Supplementary Material (ESI) for Chemical Communications


# *Supplementary Information*

## Chiroptical inversion induced by sandwiching units in chiral Polythiourethane

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### *Experimental Section*

**Measurement.** $^1$H (270 MHz) and $^{13}$C NMR (67.5 MHz) spectra were recorded on a JEOL JNM EX-270 spectrometer using tetramethylsilane (TMS) as an internal standard in $CDCl_3$, $CD_2Cl_2$, or DMSO-$d_6$. FT-IR spectra were obtained using a JASCO FT/IR-210 spectrometer. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter that was equipped with a sodium lamp as a light source. Circular dichroism (CD) spectra were measured on a JASCO J-720 spectropolarimeter. Number average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) were estimated by size-exclusion chromatography (SEC) using a Tosoh HPLC HLC-8020 system equipped with four consecutive polystyrene gel columns [TSK gels (bead size, exclusion limited molecular weight); αM (13 μm, > $1\times10^7$), α4000H (10 μm, > $1\times10^6$), α3000H (7 μm, > $1\times10^5$), and α2500H (7 μm, > $1\times10^4$)]; further, it had a refractive index and ultraviolet detectors at 40 °C. The system was operated at a flow rate of 1.0 mL/min using an *N*,*N*-dimethylformamide (DMF) solution (50 mM lithium bromide and 50 mM phosphoric acid) as an eluent. Polystyrene standards were employed for calibration. Differential scanning calorimetry (DSC) measurements were performed using an SII DSC-6200 instrument at a heating rate of 10 °C/min under nitrogen atmosphere.

**Materials.** 4(S)-(Methoxycarbonyl)-1,3-oxazolidine-2-thione(**S$_L$**), 4(S)-(methoxycarbonyl)-1,3-oxazolidine-2-thione (**S$_D$**), and 4(S)-(methoxycarbonyl)-*N*-benzoyl-1,3-oxazolidine-2-thione (**BzS$_L$**) were synthesized according to the previously reported method.[4-6] $CH_2Cl_2$ was distilled over $CaH_2$ before use. The other reagents were used as received.

**Copolymerization of S$_L$ with BzS$_L$.** *Typical procedure*: Dry $CH_2Cl_2$ (6.0 mL) and TfOMe (10 μL, 9.15 μmol, 3.04 mol% to monomers) were introduced into a polymerization tube containing **S$_L$** (0.24 g, 1.5 mmol) and **BzS$_L$** (0.40 g, 1.5 mmol). The resulting mixture remained homogeneous. After quenching with methanol (0.2 mL), the resulting mixture was poured into ethyl ether (300 mL) in order to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. Poly(**S$_L$**-*co*-**BzS$_L$**) was obtained as a colorless solid in high yield (Yield = 93%). $[\alpha]_D^{30}$ = -83.4°(*c* = 0.1 g/dL in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$): $\delta$ = 2.34 (initiating end, S-C*H*$_3$), 3.04–4.32 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.71–3.79 (6H, -OC*H*$_3$, and -OC*H*$_3$), 5.38–5.72 (2H, >C*H*-, and >C*H*-), 7.32–7.95 (5H, -C$_6$*H*$_5$), 8.29–8.87 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.87 (-*C*H$_2$-), 32. 17 (-*C*H$_2$-), 52.25 (-O*C*H$_3$), 52.67 (-O*C*H$_3$), 54.26 (-*C*H<), 59.98 (-*C*H<), 128.36, 129.39, 133.70, 134.93 (-C$_5$H$_6$), 164.40 (inversed thiourethane, -S*C*ONH-), 166.58 (-S*C*ONH-), 168.35 (-S*C*ONH-), 170.19 (-NH*C*OC$_5$H$_6$), 171.16 (-*C*OOCH$_3$), 171.20 (inversed ester, -*C*OOCH$_3$), 172.18 (-*C*OOCH$_3$) ppm. IR (KBr): 3347, 1755, 1690, 1654, 1504, 1442, 1296, 1203 cm$^{-1}$.

