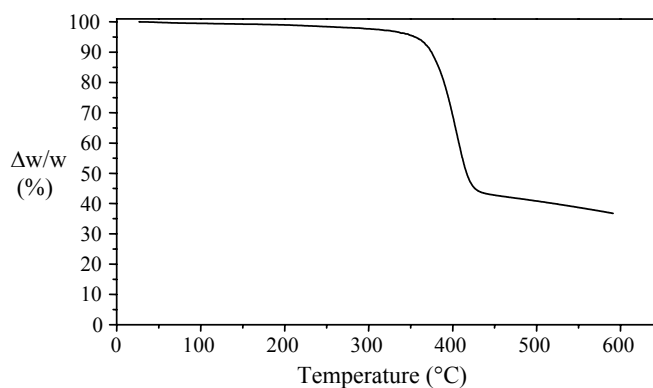


1.



TGA chart of copolymer **7** in nitrogen. Heating rate: 10°C/min.

2. Synthesis of monomers and copolymers (6-8)

2-(2-Methoxyethoxy)ethyl-p-toluenesulfonate. Under nitrogen atmosphere, 2 g (1.66×10^{-2} mole) of 2-(2-methoxyethoxy)ethanol and 7.86 g (9.96×10^{-2} mole) of pyridine were dissolved in 50 mL of freshly distilled CH_2Cl_2 . The medium was cooled in an ice bath. Tosyl chloride (2.49×10^{-2} mole; 4.74 g) was then slowly added by portions to the reaction mixture. After the addition was complete, the cooling bath was removed and the mixture was stirred at room temperature overnight. It was then hydrolyzed with a 0.1M HCl solution, extracted three times with ether, washed, dried over magnesium sulfate and concentrated under vacuum. The crude product was obtained in 85 % yield and was used without further purification. ^1H NMR (CDCl_3 , 200 MHz): 2.35 (3H, s, CH_3 -Ph), 3.37 (3H, s, OCH_3), 3.53 (2H, t, $J=5\text{Hz}$, CH_2), 3.57 (2H, t, $J=5\text{Hz}$, CH_2), 3.65 (2H, t, $J=5\text{Hz}$, CH_2), 4.16 (2H, t, $J=5\text{Hz}$, CH_2), 7.31 (2H, d, $J=8\text{Hz}$, H_{ar} of Ts), 7.8 (2H, d, $J=8\text{Hz}$, H_{ar} of Ts). ν_{max} (KBr)/ cm^{-1} : 2951, 2878, 1483, 1445, 1356, 1260, 1105, 1020, 948, 850, 796.

2-(2-Butoxyethoxy)ethyl-p-toluenesulfonate. It was prepared in a similar way as 2-(2-methoxyethoxy)ethyl-p-toluenesulfonate using 2 g (1.23×10^{-2} mole) of 2-(2-butoxyethoxy)ethanol, 5.83 g (7.38×10^{-2} mole) of pyridine dissolved in 50 mL of CH_2Cl_2 and 3.52g (1.84×10^{-2} mole) of tosyl chloride. It was obtained in 90 % yield. ^1H NMR (CDCl_3 , 200 MHz): 0.88 (3H, t, $J=5\text{Hz}$, CH_3), 1.35-1.55 (4H, m, 2 CH_2), 2.44 (3H, s, CH_3 -Ph), 3.40 (2H, t, $J=6\text{Hz}$, CH_2), 3.55 (4H, m, CH_2), 3.68 (2H, m, CH_2), 4.15 (2H, m, CH_2), 7.3 (2H, d, $J=8\text{Hz}$, H_{ar} of Ts), 7.8 (2H, d, $J=8\text{Hz}$, H_{ar} of Ts). ν_{max} (KBr)/ cm^{-1} : 2947, 2880, 1485, 1443, 1357, 1261, 1104, 1019, 942, 852, 795.

1,4-Dibromo-2,5-bis(dioxa-3,6-heptyloxy)benzene (2). Under nitrogen, a mixture containing 1.35 g (5×10^{-3} mole) of **1** and 6.51 g (2×10^{-2} mole) of Cs_2CO_3 in 40 mL of freshly distilled THF was introduced in a three necked flask equipped with a condenser. 2.6 g (9.4×10^{-3} mole) of 2-(2-methoxyethoxy)ethyl-p-toluenesulfonate in 20 mL of THF was slowly added to the reaction mixture. After the addition was complete, the mixture was refluxed for 45 hours then hydrolyzed with an iced NaOH (0.5 N) aqueous solution. The product was extracted

