Electronic Supplementary Information to:

A Chiral π-Stacked Vinyl Polymer Emitting White Circularly Polarized Light

Kento Watanabe, Takeshi Sakamoto, Makoto Taguchi, Michiya Fujiki and Tamaki Nakano*

[a]Graduate School of Chemical Sciences and Engineering
Hokkaido University
N13 W8, Kita-ku, Sapporo 060-8628, Japan

[b]Faculty of Engineering
Hokkaido University
N13 W8, Kita-ku, Sapporo 060-8628, Japan

[c]Graduate School of Materials Science
Nara Institute of Science and Technology (NAIST)
8916-5 Takayama-cho, Ikoma 630-0101, Japan

Correspondence to T. Nakano (E-mail: nakanot@eng.hokudai.ac.jp, tnakano62@gmail.com)

Experimental Details

Syntheses of poly(BBPDBF): BBPDBF monomer was available from our recent work [T. Sakamoto, K. Watanabe, Y. Shichibu, K. Konishi, S.-i. Sato and T. Nakano, *J. Polym. Sci., Part A: Polym. Chem.* 2011, **49**, 945]. The procedure is described for the polymerization at $[BBPDBF]_o/[initiator]_o$ = 10 (Supporting Information: **Tab. 1S**, run 1). A 0.10-M THF solution of optically active potassium menthoxide (initiator) was prepared according to the literature [T. Nakano, M. Tanikawa, O. Nakagawa, T. Yade and T. Sakamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 239]. In a flame-dried glass ampoule sealed with a three-way stop cock, a THF solution of BBPDBF (0.50 g, 1.13 mmol) was dissolved in dry THF (23.0 mL) under dry N_2 atmosphere. The resulting solution was cooled at -78 ^oC, and the potassium menthoxide solution (1.13 mL, 0.113 mmol) was added with a syringe to initiate the polymerization. After 48 h of initiation, polymerization was terminated by adding EtI (0.50 mL, 0.98 g, 6.25 mmol). After the addition of EtI, temperature of the reaction mixture was raised to -30^oC, and the reaction system was maintained for 1 h at this temperature until the color of the reaction system changes from deep red to pale yellow, indicating that growing

species had been completely killed. Monomer conversion was determined to be 85% by ^{1}H NMR measurements of the terminated reaction mixture with solvent peaks as internal standard. The product was purified by reprecipitation in a large amount of MeOH and dried under vacuum. The MeOH-insoluble polymer (0.41 g, 82%) was obtained as a pale yellow powder. Mn 3800, Mw/Mn 1.07; $[\alpha]_{435}^{25}$ -5^o (in THF, c = 0.5 gdL^{-1}, cell path 1 cm); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.2-5.8 (m, 14H, Ar H), 3.5-2.5 (m, 2H; main-chain CH_2), 1.2 (s, 9H; $C(CH_3)_3$), 0.7 (m, 2H; terminal $\underline{CH_2}CH_3$), -0.08 (m, 3H; terminal $CH_2\underline{CH_3}$).

CPL measurements: A film sample was made by a solution casting method using a THF solution of the poly(BBPDBF) (5 g/L). Five drops of the THF solution (ca. 30 μL) were coated onto a quartz plate (1.0 cm x 2.0 cm x 0.1 cm) using a 100-μL syringe, and THF was removed by drying under air to afford a rough-surfaced film. The film was wetted with ten drops of $CHCl_3$ (ca. 25 μL) using a 250-μL syringe, and $CHCl_3$ was slowly removed by drying under air to afford a smooth-surfaced clear film suitable for optical measurements (**Fig. 5S**). Thickness of the film was ca. 0.10 μm as measured using a Keyence VK8700 laser microscope. CPL spectra were recorded using a JASCO CPL-200 spectrometer (NAIST).

Instrumentations: Absorption spectra, fluorescent spectra, and CD spectra were recorded with a JASCO V-570, a FP-777W, and a J-820 spectrometers, respectively. Specific rotation was measured using a JASCO P-1030 digital polarimeter. TG-DTA and DSC measurments were performed on a Rigaku TG8120 and a DSC 8230 apparatuses, respectively.

Table 1S. Anionic Polymerization of **BBPDBF** in THF at -78°C for 48 h

Run	$[M]_o/[I]_o$	Conv. (%)[b]	Yield (%)[c]	Mn[d]	Mw/Mn[d]	$[\alpha]^{26}_{435}$ [e]
1	10	85	82	3800	1.07	-5°
2	20	68	61	5200	1.08	-6°

[a]$[M]_o$ =1.13 mmol. [b]Dertermined by ^{1}H NMR. [c]MeOH-insoluble part. [d]Dertermined by SEC (vs. polystyrene). [e]Conc. = 0.50 g/dL, cell length = 1 cm, solvent = THF.

