

Synthesis of Helical Rod/Coil Multiblock Copolymers by Living Block Copolymerization of Isocyanide and *o*-diisocyanobenzene by Using Arylnickel Initiators

Tetsuya Yamada,^a and Michinori Suginome^{*a}

^aDepartment of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Contents

1. General

2. Experimental Procedures

3. Determination of s.e. of poly(quinoxaline) unit in block copolymer

4. Analytical and NMR Data for New Compounds

5. CD and UV Spectra of the Polymers

(including collected CD spectra of poly-3, 4, (1R)-7, and 8–12)

1. General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^1H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, 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. CD spectra were recorded on a JASCO J-750 spectrometer. UV spectra were recorded on a JASCO V-500 spectrometer. The GPC analysis was carried out with TSKgel G4000H_{HR} (CHCl_3 , polystyrene standard). Preparative GPC was performed on JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series (CHCl_3).

THF was dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Trimethylphenylphosphine (Aldrich) and sodium borohydride (Aldrich) were used as received from the commercial sources.

Arylnickel initiator **1** was prepared by a reaction of *o*-tolyl bromide with $\text{Ni}(\text{cod})_2$ in the presence of dimethylphenylphosphine according to the literature procedure.^[1] Arylnickel initiator **2**,^[2] isocyanides **3-12**,^[3] and *o*-diisocyanobenzene **13**^[4] were prepared according to the reported procedures.

[1] (a) Ito, Y.; Ihara, E.; Murakami, M. *Polymer J.* **1992**, *24*, 298. (b) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron*, **1989**, *8*, 285.

[2] Yamada, T.; Noguchi, H.; Nagata, Y.; Sugimoto M. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 898.

[3] These monomers were prepared from the corresponding nitrobenzoyl chloride and alcohol by standard condition. See Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem. Eur. J.* **2000**, *6*, 983.

[4] Ito, Y.; Ihara, E.; Uesaka, T.; Murakami, M. *Macromolecules* **1992**, *25*, 6711-6713.

2. Experimental Procedures

2.1. Typical Procedures for the Synthesis of Poly(isocyanide)s (Table 1)

Synthesis of homopolymer poly-3 (Table 1. Entry 1): A stock solution of arylnickel initiator **1** (0.050 M in THF, 50 μ L, 2.5 μ mol) was diluted with THF (3.85 mL). To the solution was added a solution of PMe_3 in THF (1.0 M, 2.5 μ L, 2.5 μ mol). After stirring for 15 minutes, a solution of **3** (27.5 mg, 100 μ mol) in THF (1.25 mL) was added at room temperature. After 3 h, NaBH_4 (3.7 mg, 100 μ mol) was added to the reaction mixture at room temperature. After stirring for 15 min. at room temperature, water was added. Extraction with CHCl_3 followed by preparative GPC gave **poly-3** as orange solid (23.9 mg, 87% yield).

2.2. Synthesis of Triblock Copolymer 16 (Figure 2)

To a solution of arylnickel initiator **2** (0.050 M, 50 μ L, 2.5 μ mol) in THF (3.85 mL) were added a solution of PMe_3 in THF (1.0 M, 2.5 μ L, 2.5 μ mol) and then a solution of **13** (30.0 mg, 100 μ mol) in THF (1.25 mL) at room temperature. After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH_4 . This homopolymer **14** was subjected to GPC and CD analyses. To the remaining reaction mixture was added a solution of **3** (27.5 mg, 100 μ mol) in THF (1.25 mL). After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH_4 . This diblockcopolymer **15** was subjected to GPC and CD analyses. To the remaining mixture was added a solution of **13** (30.0 mg, 100 μ mol) in THF (1.25 mL). After stirring for further 1 h, NaBH_4 (3.7 mg, 100 μ mol) was added to the resulting mixture at room temperature. After stirring for 1 h at room temperature, water was added. Extraction with CHCl_3 followed by preparative GPC gave block copolymer **16** as orange solid (71.8 mg, 86% yield).

2.3. Synthesis of Triblock Copolymer 18 (Scheme 1)

To a solution of arylnickel initiator **1** (0.050 M, 50 μ L, 2.5 μ mol) in THF (3.85 mL) were added a solution of PMe_3 in THF (1.0 M, 2.5 μ L, 2.5 μ mol) and then **13** (30.0 mg, 100 μ mol) at room temperature. After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH_4 . This homopolymer was subjected to GPC analysis. To the remaining reaction mixture was added a solution of **7** (28.5 mg, 100 μ mol) in THF (1.25 mL). After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH_4 . This diblock copolymer **17**

was subjected to GPC and CD analyses. To the remaining mixture was added a solution of **13** (30.0 mg, 100 μ mol) in THF (1.25 mL). After stirring for further 1 h, NaBH₄ (3.7 mg, 100 μ mol) was added to the resulting mixture at room temperature. After stirring for 15 min. at room temperature, water was added. Extraction with CHCl₃ followed by preparative GPC gave block copolymer **18** as orange solid (66.0 mg, 78% yield).

2.4. Synthesis of Pentablock Copolymer **19** (Figure 3)

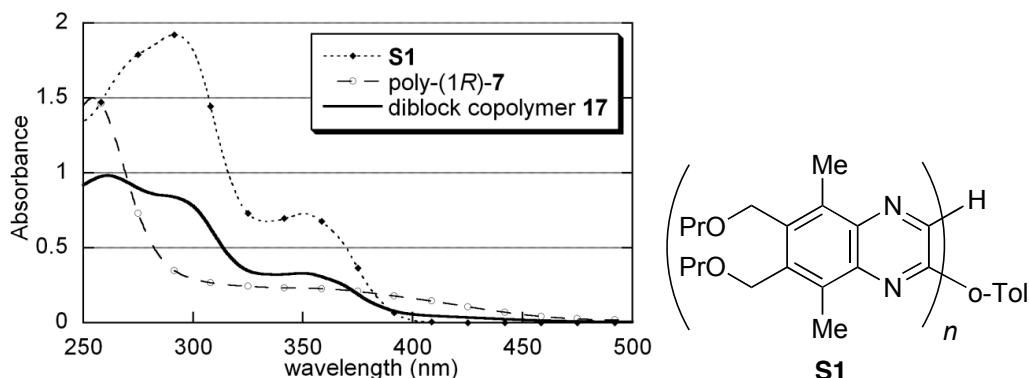
To a solution of arylnickel initiator **2** (0.050 M, 50 μ L, 2.5 μ mol) in THF (3.85 mL) were added a solution of PMe₃ in THF (1.0 M, 2.5 μ L, 2.5 μ mol) and then **13** (30 mg, 100 μ mol) at room temperature. After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH₄. This homopolymer **20** was subjected to GPC and CD analyses. To the remaining reaction mixture was added a solution of **3** (27.5 mg, 100 μ mol) in THF (1.25 mL). After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH₄. This diblock copolymer **21** was subjected to GPC and CD analyses. To the remaining mixture was added a solution of **13** (30.0 mg, 100 μ mol) in THF (1.25 mL). After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH₄. This triblock copolymer **22** was subjected to GPC and CD analyses. To the remaining reaction mixture was added a solution of **3** (27.5 mg, 100 μ mol) in THF (1.25 mL). After 1 h, a small portion of the solution was taken out from the reaction mixture and quenched by NaBH₄. This tetrablock copolymer **23** was subjected to GPC and CD analyses. To the remaining mixture was added a solution of **13** (30.0 mg, 100 μ mol) in THF (1.25 mL). After stirring for further 1 h, NaBH₄ (3.7 mg, 100 μ mol) was added to the resulting mixture at room temperature. After stirring for 15 min. at room temperature, water was added. Extraction with CHCl₃ followed by preparative GPC gave pentablock Copolymer **19** as orange solid (103 mg, 75% yield).

3. Determination of s.e. of poly(quinoxaline) unit in block copolymers

3.1. Determination of s.e. of copolymer **17**.

UV spectra of homopolymers **S1**, poly-(1*R*)-**7**, and diblock copolymer **17** are shown below.

