Supporting information

Synthesis of Optically Active Polyamines Based on Chiral 1-Cyclohexylethylamine Derivatives

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Spectral data of polymers and model compounds.

Polymer 2(R). From (R)-(+)-α-methylbenzylamine (1.82 g, 15 mmol), *p*-xylylene dibromide (3.96 g, 15 mmol), Yield 46%.; M_n = 8600, M_w = 18000, M_w/M_n = 2.1.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.39-7.15 (9H, Ph-H), 3.90-3.83 (1H, Ph-CH(CH_3)-N)), 3.57-3.34 (4H, Ph-CH_2-N), 1.41-1.31 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.8, 138.7, 128.4, 127.9, 127.8, 126.5, 55.8, 53.2, 13.6.; IR (NaCl, cm^{-1}): ν = 3020, 2970, 2930, 2820, 1510, 1450, 1370, 1120.

Polymer 2(S). From (S)-(–)-α-methylbenzylamine (1.21 g, 10 mmol), *p*-xylylene dibromide (2.64 g, 10 mmol), Yield 68%.; M_n = 18000, M_w = 28000, M_w/M_n = 1.6.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.39-7.15 (9H, Ph-H), 3.91-3.83 (1H, Ph-CH(CH_3)-N)), 3.57-3.34 (4H, Ph-CH_2-N), 1.40-1.33 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.8, 138.8, 128.4, 128.0, 127.8, 126.5, 55.8, 53.2, 13.7.; IR (NaCl, cm^{-1}): ν = 3020, 2970, 2930, 2820, 1510, 1450, 1370, 1120.

Polymer 2(Rac). From (DL)-1-methylbenzylamine (1.21 g, 10 mmol), *p*-xylylene dibromide (2.64 g, 10 mmol), Yield 78%.; M_n = 20000, M_w = 30000, M_w/M_n = 1.5.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.39-7.15 (9H, Ph-H), 3.90-3.82 (1H, Ph-CH(CH_3)-N)), 3.56-3.34 (4H, Ph-CH_2-N), 1.40-1.31 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.8, 138.8, 128.4, 128.0, 127.8, 126.5, 55.8, 53.2, 13.6.; IR (NaCl, cm^{-1}): ν = 3020, 2970, 2930, 2820, 1510, 1450, 1370, 1120.

Polymer 3(R). From 2,6-Bis(bromomethyl)naphthalene (0.315 g, 1 mmol), (R)-(+)-α-methylbenzylamine (0.121 g, 1 mmol), Yield 54%.; M_n = 6000, M_w = 13000, M_w/M_n = 2.1.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.76-7.16 (11H, Ph-H), 3.97-3.88 (1H, Ph-CH(CH_3)-N)), 3.78-3.52 (4H, Ph-CH_2-N), 1.49-1.39 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.6, 137.5, 132.6, 128.1, 127.9, 127.6, 127.1, 127.0, 126.7, 56.0, 53.6, 13.6.; IR (NaCl, cm^{-1}): ν = 3030, 2970, 2930, 2820, 1490, 1450, 1370, 1120.

Polymer 3(S). From 2,6-Bis(bromomethyl)naphthalene (0.314 g, 1 mmol), (S)-(–)-α-methylbenzylamine (0.121 g, 1 mmol), Yield 52%.; M_n = 6000, M_w = 13000, M_w/M_n = 2.2.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.78-7.17 (11H, Ph-H), 3.97-3.89 (1H, Ph-CH(CH_3)-N)), 3.78-3.53 (4H, Ph-CH_2-N), 1.50-1.40 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.6, 137.5, 132.5, 128.1, 128.0, 127.6, 127.1, 127.0, 126.7, 55.9, 53.6, 13.6.; IR (NaCl, cm^{-1}): ν = 3020, 2970, 2930, 2820, 1490, 1450, 1370, 1120.

Polymer 3(Rac). From 2,6-bis(bromomethyl)naphthalene (0.314 g, 1 mmol), (DL)-1-methylbenzylamine (0.121 g, 1 mmol), Yield 62%.; M_n = 5200, M_w = 11000, M_w/M_n = 2.2.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.77-7.17 (11H, Ph-H), 3.98-3.89 (1H, Ph-CH(CH_3)-N)), 3.79-3.52 (4H, Ph-CH_2-N), 1.50-1.39 (3H, -CH_3).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.6, 137.5, 132.5, 128.1, 127.9, 127.6, 127.1, 127.0, 126.7, 56.0, 53.6, 13.6.; IR (NaCl, cm^{-1}): ν = 3020, 2970, 2930, 2810, 1490, 1450, 1360, 1120.

