

# Tuning the Gas Separation Performances of Smectic Liquid Crystalline Polymer Membranes by Molecular Engineering

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Synthesis of 4-(3-acryloyloxypropyloxy)phenyl 4-(4-(3-acryloyloxypropyloxy) benzo-  
yloxy)benzoate (**C3**). See Scheme 1 in the main text.

## Synthesis of 3-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenoxy)propan-1-ol (**3**)

5.4 g of sodium methanolate (0.1 mol) was added to a solution of 19.5 g 4-((tetrahydro-2H-pyran-2-yl)oxy)phenol (**1**), 0.1 mol) in 80 ml of butanone under nitrogen atmosphere with vigorously stirring. After a clear solution was obtained, 3 g of sodium iodide (0.02 mol) and 8.36 ml of 3-chloropropanol (0.1 mol) were added. The mixture was refluxed for 16 hours and then evaporated under vacuum. 100 ml of diethyl ether and 25 ml of water were added and after separation, the organic layer was extracted twice with 25 ml of an aqueous 10% sodium hydroxide and with 25 ml of brine. After drying over magnesium sulfate and evaporation, an oil was obtained that slowly crystallized. 15.6 g of product (**3**) (62% yield) was obtained as a solid after washing with 150 ml of ligroin and drying over silica in a vacuum desiccator. <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 6.98 (d, J = 9.0, 2H), 6.82 (d, J = 9.0, 2H), 5.29 (m, 1H), 4.10 (t, J = 6.1, 2H), 3.91 (m, 1H), 3.84 (t, J = 6.1, 2H), 3.60 (m, 1H), 2.05 (p, J = 6.1, 2H), 1.5–2.1 (m, 7H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 152.00, 151.20, 118.20\*, 115.67\*, 97.71\*, 66.85#, 62.49#, 61.05#, 32.44#, 30.88#, 25.65#, 19.32.

## Synthesis of 3-(4-hydroxyphenoxy)propyl acrylate (**5**)

6.0 ml of acryloyl chloride (74 mmol) was added slowly to a solution of 15.5 g of 3-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenoxy)propan-1-ol (**3**), 60 mmol), 9.3 ml of N,N-dimethylaniline (74 mmol) and 20 mg of 4,6-di-tert-butyl-4-methylphenol in 80 ml dichloromethane, stirred in an ice bath under a nitrogen atmosphere. After stirring for 4 hours at room temperature, the solution was subsequently extracted twice with 25 ml of water, 25 ml of an ice-cold aqueous 1N hydrochloric acid solution and 50 ml of brine. The crude intermediate (**4**) was obtained as an oil after drying over magnesium sulfate and evaporation. The crude product was suspended in 70 ml of ethanol that contained 2 g of pyridinium 4-toluenesulfonate (0.8 mmol) and refluxed for one hour. The product was precipitated by adding the cooled ethanolic solution to a mixture of 60 g of ice and 120 ml of water with vigorously stirring. 10 g of product (**5**) (74% yield) was obtained as a white solid after washing with 40 ml of water and drying over silica in a vacuum desiccator. <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 6.70 (m, 4H), 6.43 (dd, J = 17.3, 1.5, 1H), 6.14 (dd, J = 17.3, 10.4, 1H), 5.85 (dd, J = 10.4, 1.5, 1H), 4.84 (s, 1H), 4.38 (t, J = 6.1, 2H), 4.01 (t, J = 6.1, 2H), 2.13 (p, J = 6.1, 2H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 165.91, 153.20, 149.37, 131.31#, 128.75\*, 116.44#, 116.04#, 65.41#, 62.12#, 29.12#.

