Electronic Supplementary Information

Photopolymerization of Self-Organizing Ionic Liquids

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Experimental Procedures and Analytical Data

General Methods, Instrumentation and Characterization

A Zeiss Axioskop 40 Pol transmission and polarising microscope (or an Olympus BH2 polarising microscope) equipped with a colour digital camera, a Mettler FP82 hot stage, and a Mettler Toledo FP90 central processor was used to observe defect textures of the lyotropic liquid crystalline phases using the transmission mode of the microscope. For the microscopy studies thin preparations of samples sandwiched between untreated glass slides and cover slips in contact with water were used.

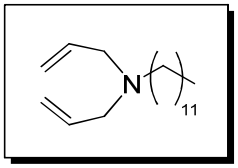
The structures of the compounds prepared were confirmed by spectroscopic methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX400 spectrometer using the signal of the deuterated solvent as lock and internal standard for chemical shift data in the δ-scale relative to TMS. Coupling constants are given in Hz.

Atmospheric Pressure Ionisation mass spectrometry was performed on a Thermo Quest LCQ instrument from Finnigan.

Infrared spectra were measured with a Shimadzu IRPrestige-21 Fourier Transformation Infrared Spectrometer at room temperature. Absorption bands are given in wave numbers (cm^{-1}).

General synthesis of compounds of type **2**[1]

The alkyl bromide was dissolved in acetonitrile and 1.5 equiv. diallylamine and 1 equiv. K_2CO_3 were added. The reaction was heated under reflux for 36 h. The suspension was filtered and the solvent removed by evaporation. Isolation of the product was carried out by column chromatography over silica gel using hexane:ethyl acetate 1:1 as the eluent.



N,*N*-Dially-*N*-dodecylamine (**2a**)

1-Bromododecane (5.00 g, 20.06 mmol), diallylamine (3.7 mL, 30.1 mmol, 1.5 equiv.), and K_2CO_3 (2.77 g, 20.06 mmol, 1 equiv.) in acetonitrile (300 mL) gave *N*,*N*-dially-*N*-dodecylamine (**2a**) (4.53 g, 17.05 mmol, 85 %) as a clear oil.

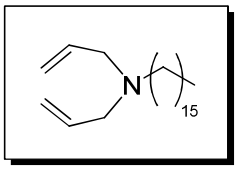
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3078, 2924, 2855, 2792, 1744, 1643, 1458, 1420, 1366, 1258, 1219, 1150, 1103, 1080, 995, 918, 718, 656, 617, 556;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (ddt, 2H, ^3J = 6.5 Hz, ^3J = 10.3 Hz, ^3J = 17.0 Hz; NCH_2-C<u>H</u>=CH_2), 5.20 – 5.10 (m, 4H; NCH_2-CH=C<u>H_2</u>), 3.11 – 3.06 (m, 4H; N<u>CH_2</u>-CH=CH_2), 2.43 – 2.38 (m, 2H; 1-H), 1.49 – 1.40 (m, 2H; 2-H), 1.35 – 1.21 (m, 18H; 3-H - 11-H), 0.88 (t, 3H, ^3J = 6.9 Hz; 12-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.85 (d; NCH_2-<u>C</u>H=CH_2), 117.24 (t; NCH_2-CH=<u>C</u>H_2), 56.84 (t; N<u>C</u>H_2-CH=CH_2), 53.38 (t; C-1), 31.91, 29.66, 29.63, 29.61, 29.60, 29.58, 29.34, 27.50, 26.87, 22.68 (10t; C-2 – C-11), 14.11 (q; C-12);

MS (positive ESI) m/z (%): 266.28 $[M+H]^+$;

HR-MS (positive ESI): Calcd. for $C_{18}H_{36}N$ $[M+H]^+$ m/z: 266.2842; Found 266.2840.