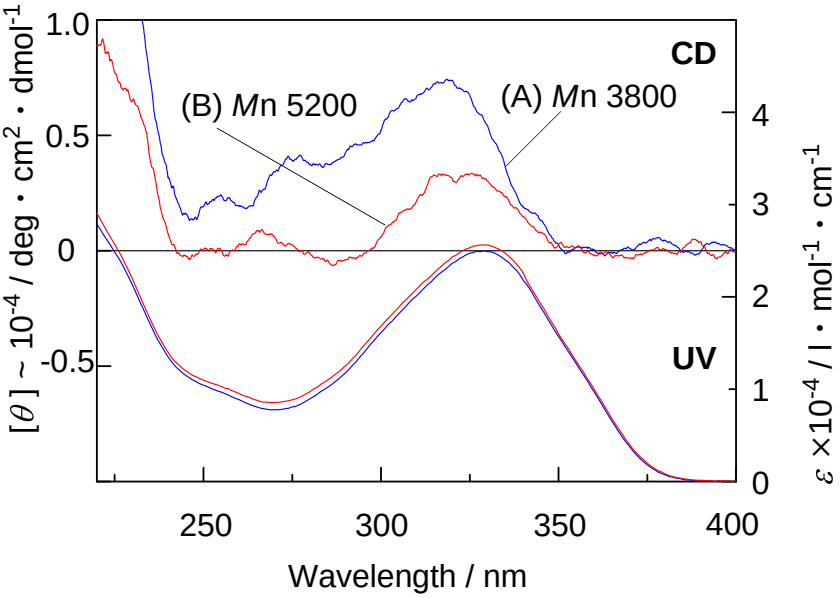

Figure 1S. CD and UV spectra of poly(BBPDBF)s obtained at [BBPDBF]/[initiator] = 10 (A) and 20 (B). [THF, 1.25 x 10^{-4} M, cell path 1 mm]

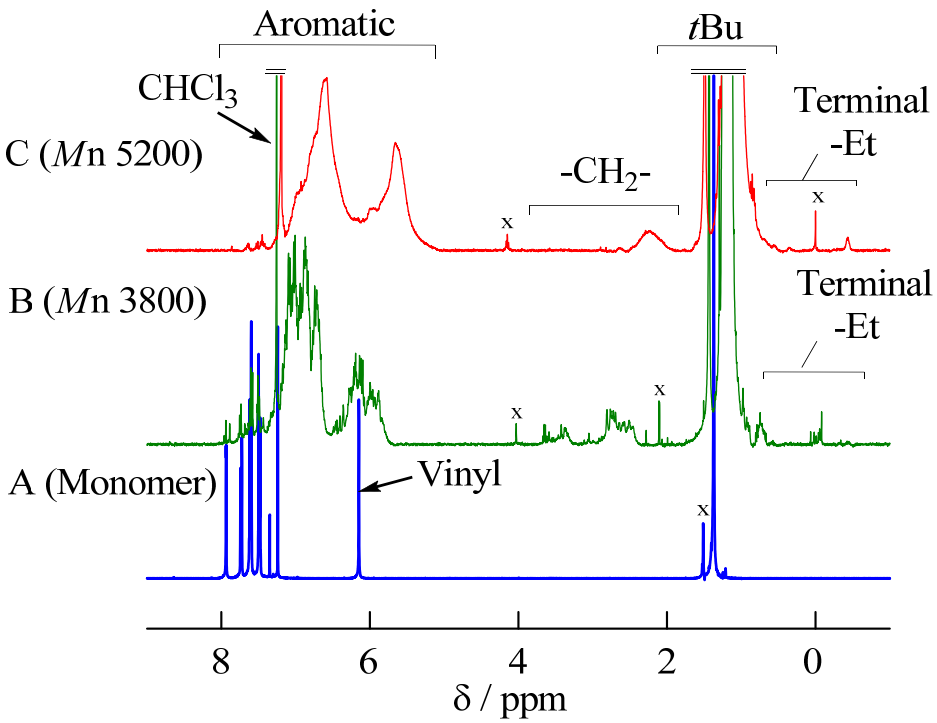

Figure 2S. ^{1}H NMR spectra of BBPDBF monomer (A) and poly(BBPDBF)s of Mn 3800 (B) and Mn 5200 (C). [400 MHz, $CDCl_3$, 23°C]