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### Synthesis of 4-(3-(acryloyloxy)propoxy)phenyl 4-hydroxybenzoate (**8**)

9.3 g of N,N'-dicyclohexylcarbodiimide (44 mmol) was added in small portions to a mixture of 9.8 g of 3-(4-hydroxyphenoxy)propyl acrylate ((**5**), 44 mmol), 9.8 g 4-((tetrahydro-2H-pyran-2-yl)oxy)benzoic acid ((**6**), 44 mmol), 0.54 g of N,N'-4-dimethylaminopyridine (4.4 mmol) and 150 ml of dichloromethane stirred in an ice bath under a nitrogen atmosphere. After stirring for 16 hours at room temperature, the solvent was evaporated after filtration over a thin layer of silica. Intermediate (**7**) was obtained as a solid after crystallization from 100 ml of ethanol. The crude intermediate was suspended in 100 ml of ethanol that contained 1.4 g of pyridinium 4-toluenesulfonate (0.8 mmol) and refluxed for two hours. The product was precipitated by adding the cooled ethanolic solution to a mixture of 45 g of ice and 90 ml of water with vigorously stirring. 13.3 g of product (**8**) (88% yield) was obtained as a white solid after washing with 40 ml of water and drying over silica in a vacuum desiccator. <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 8.12 (d, J = 9.1, 2H), 7.11 (d, J = 9.0, 2H), 6.97 (d, J = 8.9, 2H), 6.91 (d, J = 9.1, 2H), 6.43 (dd, J = 17.3, 1.5, 1H), 6.13 (dd, J = 17.3, 10.4, 1H), 5.90 (s, 1H), 5.86 (dd, J = 10.4, 1.5, 1H), 4.38 (t, J = 6.1, 2H), 4.08 (t, J = 6.1, 2H), 2.15 (p, J = 6.1, 2H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 164.95, 164.01, 163.95, 156.52, 142.24, 132.94\*, 131.31#, 128.75\*, 122.33, 122.95\*, 115.78#, 115.53#, 65.10#, 61.08#, 29.04#.

### Synthesis of 4-(3-(acryloyloxypropoxy)phenyl 4-(4-(3-(acryloyloxypropoxy)benzyloxy)benzoate (**C3**))

2.1 g of N,N'-dicyclohexylcarbodiimide (10 mmol) was added in small portions to a mixture of 3.4 g 4-(3-(acryloyloxy)propoxy)phenyl 4-hydroxybenzoate ((**8**), 10 mmol), 2.5 g 4-(3-(acryloyloxy)propoxy)benzoic acid ((**9**), 10 mmol), 0.12 g of N,N'-4-dimethylaminopyridine (1.0 mmol) and 30 ml of dichloromethane stirred in an ice bath under a nitrogen atmosphere. After stirring for 16 hours at room temperature, the solvent was evaporated after filtration over a thin layer of silica. 4.1 g of the final product (**C3**) was obtained as a white solid (71% yield) after crystallization from 50 ml of ethanol that contained 10 mg of 4-methoxyphenol. <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 8.27 (d, J = 8.7, 2H), 8.16 (d, J = 9.1, 2H), 7.36 (d, J = 8.7, 2H), 7.13 (d, J = 9.0, 2H), 7.00 (d, J = 8.9, 2H), 6.94 (d, J = 9.1, 2H), 6.45 (dd, J = 17.3, 1.5, 1H), 6.40 (dd, J = 17.3, 1.5, 1H), 6.15 (dd, J = 17.3, 10.4, 1H), 6.13 (dd, J = 17.3, 10.4, 1H), 5.85 (dd, J = 10.4, 1.5, 1H), 5.84 (dd, J = 10.4, 1.5, 1H), 4.39 (t, J = 6.1, 2H), 4.38 (t, J = 6.1, 2H), 4.17 (t, J = 6.1, 2H), 4.08 (t, J = 6.1, 2H), 2.22 (p, J = 6.2, 2H), 2.18 (p, J = 6.2, 2H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 166.29, 166.25, 164.94, 164.38, 163.47, 156.67, 155.38, 144.59, 132.58\*, 131.89\*, 131.15\*, 131.00\*, 128.48#, 128.38#, 127.15, 122.60\*, 122.17\*, 121.53, 115.29\*, 114.54\*, 64.89#, 64.86#, 61.45#, 61.27#, 28.79#, 28.65#. HRMS (MALDI-TOF): [M + Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>30</sub>O<sub>10</sub>Na: 597.17; found: 597.16.

