Nanoporous Smectic LC Polymer Networks with an Adjustable Pore Interior Based on Dynamic Covalent Chemistry

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Materials
4-(6-hydroxyhexyloxy)benzaldehyde was kindly provided by Philips Research. 4-((6-(acryloyloxy)hexyl)oxy)-benzoic acid was obtained from SYNTHON Chemicals GmbH & Co. KG. Methacryloylchloride (97%), 4-(2-aminoethyl)aniline (97%), and 3-pentylamine (97%) were obtained from Sigma Aldrich. Triethylamine (TEA, 99%) was obtained from Acros. All Solvents used were Analytical Grade and obtained from Biosolve. Dry ethanol was prepared by storing it overnight over 3Å molecular sieves (activated in an oven at 600 °C). 1 M HCl (aq.) was freshly prepared from a 37% HCl solution obtained from Sigma Aldrich. All reagents were used as received, without further purification.

Characterizations
Magnetic nuclear resonance measurements were performed on a 400 MHz Agilent Technologies 400-MR NMR Spectrometer. Infrared spectroscopy was performed on a Varian 670 IR spectrometer equipped with a transmission microscopy setup over a range of 4000-650 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and 100 scans per spectrum. Polarized light microscopy was performed on a Leica CTR600 Optical microscope equipped with polarization filters. Linkam TMS 600 hot-stage was used for temperature controlled experiments. Differential scanning calorimetry was performed on a TA Instruments Q1000 calorimeter. The samples were heated and cooled with 5 °C min⁻¹ between -40 °C and 130 °C with an isothermal equilibration of 3 minutes after each heating or cooling ramp. X-ray diffraction experiments were performed on a SAXSLAB GANESHA 300 XL system. UV-Vis spectroscopy experiments were done using a Shimadzu UV-3102 spectrophotometer.

Synthesis
4-(6-methacryloxyhexyloxy)benzaldehyde
6.02 g (27.1 mmol) of 4-(6-hydroxyhexyloxy)benzaldehyde and 9.4 mL of trimethylamine (67.5mmol, 2.50 eq.) were dissolved in 60 mL of dichloromethane (DCM). Subsequently, the flask was placed in an ice bath to allow contents to cool down to 0 °C. 3.10mL (31.7 mmol, 1.17 eq.) of methacryloylchloride was added dropwise over a time span of 10 minutes. The reaction was allowed to continue for another hour where after the ice bath was removed. The reaction mixture was stirred for 4h at room temperature. The obtained mixture was washed twice with 60mL of 1 M HCl (aq) solution and subsequently once with 30 ml saturated NaCl solution. The product was dried over MgSO₄. The product was passed over a short-plug silica column (DCM) before the solvent was removed by rotary evaporation. Yield 6.28 g pale yellow liquid (21.63mmol, 80.1%).

1H NMR (400 MHz, CDCl₃): δ = 9.88 (s, 1H), 7.82 (d, J = 8.80 Hz, 2H), 6.98 (d, J = 8.72 Hz, 2H), 6.09 (s, 1H), 5.54 (s, 1H), 4.16 (t, J = 6.61 Hz, 2H), 4.04 (t, J = 6.41 Hz, 2H), 1.94 (s, 3H), 1.84 (m, 2H), 1.72 (m, 2H), 1.50 (m, 4H).

13C NMR (100 MHz, CDCl₃): δ = 190.74, 167.45, 164.13, 156.44, 131.94, 129.77, 125.20, 114.70, 68.16, 64.53, 28.92, 28.50, 25.72, 25.64, 18.30.

FTIR (ATR): 2940 (m), 2860 (m), 2735 (w), 1714 (s), 1688 (s), 1638 (w), 1600 (s), 1577 (s), 1577 (s), 1509 (m), 1470 (w), 1453 (w), 1430 (w), 1395 (w), 1315 (m), 1297 (m), 1254 (s), 1215 (m), 1156 (s), 1100 (m), 1011 (m), 858 (w), 835 (m), 814 (m), 735 (m), 702 (w).
4-(2-aminoethyl)aniline core diimine (1)