Figure S1. UV spectra of **S1**, poly-(1*R*)-**7**, and **17**



UV spectrum of diblock copolymer **17** is assumed to be the linear combination of the UV spectra of the poly(quinoxaline) block and the poly(iminomethylene) block as shown in eq 1, in which $A_{\text{poly(quinoxaline)}}$ and $A_{\text{poly(iminomethylene)}}$ stand for absorption of the respective blocks. Since the UV spectra of the poly(quinoxaline) block and the poly(iminomethylene) block are almost equivalent to those of **S1** and poly-(1*R*)-**7**, respectively, the UV spectrum of **17** (A_{17}) can be expressed as shown in equation 2, using F_1 and F_2 as proportionality factors.

$$A_{17} = A_{\text{poly(quinoxaline)}} + A_{\text{poly(iminomethylene)}} \quad (1)$$

$$= F_1 \times A_{\text{S1}} + F_2 \times A_{\text{poly-(1R)-7}} \quad (2)$$

Nonlinear least-squares fitting of the UV spectrum of **17** against the UV spectra of **S1** and poly-(1*R*)-**7** was performed by using the Solver Function in Microsoft Office Excel 2007. Sums of the squares of the deviation were minimized by varying the proportionality factors F_1 and F_2 . These parameters were successfully converged and the final values were as follows.

$$F_1 = 0.3834, \quad F_2 = 0.2816 \quad (3)$$

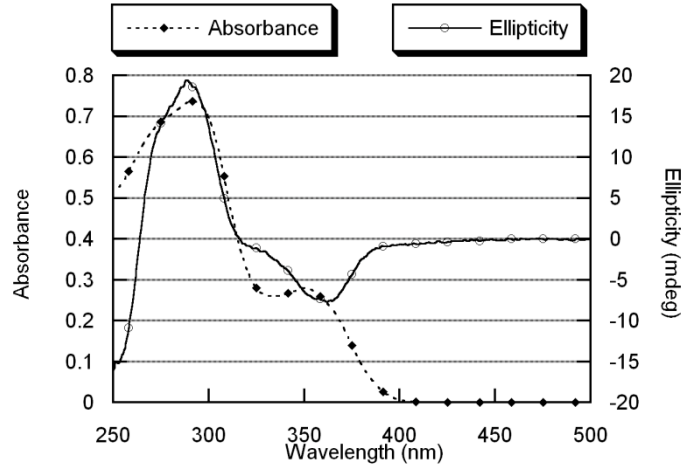
From equations 1–3, virtual UV absorption of the poly(quinoxaline) unit in copolymer **17** is expressed as shown in equation 4, which leads to the virtual UV spectrum shown in Figure S2.

$$A_{\text{poly(quinoxaline)}} = A_{17} - F_2 \times A_{\text{poly-(1R)-7}} \quad (4)$$

Likewise, virtual CD of the poly(quinoxaline) unit in copolymer **17** is expressed by equation 5, which leads to the virtual CD spectrum shown in Figure S2.

$$\theta_{\text{poly}(\text{quinoxaline})} = \theta_{17} - F_2 \times \theta_{\text{poly}-(1R)-7} \quad (5)$$

Figure S2. Virtual UV and CD spectra of poly(quinoxaline) unit in diblock copolymer **17**



From the UV and CD intensities at 366 nm, the *g* value (Kuhn's dissymmetry ratio) is obtained according to the following equation. In the equations, $\Delta\epsilon$, ϵ , $[\theta]$, and *A* stand for circular dichroism (CD), molar absorption coefficient (UV), molar ellipticity (CD), and absorbance (UV), respectively.

$$\begin{aligned} g_{\text{abs}[\text{poly}(\text{quinoxaline})]} &= \Delta\epsilon_{\text{poly}(\text{quinoxaline})} / \epsilon_{\text{poly}(\text{quinoxaline})} \\ &= [\theta]_{\text{poly}(\text{quinoxaline})} / 3298 \times \text{cl} / A_{\text{poly}(\text{quinoxaline})} \\ &= \theta_{\text{poly}(\text{quinoxaline})} / 32.98 \cdot \text{cl} \times \text{cl} / A_{\text{poly}(\text{quinoxaline})} \\ &= \theta_{\text{poly}(\text{quinoxaline})} / 32.98 A_{\text{poly}(\text{quinoxaline})} \end{aligned} \quad (6)$$

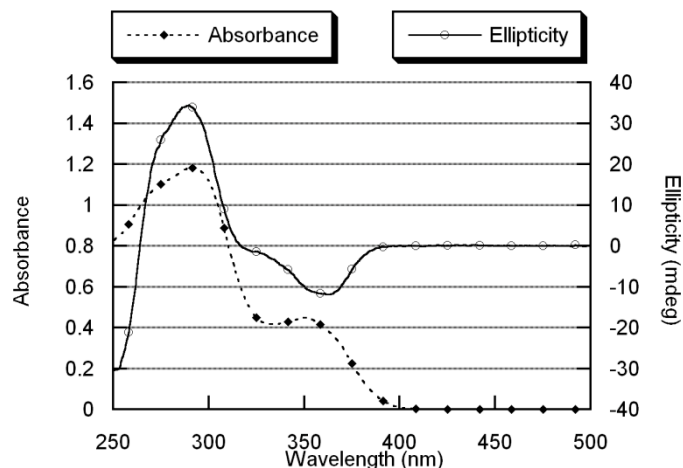
Since $\theta_{\text{poly}(\text{quinoxaline})}$ and $A_{\text{poly}(\text{quinoxaline})}$ at 366 nm are -7.268×10^{-3} and 0.2207, respectively, as shown in Figure 2, the *g* value of -9.98×10^{-4} at 366 nm is obtained. This value corresponds to 42% se for the left-handed helical structure.

3.2. Determination of s.e. of the poly(quinoxaline) block in copolymer **18**.

According to the procedure shown above for copolymer **17**, F_1 and F_2 were determined to be 0.6157 and 0.2648, respectively. Virtual UV and CD spectra of the poly(quinoxaline) block in copolymer **18** were drawn as shown in Figure S3.

The screw-sense excess of the helical rod blocks was determined to be 40% se (*M*).

Figure S3. Virtual UV and CD spectra of the poly(quinoxaline) blocks in triblock copolymer **18**



3.3. Determination of s.e. of the poly(quinoxaline) block in copolymers 19-23.

According to the procedure 3.1., suitable F_1 and F_2 were obtained from UV spectra for copolymers **19** and **21-23**. The UV and CD spectra for the poly(quinoxaline) homopolymer **20** and the virtual UV and CD spectra for the poly(quinoxaline) blocks of copolymers **19** and **21-23** are shown in Figure S4–S8. From the readings of the absorbance (UV) and the ellipticity (CD), the *g* values for polymers **19–23** are obtained as follows.

homopolymer **20**: $g_{366} = 1.87 \times 10^{-3}$ (78% s.e.)

diblock copolymer **21**: $g_{366} = 1.98 \times 10^{-3}$ (82% s.e.)

triblock copolymer **22**: $g_{366} = 8.78 \times 10^{-4}$ (37% s.e.)

tetrablock copolymer **23**: $g_{366} = 8.56 \times 10^{-4}$ (36% s.e.)

pentablock copolymer **19**: $g_{366} = 5.06 \times 10^{-4}$ (21% s.e.)

Figure S4. UV/vis absorption spectrum and CD spectrum of homopolymer **20**

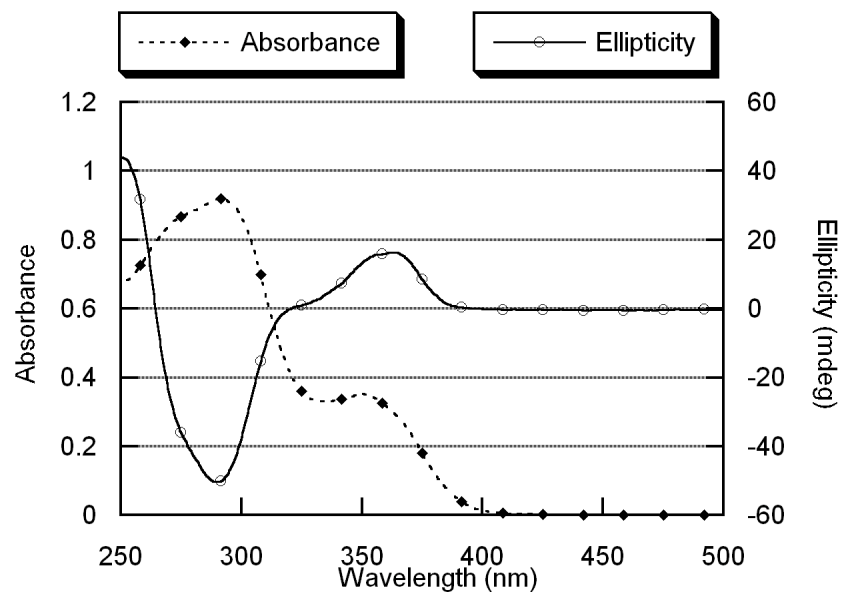


Figure S5. Virtual UV and CD spectra of the poly(quinoxaline) block in diblock copolymer **21**

