

## Supplementary Information

### SI 1. Synthesis of p-Phenylene-di[4-(2,3-epoxypropyloxy) benzoate] (LCE1)

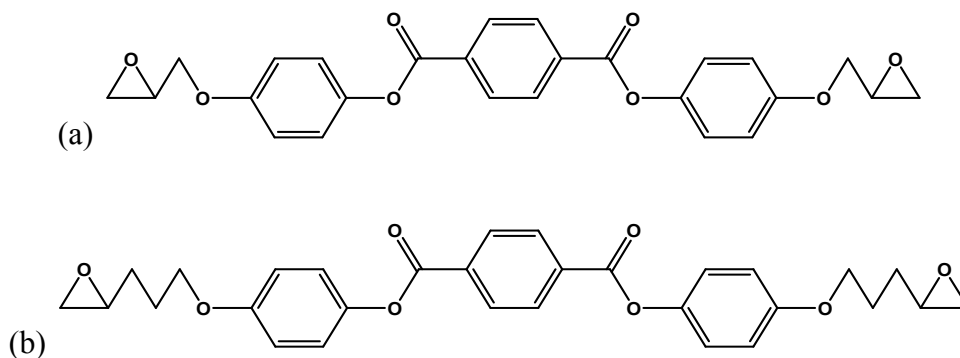
Synthetic scheme was reported by Jun Yeob Lee.[ Lee, J. Y.; Jang, J. S. *Polymer* 2006, 47, (9), 3036-3042.] A mixture of ethyl-4-hydroxybenzoate (0.6 mol, 99 g), 3-bromopropene (0.75mol, 90 g), K<sub>2</sub>CO<sub>3</sub> (0.9 mol, 126 g), and 800 ml of acetone were refluxed for 24 h. After the filtering off the solid, the solvent was evaporated away. Diethylether 400 mL and water 200 mL were poured into the remaining solution. The diethylether layer was separated and washed with 200 mL of a 10% NaOH solution three times. After evaporating away the diethylether, the residue was boiled in 900 mL of an ethanol/water (1:2) solution containing 90 g KOH until the solution was cleared. A 2N HCl solution was added to reach a pH of 2. After filtration, the solids were washed with excess water and recrystallized in ethanol to provide (4-(2-propyloxy) benzoic acid) as a white powder. A mixture of 4-(2-propyloxy) benzoic acid (0.11 mol, 21 g) and SOCl<sub>2</sub> (0.4 mol, 29 mL) was refluxed for 2 h. After evaporating excess SOCl<sub>2</sub>, 80 mL of pyridine were poured into the solution. Hydroquinone (0.55 mol, 6.3 g) was then added. The mixture was reacted in 1L of an acidified aqueous solution, filtered and washed with 500 mL of a 5% Na<sub>2</sub>CO<sub>3</sub> aqueous solution and 500 mL of water. After drying, the solid product (LCE1) was recrystallized in ethyl acetate. LCE1 was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent solvent. After evaporating away the solvent, the LCE1 product was recrystallized in ethyl acetate. The yield was 55%. <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>): δ (ppm) 8.13 (4H, d), 7.23 (4H, s), 6.99 (4H, d), 4.33 (2H, dd, CH<sub>2</sub> of glycidyl), 4.02 (2H, dd, CH<sub>2</sub> of glycidyl), 3.38 (2H, s, CH of epoxy), 2.92 (2H, dd, CH of epoxy), 2.78 (2H, dd, CH of epoxy).

LCE1 was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent solvent. After evaporation of solvent, the LCE1 product recrystallized in CH<sub>2</sub>Cl<sub>2</sub>. Transition temperatures are

following. Crystal to nematic : 182°C, nematic to isotropic : 233°C. Yield: 55%. H-NMR spectrum (CDCl<sub>3</sub>): δ (ppm) 8.13 (4H, d), 7.23 (4H, s), 6.99 (4H, d), 4.33 (2H, dd, CH<sub>2</sub> of glycidyl), 4.02 (2H, dd, CH<sub>2</sub> of glycidyl), 3.38 (2H, s, CH of epoxy), 2.92 (2H, dd, CH of epoxy), 2.78 (2H, dd, CH of epoxy).

## SI 2. Synthesis of p-Phenylene-di[4-(4,5-epoxypentyloxy) benzoate] (LCE3)

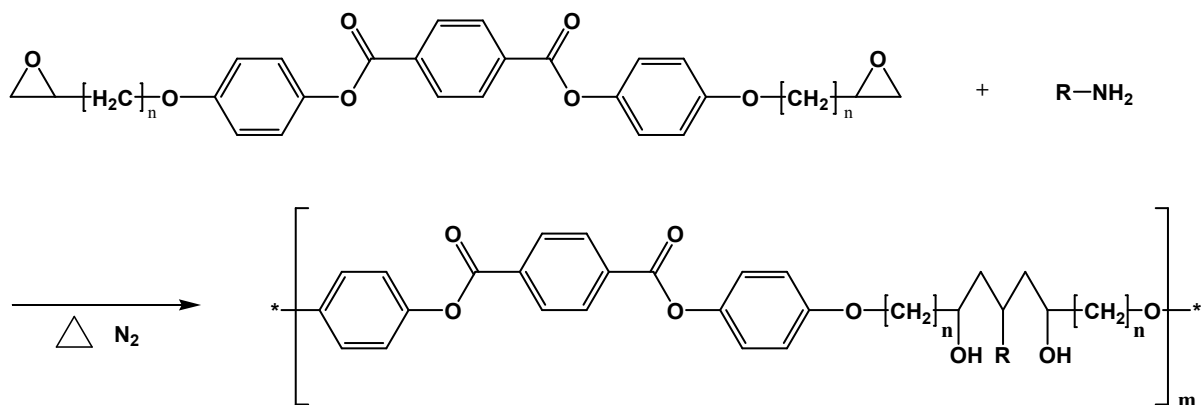
Synthetic scheme was as same as LCE1, expect using 5-bromopentene instead of 3-bromopropene. Transition temperatures are following. Crystal to smectic : 110°C, smectic to nematic : 139°C, nematic to isotropic : 235°C. Yield: 69%. H-NMR spectrum (CDCl<sub>3</sub>): δ (ppm) 8.12 (4H, d), 7.24 (4H, s), 6.96 (4H, d), 4.11 (4H, m, CH<sub>2</sub> of glycidyl), 3.01 (2H, m, CH of epoxy), 2.78 (2H, m, CH of epoxy), 2.51 (2H, m, CH of epoxy), 2.01 (4H, m, CH<sub>2</sub> of glycidyl), 1.85 (2H, m, CH<sub>2</sub> of glycidyl), 1.67 (2H, m, CH<sub>2</sub> of glycidyl).