N,*N*-Dially-*N*-hexadecylamine (**2b**)

1-Bromohexadecane (5.00 g, 16.38 mmol), diallylamine (3.1 mL, 24.6 mmol, 1.5 equiv.), and K_2CO_3 (2.26 g, 16.38 mmol, 1 equiv.) in acetonitrile (300 mL) gave *N*,*N*-dially-*N*-hexadecylamine (**2b**) (4.72 g, 14.68 mmol, 90 %) as a clear oil.

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924, 2854, 2801, 1643, 1458, 995, 918, 632, 540;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (ddt, 2H, ^3J = 6.5 Hz, ^3J = 10.3 Hz, ^3J = 17.0 Hz; NCH_2-C<u>H</u>=CH_2), 5.20 – 5.10 (m, 4H; NCH_2-CH=C<u>H_2</u>), 3.11 – 3.06 (m, 4H; N<u>CH_2</u>-CH=CH_2), 2.43 – 2.38 (m, 2H; 1-H), 1.49 – 1.40 (m, 2H; 2-H), 1.31 – 1.21 (m, 26H; 3-H - 15-H), 0.88 (t, 3H, ^3J = 6.9 Hz; 16-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.70 (d; NCH_2-$\underline{C}H$=CH_2), 117.36 (t; NCH_2-CH=$\underline{C}H_2$), 56.81 (t; $N\underline{C}H_2$-CH=CH_2), 53.36 (t; C-1), 31.92, 29.70, 29.69, 29.69, 29.68, 29.66, 29.65, 29.62, 29.61, 29.58, 29.36, 27.49, 26.82, 22.69 (14t; C-2 – C-15), 14.12 (q; C-16);

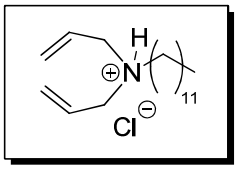
MS (EI) m/z (%): 322 (1) [M+H], 321 (2) [M], 320 (1), 294 (1), 292 (1), 280 (3), 278 (1), 252 (2), 250 (1), 236(1), 222 (1), 208 (1), 194 (1), 180 (1), 166 (1), 152 (1), 111 (10), 110 (100), 70 (6), 41 (10);

MS (positive ESI) m/z (%): 322.3 $[M+H]^+$;

HR-MS (positive ESI): Calcd. for $C_{22}H_{44}N$ $[M+H]^+$m/z: 322.3468; Found 322.3477.

General synthesis of compounds of type **3**

Compound **2** was dissolved in methanol and the acid (hydrochloric acid or hexafluorophosphoric acid) was added until a pH 1 was reached. The solvent was removed by evaporation and recrystallisation gave the desired product of type **3**.



N,*N*-Dially-*N*-dodecylammonium chloride (**3a**)

N,*N*-Dially-*N*-dodecylamine (**2a**) (0.69 g, 2.60 mmol) in methanol (10 mL) with hydrochloric acid (36 % in water) gave after recrystallisation from acetonitrile *N*,*N*-dially-*N*-dodecylammonium chloride (**3a**) (0.77 g, 2.55 mmol, 98 %) as a white solid.

m.p. 35.8 °C;

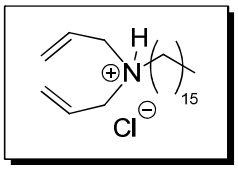
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2916, 2855, 2454, 2353, 1643, 1458, 1427, 1366, 1057, 995, 926, 725, 632;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.31 (bs, 1H), 6.10 (ddt, 2H, ^3J = 7.2 Hz, ^3J = 10.1 Hz, ^3J = 17.1 Hz; NCH_2-C$\underline{H}$=CH_2), 5.52 – 5.40 (m, 4H; NCH_2-CH=C$\underline{H_2}$), 3.61 – 3.55 (m, 4H; N$\underline{CH_2}$-CH=CH_2), 2.92 – 2.85 (m, 2H; 1-H), 1.82 – 1.73 (m, 2H; 2-H), 1.28 – 1.15 (m, 18H; 3-H - 11-H), 0.81 (t, 3H, ^3J = 6.8 Hz; 12-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.20 (t; NCH_2-CH=$\underline{C}H_2$), 125.45 (d; NCH_2-$\underline{C}H$=CH_2), 54.50 (t; $N\underline{C}H_2$-CH=CH_2), 51.18 (t; C-1), 31.71, 29.40, 29.38, 29.28, 29.19, 29.14, 28.81, 26.63, 23.13, 22.50 (10t; C-2 – C-11), 13.96 (q; C-12);

