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Synthesis and polymerization of disiloxane Si–O–Si-linked phthalonitrile monomer

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Synthesis of monomer **5**

(*a*) *2-(4-Bromophenoxy)tetrahydro-2*H*-pyran* **6**. 4-Bromophenol (5.00 g, 0.060 mol) was slowly added at 0°C to dihydropyran (6.86 g, 0.040 mol) containing 2 drops of concentrated hydrochloric acid. The mixture was stirred for 1.5 h and then 100 ml of diethyl ether was added. The organic phase was separated and washed with 50 ml of 10% NaOH. The solution was dried (Na_2SO_4) and evaporated to dryness. The residue was passed through a short pad of silica using hexane–dichloromethane mixture as eluent to give 9.95 g (98%) of product as a colorless liquid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.56–1.64 (m, 1H), 1.64–1.74 (m, 2H), 1.83–1.89 (m, 2H), 1.95–2.05 (m, 1H), 3.57–3.63 (m, 1H), 3.84–3.91 (m, 1H), 5.38 (t, 1H, *J* 3.2 Hz), 6.95 (d, 2H, *J* 9.1 Hz), 7.38 (d, 2H, *J* 9.1 Hz). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 18.6, 25.1, 30.2, 61.9, 76.8, 77.2, 96.4, 113.7, 118.2, 132.1, 156.1.

(*b*) *Dimethyl[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]silanol* **7**. This step was carried out in dry argon atmosphere. A 20 ml THF solution of 2-(4-bromophenoxy)tetrahydro-2*H*-pyran (9.90 g, 0.038 mol) was added to a mixture of magnesium turnings (1.12 g, 0.046 mol), a catalytic amount of iodine and THF (20 ml) with stirring at room temperature in 15 min. The solution of the Grignard reagent thus obtained was slowly added to a mixture of dichlorodimethylsilane (4.97 g, 0.038 mol), triethylamine (7.79 g, 0.077 mol) and THF (30 ml) in another reaction flask at 0 °C. The resulted mixture was stirred at room temperature for 1 h and then was poured into ice water, followed by careful neutralization with 5% HCl. The product was extracted with diethyl ether. The organic solution was washed with water (2×50 ml), brine (30 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was washed with hexane (2×30 ml). The product (9.21 g, 95%) was obtained as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.39 (s, 6H), 1.57–1.64 (m, 1H), 1.64–1.74 (m, 2H), 1.84–1.90 (m, 2H), 1.97–2.08 (m, 1H), 3.57–3.65 (m, 1H), 3.87–3.94 (m, 1H), 5.47 (t, 1H, *J* 3.1 Hz), 7.08 (d, 2H, *J* 8.5 Hz) 7.52 (d, 2H, *J* 8.4 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 0.1, 18.7, 25.2, 30.3, 62.0, 96.0, 116.0, 131.2, 134.5, 158.3.

(*c*) *1,3-Bis(4-hydroxyphenyl)-1,1,3,3-tetramethyldisiloxane* **8**. Dimethyl[4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]silanol (3.00 g, 0.012 mol) was dissolved in 40 ml of ethanol and the solution was treated with 0.5 ml of 5% HCl at room temperature. After stirring for 1 h, 100 ml of water was added and then the products were extracted with diethyl ether. The solution was dried (Na_2SO_4) and evaporated to dryness. The residue was purified chromatographically on silica using hexane–dichloromethane as eluent to give 1.75 g (93%) of product as a yellowish solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 0.22 (s, 12H), 6.75 (d, 4H, *J* 8.3 Hz), 7.30 (d, 4H, *J* 8.4 Hz), 9.47 (s, 2H).

(*d*) *1,3-Bis[4-(3,4-dicyanophenoxy)phenyl]-1,1,3,3-tetramethyldisiloxane* **5**. This step was carried out in dry argon atmosphere. Potassium carbonate (1.47 g, 0.010 mol) was suspended in a solution of 1,3-bis(4-hydroxyphenyl)-1,1,3,3-tetramethyldisiloxane (1.7 g, 0.005 mol) in dry DMA (20 ml). A solution of 4-nitrophthalonitrile (1.85 g, 0.010 mol) in dry DMA (10 ml) was added to the mixture. After stirring for 24 h at 70 °C, the reaction mixture was poured into ice cold water (100 ml) and dichloromethane (50 ml) was added. The organic phase was separated, washed with water (5×50 ml), brine (50 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was purified by column chromatography on silica using hexane–dichloromethane as eluent to give 1.51 g (50%) of product **5** as a yellowish glassy substance which slowly solidifies on standing. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 0.35 (s, 12H), 7.18 (d, 4H, *J* 8.5 Hz), 7.38 (dd, 2H, *J* 8.7 and 2.5 Hz), 7.64 (d, 4H, *J* 8.5 Hz), 7.77 (d, 2H, *J* 2.5 Hz), 8.08 (d, 2H, *J* 8.8 Hz). ^{13}C NMR (151 MHz, DMSO-d_6) δ: 0.8, 108.4, 115.3, 115.8, 116.7, 119.5, 122.3, 122.9, 135.2, 136.3, 136.3, 155.0, 160.6. ^{29}Si NMR δ: 1.41. Found (%): C, 67.26; H, 4.61; N, 9.88. Calc. for $C_{32}H_{26}N_4O_3Si_2$ (%): C, 67.34; H, 4.59; N, 9.82.

Curing of the monomers was performed in the presence of 4 wt% of 1,3-bis(4-aminophenoxy)benzene (APB) in a glass vial under atmosphere of dry argon. The vial was charged with the reaction mixture, melted and degassed at 120–180 °C by shaking the vial under reduced pressure. Then temperature was raised to 200 °C with the rate of 2 K min^{-1} and retained at 200 °C for 24 h under inert atmosphere. Then the temperature was raised to 375 °C (2 K h^{-1}) and kept for 8 h.