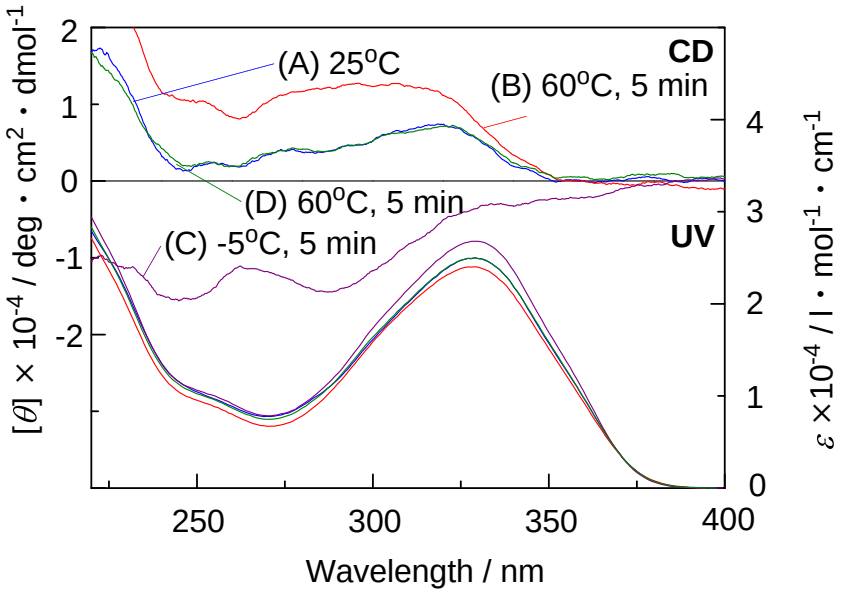

Figure 3S. CD and UV spectra of the poly(BBPDBF) of Mn 3800 recorded at 25°C (A), at 60°C after being maintained at this temperature for 5 min (B), at -5°C after being maintained at this temperature for 5 min (C), and at 25°C after being maintained at this temperature for 5 min (D). The spectra were measured in the order, A, B, C, to D. [THF, 1.25 x 10^{-4} M, cell path 1 mm]

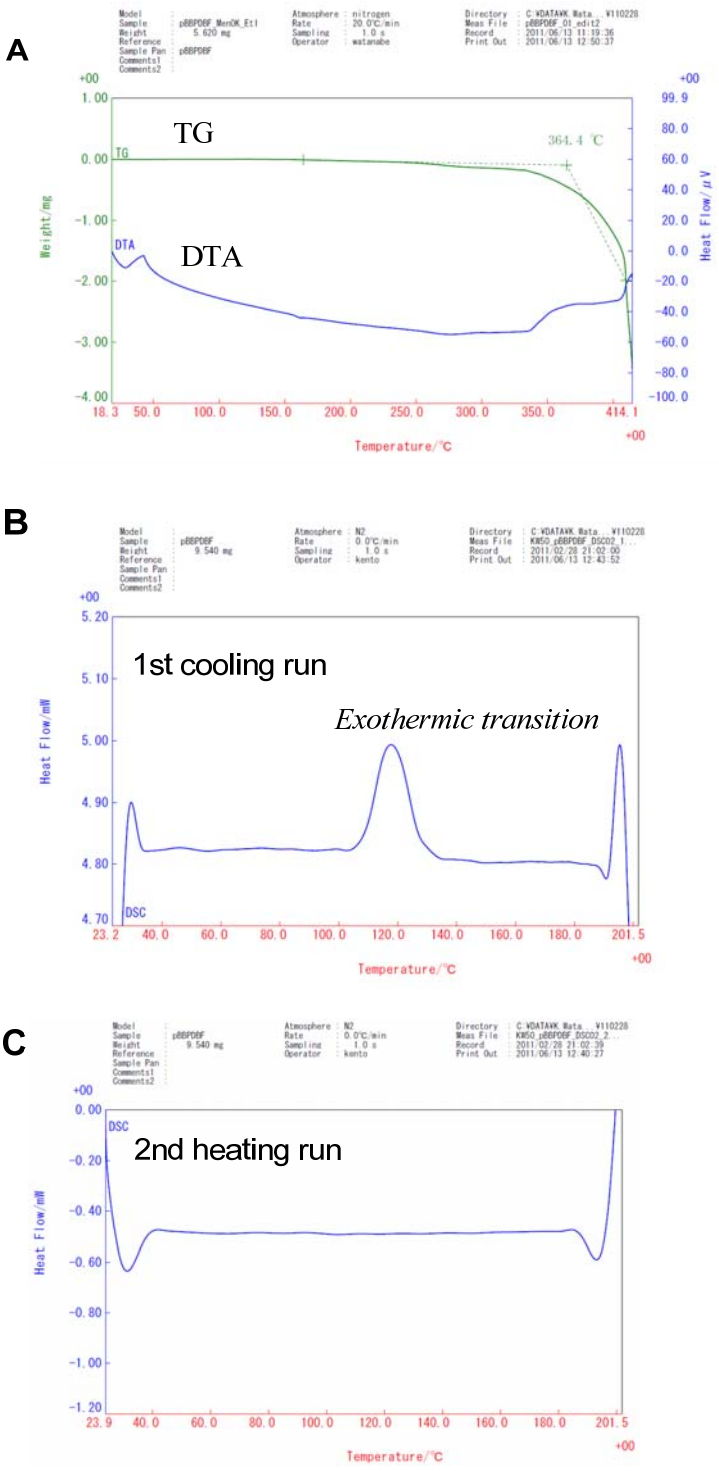

Figure 4S. TG-DTA (A) and DSC (B, C) profiles of the poly(BBPDBF) of Mn 3800.