MS (positive ESI) m/z (%): 266.28 $[M+H]^+$;

HR-MS (positive ESI): Calcd. for $C_{18}H_{36}N$ $[M+H]^+$m/z: 266.2842; Found 266.2848.



N,*N*-Dially-*N*-hexadecylammonium chloride (**3b**)

N,*N*-Dially-*N*-hexadecylamine (**2b**) (1.00 g, 3.11 mmol) in methanol (10 mL) with hydrochloric acid (36 % in water) gave after recrystallisation from acetonitrile *N*,*N*-dially-*N*-hexadecylammonium chloride (**3b**) (1.06 g, 2.96 mmol, 95 %) as a white solid.

m.p. 58.4 °C;

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2916, 2847, 2608, 2415, 2354, 1458, 1427, 1057, 995, 934, 725, 656, 625;

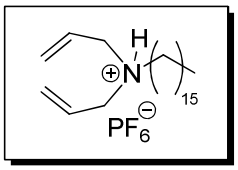
^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.58 (bs, 1H), 6.16 (ddt, 2H, ^3J = 7.2 Hz, ^3J = 10.1 Hz, ^3J = 17.1 Hz; NCH_2-C<u>H</u>=CH_2), 5.59 – 5.45 (m, 4H; NCH_2-CH=C<u>H_2</u>), 3.64 – 3.59 (m, 4H; N<u>CH_2</u>-CH=CH_2), 2.96 – 2.89 (m, 2H; 1-H), 1.87 – 1.79 (m, 2H; 2-H), 1.35 – 1.20 (m, 26H; 3-H - 15-H), 0.87 (t, 3H, ^3J = 6.9 Hz; 16-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.33 (t; NCH_2-CH=<u>C</u>H_2), 125.54 (d; NCH_2-<u>C</u>H=CH_2), 54.58 (t; N<u>C</u>H_2-CH=CH_2), 51.70 (t; C-1), 31.89, 29.67, 29.65, 29.64, 29.63, 29.60, 29.54, 29.42, 29.33, 29.33, 28.94, 26.78, 23.23, 22.66 (14t; C-2 – C-15), 14.10 (q; C-16);

MS (positive ESI) m/z (%): 322.35 $[M-Cl]^+$;

HR-MS (positive ESI): Calcd. for $C_{22}H_{44}N$ $[M-Cl]^+$m/z: 322.3468; Found 322.3468;

CHN: Calcd. for $C_{22}H_{44}NCl$: C 73.80, H 12.39, N 3.91; Found C 75.58, H 12.25, N 3.94.



N,*N*-Dially-*N*-hexadecylammonium hexafluorophosphate (**3c**)

N,*N*-Dially-*N*-hexadecylamine (**2b**) (1.00 g, 3.11 mmol) in methanol (10 mL) with hexafluorophosphoric acid (65 wt% solution in water) gave after recrystallisation from ethanol *N*,*N*-dially-*N*-hexadecylammonium hexafluorophosphate (**3c**) (1.39 g, 2.97 mmol, 96 %) as a white solid.

m.p. 73.7 °C ;

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3140, 2916, 2847, 2314, 1651, 1466, 1427, 1188, 995, 941, 833, 725, 547, 509;

