

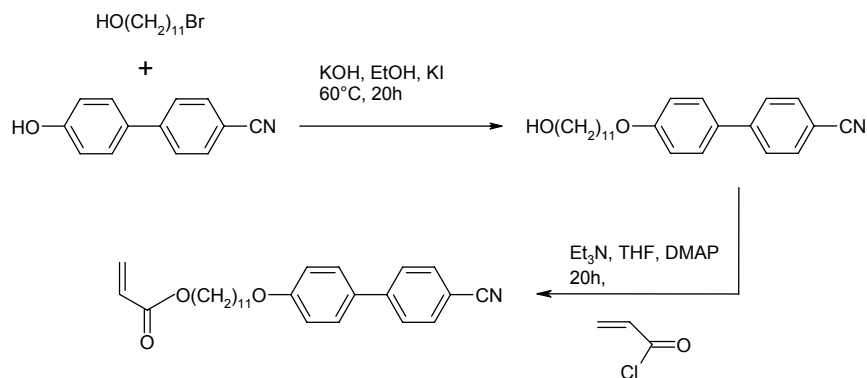
Grafting Liquid Crystalline Polymers from Cellulose Substrates using Atom Transfer Radical Polymerization

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Synthetic procedures for monomer preparation

Synthesis of 4-(11-hydroxyundecyloxy)-4'-cyanobiphenyl. 4-Hydroxy-4'-cyanobiphenyl (6.0 g, 30.8 mmol) and 11-bromo undecanol (7.74 g, 30.8 mmol) were dissolved in a mixture of ethanol/water 4/1 (300 ml) at room temperature. A solution of potassium hydroxide (2.7 g, 41 mmol) in water (22 ml) and a catalytic amount of potassium iodide was added and the system was heated to a gentle reflux under argon atmosphere for 20 h. The yellow solution was allowed to cool down to room temperature (~5h) and the crystals formed were collected by filtration, washed with cold ethanol and dried in air. Yield: 8.87g (64%). ¹H NMR (CDCl₃) □ 1.30 (m, 12H, -CH₂-), 1.47 (m, 2H, -CH₂-CH₂-CH₂-O-Ar), 1.56 (m, 2H, -CH₂-CH₂-OH), 1.81 (m, 2H, -CH₂-CH₂-O-Ar), 3.64 (t, 2H, *J* = 8.0 Hz, -CH₂-OH), 4.00 (t, 2H, *J* = 8.0 Hz, -CH₂-O-Ar), 6.99 (d, 2H, *J* = 8.0 Hz, aromatic H ortho to O-CH₂), 7.53 (d, 2H, *J* = 8.0 Hz, aromatic H meta to O-CH₂), 7.67 (m, 4H, Ar-*H* ortho and meta to -CN).

Synthesis of 11-(4'-cyanophenyl-4''-phenoxy)undecyl acrylate. 4-(11-Hydroxyundecyloxy)-4'-cyanobiphenyl (8.87 g, 24.3 mmol) was dissolved in 260 ml THF. Triethylamine (3.68 g, 36.4 mmol) and a catalytic amount of DMAP were added. Acryloyl chloride (2.26 g, 26.7 mmol) was dissolved in THF (5 ml) and added to the reaction mixture. The reaction was stirred for 20 h at RT. The reaction mixture was filtered, the solvent was evaporated and the crude mixture was re-dissolved in dichloromethane (450 ml) and purified through extraction with 10 % NaHSO₄ (3 x 100 ml), 10 % Na₂CO₃ (3 x 100 ml), and Brine (1 x 120 ml). The organic phase was dried over MgSO₄, filtered and concentrated. The acrylate-terminated LC monomer was additionally purified by medium pressure liquid chromatography (MPLC). ¹H NMR (CDCl₃) □ 1.30 (m, 12H, -CH₂-), 1.47 (m, 2H, -CH₂-CH₂-CH₂-O-Ar), 1.67 (m, 2H, -CH₂-CH₂-OH), 1.81 (m, 2H, -CH₂-CH₂-O-Ar), 4.00 (t, 2H, *J* = 8.0 Hz, -CH₂-O-Ar), 4.15 (t, 2H, *J* = 8.0 Hz, -CH₂-O-C=O), 5.81 (d, 1H, *J* = 12 Hz, -CH=CH₂), 6.12 (dd, 1H, *J* = 12 Hz, -CH=CH₂), 6.40 (d, 1H, *J* = 12 Hz, -CH=CH₂), 6.99 (d, 2H, *J* = 8.0 Hz, aromatic H ortho to O-CH₂), 7.53 (d, 2H, *J* = 8.0 Hz, aromatic H meta to O-CH₂), 7.67 (m, 4H, Ar-*H* ortho and meta to -CN).



Scheme 1 Synthesis of 11-(4'-cyanophenyl-4''-phenoxy)undecyl acrylate.

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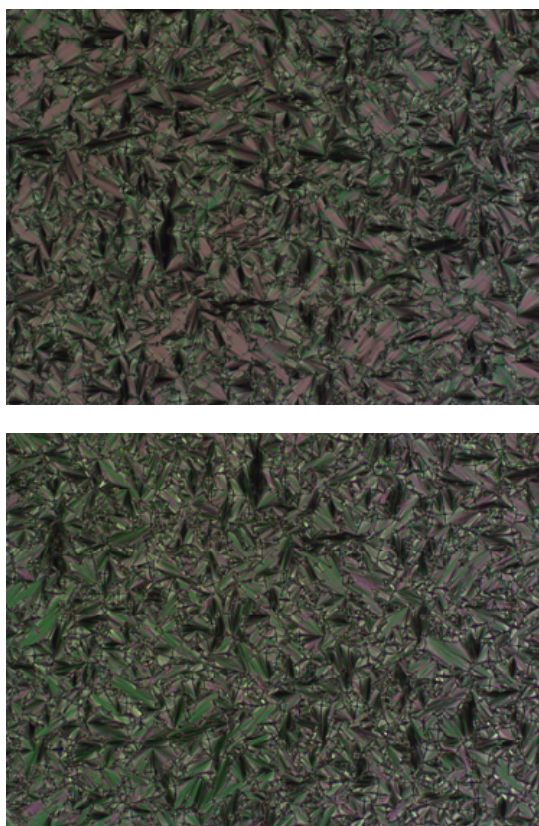


Fig. 2 Texture of the SmC phase (top) and SmA (bottom) of poly[11-(4'-cyanophenyl-4''-phenoxy)undecyl acrylate] at 29.3 °C, 21.6 °C and 123 °C respectively (crossed polarisers, magnification: x100).

Optical microscopy images presented in color

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