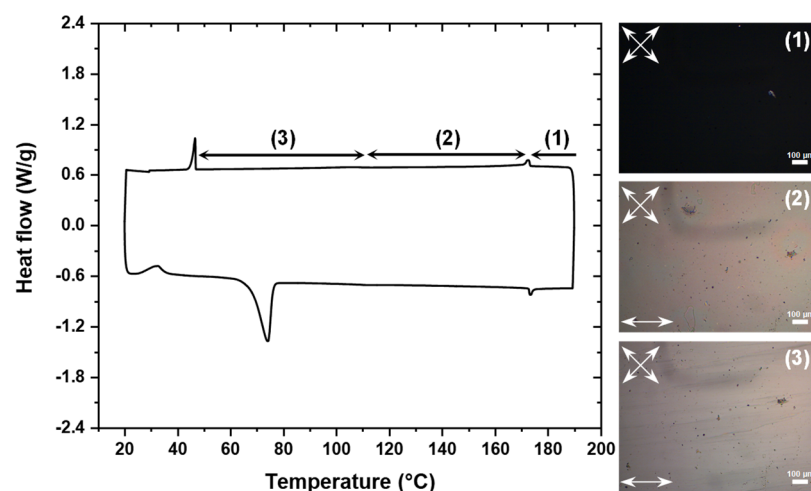
### Synthesis of 2,3-dichloro-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (**C6-Cl<sub>2</sub>**). See Scheme 2 in the main text.

2.6 ml of thionyl chloride (36 mmol) was added dropwise via syringe to a solution of 0.1 ml of N,N-dimethylformamide and 7 g of 4-(6-(acryloyloxyhexyloxy)benzoic acid ((**10**), 24 mmol) in 50 ml diethyl ether cooled in an ice bath and nitrogen was bubbled through the solution. After stirring for one hour at room temperature, 10 g of ice and 10 ml of water were added. The organic layer with the crude intermediate acid chloride (**11**) was extracted with 25 ml of brine and dried over MgSO<sub>4</sub>. The crude product was dissolved in 60 ml of dichloromethane followed by 4.2 ml of triethylamine (30 mmol). 1.8 g of 2,3-dichlorohydroquinone (**12a**), 10 mmol) was added in portions while the solution was under nitrogen and cooled in an ice bath. After stirring for 48 hours at room temperature, 60 g of ice was added, and the pH was adjusted with concentrated aqueous hydrochloric acid until pH=1. The product was obtained by extracting the organic layer with 60 ml of brine, dried over MgSO<sub>4</sub>, filtered over a thin layer of silica and the dichloromethane was

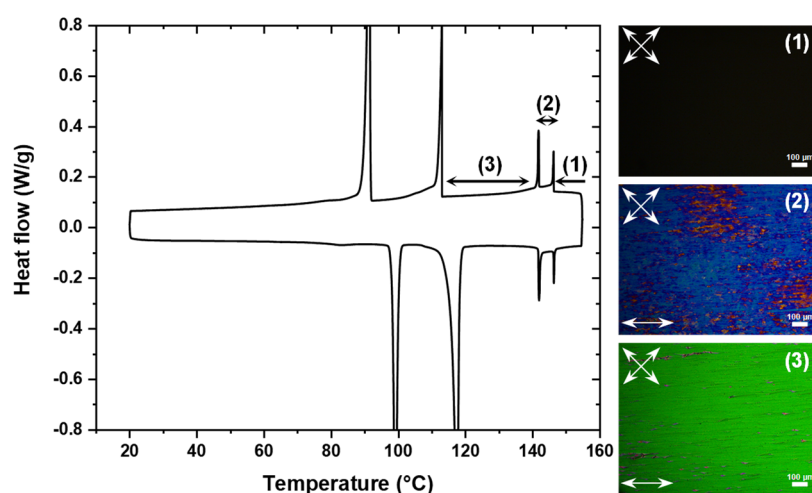
subsequently evaporated. 3.4 g of product **C6-Cl<sub>2</sub>** was obtained as a white solid (47% yield) after crystallization from 35 ml of ethyl acetate that contained 5 mg of 4-methoxyphenol. <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 8.18 (d, J = 9.0, 4H), 7.28 (s, 2H), 6.99 (d, J = 9.0, 4H), 6.41 (dd, J = 17.3, 1.5, 2H), 6.13 (dd, J = 17.3, 10.4, 2H), 5.82 (dd, J = 10.4, 1.5, 2H), 4.19 (t, J = 6.6, 4H), 4.06 (t, J = 6.4, 4H), 1.85 (p, J = 6.7, 4H), 1.73 (p, J = 7.0, 4H), 1.4–1.6 (m, 8H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 166.45, 163.98, 163.81, 146.17, 132.77\*, 130.71\*, 128.70#, 127.81, 122.07\*, 120.64, 114.60\*, 68.29#, 64.60#, 29.11#, 28.70#, 25.87#, 25.84#. HRMS (MALDI-TOF): [M + Na]<sup>+</sup> calcd for C<sub>38</sub>H<sub>40</sub>Cl<sub>2</sub>O<sub>10</sub>Na: 749.19; found: 749.17.