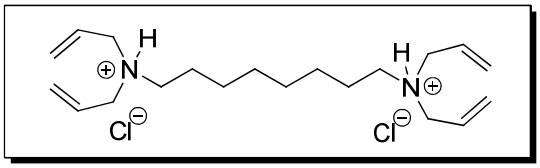
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (bs, 1H), 5.97 (ddt, 2H, ^{3}J = 7.3 Hz, ^{3}J = 10.1 Hz, ^{3}J = 17.0 Hz; NCH_2-C<u>H</u>=CH_2), 5.67 – 5.54 (m, 4H; NCH_2-CH=C<u>H_2</u>), 3.77 – 3.70 (m, 4H; NC<u>H_2</u>-CH=CH_2), 3.08 – 3.01 (m, 2H; 1-H), 1.80 – 1.70 (m, 2H; 2-H), 1.40 – 1.20 (m, 26H; 3-H - 15-H), 0.88 (t, 3H, ^{3}J = 6.8 Hz; 16-H);

^{13}C NMR (100 MHz, CDCl3): δ = 127.16 (t; NCH_2-CH=<u>C</u>H_2), 125.18 (d; NCH_2-<u>C</u>H=CH_2), 55.57 (t; N<u>C</u>H_2-CH=CH_2), 52.58 (t; C-1), 31.91, 29.69, 29.67, 29.65, 29.64, 29.63, 29.56, 29.43, 29.35, 29.29, 28.93, 26.41, 23.60, 22.68 (14t; C-2 – C-15), 14.12 (q; C-16);

^{19}F NMR (100 MHz, CDCl3): δ = -71.50 (d, J = 714.3 Hz; PF_6);

MS (positive ESI) m/z (%): 322.3 $[M\text{-}PF_6]^+$;

HR-MS (positive ESI): Calcd. for $C_{22}H_{44}N$ $[M\text{-}PF_6]^+$ m/z: 322.3468; Found 322.3478.



1,8-Bis-(*N*,*N*-diallylammonium)octane chloride (**4**)

To a solution of 1,8-bis-(*N*,*N*-diallylamino)octane (0.41 g, 1.35 mmol) in methanol (10 mL) hydrochloric acid (36% in water) was added until a pH 1 was reached. The solution was stirred for 1 h and the solvent removed by evaporation. 1,8-Bis-(*N*,*N*-diallylammonium)octane chloride (**4**) (0.49 g, 1.30 mmol, 96 %) were obtained as a white solid.

m.p. 109.4 °C;

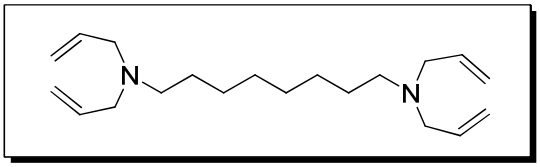
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2931, 2854, 2631, 2461, 2191, 1643, 1458, 1427, 1350, 1258, 1049, 988, 941, 887, 852, 725, 633, 516;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.33 (bs, 2H), 6.13 (ddt, 4H, ^3J = 7.2 Hz, ^3J = 10.1 Hz, ^3J = 17.1 Hz; NCH_2-C<u>H</u>=CH_2), 5.59 – 5.46 (m, 8H; NCH_2-CH=C<u>H_2</u>), 3.71 – 3.56 (m, 8H; N<u>CH_2</u>-CH=CH_2), 3.01 – 2.92 (m, 4H; 1-H), 1.92 – 1.82 (m, 4H; 2-H), 1.41 – 1.31 (m, 8H; 3-H, 4-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.12 (d; NCH_2-<u>C</u>H=CH_2), 125.76 (t; NCH_2-CH=<u>C</u>H_2), 54.48 (t; N<u>C</u>H_2-CH=CH_2), 51.84 (t; C-1), 27.92, 26.18, 23.24 (3t; C-2, C-3, C-4);

MS (positive ESI) m/z (%): 341.27 $[M\text{-}Cl]^+$, 305.30 $[M\text{-}H\text{-}2Cl]^+$;

HR-MS (positive ESI): Calcd. for $C_{20}H_{38}N_2Cl$ $[M\text{-}Cl]^+$m/z: 341.2718; Found 341.2701; Calcd. for $C_{20}H_{37}N_2$ $[M\text{-}H\text{-}2Cl]^+$m/z: 305.2951; Found 305.2952.