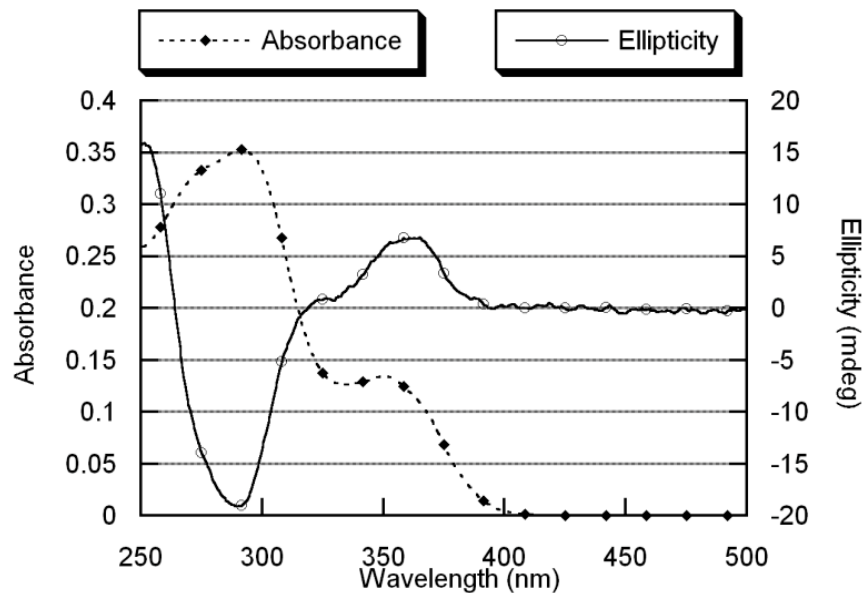


Figure S6. Virtual UV and CD spectra of the poly(quinoxaline) blocks in triblock copolymer **22**

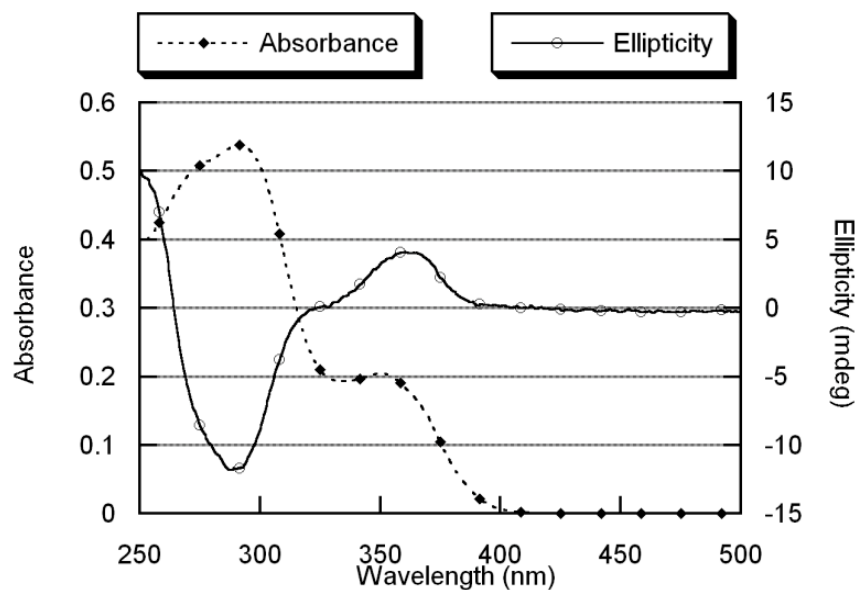


Figure S7. Virtual UV and CD spectra of the poly(quinoxaline) blocks in tetrablock copolymer **23**

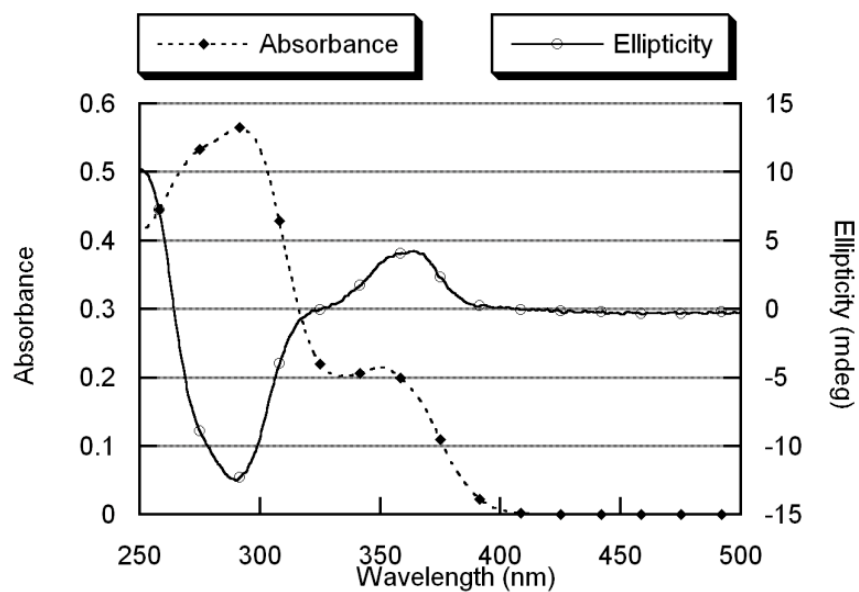
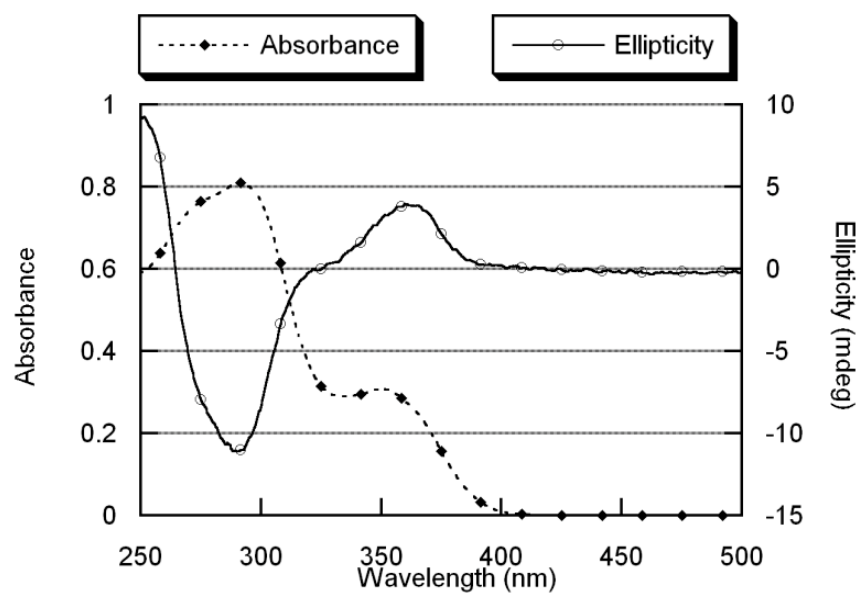


Figure S8. Virtual UV and CD spectra of the poly(quinoxaline) blocks in pentablock copolymer **19**



4. Analytical and NMR Data for New Compounds

5: ^1H NMR (400 MHz, CDCl_3) δ 0.99 (t, 7.2 Hz, 3H), 1.65 (sex, 7.2 Hz, 2H), 3.43 (dt, 6.0 Hz, 7.2 Hz, 2H), 7.43-7.46 (m, 2H), 7.78-7.82 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 11.4, 22.8, 41.9, 126.6, 128.1, 128.7, 135.6, 165.8, 166.3; IR (KBr) 2129, 1631 cm^{-1} .

8: ^1H NMR (400 MHz, CDCl_3) δ 0.10 (s, 9H), 1.13-1.17 (m, 2H), 4.42-4.46 (m, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -1.5, 17.3, 63.8, 126.3, 129.7, 130.6, 131.4, 165.0, 166.9; IR (neat) 2124, 1721 cm^{-1} Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{Si}$: C, 63.12; H, 6.93; N, 5.66. Found: C, 62.87; H, 7.05; N, 5.52.

9: ^1H NMR (400 MHz, CDCl_3) δ 1.61 (s, 9H), 7.42 (d, $J = 8.8$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 28.1, 82.0, 126.2, 129.7, 130.6, 132.8, 164.1, 166.6; IR (KBr) 2126, 1717 cm^{-1} ; Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.00; H, 6.37; N, 6.89.

10: ^1H NMR (400 MHz, CDCl_3) δ 0.95 (d, $J = 6.8$ Hz, 12H), 2.05 (octet, $J = 6.4$ Hz, 2H), 4.85 (t, $J = 6.0$ Hz, 1H), 7.46 (d, $J = 8.8$ Hz, 2H), 8.10 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 17.2, 19.4, 29.5, 84.1, 126.3, 129.7, 130.7, 131.3, 164.8, 166.9; IR (KBr) 2124, 1721 cm^{-1} ; Anal. Calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.83; H, 8.01; N, 4.85.

11: ^1H NMR (400 MHz, CDCl_3) δ 0.99 (s, 6H), 1.12 (s, 6H), 1.14-1.33 (m, 4H), 1.88 (d, $J = 12.8$ Hz, 2H), 5.29 (tt, $J = 8.8$ Hz, 3.2 Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 27.8, 32.5, 34.9, 44.4, 51.5, 71.4, 126.3, 129.7, 130.7, 131.7, 164.5, 166.8; IR (neat) 2124, 1719 cm^{-1} ; Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.39; H, 7.74; N, 5.61.

