Supporting information

Synthesis and evaluation of high-birefringence polymethacrylate having diphenyl-diacetylene LC moiety in side chain

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Instruments

The ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on a JEOL LNM-EX 400 at room temperature using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were recorded on a JASCO FT-IR 460 plus spectrometer. Gel permeation chromatography (GPC) was carried out by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSKgel G4000H_{XL} column) using tetrahydrofuran (THF) as the eluent after calibration with polystyrene standards. The transition behavior was investigated by polarizing optical microscopy (POM) (Leica DM2500P microscopy with a Mettler FP90 hot stage) and differential scanning calorimetry (Perkin Elmer DSC7) with heating and cooling scans performed at 10 °Cmin^{-1}. The transmittance of light was observed by a microscope spectroscopic method using a Nikon LV100 Pol optical microscope equipped with a USB4000 (Ocean photonics) spectrometer.

Materials

Trimethylsilylacetylene, $Pd(PPh_3)_4$, 4-(hexyloxy)benzaldehyde, 6-bromo-1-hexanol, 4-iodophenol, tetrabutylammoniumfluoride (TBAF), *tert*-butyldimethylchlorosilane and methacryloylchloride were purchased from TCI, and PPh_3, CuI, $ZnCl_2$, 2-bromo-6-naphthol, triethylamine, N-ethyldiisopropylamine, chloromethylmethylether and tetrabromomethane were purchased from Wako, and *n*-butyllithium was purchased from Kanto chemical. Unless otherwise noted, all chemical were commercially available and use as received.

Synthesis

4-(6-Hydroxyhexyloxy)iodobenzene (1)

A mixture of 4-iodophenol (5.5 g, 25.1 mmol), 6-bromo-1-hexanol (5.0 g, 27.6 mmol), potassium carbonate (4.2 g, 30.1 mmol) and DMF (50 mL) was refluxed for 18 h. The insoluble solids were removed by filtration with diethylether, and the filtrate was extracted with diethylether, washed with brine, and dried over $MgSO_4$. After removing the solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/3) to afford the title compound as a colorless solid. **Yield**: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, *J* = 8.5 Hz), 6.67 (d, 2H, *J* = 8.5 Hz), 3.92 (t, 2H, *J* = 6.5 Hz), 3.66 (dt, 2H, *J* = 4.0, 7.0 Hz,), 1.79 (tt, 2H, *J* = 6.5, 7.4 Hz), 1.64-1.36 (m, 6H), 1.26 (t, 1H, *J* = 7.0 Hz) ppm.

4-(6-Hydroxyhexyloxy)-1-(2-trimethylsilylethynyl)benzene (2)

To a mixture of 4-(6-hydroxyhexyloxy)iodobenzene (8.0 g, 25 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.050 mmol), CuI (95 mg, 0.050 mmol), PPh_3 (0.13 g, 0.050 mmol), and triethylamine (20 mL) in THF (20 mL) was added trimethylsilylacetylene (5.5 mL, 40 mmol), and it was stirred at 45 °C for 2 days. A portion of diethylether was added, and insoluble solids were removed by filtration. The filtrate was extracted with diethylether, consequently washed with aqueous 2 M HCl and brine, and dried by $MgSO_4$. After removal of solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/2) to afford the title compound as a pale yellow liquid. **Yield**: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 8.3 Hz), 6.80 (d, 2H, *J* = 8.3 Hz), 3.95 (t, 2H, *J* = 6.6 Hz), 3.69-3.63 (brm, 2H), 1.79 (tt, 2H, *J* = 6.6, 6.6 Hz), 1.64-1.1.39 (m, 6H), 1.26 (t, 1H, *J* = 7.2 Hz) ppm.