with ether (3x30 mL), washed with NH₄Cl (0.1N), dried over magnesium sulfate and concentrated under vacuum. **2** was obtained as a pale yellow solid (2.35 g, 5 x 10⁻³ mole, 53%). m.p. 53-55°C; Anal. Calcd for (C₁₆H₂₄O₆Br₂): C, 40.68; H, 5.08; Br, 33.90. Found: C, 40.48; H, 5.16; Br, 32.92. ¹H NMR (CDCl₃, 200 MHz) 3.39 (6H, s, OMe), 3.56 (4H, t, *J*= 5Hz, CH₂-OMe), 3.77 (4H, t, *J*= 5Hz, CH₂-CH₂-OMe), 3.85 (4H, t, *J*= 5Hz, CH₂-CH₂-OPh), 4.15 (4H, t, *J*= 5Hz, CH₂-OPh), 7.15 (2H, s, H_{phenyl}). ¹³C NMR (CDCl₃, 200MHz) 59.0, 69.5, 70.2, 71.0, 72.0, 111.3, 119.1, 150.2. ν_{\max} (KBr)/cm⁻¹: 3081, 2899, 2727, 1619, 1461, 1260, 1100, 915, 804. MS: *m/z*: 472 (M).

1,4-Dibromo-2,5-bis(dioxa-3,6-decyloxy)benzene (3). **3** was prepared as described for **2** using 1.35 g (5 x 10⁻³ mole) of **1**, 6.51 g (2 x 10⁻² mole) of Cs₂CO₃ in 40 mL of THF and 3 g (9.4 x 10⁻³ mole) of 2-(2-butoxyethoxy)ethyl-p-toluenesulfonate diluted in 20 mL of dry THF. **3** was obtained as a brown oil (2.68 g, 4.8 x 10⁻³ mole, 51%). Anal. Calcd for (C₂₂H₃₆O₆Br₂): C, 47.52; H, 6.55; Br, 28.76. Found: C, 47.63; H, 6.69; Br, 27.79. ¹H NMR (CDCl₃, 200 MHz) 0.90 (6H, t, *J*=6Hz, CH₃), 1.33 (4H, m, CH₂-CH₃), 1.57 (4H, m, CH₂-CH₂-CH₃), 3.47 (4H, t, *J*=5Hz, CH₂-O), 3.62-3.73 (8H, m, -CH₂-CH₂-OBu), 3.87 (4H, t, *J*=5Hz, CH₂-CH₂OAr), 4.12 (4H, t, *J*=5Hz, CH₂-OAr), 7.15 (2H, s, H_{phenyl}). ¹³C NMR (CDCl₃, 200MHz) 12.7, 18.0, 30.5, 68.3, 69.0, 69.9, 70.0, 70.9, 110.1, 118.0, 149.1. ν_{\max} (KBr)/cm⁻¹: 2947, 2861, 1485, 1452, 1357, 1219, 1128, 1066, 938, 852, 780. MS: *m/z*: 554 (M-2).

1,4-Bis(trioxa-3,6,9-decyloxy)benzene (4). Under nitrogen, 9.43 g (4.77 x 10⁻² mole) of hydroquinone bis(2-hydroxyethyl)ether diluted in 100 mL of DMSO and 13.3 g (0.235 mole) of powdered KOH were introduced into a three necked flask equipped with a condenser. 26.13 g (9.5 10⁻² mole) of 2-(2-methoxyethoxy)ethyl-p-toluenesulfonate in 50 mL of DMSO were slowly added to the reaction mixture. After the addition was complete, the mixture was stirred for 72 hours at room temperature. The medium was hydrolyzed and the product was extracted with ether (3 x 40 mL), washed with water to neutrality, dried over magnesium sulphate and concentrated under vacuum. **4** was obtained as a pale yellow oil (14.57 g, 3.63 x 10⁻² mole, 76%). Anal. Calcd for (C₂₀H₃₄O₈): C, 59.71; H, 8.45. Found: C, 59.35; H, 8.69. ¹H NMR (CDCl₃, 200 MHz) 3.38 (6H, s, OMe), 3.56 (4H, t, *J*= 5Hz, CH₂-OMe), 3.70 (12H, m, CH₂), 3.82 (4H, t, *J*= 6Hz, CH₂-CH₂OAr), 4.07 (4H, t, *J*= 5Hz, CH₂-OAr), 6.83 (4H, s, H_{phenyl}). ¹³C NMR (CDCl₃, 200MHz) 58.4, 67.5, 69.3, 69.9, 70.0, 70.2, 71.3, 115.0, 152.5. ν_{\max} (KBr)/cm⁻¹: 2880, 1642, 1509, 1452, 1283, 1233, 1124, 1062, 938, 823, 747. MS: *m/z*: 402 (M).