12: ^1H NMR (400 MHz, CDCl_3) δ 0.98-1.31 (m, 12H), 1.65-1.76 (m, 10H), 4.89 (t, 6.0 Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 8.09 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 26.0, 26.1, 26.3, 27.6, 30.0, 38.5, 82.9, 126.4, 129.7, 130.8, 131.5, 164.9, 166.8; IR (neat) 2122, 1723 cm^{-1} .

Monomers **3**, **4**, **6** and (1*R*)-**7** are known compounds. CAS numbers of these monomers are shown below.

3: 205495-60-9

4: 288154-56-3

6: 602262-09-3

(1*R*)-**7**: 254116-83-1

2. polymers

Poly-3 (achiral initiator, Table1, Entry 1): ¹H NMR (400MHz, CDCl₃) δ 1.28 (br, 10*n*H), 4.99 (br, 4*n*H), 5.72-8.56 (m, 3*n*H).

Poly-4 (achiral initiator, Table1, Entry 2): ¹H NMR (400MHz, CDCl₃) δ 1.01 (br, 3*n*H), 1.63 (br, 2*n*H), 3.48-4.74 (m, 2*n*H), 5.38-8.46 (m, 4*n*H).

Poly-(1*R*)-7 (Table1, Entry 5): ¹H NMR (400MHz, CDCl₃) δ 0.22-2.58 (m, 18*n*H), 4.92 (br, *n*H), 5.97 (br, 2*n*H), 6.50-8.04 (m, 2*n*H).

Poly-3 (chiral initiator, Table1, Entry 6): ¹H NMR (400MHz, CDCl₃) δ 0.93 (br, 6*n*H), 1.58 (br, 4*n*H), 2.91-4.78 (m, 4*n*H), 5.22-8.56 (m, 3*n*H).

Poly-4 (chiral initiator, Table1, Entry 7): ¹H NMR (400MHz, CDCl₃) δ 1.27 (br, 5*n*H), 4.99 (br, 2*n*H), 5.86-8.10 (m, 4*n*H).

Poly-8 (Table1, Entry 8): ¹H NMR (400MHz, CDCl₃) δ 0.08 (br, 9*n*H), 1.00 (br, 2*n*H), 3.63-4.76 (m, 2*n*H), 5.83 (br, 2*n*H), 6.56-8.20 (m, 2*n*H).

Poly-9 (Table1, Entry 9): ¹H NMR (400MHz, CDCl₃) δ 1.43 (br, 9*n*H), 5.90 (br, 2*n*H), 6.36-8.02 (m, 2*n*H).

Poly-10 (Table1, Entry 10): ¹H NMR (400MHz, CDCl₃) δ 1.05 (br, 16*n*H), 1.74 (br, 2*n*H), 5.03 (br, *n*H), 5.76 (br, 2*n*H), 6.22-7.94 (m, 2*n*H).

Poly-11 (Table1, Entry 11): ¹H NMR (400MHz, CDCl₃) δ 0.84 (br, 12*n*H), 1.90 (br, 2*n*H), 4.63 (br, *n*H), 5.92 (br, 2*n*H), 6.70-8.10 (m, 2*n*H).

Poly-12 (Table1, Entry 12): ^1H NMR (400MHz, CDCl_3) δ 0.38-2.12 (m, 22nH), 4.63 (br, nH), 5.03 (br, 2nH), 6.64-8.16 (m, 2nH).

Triblock copolymer 16a: ^1H NMR (400MHz, CDCl_3) δ 0.90 (br, $(6(n+l)+6m)\text{H}$), 1.60 (br, $(4(n+l)+4m)\text{H}$), 2.35 (br, $6(n+l)\text{H}$), 3.46 (br, $4(n+l)\text{H}$), 4.57 ($4(n+l)+4m\text{H}$). The sp^2 -protons on benzene ring of monoisocyanide **3** were not detectable by NMR measurements.

Triblock copolymer 16b: ^1H NMR (400MHz, CDCl_3) δ 0.90 (br, $(6(n+l)+6m)\text{H}$), 1.60 (br, $(4(n+l)+4m)\text{H}$), 2.35 (br, $6(n+l)\text{H}$), 3.47 (br, $4(n+l)\text{H}$), 4.56 ($4(n+l)+4m\text{H}$). The sp^2 -protons on benzene ring of monoisocyanide **3** were not detectable by NMR measurements.

Triblock copolymer 16c: ^1H NMR (400MHz, CDCl_3) δ 0.90 (br, $(6(n+l)+6m)\text{H}$), 1.60 (br, $(4(n+l)+4m)\text{H}$), 2.34 (br, $6(n+l)\text{H}$), 3.45 (br, $4(n+l)\text{H}$), 4.56 ($4(n+l)+4m\text{H}$), 5.86-7.80 (m, $3m\text{H}$).

Triblock copolymer 18: ^1H NMR (400MHz, CDCl_3) δ 0.91 (br, $6(n+l)\text{H}$), 1.60 (br, $4(n+l)\text{H}$), 2.35 (br, $6(n+l)\text{H}$), 0.24-2.67 (br, $18m\text{H}$), 3.47 (br, $4(n+l)\text{H}$), 4.57 (br, $(4(n+l)+m)\text{H}$), 5.95 (br, $2m\text{H}$), 6.32-8.04 (m, $2m\text{H}$).

pentablock copolymer 19: ^1H NMR (400MHz, CDCl_3) δ 0.90 (br, $\{6(n+l+j)+6(m+k)\}\text{H}$), 1.27 (br, $4(m+k)\text{H}$), 1.60 (br, $4(n+l+j)\text{H}$), 2.35 (br, $6(n+l+j)\text{H}$), 3.47 (br, $4(n+l+j)\text{H}$), 4.56 (br, $4(n+l+j)\text{HH}$), 4.98 (br, $4(m+k)\text{H}$), 5.86-7.80 (m, $3m\text{H}$).

5. CD and UV Spectra of the Polymers

Figure S9. Collected CD spectra of poly(*N*-aryliminomethylene)s poly-3, poly-4, poly-(1*R*)-7, poly-8, poly-9, poly-10, poly-11, and poly-12. Individual CD charts are shown below in Figure S10–S17.

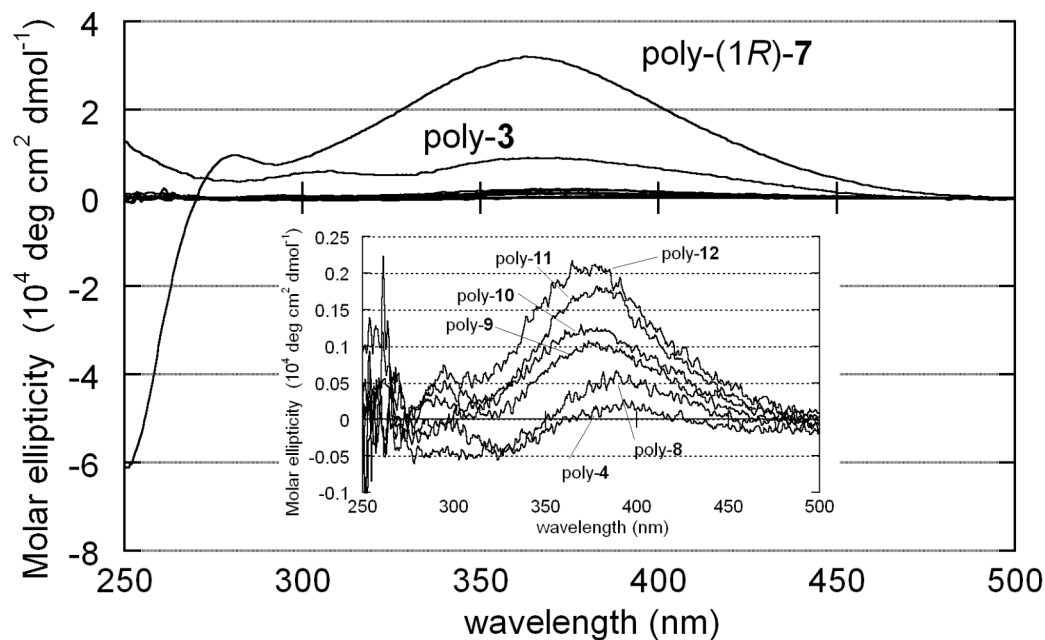


Figure S10. UV/vis absorption spectrum and CD spectrum of **Poly-(1*R*)-7** (Table1, Entry 5)