4-(6-Hydroxyhexyloxy)-1-ethynylbenzene (3)

To a solution of 4-(6-hydroxyhexyloxy)-(2-trimethylsilylethynyl)benzene (3.07 g, 14.1 mmol) in THF (50 mL) was added TBAF (1.0 M in THF solution, 16 mL, 16 mmol), and stirred for 15 min at room temperature. A portion of water was added, and the mixture was extracted with diethylether, washed with brine and dried over $MgSO_4$. After removal of solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/3) to afford the title compound as a colorless solid. **Yield**: 68%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, 2H, *J* = 8.8 Hz), 6.82 (d, 2H, *J* = 8.8 Hz), 3.96 (t, 2H, *J* = 6.5 Hz), 3.68-3.64 (brm, 2H), 2.99 (s, 1H), 1.80 (tt, 2H, *J* = 6.5, 7.4 Hz), 1.64-1.41 (m, 6H), 1.22 (brm, 1H) ppm.

4-[6-(*tert*-Butyldimethylsiloxy)hexyloxy]-1-ethynylbenzene (4)

To a solution of **3** (1.10 g, 5.00 mmol) and imidazole (0.45 g, 6.50 mmol) in CH_2Cl_2 (30 mL) was added tert-butyl-dimethyl-silylchloride (0.98 g, 6.50 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (eluent: ethyl acetate/ hexane = 1/10) to afford the title compound as a colorless liquid. **Yield**: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41, (d, 2H, *J* = 8.6 Hz), 6.82 (d, 2H, *J* = 8.8 Hz), 3.95 (t, 2H, *J* = 6.5 Hz), 3.61 (t, 2H, *J* = 6.5 Hz), 2.99 (s, 1H), 1.79 (tt, 2H, *J* = 6.5, 7.3 Hz), 1.56-1.34 (m, 6H), 0.89 (s, 9H), 0.04 (s, 6H) ppm.

4-(2,2-Dibromoethenyl)-1-hexyloxybenzene (5)

A solution of PPh_3 (10.5 g, 40 mmol) in CH_2Cl_2 was added tetrabromomethane (6.6 g, 20 mmol) at 0 °C. After stirring for 15 min, 4-hexyloxybenzaldehyde (2.10 g, 10 mmol) was added to the mixture, and it was stirred for further 3 h. A portion of methanol and water were sequentially added, and the mixture was extracted with chloroform, sequentially washed with aqueous NaS_2O_3 and brine, and dried over MgSO4. After removal of solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/10) to afford the title compound as a colorless liquid. **Yield**: >99%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50, (d, 2H, *J* = 7.8 Hz), 7.40 (s, 1H), 6.88 (d, 2H, *J* = 7.8 Hz), 3.96 (t, 2H, *J* = 6.6 Hz), 1.78 (tt, 2H, *J* = 6.6, 7.4 Hz), 1.49-1.29 (m, 6H), 0.91 (t, 3H, *J* = 7.1 Hz) ppm.

2-Bromo-1-(4-hexyloxyphenyl)-4-[4-(6-*tert*-butyldimethylsiloxyhexyloxy)phenyl]-1-(Z)butene-3yne (6)

To a solution of acetylene **4** (1.9 g, 5.7 mmol) in THF (30 mL) was added *n*-BuLi (2.6 M in hexane, 2.2 mL, 5.8 mmol) at -78 °C. After stirring 30 min, a solution of dry $ZnCl_2$ (0.79 g, 5.8 mmol) in THF (15 mL) was added to the mixture, and it was stirred for further 15 min. The mixture was allowed to warm to room temperature over 30 min. This mixture was added to another flask at 0 °C, which contained a mixture of dibromostyrene **5** (2.0 g, 5.7 mmol) and $Pd(PPh_3)_4$ (0.33 g, 0.28 mmol) in THF (5 mL). After stirring at 0 °C for 2 days, a portion of aqueous NH_4Cl was added, and it was extracted with diethylether, sequentially washed with aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. After removal of solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/10) to afford the title compound as a colorless solid. **Yield**: 47%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, 2H, *J* = 8.8 Hz), 7.41 (d, 2H, *J* = 8.8 Hz), 7.21 (s, 1H), 6.89 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 3.97 (dt, 4H, *J* = 6.0, 6.3 Hz), 3.62 (t, 2H, *J* = 6.5 Hz), 1.86-1.73 (m, 4H), 1.53-1.31(m, 12H), 0.93-0.88 (m, 12H), 0.05 (s, 6H) ppm.