Synthesis of 2,6-Bis(bromomethyl)naphthalene. 2,6-Dimethylnaphthalene (3.24 g 20 mmol)

and NBS (4.45 g 50 mmol) were dissolved in tetrachloromethane at room temperature under Ar. Benzoyl peroxide (0.35 g) was added to a mixture and was stirred for 30 minutes, then heated slowly to reflux, and maintained at reflux for 6 h. The mixture was cooled, filtered and recrystallized from chloroform to give 2,6-Bis(bromomethyl)naphthalene as a yellow powder in 23% yield.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.80 (m, 2H), 7.53, 7.51 (dd, *J* = 1.48, 1.48 Hz, 1H), 4.66 (s, 4H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 135.9, 132.8, 128.8, 127.7, 127.4, 33.8.; IR (NaCl, cm^{-1}): ν = 3050, 3020, 2970, 2920, 1500, 1440, 1210, 890, 830, 700, 670, 600, 570, 480.

Model Compound 5(R). From (R)-(+)-α-methylbenzylamine (0.59 g, 4.8 mmol), benzylbromide (1.71 g, 10 mmol), yield 13%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.41-7.19 (m, 15H), 3.92 (q, *J* = 6.8 Hz, 1H), 3.61, 3.46 (dd, *J* = 13.9, 13.9 Hz, 4H), 1.43 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.7, 140.4, 128.6, 128.2, 128.0, 127.9, 126.7, 56.2 53.6, 13.8.; IR (NaCl, cm^{-1}): ν = 3060, 3030, 2970, 2930, 2830, 1490, 1450, 1380, 1120.

Model Compound 5(S). From (S)-(–)-α-methylbenzylamine (0.18 g, 1.5 mmol), benzylbromide (0.51 g, 0.36 mmol), yield 53%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.41-7.19 (m, 15H), 3.92 (q, *J* = 6.8 Hz, 1H), 3.60, 3.45 (dd, *J* = 13.9, 13.9 Hz, 4H), 1.43 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.7, 140.4, 128.6, 128.1, 128.0, 127.9, 126.69, 126.67, 56.1 53.5, 13.7.; IR (NaCl, cm^{-1}): ν = 3060, 3020, 2970, 2930, 2830, 1490, 1450, 1370, 1130.

Model Compound 5(Rac). From (DL)-α-methylbenzylamine (0.18 g, 1.5 mmol), benzylbromide (0.51 g, 0.36 mmol), Yield 53%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.41-7.19 (m, 15H), 3.92 (q, *J* = 6.8 Hz, 1H), 3.60, 3.46 (dd, *J* = 13.9, 13.9 Hz, 4H), 1.43 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.7, 140.4, 128.6, 128.1, 128.0, 127.9, 126.70, 126.67, 56.1 53.5, 13.7.; IR (NaCl, cm^{-1}): ν = 3060, 3030, 2970, 2920, 2840, 1490, 1450, 1360, 1140.

Model Compound 6(R). From (R)-(+)-α-methylbenzylamine (0.090 g, 0.74 mmol), 2-bromomethylnaphthalene (0.31 g, 1.4 mmol), Yield >99%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.24 (m, 19H), 3.99 (q, *J* = 6.8 Hz, 1H), 3.80, 3.65 (dd, *J* = 13.7, 13.7 Hz, 4H), 1.51 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.6, 138.0, 133.3, 132.7, 128.1, 128.0, 127.9, 127.63, 127.58, 127.2 127.1, 126.8, 125.8, 125.4, 56.2, 53.4, 13.7.; IR (NaCl, cm^{-1}): ν = 3050, 3020, 2970, 2930, 2820, 1510, 1450, 1370, 1120.

Model Compound 6(S). From (S)-(–)-α-methylbenzylamine (0.088 g, 0.73 mmol), 2-bromomethylnaphthalene (0.31 g, 1.4 mmol), Yield 96%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.24 (m, 19H), 3.99 (q, *J* = 6.8 Hz, 1H), 3.80, 3.65 (dd, *J* = 13.7, 13.7 Hz, 4H), 1.51 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.6, 138.0, 133.3, 132.7, 128.1, 128.0, 127.9, 127.62, 127.56, 127.2 127.1, 126.8, 125.8, 125.4, 56.1, 53.7, 13.6.; IR (NaCl, cm^{-1}): ν = 3050, 3030, 2970, 2930, 2820, 1510, 1450, 1360, 1120.

