

## Supporting Information

# Design and Investigation of a Side-Chain Liquid Crystalline Polysiloxane with a N<sub>tb</sub>-Phase-Forming Side Chain

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### S1. Yield calculation on polymers

#### PCN

The siloxane unit is the repeating unit of the polymer backbone, at 60.1 g/mol in molecular weight. Therefore, 0.228 g of polymer backbone which, except for the end groups, consists of the repeating units of the siloxane unit. It can be assumed that the molar amounts were:

$$\frac{0.228 \text{ g}}{60.1 \text{ g/mol}} = 3.8 \times 10^{-3} \text{ mol}$$

The molecular weight of repeating units of siloxane unit which contains 4'-(pent-4-en-1-yloxy)-[1,1'-biphenyl]-4-carbonitrile is 323.1 g/mol. The isolated yield of the polymer **PCN** can be calculated as:

$$\frac{0.25 \text{ g}}{\frac{323.1 \text{ g/mol}}{3.8 \times 10^{-3} \text{ mol}}} = 20.4 \%$$

#### HP1

The siloxane unit is the repeating unit of the polymer backbone, at 60.1 g/mol in molecular weight. Therefore, 0.01g of polymer backbone which, except for the end groups, consists of the repeating units of the siloxane unit. It can be assumed that the molar amounts were:

$$\frac{0.01 \text{ g}}{60.1 \text{ g/mol}} = 0.166 \times 10^{-3} \text{ mol}$$

The molecular weight of repeating units of the siloxane unit which contains monomer 1 is 730.4 g/mol. The isolated yield of the **HP1** can be calculated as:

$$\frac{0.031 \text{ g}}{\frac{730.4 \text{ g/mol}}{0.166 \times 10^{-3} \text{ mol}}} = 25.6 \%$$

#### CoP1

The calculation on the actual molar ratio of the monomers for the reaction is based on <sup>1</sup>HNMR results:

The signal with the chemical shift at δ 3.86 ppm belongs to the -CH<sub>2</sub>-O group, integration of which is 4. While the chemical shift above 6.5 ppm is associated with the phenyl ring protons, integration of which is 28. Assuming that there is x mol of 4'-(pent-4-en-1-yloxy)-[1,1'-biphenyl]-4-carbonitrile, and y mol of **M1**. The calculation of each group of protons can be performed by integration of the <sup>1</sup>HNMR signals.

$$\begin{cases} 2x + 2y = 4 \\ 8x + 18y = 28 \end{cases} \rightarrow \begin{cases} x = 0.8 \\ y = 1.2 \end{cases}$$

Therefore, the actual mol ratio is (**M1**: **MCN**=1.2:0.8).

The siloxane unit is the repeating units of the polymer backbone, with a molecular weight of 60.1 g/mol. Therefore, 0.051g of poly(methylhydrosiloxane) consists of almost all the repeating units of siloxane backbone, and it can be assumed that the molar amount will be.

$$\frac{0.051g}{60.1 g/mol} = 8.5 \times 10^{-4} mol$$

As the actual molar ratio of the monomers is (**M1**: **MCN**=1.2:0.8). The molecular weight of repeating units of siloxane unit which contains monomer 1 is 730.4 g/mol, whereas the compound containing monomer 4'-(pent-4-en-1-yloxy)-[1,1'-biphenyl]-4-carbonitrile is 323.13 g/mol.