**Poly(S$_D$-*co*-BzS$_L$)** (from **S$_D$** (1.5 mmol) and **BzS$_L$** (1.5 mmol)): Yield = 94%. $[\alpha]_D^{30}$ = -94.8° (*c* = 0.1 g/dL in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$): $\delta$ = 2.34 (initiating end, S-C*H*$_3$), 2.68–4.15 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.70–3.81 (6H, -OC*H*$_3$, and -OC*H*$_3$), 4.80–5.56 (2H, >C*H*-, and >C*H*-), 7.27–7.62 (5H, -C$_6$*H*$_5$), 7.80–8.51 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.56 (-*C*H$_2$-), 32. 12 (-*C*H$_2$-), 52.19 (-O*C*H$_3$), 52.58 (-O*C*H$_3$), 54.21 (-*C*H<), 59.90 (-*C*H<), 128.44, 129.48, 132.27, 133.79 (-*C*$_5$H$_6$), 166.58 (-S*C*ONH-), 168.37 (-S*C*ONH-), 170.18 (-NH*C*OC$_5$H$_6$), 171.24 (-*C*OOCH$_3$), 172.15 (-*C*OOCH$_3$) ppm. IR (KBr): 3302, 1749, 1690, 1658, 1512, 1442, 1296, 1247, 1203 cm$^{-1}$.

**Block copolymerization of S$_L$ with BzS$_L$.** *Typical procedure*: A solution of **S$_L$** (0.24 g, 1.5 mmol) and TfOMe (10 μL, 9.15 μmol, 3.04 mol% to monomer) in dry $CH_2Cl_2$ (3.0 mL) was placed in a polymerization tube under nitrogen atmosphere. The resulting mixture was subjected to polymerization at 30 °C for 16 h under nitrogen. After **S$_L$** was completely consumed, a solution of **BzS$_L$** (0.40 g, 1.5 mmol) in $CH_2Cl_2$ (3.0 mL) was added to the polymerization mixture. The reactive mixture was stirred at 30 °C for 4 d, quenched with

methanol, and poured into ethyl ether in order to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. Poly(**$S_L$**-*b*-**$BzS_L$**) was obtained as a colorless solid in quantitative yield. $[\alpha]_D^{30}$ = -43.2° (*c* = 0.1 g/dL in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$): $\delta$ = 2.34 (initiating end, S-C*H*$_3$), 2.72–4.15 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.73–3.79 (6H, -OC*H*$_3$, and -OC*H*$_3$), 4.39–5.58 (2H, >C*H*-, and >C*H*-), 7.27–7.76 (5H, -$C_6H_5$), 7.82–8.48 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.54 (-*C*H$_2$-), 32.16 (-*C*H$_2$-), 52.15 (-O*C*H$_3$), 52.42 (-O*C*H$_3$), 54.25 (-*C*H<), 59.88 (-*C*H<), 128.42, 129.43, 132.29, 133.74 (-$C_5H_6$), 166.56 (-S*C*ONH-), 168.32 (-S*C*ONH-), 170.14 (-NH*C*O$C_5H_6$), 171.25 (-*C*OOCH$_3$), 172.14 (-*C*OOCH$_3$) ppm. IR (KBr): 3301, 1744, 1691, 1658, 1512, 1447, 1295, 1246, 1203 cm$^{-1}$.

**Poly(**$S_D$-*b*-$BzS_L$**):** Yield = quantitative. $[\alpha]_D^{30}$ = -198.5° (*c* = 0.1 g/dL in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$): $\delta$ = 2.34 (initiating end, S-C*H*$_3$), 2.76-3.95 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.73–3.79 (6H, -OC*H*$_3$, and -OC*H*$_3$), 4.40–5.54 (2H, >C*H*-, and >C*H*-), 7.27–7.88 (5H, -$C_6H_5$), 7.96–8.64 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.43 (-*C*H$_2$-), 31. 99 (-*C*H$_2$-), 52.10 (-O*C*H$_3$), 52.49 (-O*C*H$_3$), 54.16 (-*C*H<), 59.55 (-*C*H<), 128.42, 129.44, 132.26, 133.79 (-$C_5H_6$), 166.51 (-S*C*ONH-), 168.35 (-S*C*ONH-), 170.09 (-NH*C*O$C_5H_6$), 171.22 (-*C*OOCH$_3$), 172.15 (-*C*OOCH$_3$) ppm. IR (KBr): 3301, 1743, 1694, 1657, 1511, 1444, 1298, 1244, 1204 cm$^{-1}$.