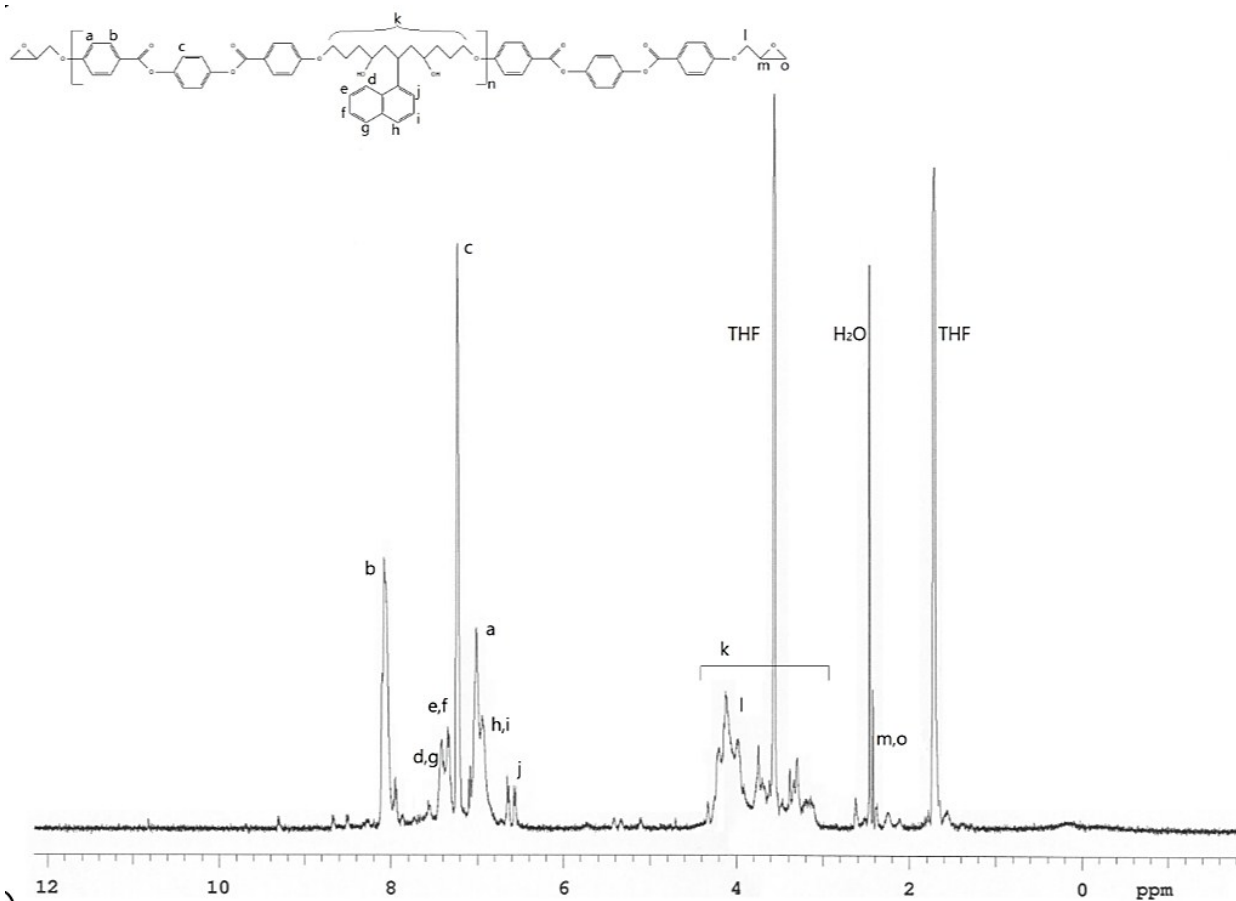
SI Figure 1 Chemical structure of LCE1 (a) and LCE3 (b).

## SI 3. Polymerization and NMR spectrum of PDEA3

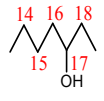
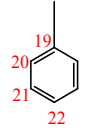
Diepoxide (LCE1 and LCE3) and the primary monoamine (aniline) were fed into round flask with magnetic stirrer and condenser; the mol ratio of LCE : amine was 1 : 1. LCE/amine LCP was polymerized at 250°C, 30 min in nitrogen atmosphere.



where R is phenyl.



**SI Table 1**  $^{13}\text{C}$ -NMR spectra of PDEA3 ( $\delta$  in ppm).

LCP	PDEA3		
C atom	R		
			
14	68.6	1	164.7
15	24.5	2	116.1
16	31.2	3	132.7
17	68.0	4	123.7
18	66.2	5	165.3
19	149.2	6	150.1
20	113.1	7	123.8
21	128.9	8	70.5
22	117.0	9	51.2
		10	45.3