1,8-Bis-(*N*,*N*-diallylamino)octane (**5**)

1,8-Dibromooctane (5.00 g, 18.4 mmol), *N*,*N*-diallylamine (5.36 g, 55.1 mmol, 3 equiv.), and potassium carbonate (5.08 g, 36.8 mol, 2 equiv.) in acetonitrile (300 mL) were heated under reflux for 48 h. The solids were removed by filtration and the solvent removed by evaporation to leave a yellow oil. The product was isolated by column chromatography over silica gel using ethyl acetate as the eluent, to leave, after removal of solvents, 1,8-bis-(*N*,*N*-diallylamino)octane (**5**) (2.48 g, 8.14 mmol, 54 %) as a clear oil.

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924, 2854, 2793, 1643, 1451, 1419, 1258, 1150, 1080, 995, 918, 633, 540;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (ddt, 4H, ^3J = 6.5 Hz, ^3J = 10.3 Hz, ^3J = 17.0 Hz; NCH_2-C<u>H</u>=CH_2), 5.20 – 5.10 (m, 8H; NCH_2-CH=C<u>H_2</u>), 3.08 (ddd, 8H, ^4J = 1.2 Hz, ^3J = 6.5 Hz; N<u>CH_2</u>-CH=CH_2), 2.43 – 2.37 (m, 4H; 1-H), 1.49 – 1.40 (m, 4H; 2-H), 1.30 – 1.22 (m, 8H; 3-H, 4-H);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.79 (d; NCH_2-$\underline{C}H$=CH_2), 117.08 (t; NCH_2-CH=$\underline{C}H_2$), 56.76 (t; $N\underline{C}H_2$-CH=CH_2), 53.27 (t; C-1), 29.43, 27.34, 26.81 (3t; C-2, C-3, C-4);

MS (positive ESI) m/z (%): 305.30 $[M+H]^+$;

HR-MS (positive ESI): Calcd. for $C_{20}H_{37}N_2$ $[M+H]^+$m/z: 305.2951; Found 305.2962.

Polymerization

Approximately 1 - 2 % by wt. of photoinitiator 1-hydroxycyclohexylphenyl ketone was added to the salt, and after addition of water the mixture was spread onto a suitable substrate, usually glass slide in our case. Polymerization was then effected using a domestic low-power (75 W) UVA sunlamp.

Micrographs of POM textures

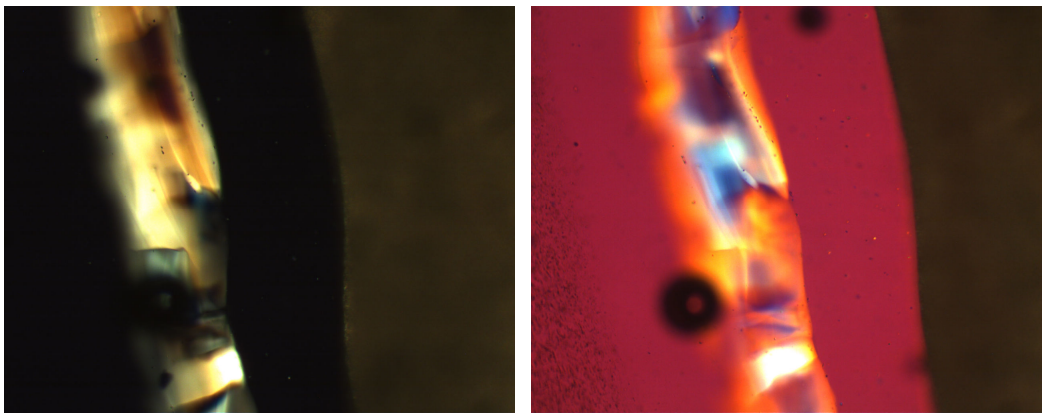


Fig. A1 POM textures of cubic and hexagonal phase of **3a** with water before polymerization without (left) and with (right) λ/4 (530 nm) plate. Picture was taken at room temperature (×100).