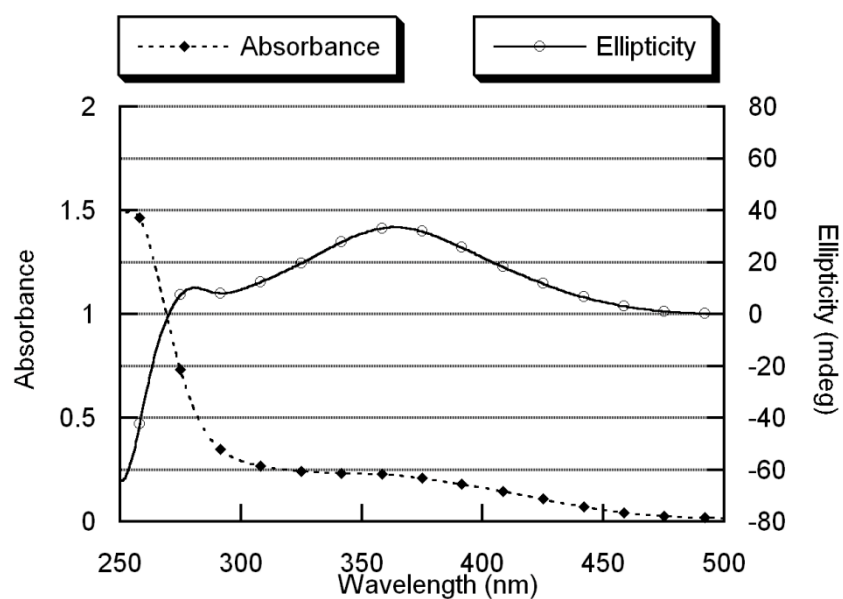


Figure S11. UV/vis absorption spectrum and CD spectrum of **Poly-3** (chiral initiator, Table1, Entry 12)

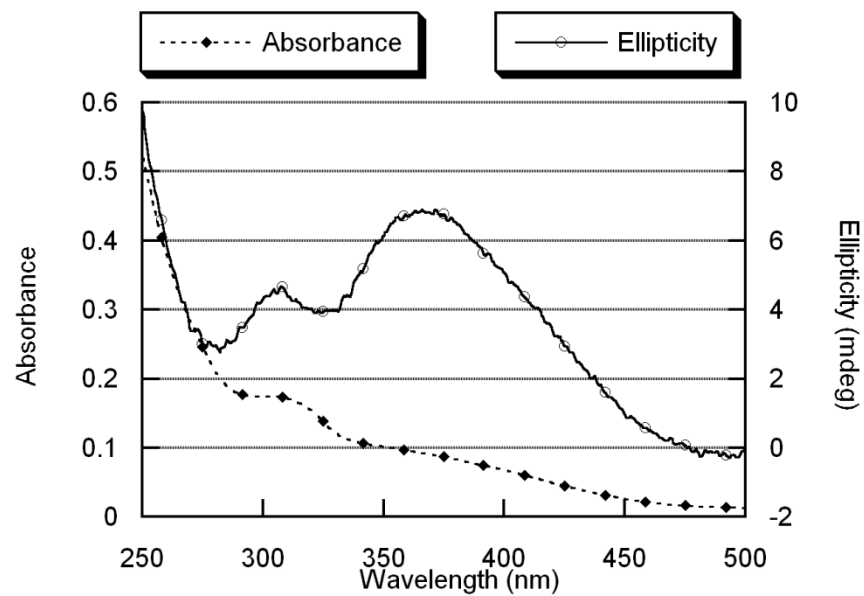


Figure S12. UV/vis absorption spectrum and CD spectrum of **Poly-4** (chiral initiator, Table1, Entry 6)

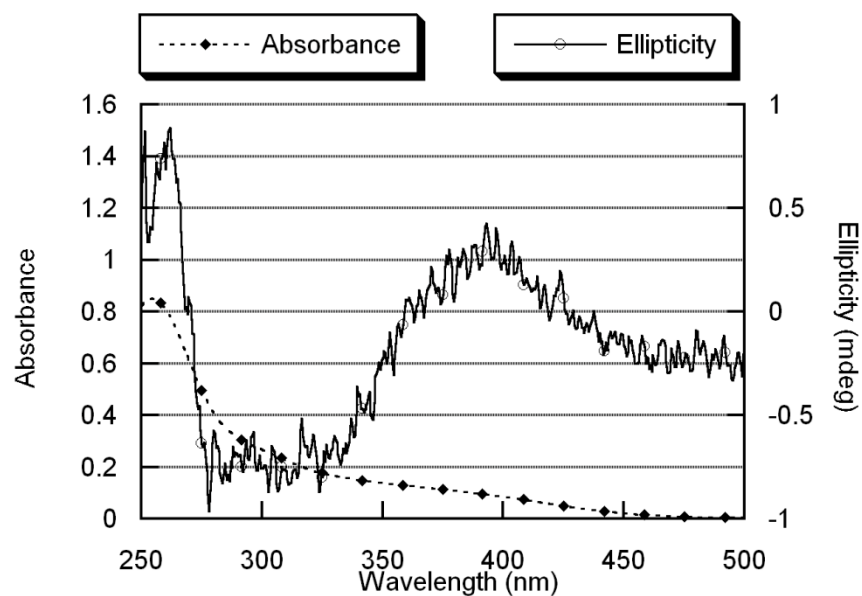


Figure S13. UV/vis absorption spectrum and CD spectrum of **Poly-8** (Table1, Entry 7)

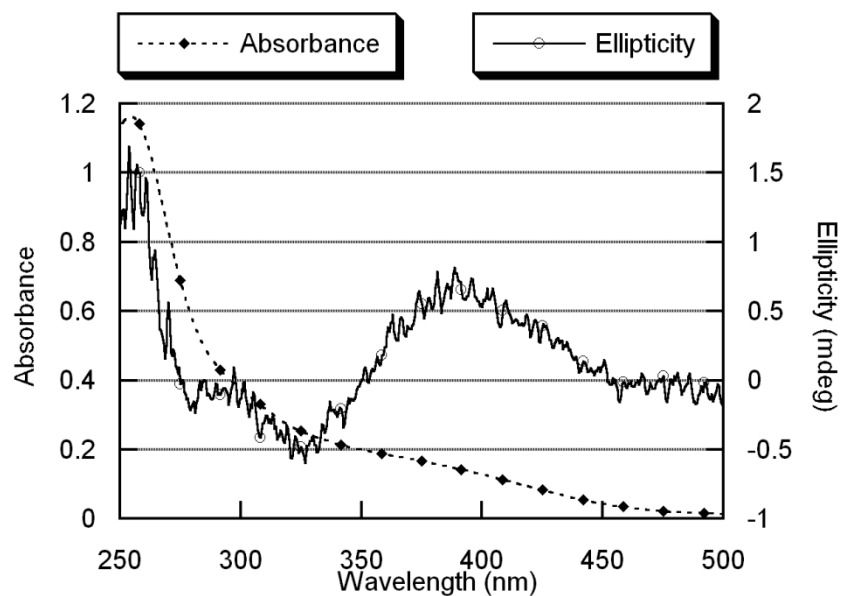


Figure S14. UV/vis absorption spectrum and CD spectrum of **Poly-9** (Table1, Entry 8)

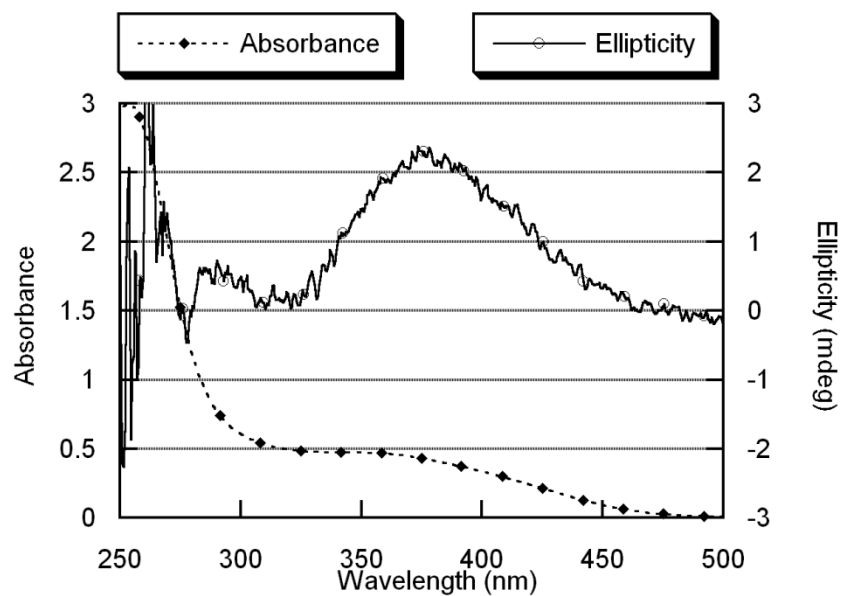


Figure S15. UV/vis absorption spectrum and CD spectrum of **Poly-10** (Table1, Entry 9)