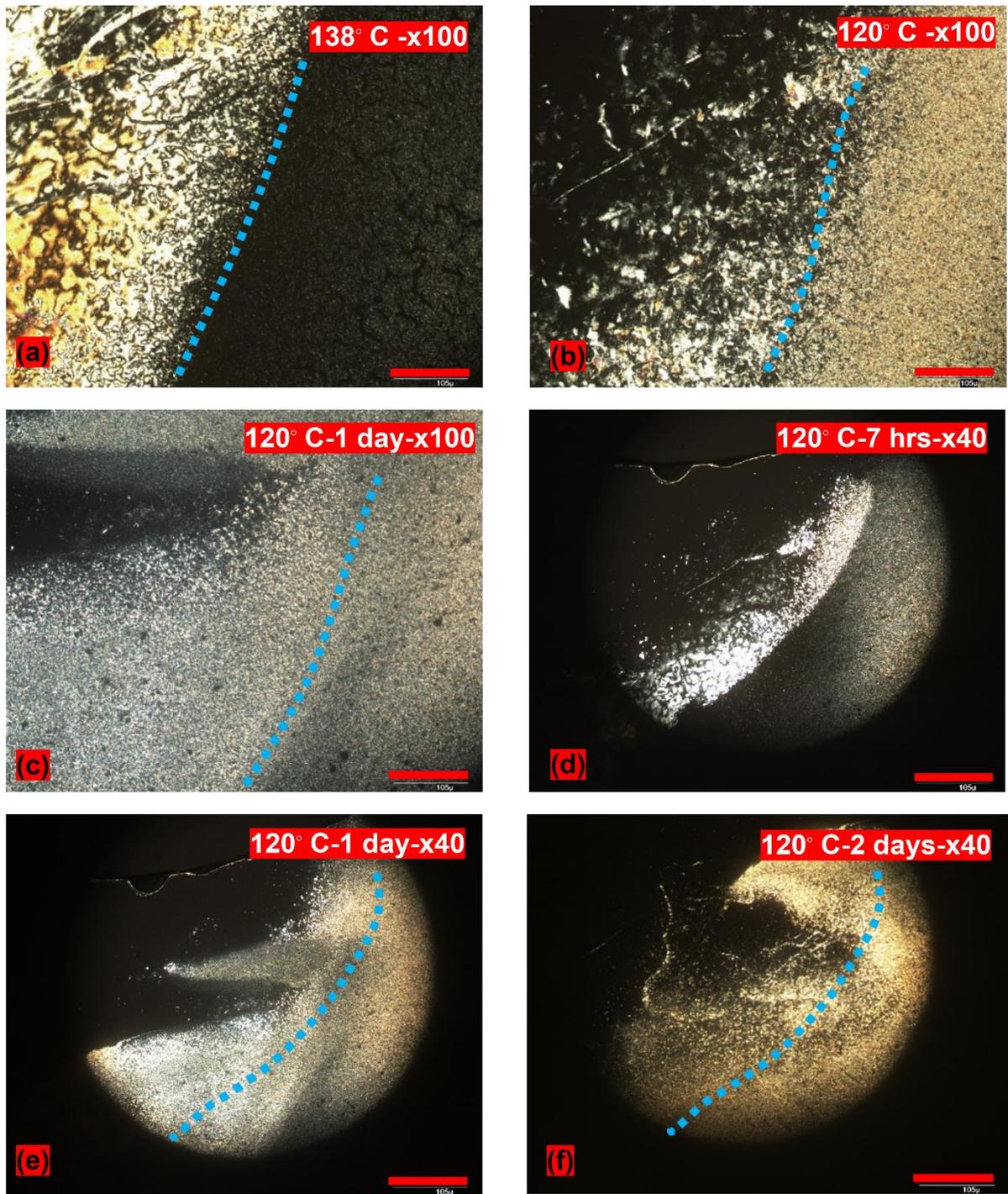
$$0.102g = 1.2 a \times 730.40 + 0.8 a \times 323.13$$

$$\text{Thus } a = 0.09 \times 10^{-3} mol,$$

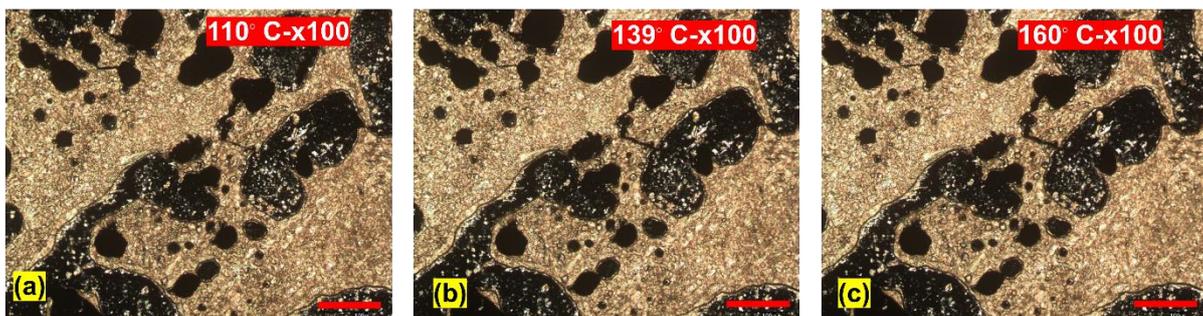
The isolated yield of the **CoP 1** can be calculated as:

$$\text{Isolated yield} = \frac{\text{actual yield}}{\text{theoretical yield}} = \frac{(1.2 a + 0.8 a) mmol}{0.85 mmol} = \frac{2 \times 0.09 mmol}{0.85 mmol} = 21.2 \%$$

## S2. OPM textures



**Figure S1.** Textures of the contact of **HP1** with **DTC5C7**, displayed by polarized optical microscopy. The scale bar is  $105\mu\text{m}$ , for magnification  $\times 100$ ; the scale bar is  $42\mu\text{m}$ , for magnification  $\times 40$ . On the left side of the slides, **DTC5C7** is located, on the right side of the slides, **HP1** is located, the blue dash line indicates the initial separation line of the binary mixtures (a) texture at  $138^\circ\text{C}$ , **DTC5C7** at nematic phase on the left side (b) texture at  $120^\circ\text{C}$ , **DTC5C7** in the  $N_b$  phase on the left-side (c) texture at  $120^\circ\text{C}$ , after annealing for 1 day, both sides gradually merge (d) textures at  $120^\circ\text{C}$ , after annealing for 7hrs, magnification as  $\times 40$  (e) texture at  $120^\circ\text{C}$ , after annealing for 1 day, where **DTC5C7** shows the  $N_b$  phase, magnification as  $\times 40$  (f) texture at  $120^\circ\text{C}$  after annealing for 2 days, magnification as  $\times 40$



**Figure S2.** Defec texture of homopolymer 1 (HP1), as by polarized optical microscopy. The scale bar is 105 $\mu$ m, for magnification  $\times$ 100. (a) at 110 °C (b) at 139 °C (c) at 160 °C.