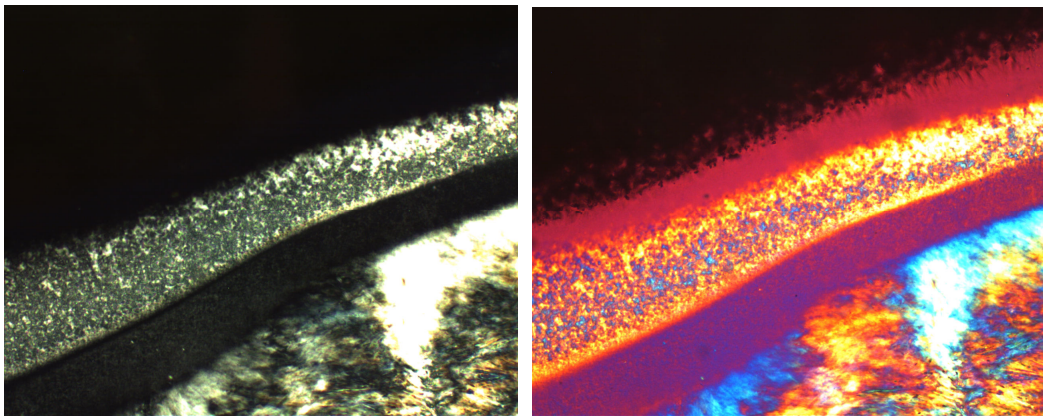


Fig. A2 POM textures of cubic and hexagonal phase of **3a** with water after polymerization without (right) and with (left) λ/4 (530 nm) plate. Picture was taken at room temperature (×100).

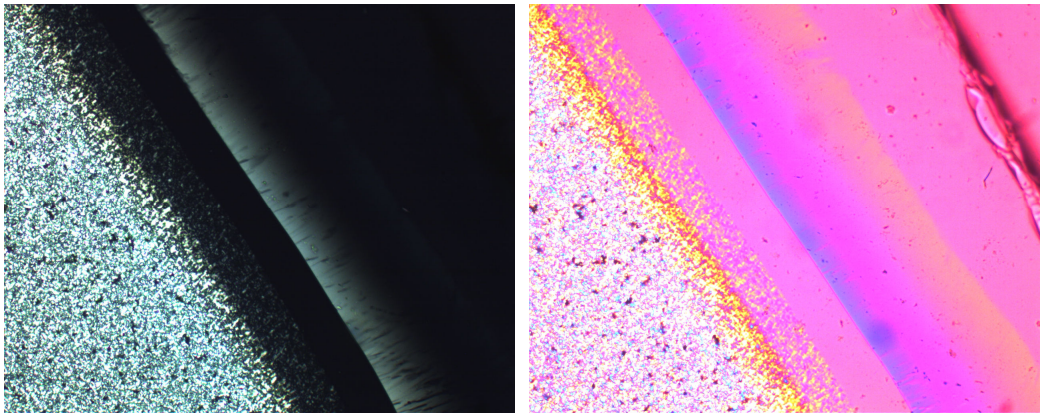


Fig. A3 POM textures of lamellar, cubic, and hexagonal phase of **3b** with water before polymerization without (left) and with (right) λ/4 (530 nm) plate. Picture was taken at room temperature (×100).