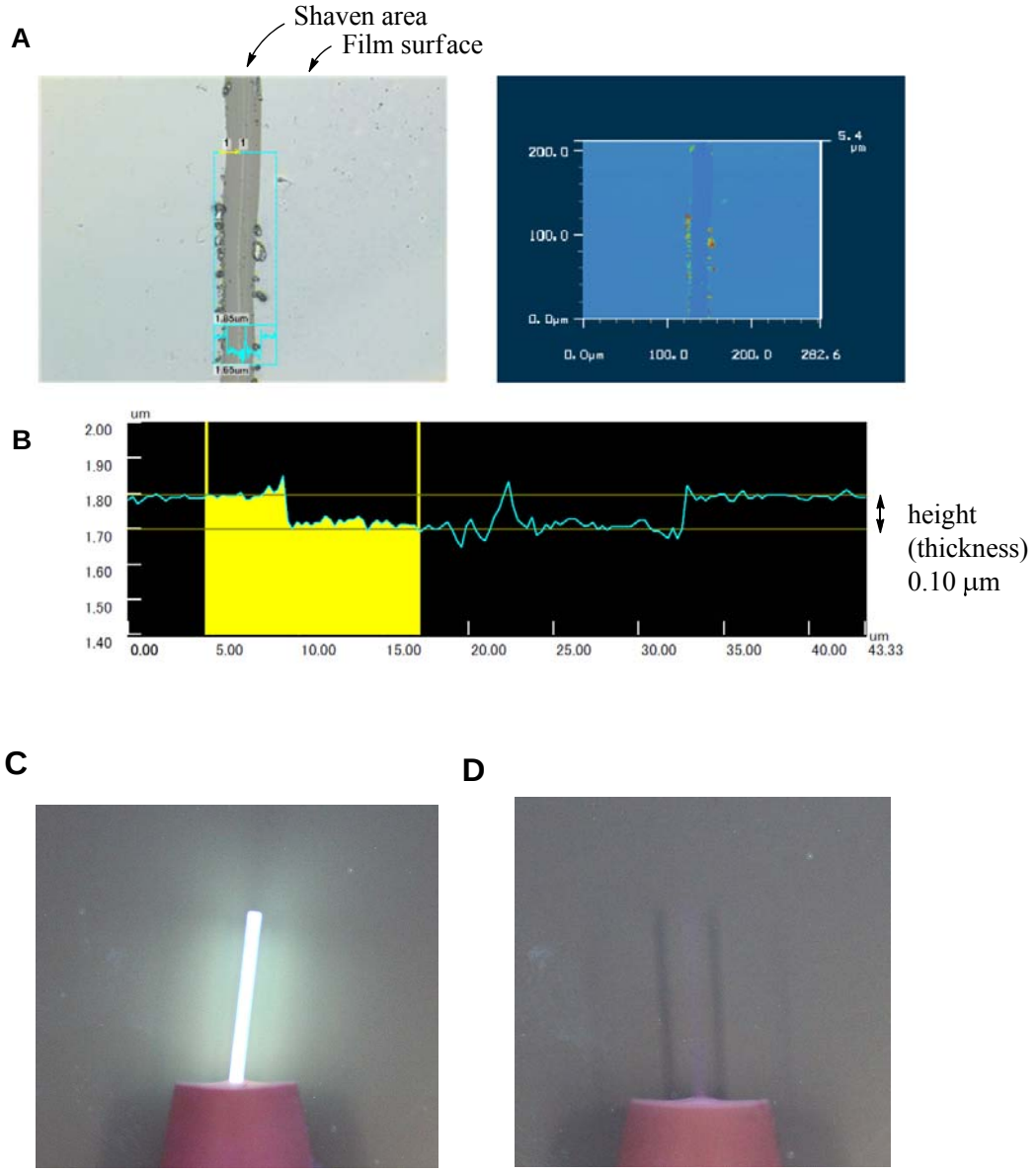

Figure 5S. Photographs of a thin film sample of the poly(BBPDBF) of Mn 3800. Laser microscopic images of film surface partially shaven for height measurement (A), the height profile obtained from A (B), and side-view images of quartz plates coated with (C) and without (D) poly(BBPDBF) film taken upon black light excitation (λ_{ex} 365 nm).