**Block copolymerization of $BzS_L$ with a mixture of $S_L$ and $BzS_L$.** *Typical procedure*: A solution of **$BzS_L$** (0.27 g, 1.0 mmol) and TfOMe (19 μL, 16.7 μmol, 16.7 mol% to monomer) in dry $CH_2Cl_2$ (2.0 mL) was placed in a polymerization tube under a nitrogen atmosphere. The resulting mixture was subjected to polymerization at 30 °C for 16 h under nitrogen. After **$BzS_L$** was completely consumed, a solution of **$S_L$** (0.48 g, 3.0 mmol) and **$BzS_L$** (0.53 g, 2.0 mmol) in $CH_2Cl_2$ (10 mL) was added to the reactive solution. The resulting mixture was stirred at 30 °C for 4 d, quenched with methanol, and poured into ethyl ether to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum. Poly(**$BzS_L$**-*b*-(**$S_L$**-*co*-**$BzS_L$**)) was obtained as a colorless solid. Yield = 95%. $[\alpha]_D^{30}$ = -159.7° (*c* = 0.1 g/dL in $CH_2Cl_2$). $T_m$ = 119.9 °C (15.6 mJ/mg). $^1$H NMR ($CDCl_3$): $\delta$ = 2.33 (initiating end, S-C*H*$_3$), 2.74-4.25 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.73–3.79 (6H, -OC*H*$_3$, and -OC*H*$_3$), 4.40–5.74 (2H, >C*H*-, and >C*H*-), 7.27–7.77 (5H, -$C_6H_5$), 7.80–8.55 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.87 (-*C*H$_2$-), 32. 17 (-*C*H$_2$-), 52.24 (-O*C*H$_3$), 52.68 (-O*C*H$_3$), 54.25 (-*C*H<), 59.99 (-*C*H<), 128.45, 129.47, 133.80, 134.92 (-$C_5H_6$), 164.38 (-S*C*ONH-), 168.35 (-S*C*ONH-), 170.19 (-NH*C*O$C_5H_6$), 171.16 (-*C*OOCH$_3$), 172.18 (-*C*OOCH$_3$) ppm. IR (KBr): 3313, 1747, 1693, 1649, 1302, 1252, 1205 cm$^{-1}$.

**Poly(**$BzS_L$-***b***-($S_D$-***co***-$BzS_L$)):** Yield = 98%. $[\alpha]_D^{30}$ = -196.5° (*c* = 0.1 g/dL in $CH_2Cl_2$). $T_m$ = 147.1 °C (39.6 mJ/mg). $^1$H NMR ($CDCl_3$): $\delta$ = 2.33 (initiating end, S-C*H*$_3$), 2.61—4.27 (4H, -C*H*$_2$-, and -C*H*$_2$-), 3.74–3.79 (6H, -OC*H*$_3$, and -OC*H*$_3$), 4.26–5.90 (2H, >C*H*-, and >C*H*-), 7.38–7.94 (5H, -$C_6H_5$), 8.00–8.55 (1H, -N*H*-) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.58 (-*C*H$_2$-), 32. 13 (-*C*H$_2$-), 52.22 (-O*C*H$_3$), 52.61 (-O*C*H$_3$), 54.20 (-*C*H<), 59.92 (-*C*H<), 128.45, 129.47, 132.25, 133.77 (-$C_5H_6$), 166.50 (-S*C*ONH-), 168.30 (-S*C*ONH-), 170.13 (-NH*C*O$C_5H_6$), 171.20 (-*C*OOCH$_3$), 172.11 (-*C*OOCH$_3$) ppm. IR (KBr): 3303, 1743, 1692, 1657, 1512, 1445, 1295, 1247, 1206 cm$^{-1}$.