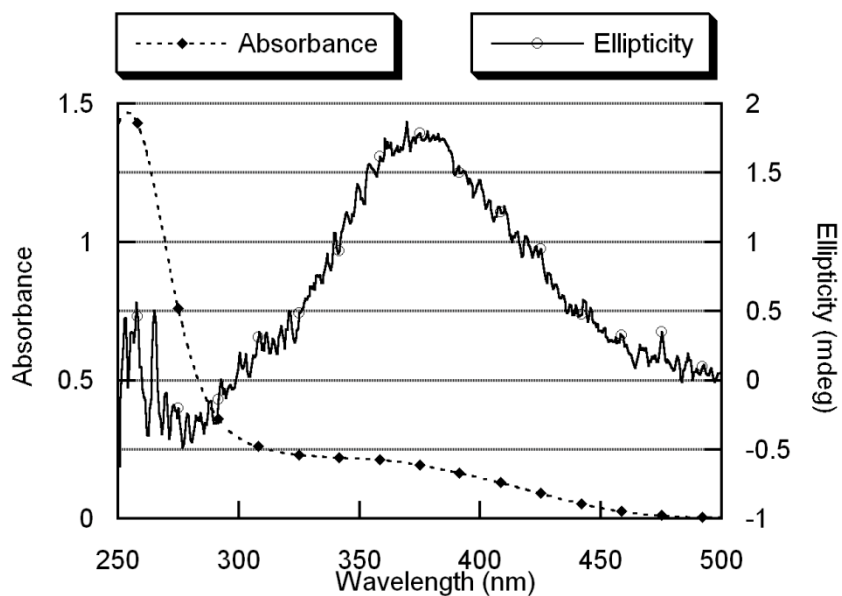


Figure S16. UV/vis absorption spectrum and CD spectrum of **Poly-11** (Table1, Entry 10)

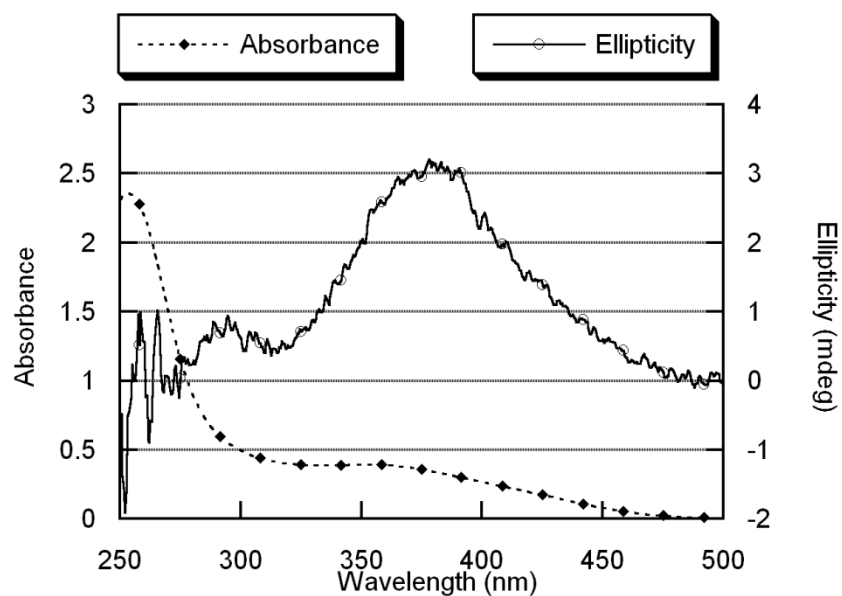


Figure S17. UV/vis absorption spectrum and CD spectrum of **Poly-12** (Table1, Entry 11)

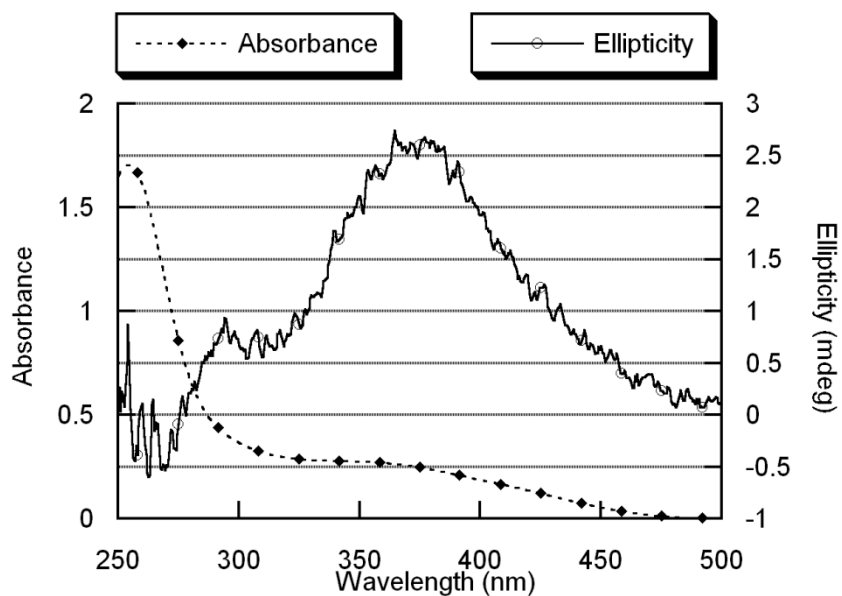


Figure S18. UV/vis absorption spectrum and CD spectrum of **Homopolymer 14** (Figure 2)

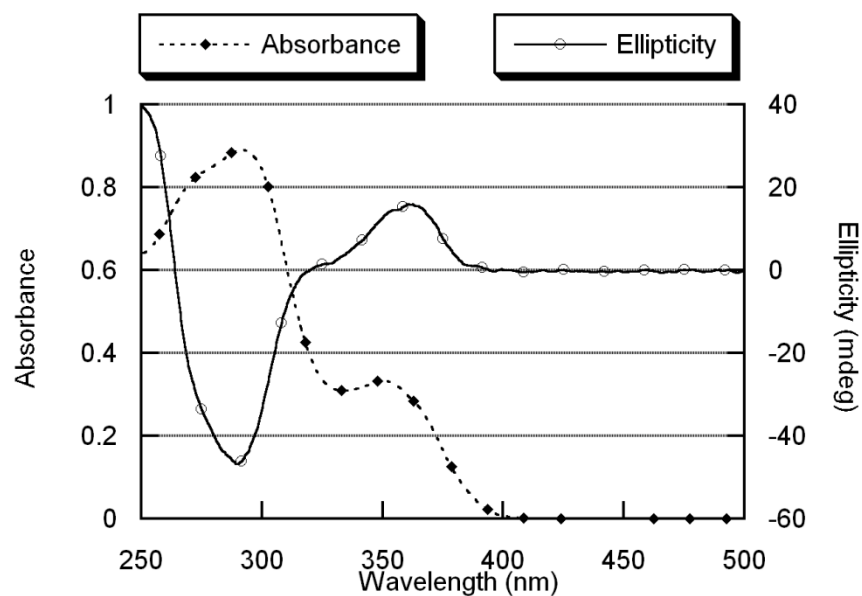


Figure S19. UV/vis absorption spectrum and CD spectrum of **Diblock copolymer 15a** (Figure 2)

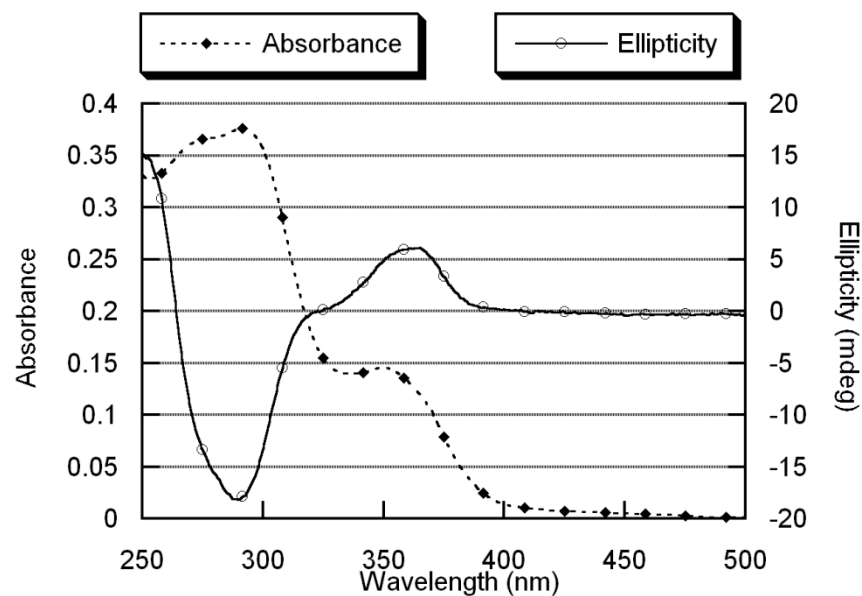


Figure S20. UV/vis absorption spectrum and CD spectrum of **Diblock copolymer 15b** (Figure 2)