Model Compound 6(Rac). From (DL)-1-methylbenzylamine (0.090 g, 0.74 mmol), 2-bromomethylnaphthalene (0.31 g, 1.4 mmol), Yield >99%.; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.82-7.26 (m, 19H), 3.99 (q, *J* = 6.8 Hz, 1H), 3.80, 3.65 (dd, *J* = 13.7, 13.7 Hz, 4H), 1.51 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 142.5, 137.9, 133.3, 132.7, 128.1, 128.0, 127.9, 127.61, 127.55, 127.2 127.1, 126.8, 125.8, 125.4, 56.1, 53.7, 13.6.; IR (NaCl, cm^{-1}): ν = 3050, 3020, 2970, 2930, 2820, 1510, 1450, 1360, 1120.

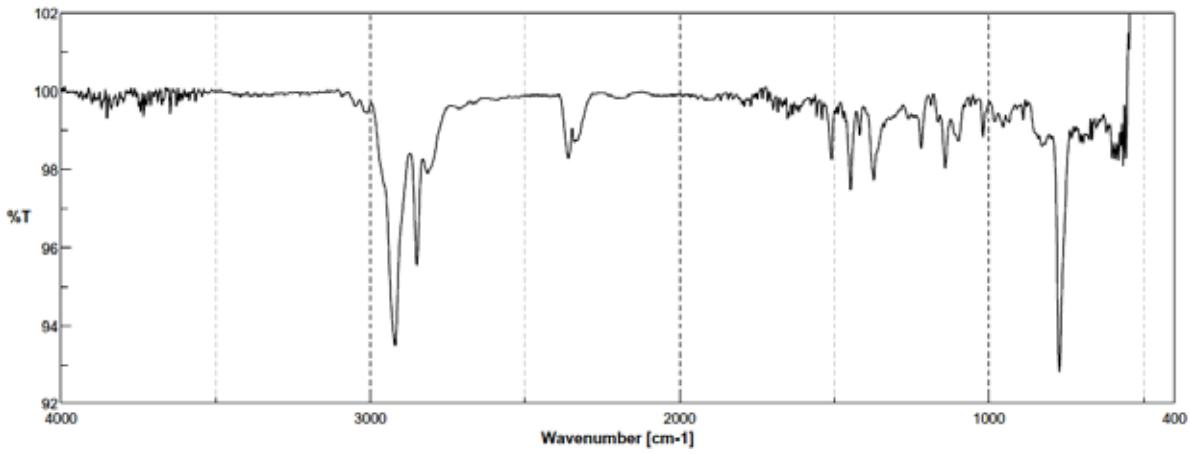

Figure S1. FT-IR spectrum of polymer **1(R)**. There was no peak of the quaternary amines

around 3000 cm^{-1}.