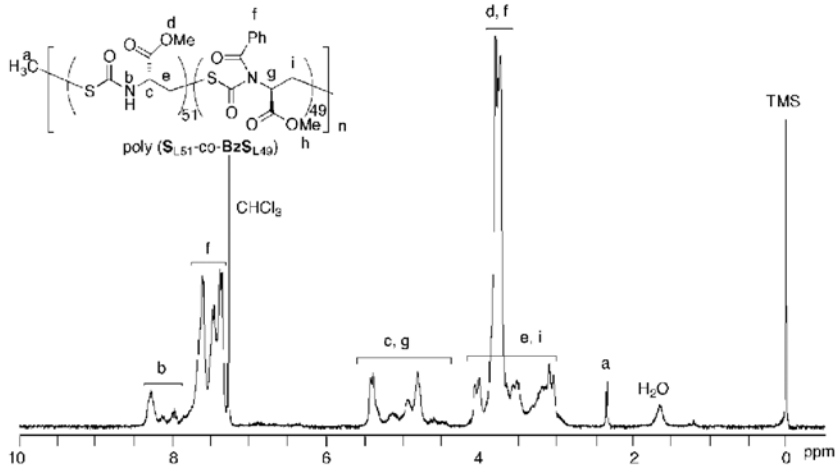


**Fig. 1S** $^1$H NMR spectra ($CDCl_3$) of poly(**$S_{L51}$**-*co*-**$BzS_{L49}$**).

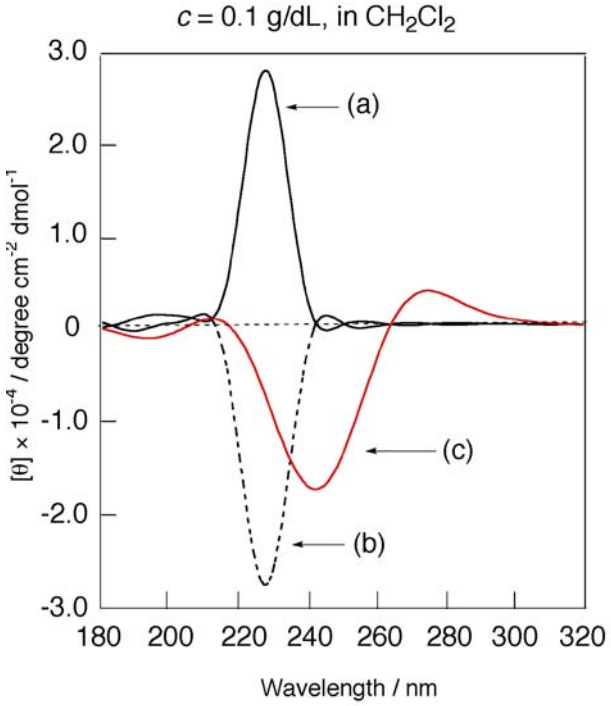


**Fig. 2S** CD spectra of (a) poly(**S**$_{\mathbf{L}}$) ($M_n$ = 3300, $M_w/M_n$ = 1.14), (b) poly(**S**$_{\mathbf{D}}$) ($M_n$ = 3500, $M_w/M_n$ = 1.14), and (c) poly(**BzS**$_{\mathbf{L}}$) ($M_n$ = 3500, $M_w/M_n$ = 1.19).

