

Supporting Information

Unique Molecular Orientation in a Smectic Liquid Crystalline Polymer Film Attained by Surface-Initiated Graft Polymerization

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Synthesis

The synthetic strategy is shown in Scheme S1. ^1H -NMR spectra were recorded on a JEOL 270GXS instrument spectrometer operating at 270MHz using tetramethylsilane as the internal standard for the chloroform solutions.

4-[(4'-Pentylphenyl)azo] phenol

4-Pentylaniline (25.8 g, 158 mmol) was dissolved in a mixture of concentrated hydrochloric acid (25 mL) and water (150 mL). Sodium nitrate (15.9 g, 230 mmol) in water (80 mL) was added dropwise to the above solution at 5 °C. An aqueous solution (800 mL) dissolving phenol (22.0 g, 234 mmol), sodium hydroxide (9.30 g, 233 mmol) was then added dropwise under vigorous stirring. The solution was stirred for 2 h at 5 °C and 3 h at room temperature. After this solution was neutralized with a diluted hydrochloric acid aqueous solution, the precipitate was filtered off and dissolved in ethyl acetate. The solution was washed with a NaCl aqueous solution, and then, dried over anhydrous magnesium sulfate. The precipitate was recrystallized from hexane twice to give yellow platelet crystals.

Yield: 25.1 g (59.1 %), ^1H NMR(δ [ppm], CDCl_3): 0.89 (3H, t, $J = 7$ Hz, CH₃–), 1.24–1.35 (4H, m, –CH₂–), 1.64 (2H, t, $J = 7$ Hz, –CH₂–), 2.65 (2H, t, $J = 8$ Hz, –CH₂–Ph), 5.27 (1H, s, –OH), 6.90 (2H, d, $J = 9$ Hz, Ph–H), 7.28 (2H, d, $J = 9$ Hz, Ph–H), 7.77–7.84 (4H, m, Ph–H).

4-(10-Hydroxydecyloxy)-4'-pentylazobenzene

Potassium carbonate (10.3 g, 74.5 mmol) and potassium iodide (1.24 g, 7.47 mmol) were added to 4-[(4'-Pentylphenyl)azo]phenol (10.0 g, 37.3 mmol) in dry *N,N'*- dimethylformamide (DMF) (60ml), and then mixture was stirred for 30 min at 70 °C. 10-Bromodecanol (13.3 g, 56.1 mmol) in dry DMF (40ml) was added dropwise to the solution. The mixture was stirred for 6h at 70 °C. The reaction mixture was pored into water. A precipitated yellow solid was filtered, washed with water for several times, and dried in vacuum. The solid was recrystallized from methanol.

Yield: 14.7 g (84.1 %), ^1H NMR(δ [ppm], CDCl_3): 0.90 (3H, t, $J = 7$ Hz, CH_3-), 1.31–1.80 (22H, m, – CH_2-), 2.67 (2H, t, $J = 8$ Hz, – CH_2-Ph), 4.02 (2H, t, $J = 8$ Hz, – OCH_2-), 4.14 (2H, t, $J = 8$ Hz, – OCH_2-), 6.94 (2H, d, $J = 9$ Hz, Ph–H), 7.29 (2H, d, $J = 9$ Hz, Ph–H), 7.79 (2H, d, $J = 9$ Hz, Ph–H), 7.88 (2H, d, $J = 9$ Hz, Ph–H).

4-(10-Methacryloydecyloxy)-4'-pentylazobenzene (3)

4-(10-Hydroxydecyloxy)-4'-pentylazobenzene (14.0 g, 29.9 mmol) and triethylamine (4.54 g, 4.82 mmol) was dissolved in dry tetrahydrofuran (THF) solution (40 mL). A dry THF solution (10 ml) containing methacryloyl chloride (4.69 g, 4.82 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred for 30 min at 0 °C and 12 h at room temperature. The reaction mixture was evaporated, and ethyl acetate was added. The solution was washed with water, and brine, and then, dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was recrystallized from methanol twice. Yellow solid was obtained.

Yield: 9.34 g (63.5 %), ^1H NMR(δ [ppm], CDCl_3): 0.90 (3H, t, $J = 7$ Hz, CH_3-), 1.33–1.84 (22H, m, – CH_2-), 1.94 (3H, s, = $\text{C}(\text{CH}_3)_2$), 2.67 (2H, t, $J = 8$ Hz, – CH_2-Ph), 4.02 (2H, t, $J = 8$ Hz, – OCH_2-), 4.14 (2H, t, $J = 8$ Hz, – OCH_2-), 5.54 (1H, s, $\text{CH}_2=\text{C}-$), 6.09 (1H, s, $\text{CH}_2=\text{C}-$), 6.94 (2H, d, $J = 9$ Hz, Ph–H), 7.29 (2H, d, $J = 9$ Hz, Ph–H), 7.799 (2H, d, $J = 9$ Hz, Ph–H), 7.88 (2H, d, $J = 9$ Hz, Ph–H).