Synthesis of 2-chloro-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (**C6-Cl<sub>1</sub>**). See Scheme 2 in the main text.

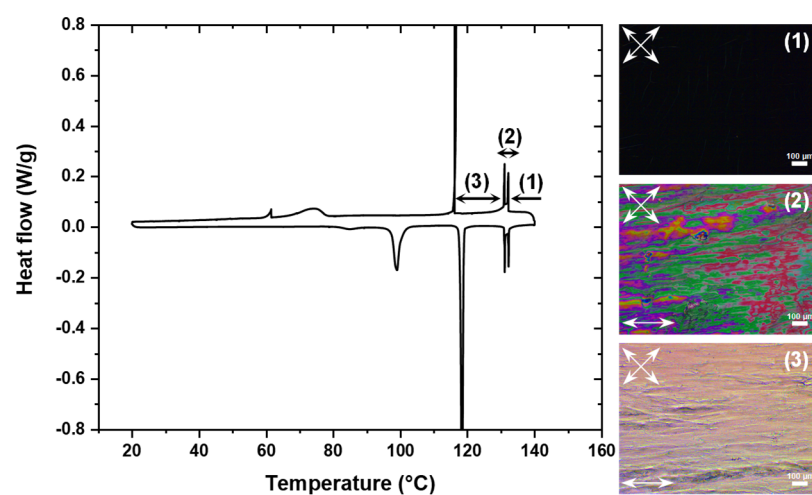
**C6-Cl<sub>1</sub>** was obtained with a yield of 60% in a similar way as described for the synthesis of 4-di-(4-(6-(acryloyloxy)hexyloxy)benzyloxy)-2,3-dichlorobenzene (**C6-Cl<sub>2</sub>**), but 2,3-dichlorohydroquinone (**12b**) was replaced by 2-chlorohydroquinone (**12a**). <sup>1</sup>H-NMR (400 MHz,  $\delta$  in ppm, J in Hz): 8.18 (d, J = 9.0, 2H), 8.13 (d, J = 9.0, 2H), 7.39 (d, J = 2.7, 1H), 7.32 (d, J = 8.8, 1H), 7.19 (dd, J = 8.8, 2.7, 1H), 6.98 (d, J = 9.0, 2H), 6.97 (d, J = 9.0, 2H), 6.41 (dd, J = 17.3, 1.5, 2H), 6.13 (dd, J = 17.3, 10.4, 2H), 5.82 (dd, J = 10.4, 1.5, 2H), 4.19 (t, J = 6.6, 4H), 4.06 (t, J = 6.5, 4H), 1.85 (p, J = 6.7, 4H), 1.73 (p, J = 7.0, 4H), 1.4–1.6 (m, 8H). <sup>13</sup>C-NMR (101 MHz,  $\delta$  in ppm, \*: CH or CH<sub>3</sub>, #: CH<sub>2</sub>): 166.44, 164.56, 164.06, 163.84, 163.80, 148.81, 145.04, 132.69\*, 132.52\*, 130.70\*, 128.70#, 127.62, 124.35\*, 123.92\*, 121.31\*, 121.15, 120.94, 114.52\*, 68.26#, 64.60#, 29.11#, 28.69#, 25.86#, 25.84#. [M + Na]<sup>+</sup> calcd for C<sub>38</sub>H<sub>41</sub>ClO<sub>10</sub>Na: 715.23; found: 715.22.