1-(4-Hexyloxyphenyl)-4-{4-[6-(*tert*-butyldimethylsiloxy)hexyloxy]phenyl}-1,3-butadiyne (7)

To a solution of compound **6** (1.60 g, 2.60 mmol) in THF (20 ml) was added tetra-*n*-butylammonium fluoride (1.0 M in THF, 4.80 mL, 4.80 mmol), and the mixture was stirred for 1 day at room temperature. A portion of water was added, and the mixture was extracted with chloroform, washed with brine, and dried over $MgSO_4$. After removal of solvents, the residue was purified by silica gel column chromatography ($CHCl_3$/EtOAc/hexane = 1/1/1) to afford the title compound as a colorless solid. **Yield**: 96%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44, (dd, 2H, *J* = 4.4 Hz), 7.44, (dd, 2H, *J* = 4.4 Hz), 6.83 (d, 2H, *J* = 4.4 Hz), 6.83 (d, 2H, *J* = 4.4 Hz), 3.98-3.94 (m, 4H), 3.66 (t, 2H, *J* = 6.6 Hz), 1.83-1.74 (m, 4H), 1.64-1.33 (m, 12H), 1.27-1.20 (brs, 1H) 0.90 (t, 3H, *J* = 6.8 Hz) ppm; **HRMS** (FAB) M^+ Calcd for $C_{28}H_{34}O_3$ 418.2503; Found, 418.2500.

1-(4-Hexyloxyphenyl)-4-[4-(6-hydroxyhexyloxy)phenyl]-1,3-butadiyne (8)

To a solution of compound **7** (0.97 g, 2.30 mmol) and triethylamine (3.00 ml, 3.00 mmol) in CH_2Cl_2 (35 mL) was added methacryloyl chloride (0.29 mL, 3.00 mmol), and the mixture was stirred at room temperature for 7 h. A portion of 2 M HCl was added, and the mixture was extracted with chloroform, washed with water, and dried over $MgSO_4$. After removal of solvents, the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/2) to afford the title compound as a colorless solid. **Yield**: 67%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, *J* = 4.3 Hz), 7.44 (d, 2H, *J* = 4.3 Hz), 6.83 (d, 2H, *J* = 4.4 Hz), 6.83 (d, 2H, *J* = 4.4 Hz), 6.10 (d, 1H, *J* = 1.7 Hz), 5.55 (d, 1H, *J* = 1.7 Hz), 4.16 (t, 2H, *J* = 6.6 Hz), 3.98-3.94 (m, 4H), 1.94 (s, 3H), 1.82-1.67 (m, 6H), 1.53-1.31 (m, 10H), 0.91 (t, 3H, *J* = 6.7 Hz) ppm; **^{13}C NMR** (400 MHz, $CDCl_3$) δ 167.5, 159.8, 159.7, 136.4, 134.0, 134.0, 125.2, 114.6, 114.6, 113.7, 113.6, 81.3, 81.2, 72.9, 72.8, 68.1, 67.8, 64.6, 31.5, 29.1, 29.0, 28.5, 25.7, 25.7, 25.6, 22.6, 18.3, 14.0 ppm; **HRMS** (FAB) M^+ Calcd for $C_{32}H_{38}O_4$ 486.2770; Found, 486.2774.

Polymerization

To a Schlenk tube, which contained **8** (0.10 g, 0.21 mmol) and THF (0.41 ml) was added dropwise BuLi (2.6 M in hexane, 3.9 μL, 0.010 mmol) at 0 °C, and the mixture was stirred for 24 h at the same temperature. The mixture was poured dropwise into excess methanol, and it was filtrated. The solids were purified by reprecipitation with MeOH to afford the title polymer as a colorless solid. The polymerization result explained following: **Yield** = 40%, Mn = 7990, Mw / Mn = 1.69. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.35 (brm, 4H), 6.85-6.74 (brm, 4H), 4.02-3.81 (br, 6H), 1.82-1.08 (brm, 23H), 1.94 (s, 3H), 0.93-0.81 (m, 3H) ppm.