4.02 g (13.84 mmol) of 6-(4-formylphenoxy)hexylmethacrylate and 0.82 mL (6.23 mmol) of 4-(2-aminoethyl)aniline were dissolved in 25.5 mL of dry ethanol (3Å molecular sieves). A small amount of grinded molecular sieves was added to the mixture. The mixture was heated up to the boiling temperature and refluxed for 90 minutes. Subsequently, the mixture was slowly cooled down to room temperature. Whereafter it cooled down further to −20 °C. The crystals were filtrated and washed with dry and cold ethanol (−20°C). The residue was recrystallized twice from ethanol. Yield 3.15 g of off-white solid (4.63 mmol, 74.3%)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1H), 8.09 (s, 1H), 7.81 (d, $J = 8.6$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 2H), 6.09 (s, 2H), 5.54 (s, 2H), 4.16 (td, $J = 6.5$, 2.0 Hz, 4H), 4.00 (dt, $J = 12.7$, 6.4 Hz, 4H), 3.83 (t, $J = 7.3$ Hz, 2H), 3.00 (t, $J = 7.4$ Hz, 2H), 1.94 (s, 6H), 1.82 (h, $J = 6.7$ Hz, 4H), 1.76 – 1.05 (m, 4H), 1.57 – 1.40 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ = 167.49, 161.65, 161.07, 160.83, 159.13, 150.33, 137.49, 136.48, 130.38, 129.72, 129.56, 129.20, 129.00, 125.20, 120.81, 114.62, 114.45, 67.93, 67.85, 64.60, 63.16, 37.17, 29.08, 28.55, 25.79, 25.72, 18.33.

IR (ATR) 2939 (m), 2867 (w), 1710 (m), 1640 (w), 1623 (w), 1605 (m), 1571 (m), 1510 (m), 1474 (w), 1460 (w), 1426 (w), 1419 (w), 1375 (w), 1323 (m), 1302 (m), 1242 (s), 1163 (s), 1109 (m), 1074 (w), 1048 (w), 1013 (m), 975 (w), 959 (w), 937 (m), 886 (w), 832 (m), 816 (m), 801 (m), 729 (w).
Ethane-1,2-diylbis(4,1-phenylene) bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (2)

$^1$H NMR (399 MHz, Chloroform-$d$) δ 8.14 (d, $J = 8.9$ Hz, 4H), 7.23 (d, $J = 8.6$ Hz, 4H), 7.12 (d, $J = 8.5$ Hz, 4H), 6.96 (d, $J = 8.9$ Hz, 4H), 6.41 (dd, $J = 17.3, 1.5$ Hz, 2H), 6.13 (dd, $J = 17.3, 10.4$ Hz, 2H), 5.82 (dd, $J = 10.4, 1.5$ Hz, 2H), 4.18 (t, $J = 6.6$ Hz, 4H), 4.05 (t, $J = 6.4$ Hz, 4H), 2.95 (s, 4H), 1.84 (p, $J = 6.5$ Hz, 4H), 1.73 (p, $J = 6.8$ Hz, 4H), 1.57 - 1.44 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ = 166.32, 165.06, 163.37, 149.26, 138.99, 132.26, 130.58, 129.40, 128.57, 121.76, 121.61, 114.25, 68.07, 64.48, 37.35, 29.01, 28.56, 25.74, 25.72.
Methods

Preparation of LC Cells.
30x30 mm glass slides were first wiped clean using ethanol, sonicated in ethanol for 20 minutes where after they were exposed 20 minutes to a UV-Ozone treatment. A thin layer of polyimide was applied to the glass slides by spincoating. The coated glass slides were precured at 90 °C for 10 minutes where after they were cured at 180°C for half an hour. After curing, the glass plates were rubbed using a velvet cloth to induce a homogeneous alignment direction. Subsequently the glass slides were glued together using a photopolymerizable glue containing 18 μm beads to obtain a well-defined spacing between the glass plates. The glass plates glued together with their rub-direction anti-parallel.

Preparation of LC Networks
A mixture containing 1 (bisimine) and 2 (cross-linker) in an 8:2 weight ratio was used to prepare liquid crystalline networks. 1 wt.% photo initiator (IRGACURE 819) and 0.5 wt.% inhibitor (TBHQ) was added to perform the photopolymerization. All compounds were dissolved in dichloromethane to obtain a homogeneous mixture. The dichloromethane was removed in vacuo after mixing. 18 μm thick films were prepared by capillary suction of LC-monomer mixture in the melt (125 °C) between two accurately spaced glass slides (LC cell). After filling of the cell, the mixture was cooled with 1 °C/min to 80 °C. Subsequently, the polymerization was performed by UV irradiation using a EXFO OmniCure® S2000 spot UV curing lamp for 900 seconds.