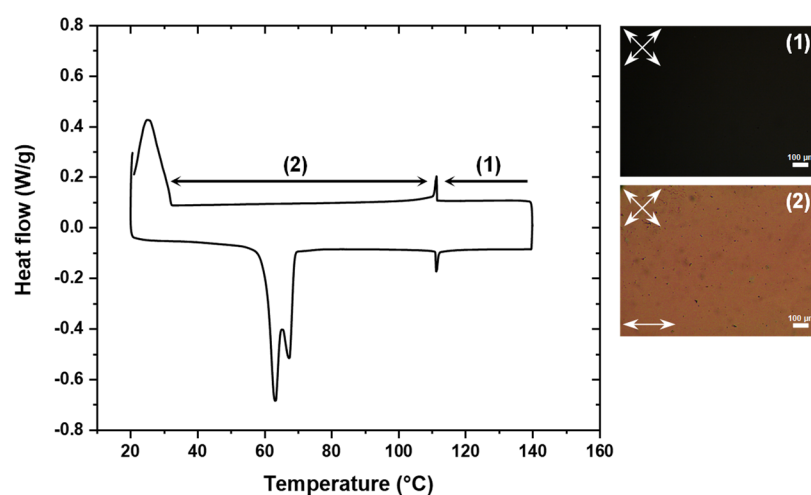
**Figure S1.** DSC measurement and POM images of **C3**, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



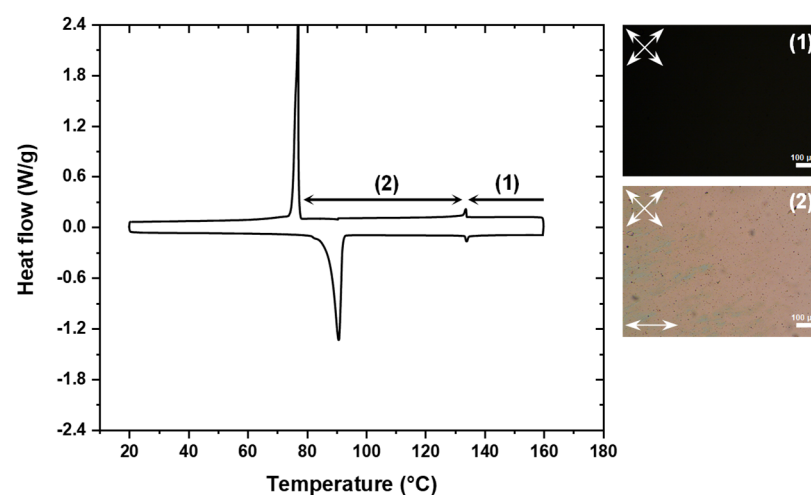
**Figure S2.** DSC measurement and POM images of C6, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



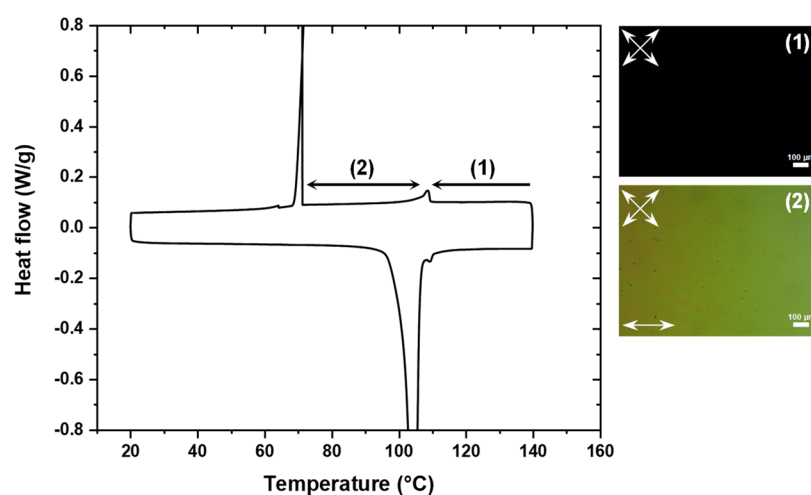
**Figure S3.** DSC measurement and POM images of C11, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



