Macromolecules

Macromolecules, 1996, 29(3), 1082-1084, DOI:10.1021/ma951414t

Synthesis and Characterization of R-4, R-5, 6, R-7 and rac-7.

(R)-6,6'-Dibromo-2,2'-dihexyloxy-1,1'-binaphthyl, R-4: To a solution of (R)-6,6'-dibromo-1,1'-bi-2-naphthol, R-3 (4.88 g, 11 mmol), in acetone (70 mL) was added 1-iodohexane (12.0 g, 56.5 mmol) and K_2CO_3 (7.0 g, 50.7 mmol). The mixture was heated to reflux and the reaction was monitored by ^1H NMR and TLC. After 24 h, the solvent was evaporated, and water (30 mL) was added to the mixture, which was then extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with Na_2SO_3 solution and brine, and then dried over Na_2SO_4. After evaporation of the solvent, excess 1-iodohexane was recovered by distillation under reduced pressure, and an oily residue was obtained. Flash chromatography of the oil on silica gel by using EtOAc/hexanes as the eluent gave pure R-4 (6.40 g, 95%). The oil solidifies after standing at rt. mp 56.5 - 58.0 °C. $[\alpha]_D = 25.9°$ (c = 0.52, THF). FT-IR (KBr) cm^{-1} 1616 (w), 1581 (s), 1492 (s), 1468 (s), 1338 (s), 1263 (s), 1238 (s), 1076 (s), 1022 (m), 939 (m), 895 (m), 871 (m), 815 (m), 790 (m). UV-vis λ_{max} (CH_2Cl_2) nm 350, 284, 256. ^1H NMR (270 MHz, $CDCl_3$) δ 0.74 (t, *J* = 6.6 Hz, 6 H, -C*H*$_3$), 1.01 (m, 8 H, -C*H*$_2$C*H*$_2$CH$_3$), 1.38 (m, 4 H, -OCH$_2$C*H*$_2$-), 3.90 (m, 4 H, -OC*H*$_2$-), 6.98 (d, *J* = 8.8 Hz, 2 H), 7.25 (dd, *J* = 8.8, 2.2 Hz, 2 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.99 (d, *J* = 2.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 13.90, 22.46, 25.29, 29.25, 31.26, 69.52, 116.40, 117.22, 120.05, 127.10, 128.37, 129.43, 129.74, 130.19, 132.57, 154.77. MS *m/z* 612 (M^+), 528, 364. Anal. Calcd for $C_{32}H_{36}O_2Br_2$: C, 62.76; H, 5.8. Found: C, 62.91; H, 5.60.

(R)-2,2'Dihexyloxy-1,1'-binaphthyl-6,6'-diboronic acid, R-5: To a mixture of Mg (288 mg, 12 mmol) in THF (5 mL) was slowly added a THF solution (15 mL) of R-4 (3.06 g, 5 mmol) and $ClCH_2CH_2Cl$ (0.198 g, 2 mmol) over 30 min at 60 °C under N_2. The mixture was then gently refluxed for 6 h to give a homogeneous solution of the bifunctional Grignard reagent. This solution was then slowly added to a solution of $B(OMe)_3$ (2.74 g, 26.4 mmol) in Et_2O (30 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 48 h. 1N HCl (50 mL) was added at 0 °C and the resulting solution was extracted with EtOAc (3 x 50 mL).

The combined organic layers were washed with brine, and dried over Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by flash chromatography on silica gel (EtOAc/hexanes) to give R-**5** (1.36 g) in 50.2% yield. mp 287-290 °C. $[\alpha]_D$ = 35.6° (c = 0.22, DMSO). FT-IR (KBr) cm^{-1} 3441 (s), 1620 (s), 1467 (s), 1398 (s), 1377 (s),1315 (s), 1244 (s), 1078 (w), 1047 (m), 908 (w), 831 (w). UV-vis λ_{max} (MeOH) nm 346, 266, 234. ^1H NMR (400 MHz, DMSO-d_6) δ 0.65 (t, *J* = 6.8 Hz, 6 H, -CH_3), 0.92 [m, 12 H, -$(CH_2)_3CH_3$], 1.31 (m, 4 H, OCH_2CH_2-), 3.92 (m, 4 H, -OCH_2-), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.50 (d, *J* = 9.1 Hz, 2 H), 7.53 (d, *J* = 8.6 Hz, 2 H), 7.99 (d, *J* = 9.1 Hz, 2 H), 8.08 [s, 4 H, -$B(OH)_2$], 8.36 (s, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 13.94, 22.10, 24.96, 28.96, 30.90, 68.66, 115.29, 119.30, 123.53, 128.30, 128.70, 129,99, 130.88, 134.78, 135.52, 154.84. HRMS (Electron Spray) *m/e* calcd for $C_{32}H_{40}O_6B_2 + H^+$: 543.3089, obsd: 543.3083.

Rac-4 and rac-5 were prepared similarly.