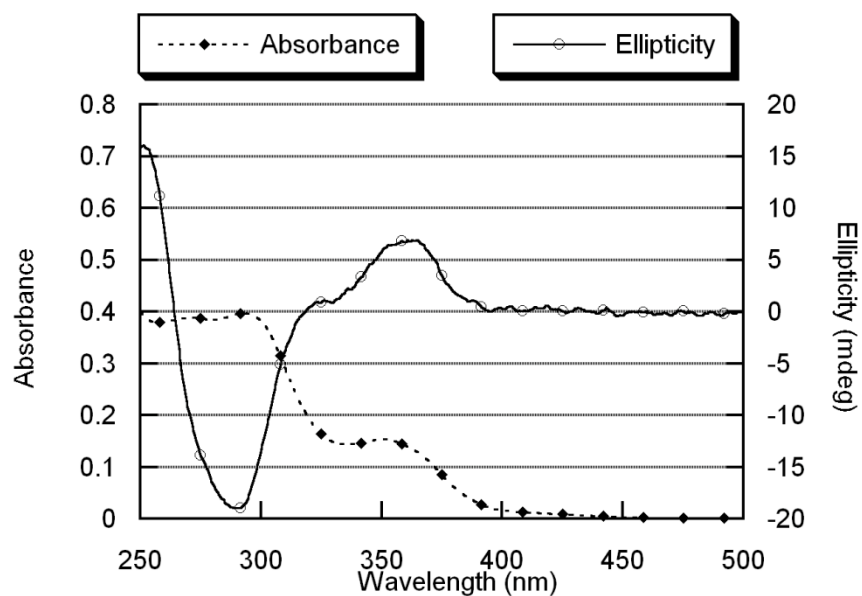


Figure S21. UV/vis absorption spectrum and CD spectrum of **Diblock copolymer 15c** (Figure 2)

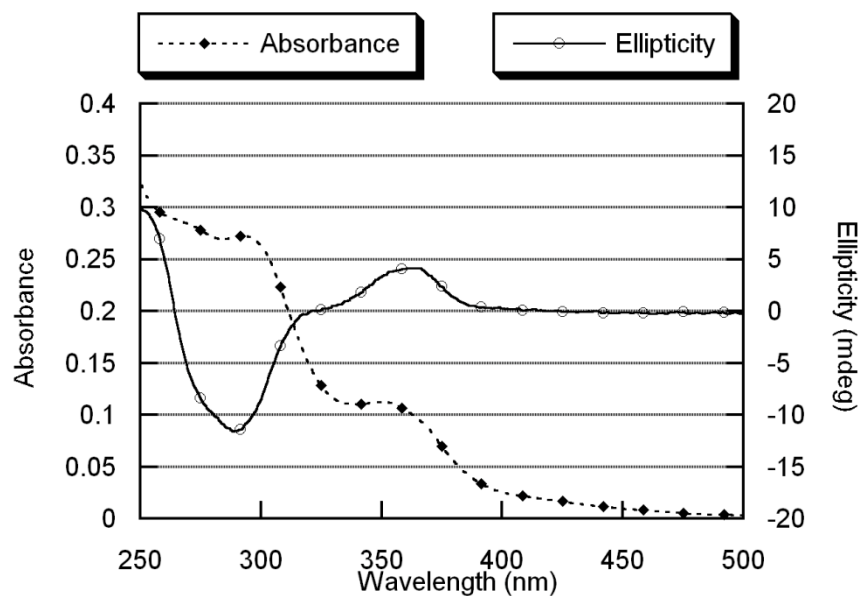


Figure S22 UV/vis absorption spectrum and CD spectrum of **Triblock copolymer 16a** (Figure 2)

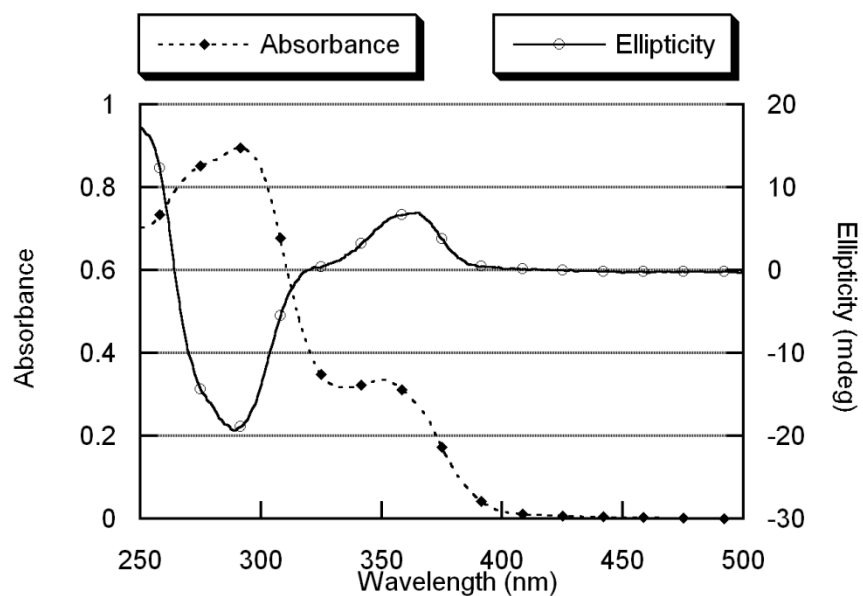


Figure S23. UV/vis absorption spectrum and CD spectrum of **Triblock copolymer 16b** (Figure 2)

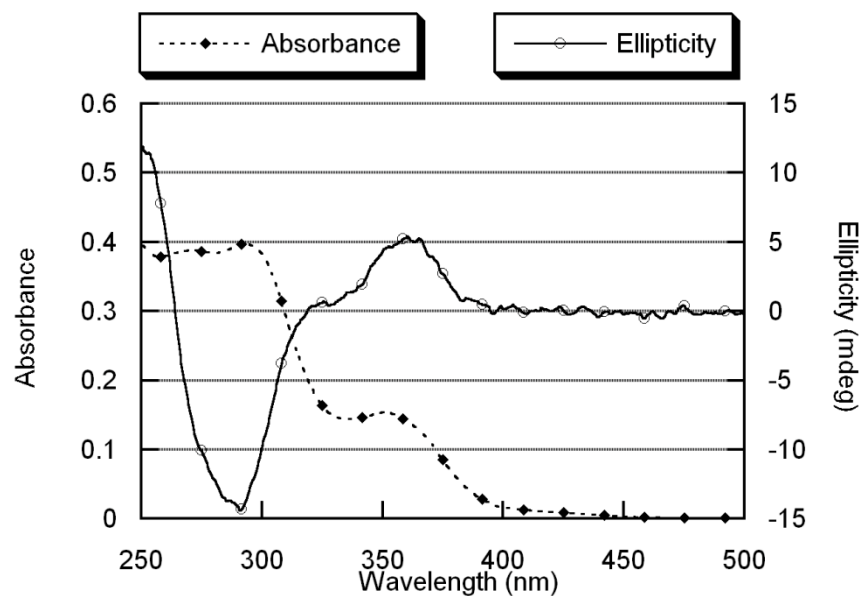


Figure S24. UV/vis absorption spectrum and CD spectrum of **Triblock copolymer 16c** (Figure 2)

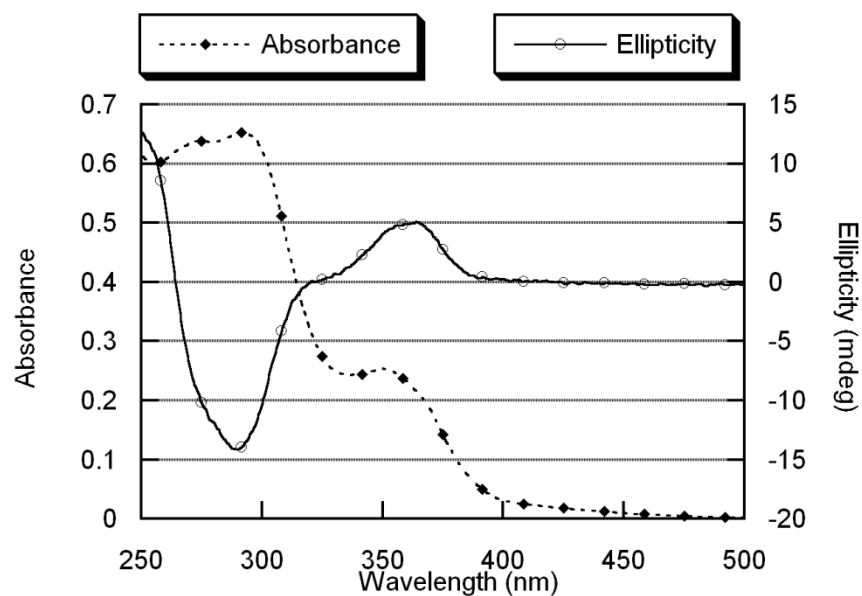


Figure S25. UV/vis absorption spectrum and CD spectrum of **Diblock copolymer 17** (Scheme 1)