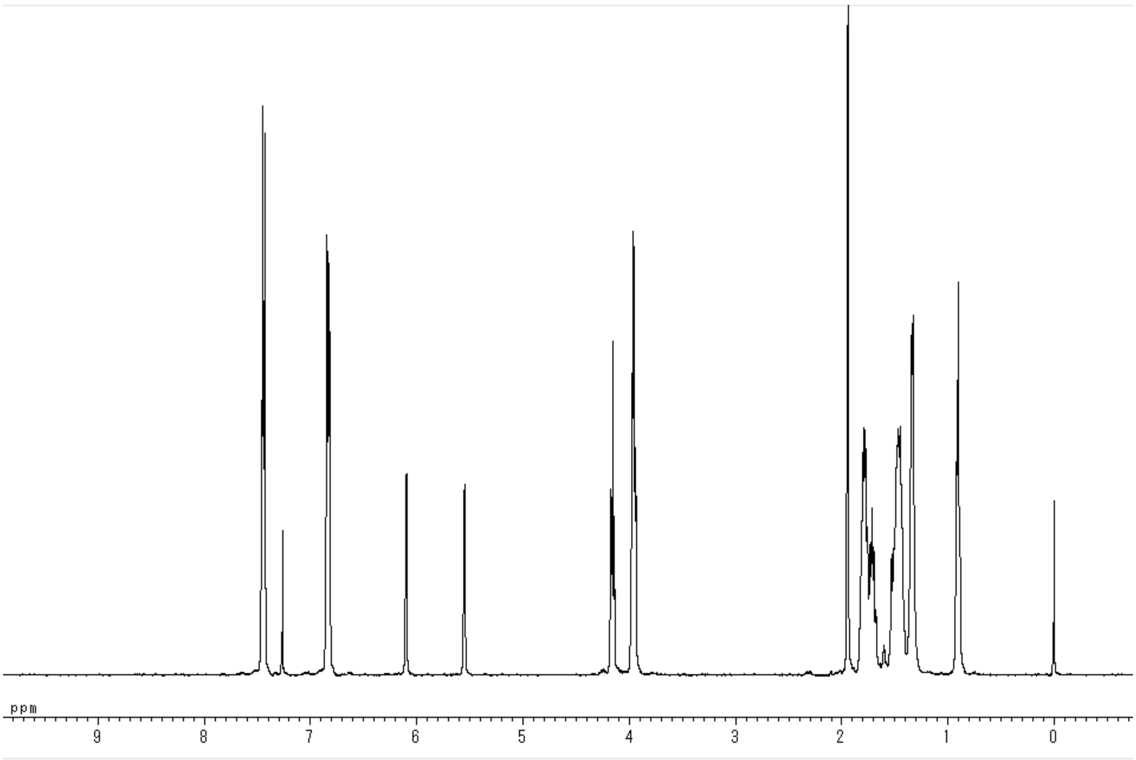

Fig. S1 ^{1}H NMR spectrum of monomer **8** (400 MHz, $CDCl_3$).