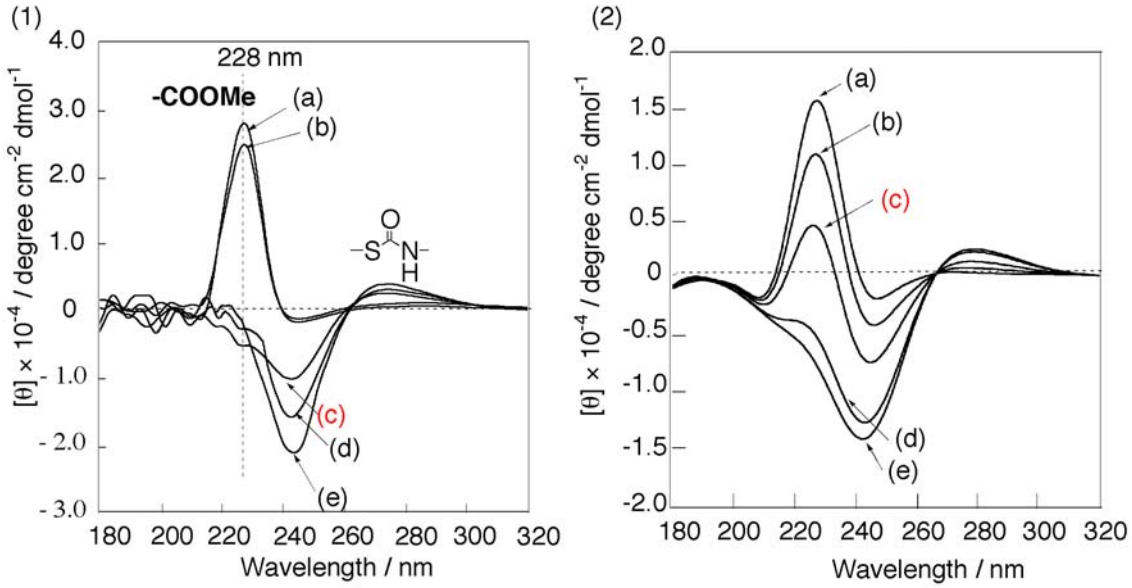


**Fig. 3S** The observed Cotton effect curves (1) and linearly combined presumable Cotton effect curves (2) of the obtained copolymers [(a) poly(**S**$_{\mathbf{L}91}$-*co*-**BzS**$_{\mathbf{L}9}$), (b) poly(**S**$_{\mathbf{L}74}$-*co*-**BzS**$_{\mathbf{L}26}$), (c) poly(**S**$_{\mathbf{L}51}$-*co*-**BzS**$_{\mathbf{L}49}$), (d) poly(**S**$_{\mathbf{L}16}$-*co*-**BzS**$_{\mathbf{L}84}$), and (e) poly(**S**$_{\mathbf{L}7}$-*co*-**BzS**$_{\mathbf{L}93}$)].

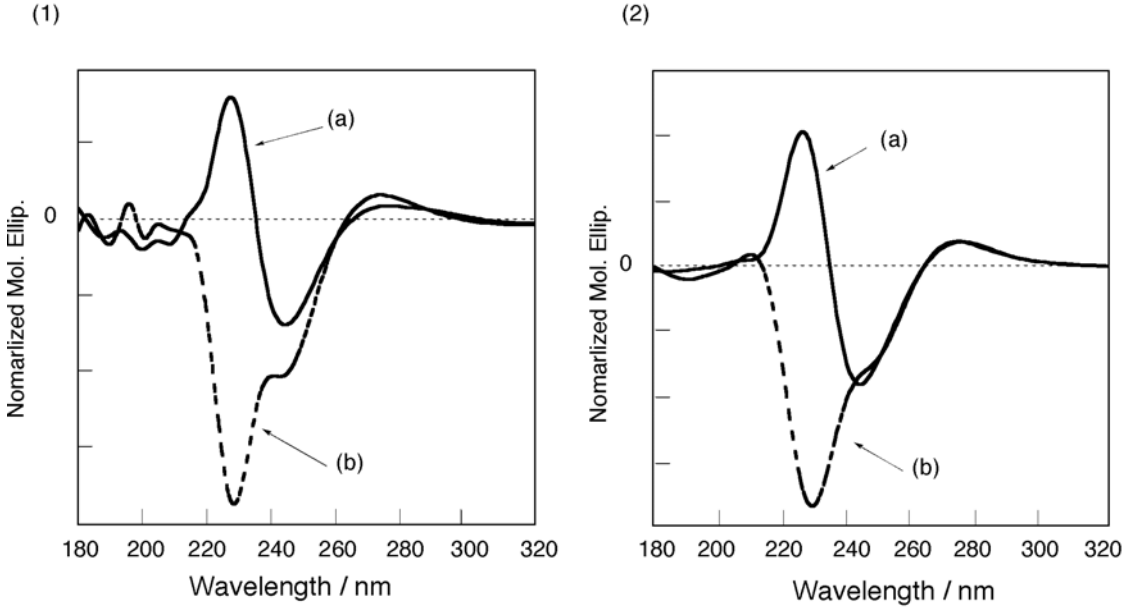


**Fig. 4S** The observed Cotton effects curves (1) and linearly combined presumable Cotton effect curves (2) of the obtained block copolymers [(a) poly($\mathbf{S_{L53}}$-*b*-$\mathbf{BzS_{L47}}$) and (b) poly($\mathbf{S_{D50}}$-*b*-$\mathbf{BzS_{L50}}$)].

