* = (*S*)-2-butyl
7f : R* = (*S*)-2-octyl

addition to a definite peak at 253 nm.[13] Copolymer **6a** containing tetraphenylporphyrin units, on the other hand, showed several absorption peaks characteristic of a metal-free porphyrin: namely, Soret bands at 405 and 419 nm and four weak bands between 500 and 670 nm (the so-called Q bands), in addition to a peak at 253 nm, which was also seen for **7a**.[10] The CD spectrum of **7a** consists of a broad positive envelope and a sharp trough corresponding, respectively, to the absorption shoulder at 364 nm and peak at 253 nm. The CD spectrum of **6a** is essentially similar in shape except in the Soret region (380–450 nm), which indicates that the helicity of **6a** and **7a** is the same. Subtraction of the CD spectrum of **7a** from that of **6a** (the inset in Figure 1) showed a positive-to-negative pattern (the positive CD couplet) on going from longer to shorter wavelengths, and corresponds to the Soret band. Thus, the CD spectrum in this region of copolymer **6a** is produced by the superimposition of this positive CD couplet and the broad CD envelope originating from the homopolymer main chain. Triblock copolymers with a different composition of **2a** and **4** were systematically prepared down to **2a**/**4**/**2a** = 49/2/49. As the content of the porphyrin monomer **4** decreased, the intensity of the Soret band consequently decreased and the higher energy component of the two split Soret bands in the electronic spectra was lost. The triblock

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copolymer (**2a**/**4**/**2a** = 49/2/49) showed a single positive couplet arising from the Soret band in the CD spectra at the same wavelength as the lower energy component of the split Soret band in **6a**, which suggests that the CD sign of the Soret band unambiguously reflects the helical sense of the main chain. Thus, the helicity of **6a**, and thus accordingly **7a**, can then be determined to be right-handed from the change of the CD sign in the Soret band region.[11, 12]

This methodology using a triblock porphyrin copolymer has successfully been applied to the determination of the helicity of other helical chiral poly(aryl isocyanide)s (Table 2).[14] For example, the CD spectrum of copolymer **6b** prepared from **2b** and **4** showed a negative Cotton effect at 364 nm (Figure 2). The differential CD spectrum obtained from **6b** and **7b** exhibits negative CD couplets of the Soret band. These CD spectra are exactly mirror images of those of **6a** and **7a**, which suggests that **6b** has a left-handed helical structure. Comparison of the sign of the $\Delta\varepsilon_{364}$ band to the helical sense determined by the CD sign of the exciton coupling of the Soret band reveals that the positive $\Delta\varepsilon_{364}$ band is indicative of a right-handed helix, while the negative signal indicates a left-handed helix.[11, 12] It should be noted that the present relationship between the sign of the $\Delta\varepsilon_{364}$ band and the helical sense of poly(aryl isocyanide)s is opposite to that assigned in a previous study[15] in which it was estimated from the theoretical CD calculation of poly(*t*ert-butyl isocyanide)s.[7]

Table 2. CD signs and helical sense of triblock copolymers **6**.

polymer	R*	M_n[a]	M_w/M_n[a]	$\Delta\varepsilon_{364}$[b]	2nd Cotton effect[c]	1st Cotton effect[c]	Helical sense
6a	(L)-menthyl	15300	1.10	+	−	+	*P*
6b	(D)-menthyl	13800	1.10	−	+	−	*M*
6c	(D)-isomenthyl	13300	1.10	−	+	−	*M*
6d	(D)-neomenthyl	13700	1.09	−	+	−	*M*
6e	(*S*)-2-butyl	13700	1.14	−	+	−	*M*
6f	(*S*)-2-octyl	15000	1.09	−	+	−	*M*

[a] Determined by gel-permeation chromatography using polystyrene standards. [b] In $CHCl_3$ at room temperature. [c] The sign of the Soret band in the differential CD spectra between triblock copolymers **6** and homopolymers **7**.

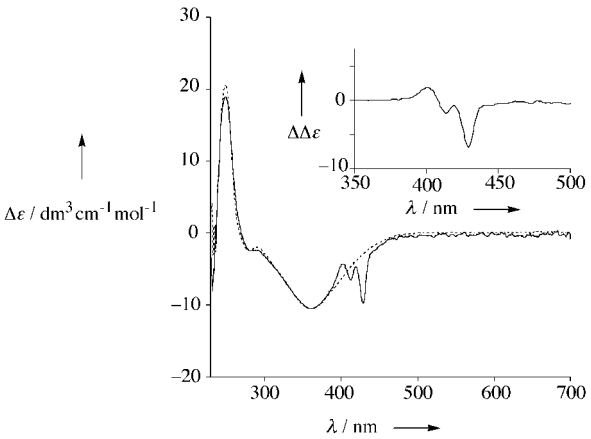

Figure 2. CD spectra of triblock copolymer **6b** and homopolymer **7b** in $CHCl_3$ at room temperature (——: **6b**, - - - -: **7b**). The inset indicates substraction of the CD spectrum in the Soret band region ($\Delta\Delta\varepsilon = \Delta\varepsilon(\mathbf{6b}) - \Delta\varepsilon(\mathbf{7b})$).

In conclusion, we have developed a novel method of determining the helical sense of poly(aryl isocyanide)s by using the porphyrin chromophore. This is the first example of the experimental determination of the helical sense of poly(aryl isocyanide)s and may be applicable to other helical polymers.

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