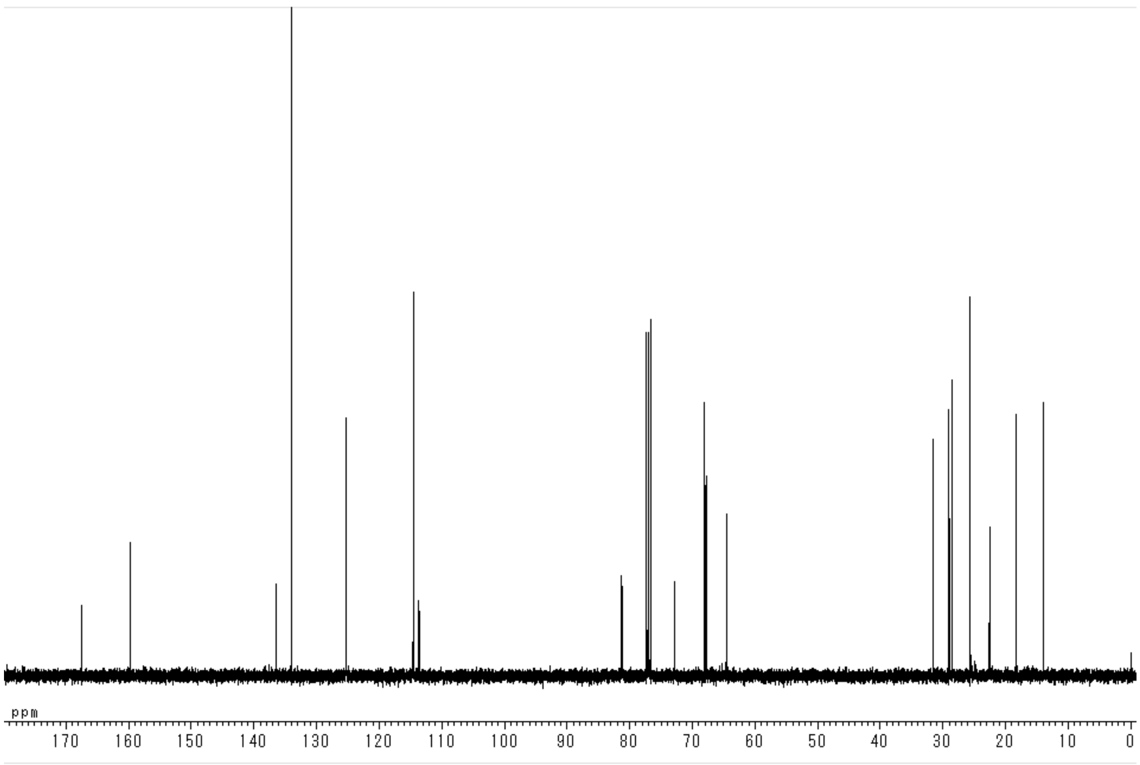

Fig. S2 ^{13}C NMR spectrum of monomer **8** (400 MHz, $CDCl_3$).