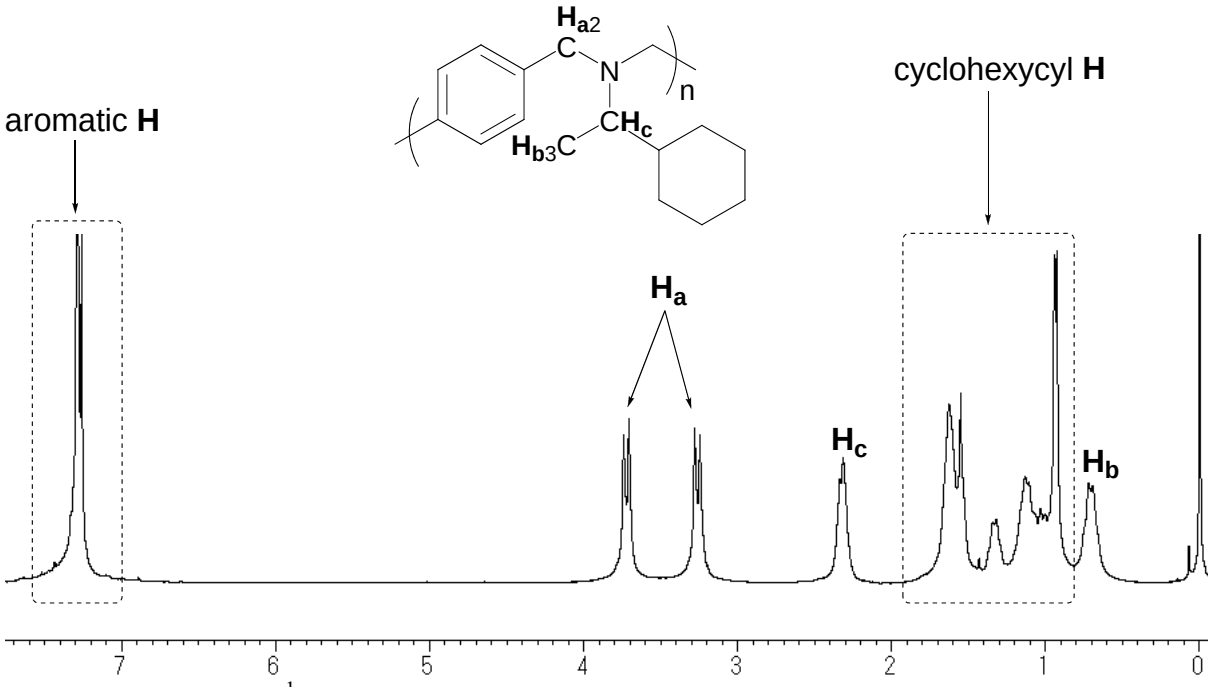

Figure S2. ^{1}H NMR spectrum of polymer **1(R) (**400 MHz, $CDCl_3$, ppm**)**.

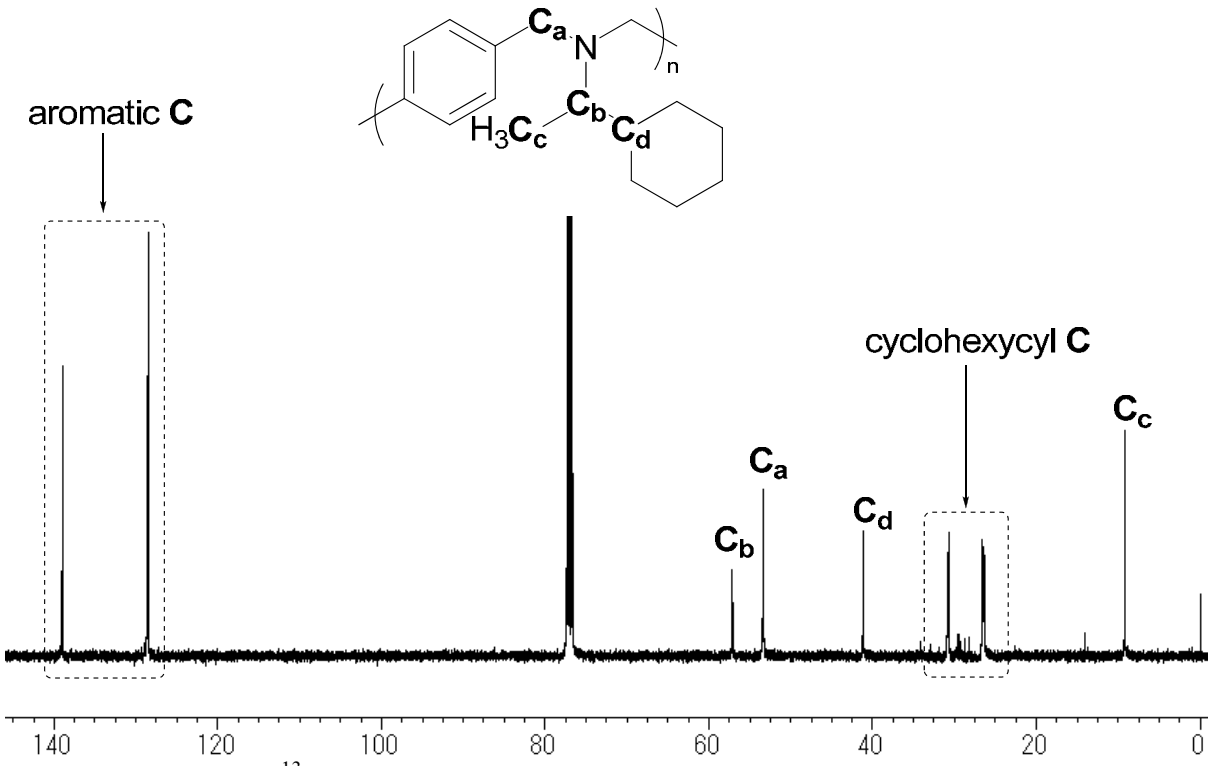

Figure S3. ^{13}C NMR spectrum of polymer **1(R) (**100 MHz, $CDCl_3$, ppm**)**.