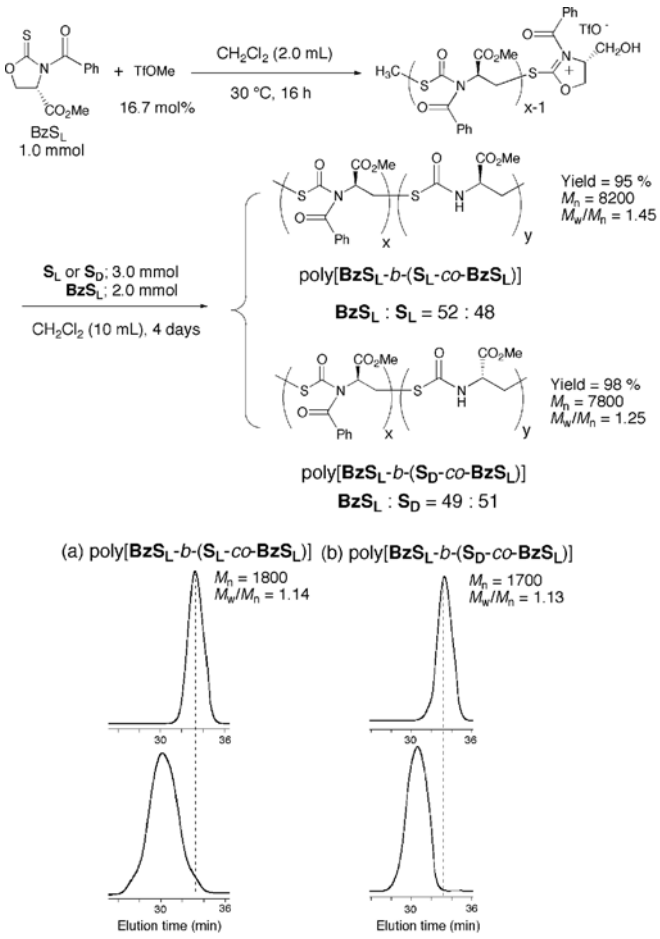


**Fig. 5S** Synthesis of block copolymers poly($\mathbf{BzS_L}$-*b*-($\mathbf{S_D}$-*co*-$\mathbf{BzS_L}$)) and poly($\mathbf{BzS_L}$-*b*-($\mathbf{S_L}$-*co*-$\mathbf{BzS_L}$)).

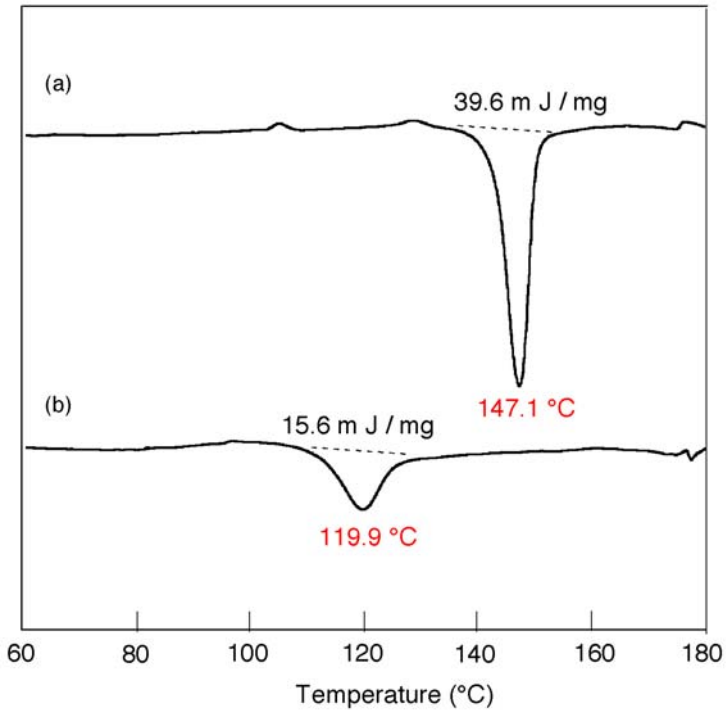


**Fig. 6S** DSC traces of (a) poly(**BzS$_L$**-*b*-(**S$_D$**-*co*-**BzS$_L$**)) and (b) poly(**BzS$_L$**-*b*-(**S$_L$**-*co*-**BzS$_L$**)).