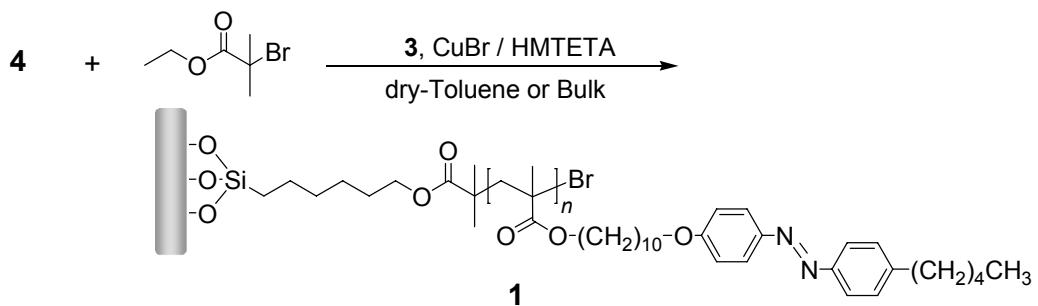
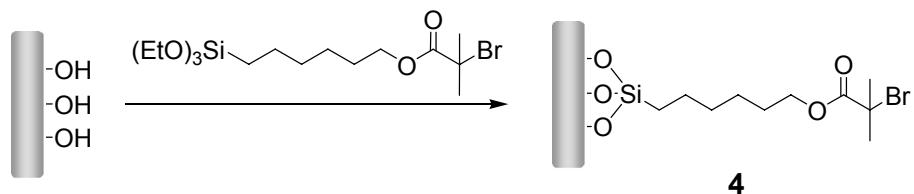
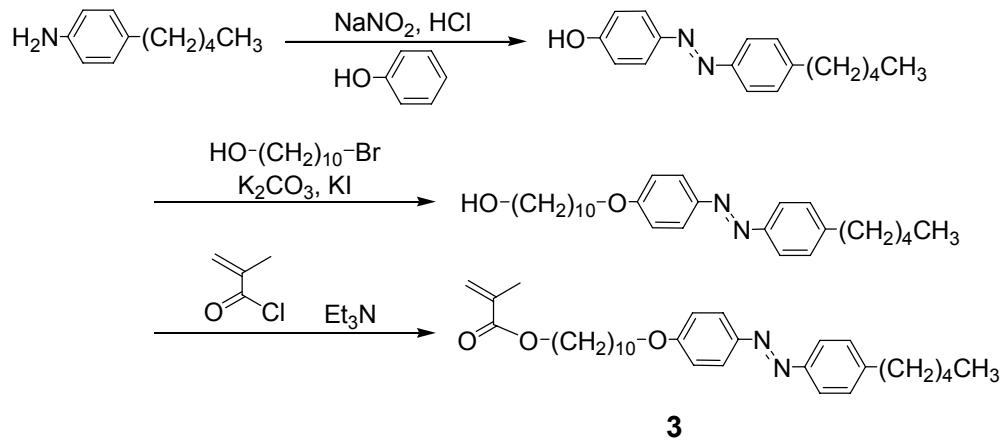
Modification of the initiator onto silicon substrates (4)

Cleaned silicon wafer or quartz substrates were placed into a Teflon container. The container was sealed and placed in an oven maintained at 150 °C for 1 h. Then, a glass cup filled with (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane liquid (about 50mg) was put together and maintained at 150 °C for 3 h. The BHE liquid in the vessel vaporized and reacted with the hydroxyl groups on the

sample surface. Subsequently, the container was opened and placed at 150 °C for 1h. After the surface reaction, the samples treated with BHE were dipped into dehydrated toluene and ethanol successively and washed by ultrasonic bath for 5 min. Finally, the samples were dried under vacuum and stored in nitrogen atmosphere.

Surface-initiated atom transfer radical polymerization (1)

In a typical synthesis, the surface initiated ATRP was carried out at 80°C in toluene. 15 mg (0.1 mmol) of Cu(I)Br, 492 mg (1.0 mmol) of the Az containing monomer **3**, 2.0 mg (0.01 mmol) of ethyl-2-bromoisobutyrate as a free initiator, and 23.0 mg (0.1 mmol) of 1, 1, 4, 7, 10, 10-hexamethyltriethylentetraamine as a ligand were dissolved in 1.25 ml of dry toluene and filled with nitrogen. In glove box, initiator-modified quartz or silicon substrates were added in polymerization solution, sealed and placed in the 80 °C oil bath for 12h. After polymerization, polymer grafted substrates were washed with THF for several times to remove unreacted monomer and free polymer, and dried at room temperature.



Scheme S1. T. Uekusa et al.