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\text{Absorbance (a.u.)}
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\text{Wavenumbers (cm}^{-1}\text{)}
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Figure S1. FTIR spectra of the monomer mixture (dashed) and the bisimine polymer network (solid). A clear reduction of intensity of vibration at 1640 (C=C str), and a disappearance of the bands at 1410 (=CH}_2 \text{ def. vib) and 1320 cm}_1 \text{ (=C-H rocking) was observed, indicating the conversion of methacrylate bonds. N.B. The vibration at 1640 cm}_1 \text{ is overlapping with the imine C=N str. vibration.}

Removal of the bisimine template: Formation of the aldehyde
After the preparation of the LC network films the films were removed from their cells and cut into squares of approximately 5x5 mm² and placed in a freshly prepared 0.5 M HCl in a 50 vol.% THF/water mixture. After approx. 20 hours at room temperature (r.t., 20 °C) the films were transferred to pure THF. The films were replaced into pure THF for at least two times to ensure that all diamine was removed from the polymer film.

Dimension changes of the material
Small rectangular pieces of approximately 2 mm² (with the edges along and perpendicular to the alignment) were cut from the pristine bisimine film. Their dimensions were measured by microscopy. Subsequently, the pieces were exposed to 0.5 M HCl in a 50 vol.% THF/water mixture. After approx. 20 hours at room temperature the pieces were washed with pure THF, dried, and remeasured by optical microscopy. 4 samples were measured and for each sample 2 sides parallel and 2 sides perpendicular to the alignment were measured. (given error in the manuscript is ±SD)
Preparation of imine interior membranes
An imine modified interior was prepared by immersing an aldehyde functional film to a 1 M amine solution containing 0.1 M acetic acid in THF and allowing it to react for approx. 20 hours at RT. Subsequently, the films were transferred to pure THF. The THF solution was replaced twice to remove remaining reactants.

Preparation of sec-amine interior membranes
The imines in the interior were reduced to sec-amines by the reduction using sodium triacetoxyborohydride. Imine modified membranes were directly transferred from the amine/acetic acid solution to a solution containing 0.05 M Na(AcO)$_3$BH / 0.075 M acetic acid in THF. After approx. 20 hours at RT the films were removed from the solution and transferred to pure THF. The THF was replaced at least two times to ensure all reagents were removed.

Figure S2. Azimuthal integration of the x-ray diffraction patterns of the pristine bisimine network and the aldehyde functional material.
Phase behavior of compound 1 (bisimine)

Figure S3. DSC thermogram of compound 1 (exo. down). In the cooling curve 4 transitions were observed. At 102 °C (I-SmA), 94 °C (SmA-SmC), 78 °C (SmC-SmX), and at -12 °C (SmX-Cr).

Figure S4. Polarized light microscopy images at various temperatures. a) I-SmA transition at 106 °C. b) SmA phase at 100 °C. c) SmA-SmC transition at 94 °C. d) SmC phase at 83 °C. e) SmX phase at 70 °C. f) The same SmX phase at 25 °C.
Phase behavior of 80 wt. % 1 (bisimine) + 20 wt. % 2 (cross-linker)

Figure S5. DSC thermogram of compound 1 (exo. down). In the cooling curve 5 transitions were observed. At 120 °C (I-N), 117 °C (N-SmA), 104 °C (SmA-SmC), 78 °C (SmC-SmX), and at -32 °C (SmX-Cr).

POM analysis

Figure S6. Polarized light microscopy images at various temperatures. a) N mesophase at 120 °C (while shearing). b) SmA phase at 115 °C. c) SmA-SmC transition at 105 °C. d) SmC phase at 90 °C. e) SmC-SmX phase transitions at 79 °C. f) SmX phase at 30 °C.
Preparation of aromatic imine interior membranes

Figure S6. Incorporation of aromatic amines. a) Chemical structures of 4-fluoroaniline (4FA) and 4-aminoazobenzene (4AAzo). b & c) Transmission FTIR spectra of the aldehyde functional network (short-dash line) and the 4FA and 4AAzo imine networks (solid line), respectively.

Binding affinity of amines
Aldehyde functional films were exposed to a solution containing 250 mM aliphatic amine, 250 mM aromatic amine, and 100 mM acetic acid. After approximately 20 hours, the films were removed from the solution, washed with THF, and dried. The obtained films were analyzed by transmission FTIR. In figure S7 one can see that that only the aliphatic amines were incorporated.

Figure S7. Incorporation of aromatic amines. a) Chemical structures of 4-fluoroaniline (4FA) and 4-aminoazobenzene (4AAzo). b & c) Transmission FTIR spectra of the aldehyde functional network (short-dash line) and the 4FA and 4AAzo imine networks (solid line), respectively.