1,4-Bis(*p*-bromostyryl)benzene, 6: To a solution of *p*-bromobenzaldehyde (1.85 g, 10 mmol) and *p*-xylylene-bis-(triphenylphosphonium) chloride (3.50 g, 5 mmol) in EtOH, a solution of lithium (0.1 g, 14 mmol) in EtOH (15 mL) was added over 1 h during which the product precipitated out as a yellow solid . The reaction mixture was stirred at rt for additional 2 h. Filtration and recrystallization from EtOAc gave **6** as light yellow crystals (1.40 g, 64%). mp 174.0 - 179.0 °C. FT-IR (KBr) cm^{-1} 1631 (w), 1581 (m), 1508 (m), 1485 (s), 1421 (m), 1400 (m), 1068 (s), 1010 (s), 970 (s), 947 (w), 885 (s), 835 (s), 810 (s), 758 (m), 733 (m), 565 (s), 515 (s). UV-vis λ_{max} (CH_2Cl_2) nm 342, 288, 242. ^1H NMR (270 MHz, acetone-d_6, cis-trans isomers) δ 6.56 (m, 2.16 H, C*H*=C*H*), 7.02-7.48 (m, 12 Ar-*H* + 1.84 C*H*=C*H*). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$, cis-trans isomers) δ 121.37, 126.47, 127.47, 127.95, 128.87, 129.14, 129.24, 130.51, 131.36, 136.01, 136.19, 136.40. MS *m/z* 440 (M^+), 360, 279, 202, 139, 77. Anal. Calcd for $C_{22}H_{16}Br_2$: C, 60.02; H, 3.63. Found: C, 60.28; H, 3.79.

Polymer R-7: To a mixture of R-**5** (544 mg, 1 mmol) and **6** (440 mg, 1 mmol) in THF (10 mL) and K_2CO_3 (15 mL, 1 M), a solution of $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) in THF (5 mL) was

added. The reaction mixture was refluxed for 48 h. The organic layer was diluted with CH_2Cl_2 (100 mL) and washed with 1N HCl (30 mL) and brine. After removal of the solvent, a solid was obtained, which was dissolved in THF and precipitated twice with MeOH. The solid, R-**7**, was isolated by centrifugation and removal of the solution with pipette, and was dried under vacuum at room temperature for 24 h. The yield of R-**7** was 95% (695 mg). $[\alpha]_D$ = -351° (c = 0.38, THF). GPC (THF, polystyrene standard): M_n = 20,000, M_w = 67,000, PDI = 3.4. DSC: T_g = 211.4 °C. TGA: T_{onset} = 339.6 °C. UV-vis λ_{max} (CH_2Cl_2) nm 390, 268. FT-IR (KBr) cm^{-1} 1622 (w), 1593 (s), 1518 (w), 1493 (s), 1462 (s), 1402 (w), 1343 (s), 1275 (s), 1244 (s), 1094 (m), 1055 (s), 1018 (w), 961 (w), 945 (w), 817 (s) . ^1H NMR (400 MHz, $CDCl_3$, broad peaks) δ 0.70 (CH_3), 1.00 [-(CH_2)$_2$$CH_3$], 1.42 (-$CH_2CH_2$O-), 3.96 (-O$CH_2$-), 6.61 (-$CH$=$CH$-), 7.11-7.69 (Ar-$H$, -$CH$=$CH$-), 8.00-8.11 (Ar-$H$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.88, 22.43, 25.31, 29.32, 31.28, 69.65, 116.11, 120.37, 125.45, 126.06, 126.34, 126.83, 126.90, 127.29, 128.13, 129.28, 129.33, 129.40, 133.44, 135.40, 135.94, 135.99, 136.19, 136.65, 139.86, 140.35, 154.74. Anal. Calcd for $C_{54}H_{52}O_2$: C, 88.53; H 7.10. Found: C, 87.79; H, 7.30.

Polymer rac-7: Rac-**7** was prepared similarly to R-**7** in 96% yield. GPC (THF, polystyrene standard): M_n = 17,000, M_w = 48,000, PDI = 2.8. DSC: T_g = 203.4 °C. TGA: T_{onset} = 391.4 °C. UV-vis λ_{max} (CH_2Cl_2) nm 392,268. FT-IR (KBr) cm^{-1} 1622 (w), 1593 (s), 1518 (m), 1493 (s), 1462 (s), 1402 (m), 1343 (s), 1275 (s), 1244 (s), 1094 (m), 1055 (m), 1018 (m), 961 (m), 945 (w), 817 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (-CH_3), 1.00 [-(CH_2)$_2$$CH_3$], 1.42 (-$CH_2CH_2$O-), 3.96 (-O$CH_2$), 6.61 (-$CH$=$CH$-), 7.03-7.71 (Ar-$H$, -$CH$=$CH$-), 7.97-8.11(Ar-$H$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.94, 22.46, 25.34, 29.34, 31.31, 69.68, 116.13, 120.39, 125.47, 126.08, 126.36, 126.85, 126.92,127.31, 128.15, 129.30, 129.35, 129.42, 133.46, 135.42, 135.96, 136.01,136.21, 136.67, 139.89, 140.37, 154.76. Anal. Calcd for $C_{54}H_{52}O_2$: C, 88.53; H, 7.10. Found: C, 87.54; H, 7.13.