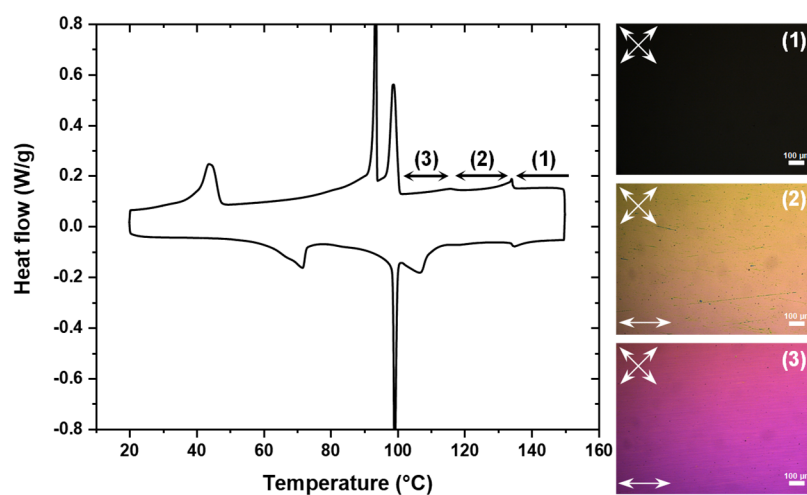
**Figure S4.** DSC measurement and POM images of **C6-Cl<sub>1</sub>**, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1) and nematic (2) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



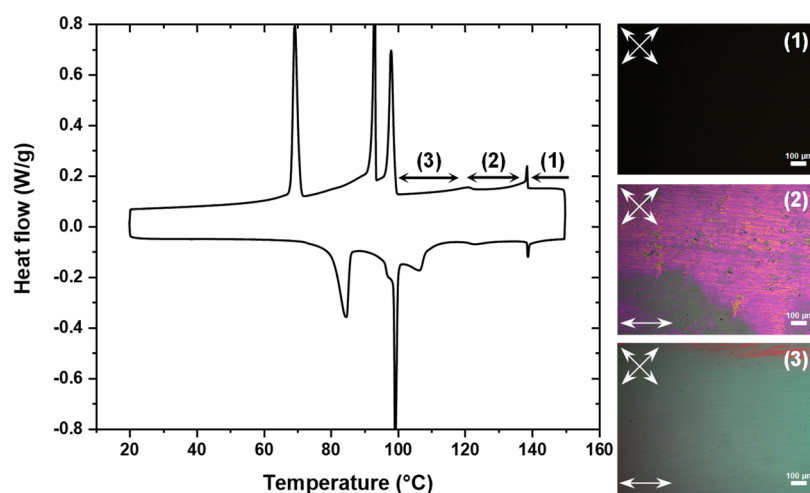
**Figure S5.** DSC measurement and POM images of **C6-Cl<sub>2</sub>**, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1) and nematic (2) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



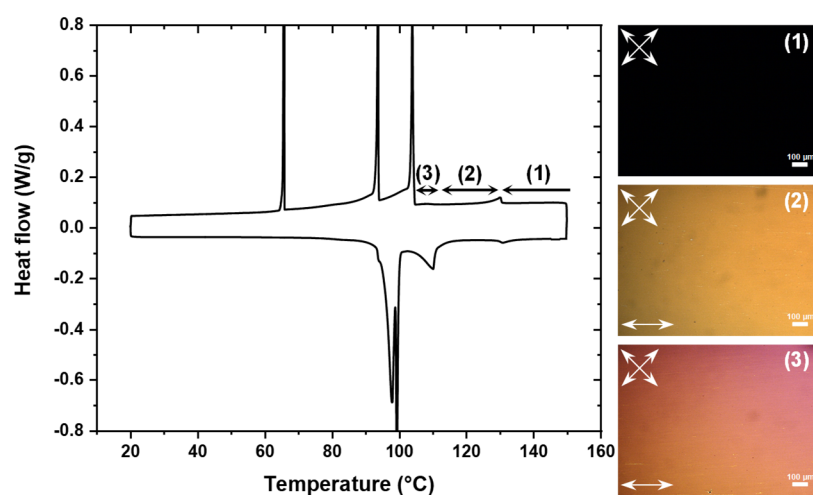
**Figure S6.** DSC measurement and POM images of C6-F<sub>4</sub>, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1) and nematic (2) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.