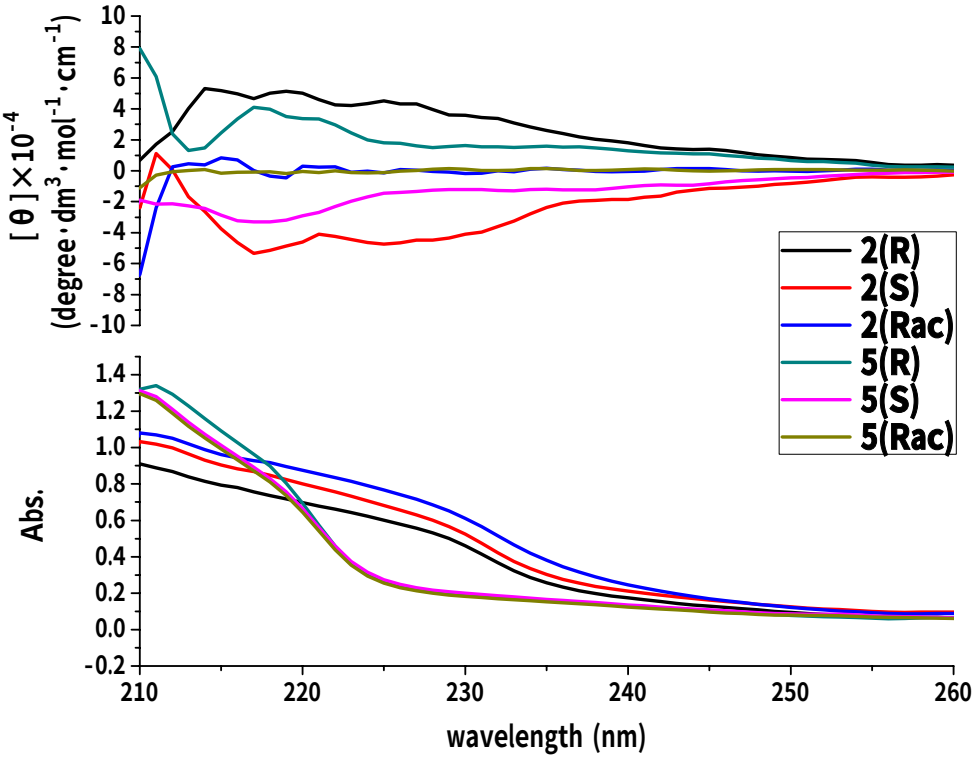

Figure S4. CD and UV-vis spectra of polymer **2** and model compound **5** (THF, 20°C, 210-260 nm, c 5×10^{-5} M for **2** and **5**).

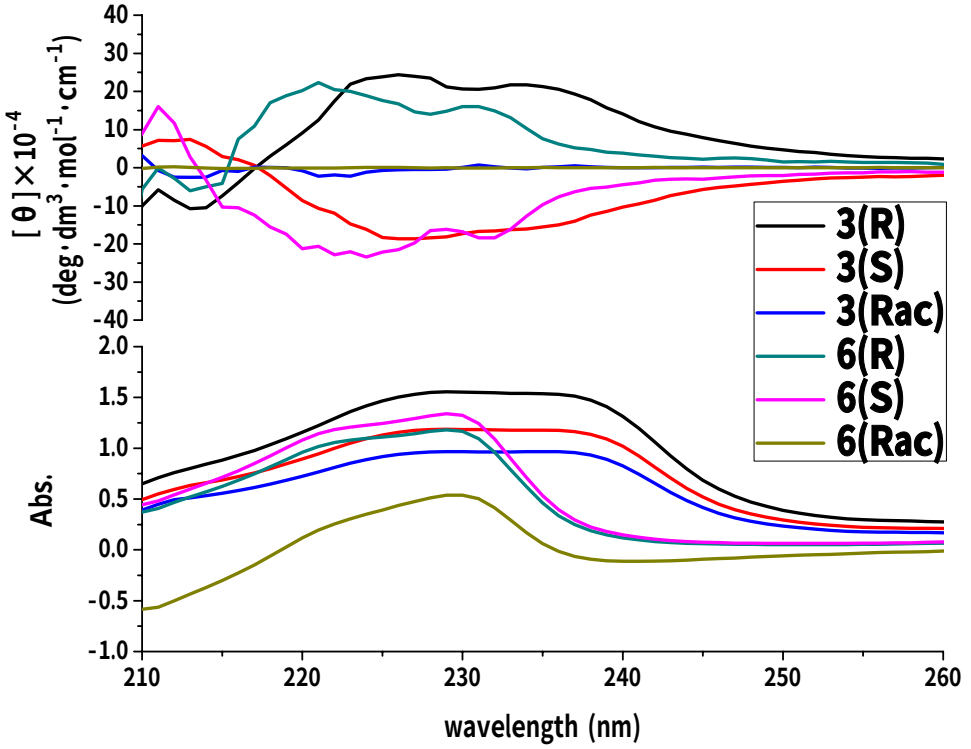

Figure S5. CD and UV-vis spectra of polymer **3** and model compound **6** (THF, 20°C, 210-260 nm, c 2×10^{-5} M for **3,** c 1×10^{-5} M for **6**).