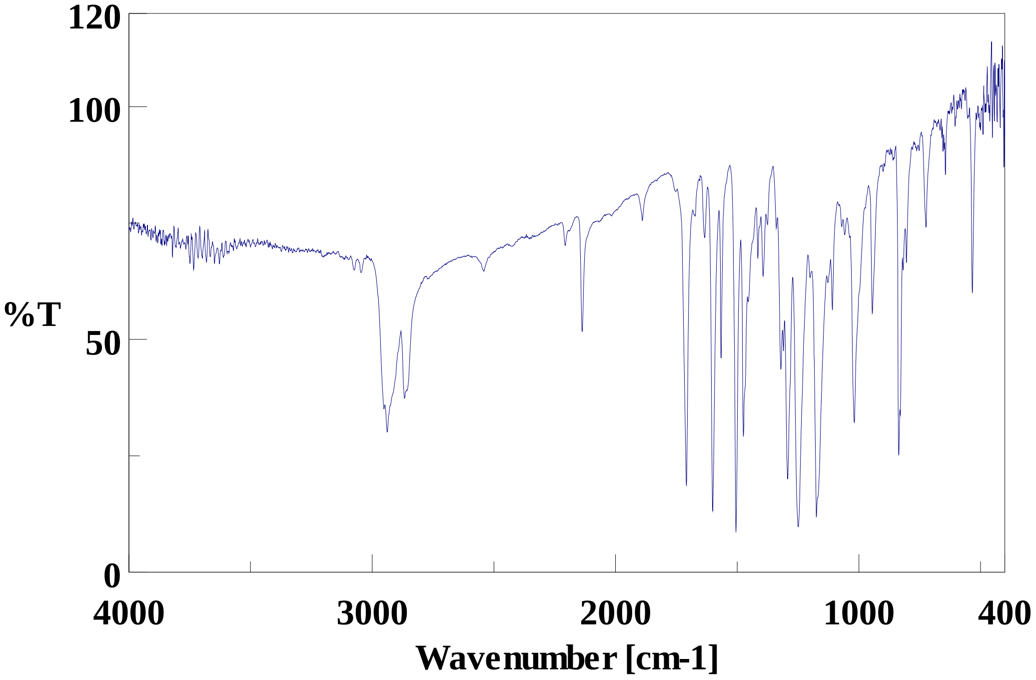

Fig. S3 FT-IR spectrum of monomer **8** (KBr).

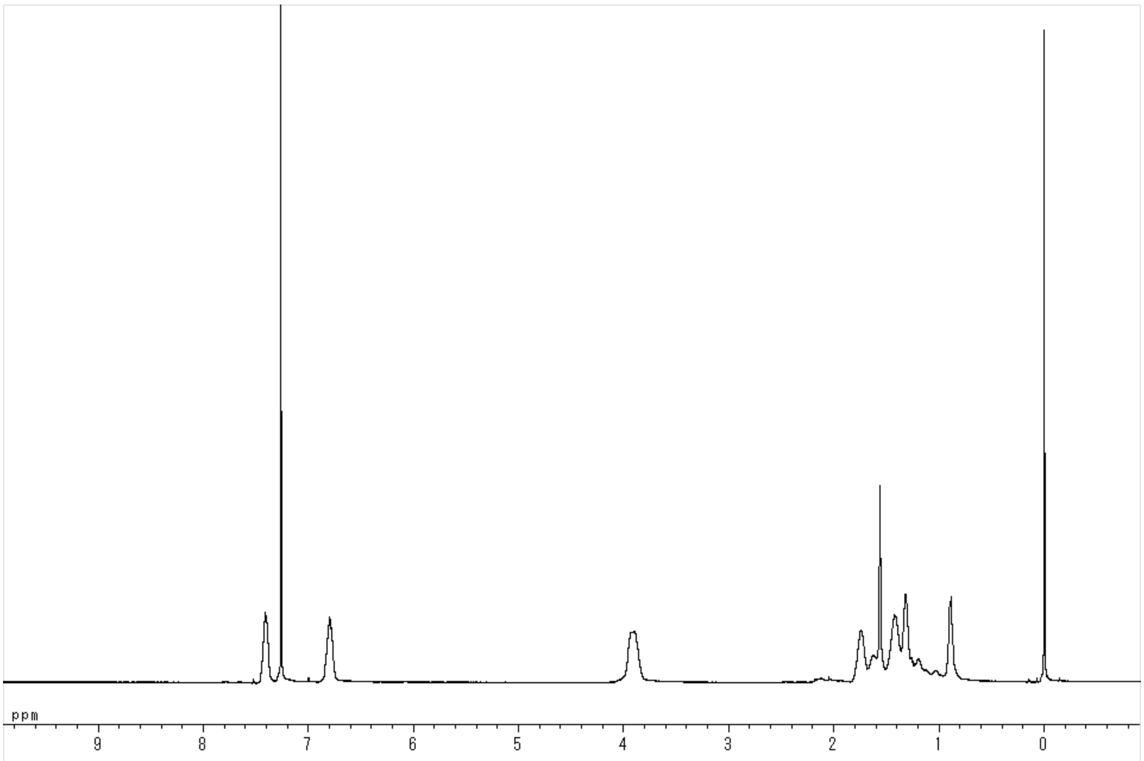

Fig. S4 ^{1}H NMR spectrum of SPM-DPDA-OC*6* (400 MHz, $CDCl_3$).