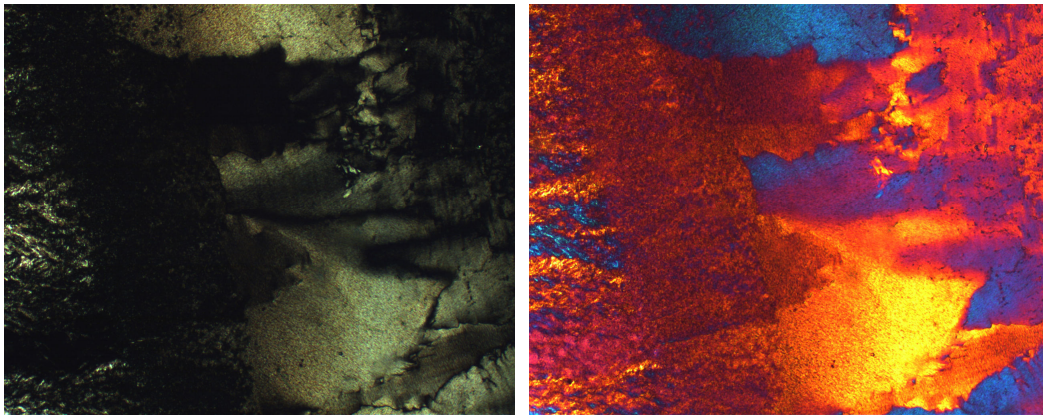


Fig. A4 POM textures of lamellar, cubic, and hexagonal phase of **3b** with water after polymerization without (left) and with (right) λ/4 (530 nm) plate. Picture was taken at room temperature (×100).

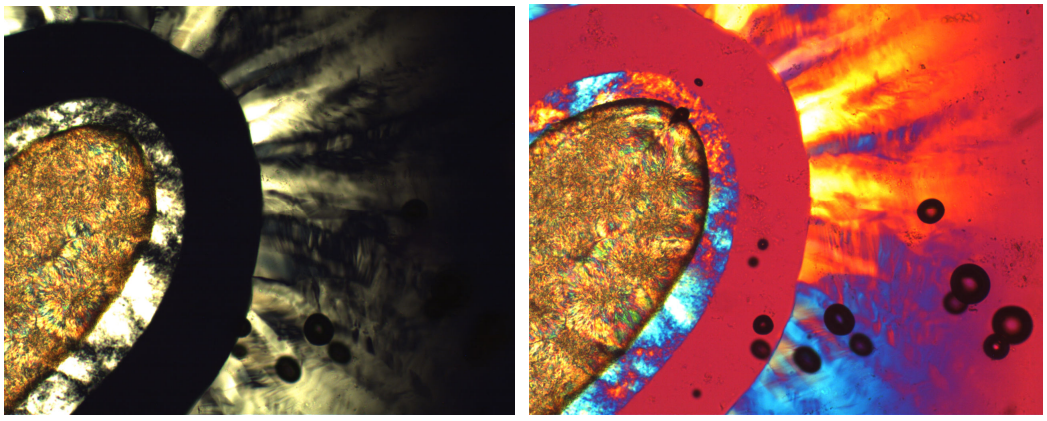


Fig. A5 POM textures of the lamellar, cubic, and hexagonal phase of 9 mol% of **4** and 91 mol% **3b** with water before polymerisation without (left) and with (right) λ/4 (530 nm) plate. Picture was taken at room temperature (×100).