**Figure S7.** DSC measurement and POM images of a LC mixture consisting of a 7:3 ratio (in wt%) between C6 and C6-Cl, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

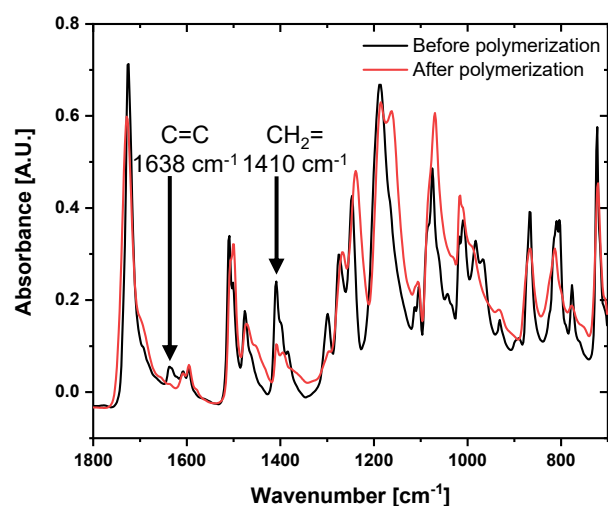


**Figure S8.** DSC measurement and POM images of a LC consisting of a 7:3 ratio (in wt%) between C6 and C6-Cl<sub>2</sub>, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

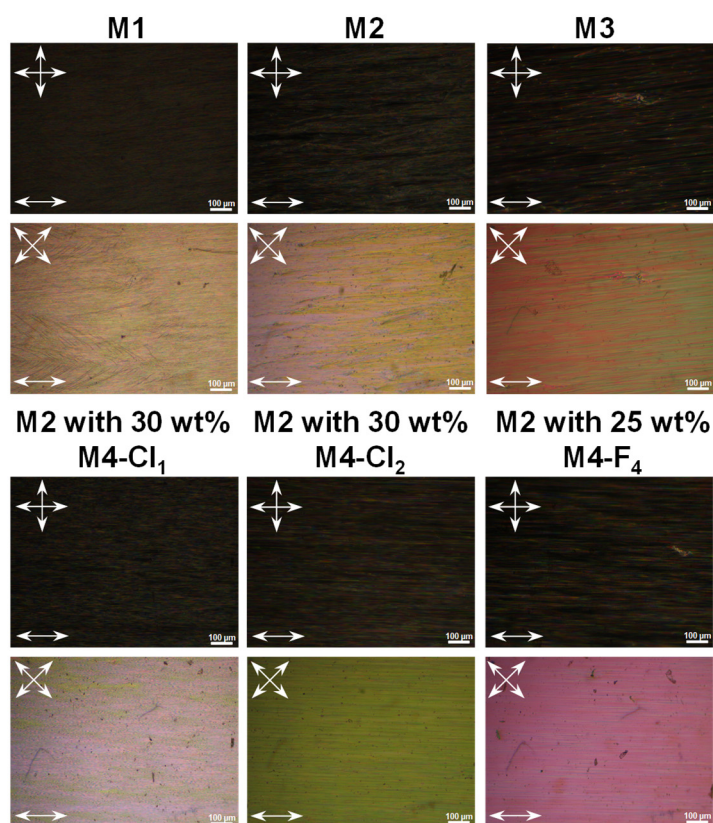


**Figure S9.** DSC measurement and POM images of a LC consisting of a 3:1 ratio (in wt%) between C6 and C6-F<sub>4</sub>, a photoinitiator and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2) and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.





**Figure S10.** FT-IR analysis of C6 before and after polymerization. All other LCs show similar graphs before and after polymerization.