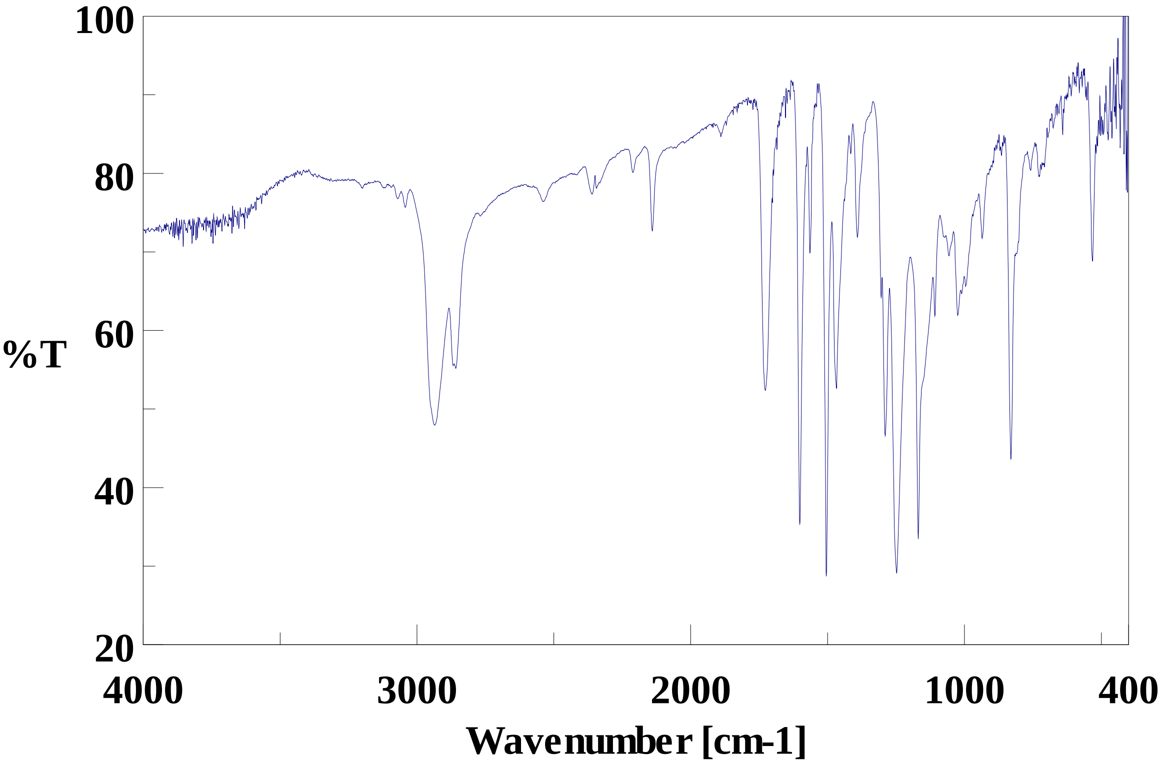

Fig. S5 FT-IR spectrum of SPM-DPDA-OC*6* (KBr).

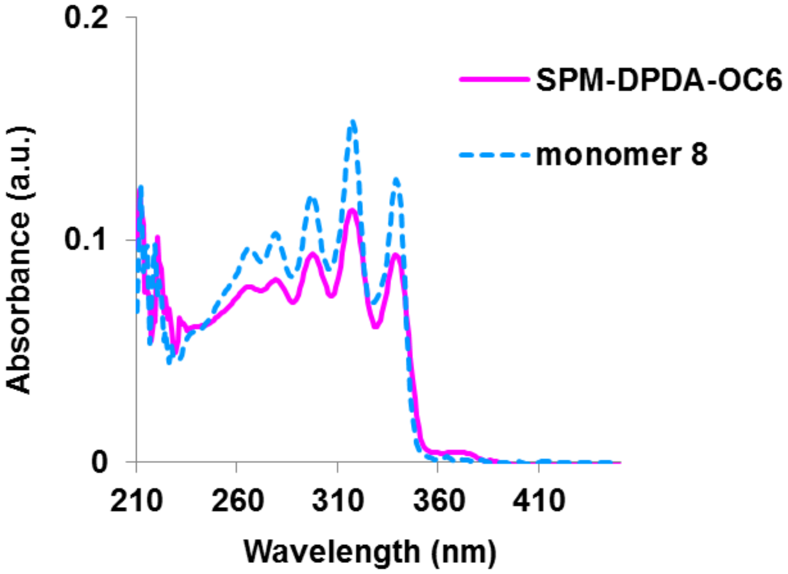

Fig. S6 UV-visible spectra of SPM-DPDA-OC*6* and monomer 8.