1,4-Dibromo-2,5-bis(trioxa-3,6,9-decyloxy)benzene (5). Under nitrogen, 2.46 g (6.1 x 10⁻³ mole) of **4**, diluted with 50 mL of CHCl₃, was introduced into a three necked flask equipped with a condenser and a dropping funnel. 1 mL of bromine diluted with 10 mL of CHCl₃ was then added dropwise to the reaction mixture. After

the addition was complete, the mixture was stirred for 2 hours at room temperature and then refluxed for 24 h. After cooling, the medium was hydrolyzed with a NaOH (0.5 N) aqueous solution and the product was extracted with ether (3x40 mL), washed with water to neutrality, dried over magnesium sulphate and concentrated under vacuum. A yellow oil was obtained and was purified on a silica gel column using CH₂Cl₂ as eluent to give **5** in 79% yield (2.7 g; 4.53 x 10⁻³ mole). M.p. 34-35°C; Anal. Calcd for (C₂₀H₃₂O₈Br₂): C, 42.84; H, 5.75. Found: C, 42.43; H, 5.40. ¹H NMR (CDCl₃, 200 MHz) 3.38 (6H, s, OMe), 3.52 (4H, t, *J* = 5 Hz, CH₂-OMe), 3.72-3.61 (8H, m, OCH₂), 3.77 (4H, t, *J* = 5 Hz, ArOCH₂-CH₂-OCH₂), 3.86 (4H, t, *J* = 5 Hz, ArOCH₂-CH₂) 4.12 (4H, t, *J* = 5 Hz, ArOCH₂), 7.15 (2H, s, H_{phenyl}). ¹³C NMR (CDCl₃, 200 MHz) 59.0, 69.6, 70.2, 70.6, 70.7, 71.1, 72.0, 111.4, 119.2, 150.3. ν_{\max} (KBr)/cm⁻¹: 2880, 1738, 1490, 1447, 1352, 1204, 1128, 1061, 942, 847, 780. MS: *m/z*: 560 (M).

Copolymer (6). In a 50 mL Schlenk tube equipped with a condenser was dissolved, under a nitrogen atmosphere and at room temperature, 21.4 mg (1.8 x 10⁻⁵ mole) of Pd(PPh₃)₄ in 10 mL of a THF/DMF (1:1) solvent mixture. 1.86 x 10⁻³ mole (0.8784 g) of **2** and 1.86 x 10⁻³ mole (1.231 g) of 2,5-bis-(tributylstannyl)thiophene were introduced by syringe. The reaction mixture was stirred at 80°C for three days. It was then cooled down and a red precipitate formed upon addition of methanol. The solid was filtered, washed with methanol and dried under vacuum to give 0.614 g of **6**. (Yield : 84 %); ¹H NMR (CDCl₃, 400 MHz) 3.31 (6H, s, OMe), 3.53 (4H, t, *J* = 5 Hz, CH₂), 3.69 (4H, m, CH₂), 3.92 (4H, m, CH₂), 4.28 (4H, m, CH₂), 7.4 (2H, s, H_{thienyl}), 7.53 (2H, s, H_{phenyl}); ν_{\max} (KBr)/cm⁻¹: 2963, 1490, 1455, 1404, 1261, 1214, 1107, 802, 700; Found: C, 57.90; H, 6.28; S, 7.61.

Copolymer (7). Copolymer **7** was obtained as above with 32.81 mg (2.8 x 10⁻⁵ mole) of Pd(PPh₃)₄, 2.8 x 10⁻³ mole (1.58 g) of **3** and 2.8 x 10⁻³ mole (1.881 g) of 2,5-bis-(tributylstannyl)thiophene in 10 mL of THF/DMF (50 : 50) mixture. Yield: 90% (1.22 g). ¹H NMR (CDCl₃, 400 MHz) 0.81 (6H, t, *J* = 4 Hz, CH₃), 1.28 (4H, m, CH₂), 1.48 (4H, m, CH₂), 3.38 (4H, t, *J* = 5 Hz, CH₂) 3.55 (4H, m, CH₂), 3.69 (4H, m, CH₂), 3.92 (4H, m, CH₂), 4.24 (4 H, m, CH₂), 7.3 (2H, s, H_{thienyl}), 7.55 (2H, s, H_{phenyl}); ν_{\max} (KBr)/cm⁻¹: 2947, 2851, 1490, 1452, 1438, 1357, 1219, 1119, 857, 800; Found: C, 63.77; H, 8.20; S, 7.16.

Copolymer (8). As above, copolymer **8** was obtained by use of 13.17 mg (1.1 x 10⁻⁵ mole) of Pd(PPh₃)₄, 1.14 x 10⁻³ mole (0.640 g) of **5** and 1.14 x 10⁻³ mole (0.7565 g) of 2,5-bis-(tributylstannyl)thiophene in 10 mL of THF/DMF (50 : 50) mixture. Yield: 89 % (0.49 g); ¹H NMR (CDCl₃, 400 MHz) 3.27 (6H, s, CH₃), 3.44 (4H, m, CH₂), 3.55 (4H, m, CH₂), 3.58 (4H, m, CH₂), 3.63 (4H, m, CH₂), 3.70 (4H, m, CH₂), 3.91 (4H, m, CH₂), 4.24 (4H, m, CH₂), 7.3 (2H, s, H_{thienyl}), 7.54 (2H, s, H_{phenyl}); ν_{\max} (KBr)/cm⁻¹: 2947, 1733, 1642, 1490, 1452, 1400, 1347, 1257, 1214, 1104, 933, 852, 800, 695; Found: C, 54.73; H, 6.70; S, 5.81.