**Figure S11.** POM images of the polymerized LC membranes. POM images show different birefringence caused by molecular order and orientation. The single arrow represents the alignment direction. The axes of the crossed polarizers are represented by the crossed arrows.



**Table S1.** Phase transition values of the used LC mixtures.

Compound/ Mixtures	Isotropic [°C]	Nematic [°C]	Smectic C [°C]
C3	>174	174-113	113-48
C6	>146	146-142	142-113
C11	>132	132-131	131-116
C6 with 30 wt% C6-Cl <sub>1</sub>	>134	134-115	115-101
C6 with 30 wt% C6-Cl <sub>2</sub>	>139	139-122	122-100
C6 with 25 wt% C6-F <sub>4</sub>	>131	131-110	110-105

**Table S2.** Permeabilities (He, CO<sub>2</sub> and N<sub>2</sub>) of smectic LC membranes with various layer spacings at 40 °C.

Permeability in Barrer [(cm <sup>3</sup> *cm)/(cm <sup>2</sup> *s*cmHg)] at 40 °C			
Gas	C3	C6	C11
He	1.23 ± 0.01	1.80 ± 0.01	2.52 ± 0.05
CO <sub>2</sub>	0.22 ± 0.01	0.41 ± 0.01	0.86 ± 0.02
N <sub>2</sub>	0.020 ± 0.001	0.031 ± 0.001	0.065 ± 0.004

**Table S3.** Ideal gas selectivities of smectic LC membranes with various layer spacings at 40 °C.

Ideal selectivity at 40 °C			
Gas pair	C3	C6	C11
He/N <sub>2</sub>	61.1 ± 0.1	58.4 ± 0.7	39.0 ± 2.3
CO <sub>2</sub> /N <sub>2</sub>	10.9 ± 0.1	13.1 ± 0.1	13.3 ± 0.8
He/CO <sub>2</sub>	5.6 ± 0.1	4.4 ± 0.1	2.9 ± 0.1

**Table S4.** The kinetic diameter, critical temperature and quadrupole moment of He, CO<sub>2</sub> and N<sub>2</sub>.

Gas species	Kinetic diameter [Å]	Critical temperature [K]	Quadrupole moment [cm <sup>2</sup> ] · 10 <sup>40</sup>
He	2.60	5.19	0.00
CO <sub>2</sub>	3.30	304.13	-13.71
N <sub>2</sub>	3.64	126.20	-4.91

**Table S5.** Permeabilities (He, CO<sub>2</sub> and N<sub>2</sub>) of smectic LC membranes with halogenated LCs at 40 °C.

Permeability in Barrer [(cm <sup>3</sup> *cm)/(cm <sup>2</sup> *s*cmHg)] at 40 °C				
Gas	C6	C6 with 30 wt% C6-Cl <sub>1</sub>	C6 with 30 wt% C6-Cl <sub>2</sub>	C6 with 25 wt% C6-F <sub>4</sub>
He	1.80 ± 0.01	1.79 ± 0.01	1.99 ± 0.03	2.12 ± 0.03
CO <sub>2</sub>	0.41 ± 0.01	0.47 ± 0.01	0.50 ± 0.01	0.60 ± 0.01
N <sub>2</sub>	0.031 ± 0.001	0.031 ± 0.001	0.032 ± 0.001	0.037 ± 0.001

**Table S6.** Ideal gas selectivities of smectic LC membranes with halogenated LCs at 40 °C.

Gas pair	Ideal selectivity at 40 °C			
	C6	C6 with 30 wt% C6-Cl <sub>1</sub>	C6 with 30 wt% C6-Cl <sub>2</sub>	C6 with 25 wt% C6-F <sub>4</sub>
He/N <sub>2</sub>	58.4 ± 0.7	57.2 ± 0.8	62.2 ± 2.0	58.2 ± 1.1
CO <sub>2</sub> /N <sub>2</sub>	13.1 ± 0.1	15.0 ± 0.1	15.5 ± 0.3	16.4 ± 0.2
He/CO <sub>2</sub>	4.4 ± 0.1	3.8 ± 0.1	4.0 ± 0.1	3.5 ± 0.1