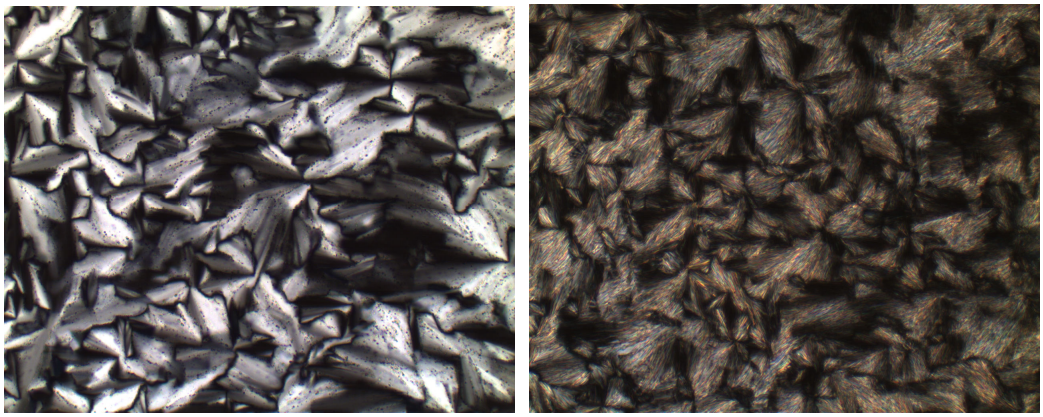


Fig. A6 POM textures of hexagonal phase of **3b** with water before (left) and after (right) polymerisation at room temperature (×100).

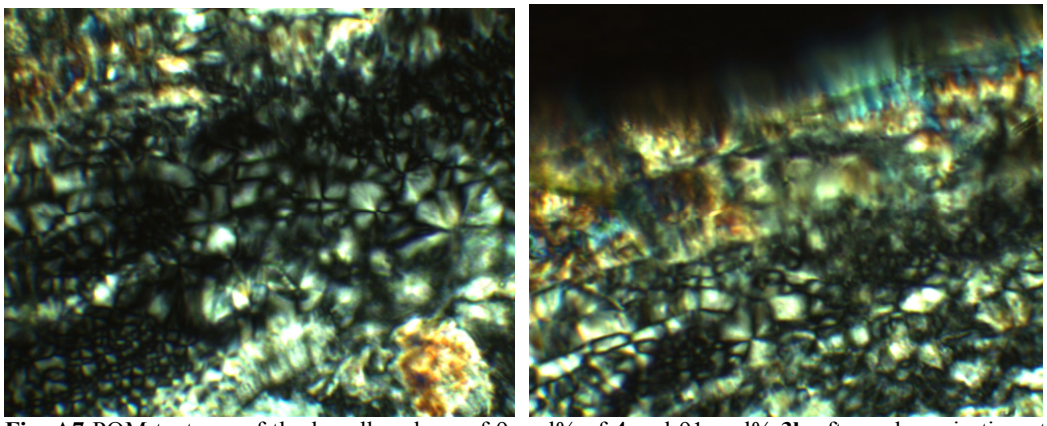


Fig. A7 POM textures of the lamellar phase of 9 mol% of **4** and 91 mol% **3b** after polymerisation at 70 °C (left) and 120 °C (right) (×100).

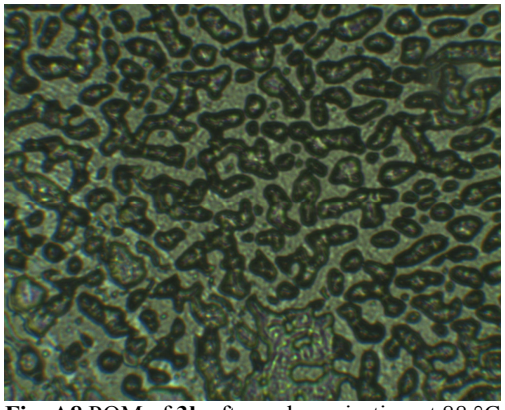


Fig. A8 POM of **3b** after polymerisation at 88 °C (×100).

[1] Further synthesis of compounds **2a** and **2b**: a) I.G.Farbenindustrie, DE681850, 1933; Fortschr. Teerfarbenfabr. Verw. Industriezweige, vol. 24, 387; b) A. R. Katritzky, J. Yao, M. Qi, *J. Org. Chem.*, 1998, **63**, 5232 – 5234; c) H. Fuhrmann, I. Grassert, G. Holzhüter, C. Grüttner, G. Oehme, *New J. Chem.*, 2002 , **26**, 1675 – 1681; d) K. D. Schmitt, *J. Org. Chem.*, 1995, **60**, 5474 – 5479.