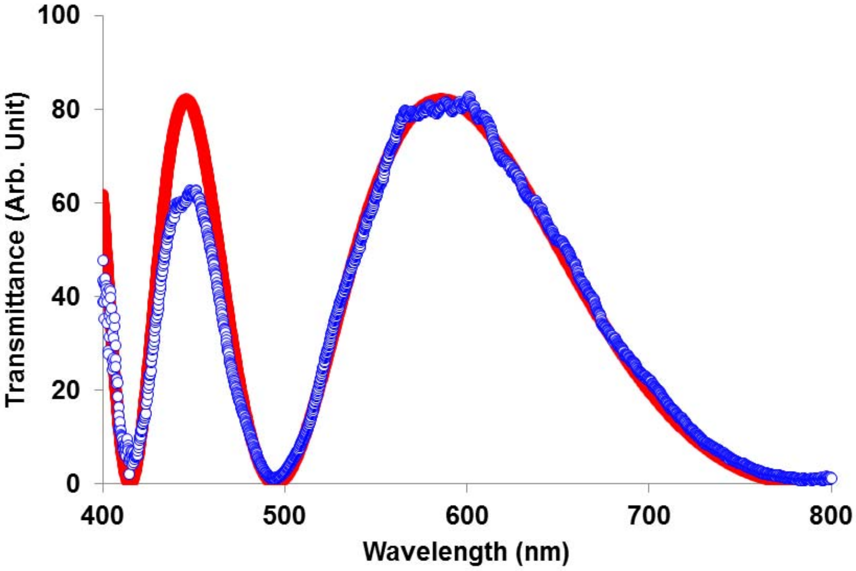

Fig. S7 Wavelength dependence of light intensity (open circles) transmitted of SPM-DPDA-OC*6* under cross polarization condition. And the solid curve is the fitting of equation (1).

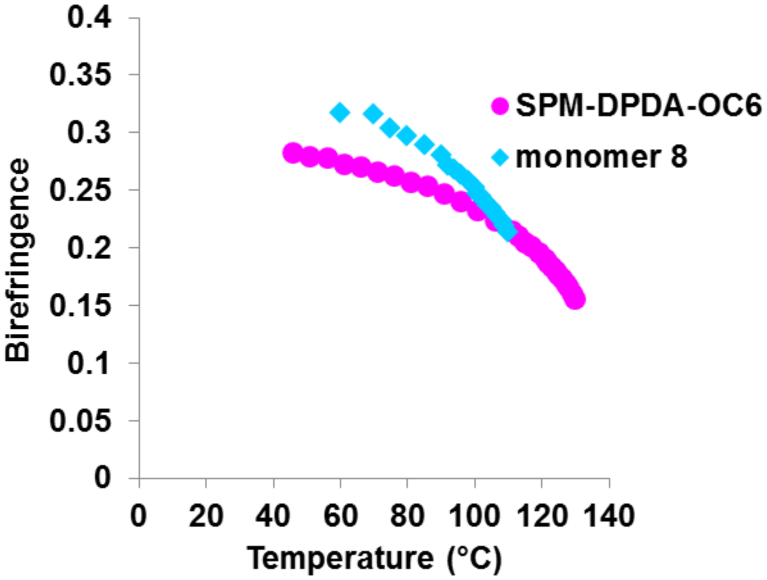

Fig. S8 Temperature dependence of birefringence measured at wavelength of 550 nm for SPM-DPDA-OC*6* and monomer 8.