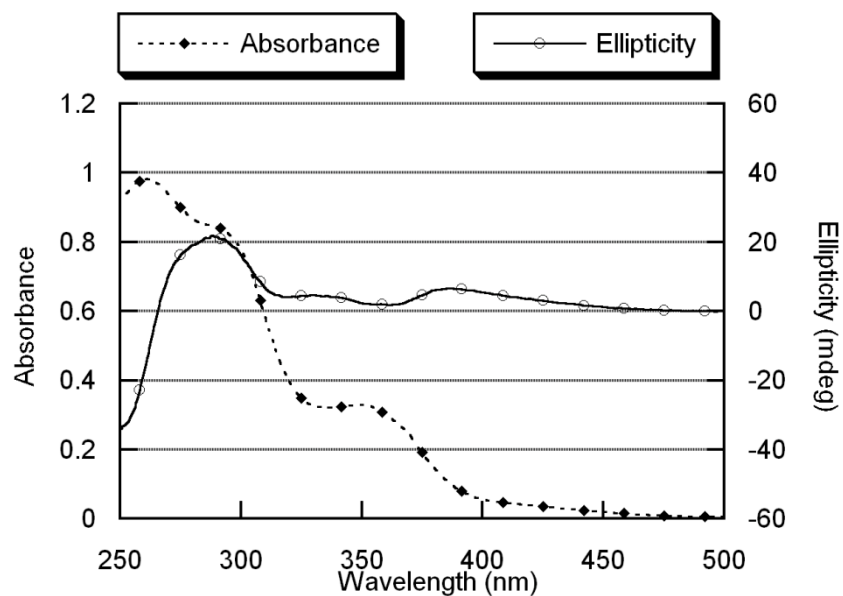


Figure S26. UV/vis absorption spectrum and CD spectrum of **Triblock copolymer 18** (Scheme 1)

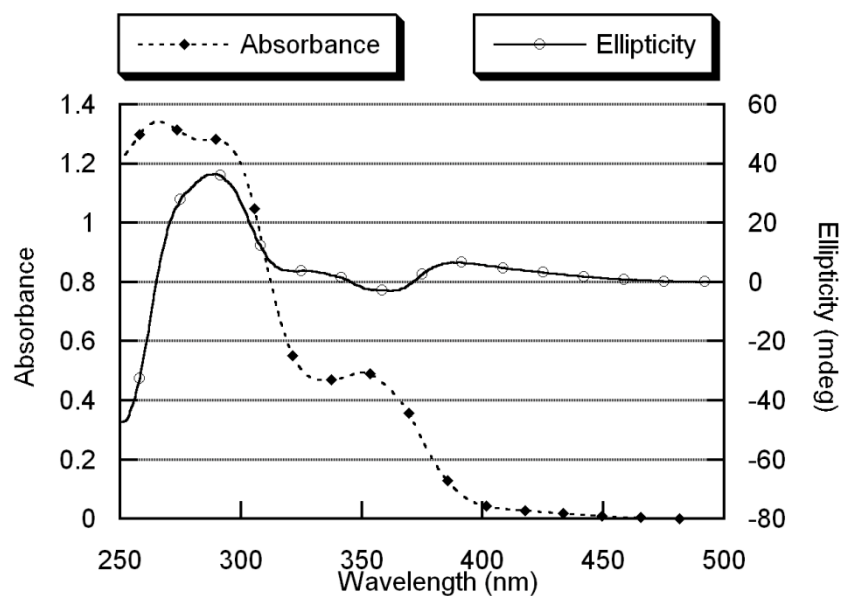


Figure S27. UV/vis absorption spectrum and CD spectrum of **Diblock copolymer 21** (Figure 3)

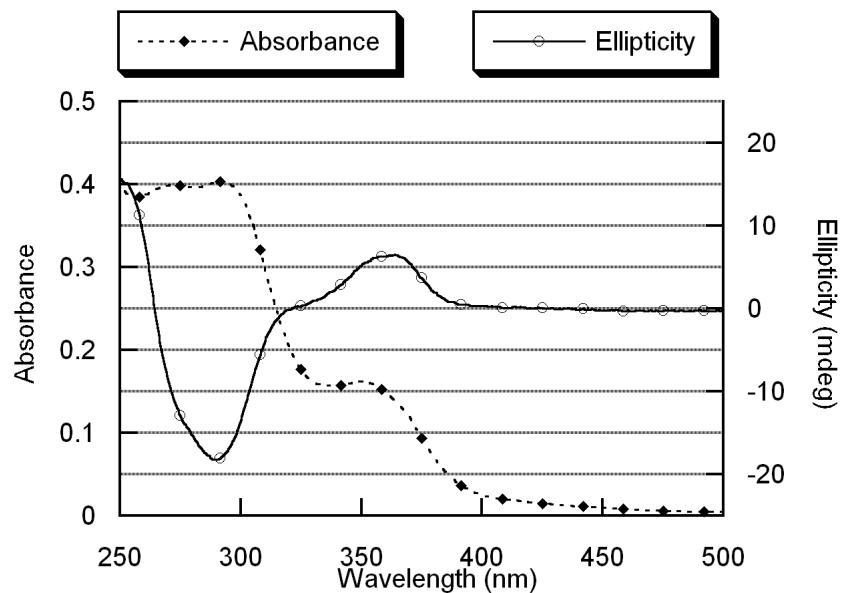


Figure S28. UV/vis absorption spectrum and CD spectrum of **Triblock copolymer 22** (Figure 3)

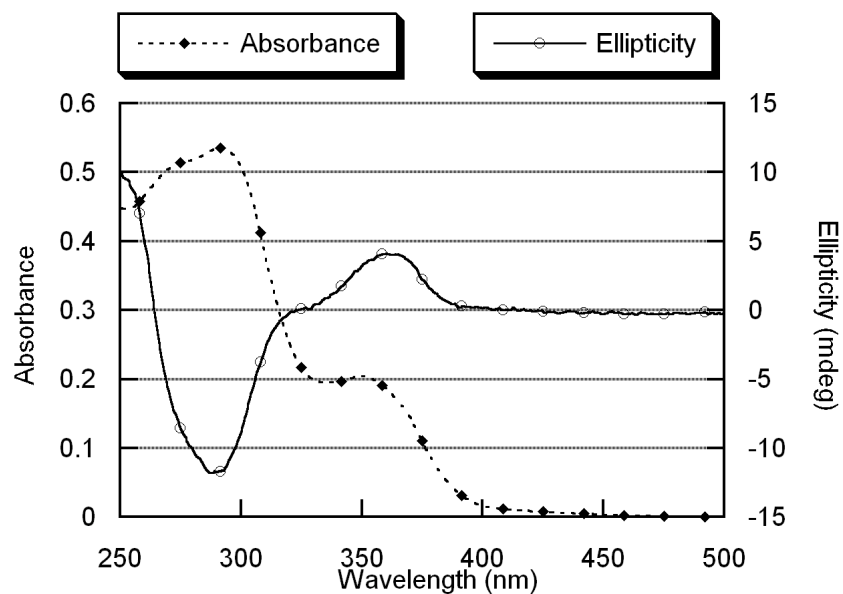


Figure S29. UV/vis absorption spectrum and CD spectrum of **Tetrablock copolymer 23** (Figure 3)

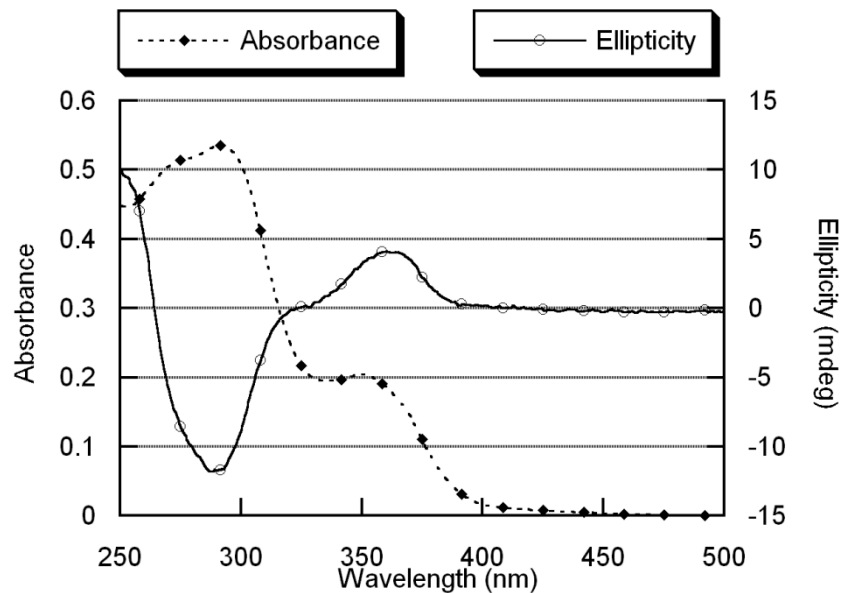


Figure S30. UV/vis absorption spectrum and CD spectrum of **Pentablock copolymer 19** (Figure 3)

