

mmol) of 4-iodophenol and 12.7 g (318 mmol) of sodium hydroxide in 120 mL of dimethyl sulfoxide was heated at 80 °C with stirring until sodium hydroxide was completely dissolved. Then 32.3 g (117 mmol) of 1,14-dichloro-3,6,9,12-tetraoxatetradecane was added to the mixture. After stirring at 100 °C for 4 h, the reaction mixture was diluted with 200 mL of water and extracted with four 200 mL portions of toluene. The extracts were washed with 200 mL of 2 mol·L⁻¹ aqueous sodium hydroxide solution and water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was recrystallized from toluene to give 52.3 g of **3** (yield, 69.4%) as a white powder. Mp: 102–103 °C. ¹H NMR (CDCl₃): δ 3.64 (s, 4H, CH₂), 3.68 (s, 8H, CH₂), 3.75–3.95 (m, 4H, ArOCH₂CH₂), 3.95–4.20 (m, 4H, ArOCH₂), 6.68, 7.53 (d, 8H, *J* = 9.01 Hz, aromatic). Anal. Calcd for C₂₂H₂₈I₂O₆ (642.27): C, 41.14; H, 4.39; I, 39.52. Found: C, 41.09; H, 4.40; I, 39.63.

Synthesis of 1,14-Bis{[4-(trimethylsilyl)ethynyl]phenoxy}-3,6,9,12-tetraoxatetradecane (4). To a solution of 23 g (35.8 mmol) of **3**, 1.1 g (1.57 mmol) of bis(triphenylphosphine)palladium(II) chloride, and 228 mg (0.72 mmol) of copper(I) iodide in 300 mL of dry piperidine was added 12 mL (85 mmol) of (trimethylsilyl)acetylene at 50 °C. After 7 h, the white precipitate was removed. The precipitate was then washed with toluene. The filtrate was evaporated, and the residue was treated with 200 mL of water and extracted with toluene (100 mL × 4). The extracts were dried, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/methanol (v/v, 97:3) and then with dry chloroform. A raw product free from solvent was recrystallized from hexane/ether (v/v, 50:50) to give 15.6 g of **4** (yield, 75.0%) as a light beige flake crystal. Mp: 77–78 °C. ¹H NMR (CDCl₃): δ 0.25 (s, 18H, SiCH₃), 3.65 (s, 4H, CH₂), 3.69 (s, 8H, CH₂), 3.75–3.93 (m, 4H, ArOCH₂CH₂), 4.10–4.20 (m, 4H, ArOCH₂), 6.86, 7.43 (d, 8H, *J* = 9.01 Hz, aromatic). Anal. Calcd for C₃₂H₄₆O₆Si₂ (582.89): C, 65.94; H, 7.95. Found: C, 65.92; H, 7.90.

Synthesis of 1,14-Bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (1). A solution of 5.0 g (8.57 mmol) of **4** and 3.1 g (29.1 mmol) of Na₂CO₃ in 100 mL of MeOH was stirred at 30 °C for 3 h. The reaction mixture was diluted with 500 mL of water and then

extracted with five 200 mL portions of toluene. The extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/methanol (v/v, 97:3) and then with dry chloroform to produce a raw product. The compound was recrystallized from ether to give 3.3 g of **1** (yield, 88%) as a light yellow flake crystal. Mp: 51–52 °C. ¹H NMR (CDCl₃): δ 2.99 (s, 2H, HC≡), 3.64 (s, 4H, CH₂), 3.67 (s, 8H, CH₂), 3.72–3.89 (m, 4H, ArOCH₂CH₂), 4.04–4.17 (m, 4H, ArOCH₂), 6.83, 7.40 (d, 8H, *J* = 9.01 Hz, aromatic). ¹³C NMR (CDCl₃): δ 67.42 (ArOCH₂), 69.56 (ArOCH₂CH₂), 70.81, 70.58, 70.58 (CH₂), 75.88 (HC≡), 83.60 (≡C–), 114.27, 133.49, 114.54, 159.10 (aromatic). Anal. Calcd for C₂₆H₃₀O₆ (438.52): C, 71.21; H, 6.90. Found: C, 71.31; H, 6.93.

Cyclopolymerization. The polymerizations were carried out with WCl₆ and MoCl₅ in toluene, with W(CO)₆/hν and Mo(CO)₆/hν in CCl₄, and with [Rh(bhd)-Cl]₂ in chloroform. After 24 h at 30 °C, the polymerization mixture was poured into a large amount of *n*-hexane, and the polymer was purified by reprecipitation from chloroform/ether.

References and Notes

- (1) Kakuchi, T.; Matsunami, S.; Kamimura, H.; Ishii, F.; Uesaka, T.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.*, accepted.
- (2) (a) Kakuchi, T.; Haba, O.; Yokota, K. *Macromolecules* **1992**, *25*, 4854–4858. (b) Kakuchi, T.; Aoki, K.; Haba, O.; Yokota, K. *Polym. J.* **1993**, *25*, 839–845.
- (3) (a) Hashimoto, H.; Kakuchi, T.; Haba, O.; Yokota, K. *Macromolecules* **1992**, *25*, 1828–1831. (b) Kakuchi, T.; Hashimoto, H.; Harada, Y.; Satoh, T.; Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 751–759.
- (4) (a) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 1697. (b) Kang, K.-L.; Kim, S.-H.; Cho, H.-N.; Choi, K.-Y.; Choi, S.-K. *Macromolecules* **1993**, *26*, 4539 and references cited therein. (c) Fox, H. H.; Wolf, M. O.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.
- (5) Masuda, T.; Kawasaki, M.; Okano, Y.; Higashimura, T. *Polym. J.* **1982**, *14*, 371.
- (6) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.
- (7) Furlani, A.; Licoccia, S.; Russo, M. V. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 991.
- (8) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105.
- (9) Pedersen, C. J. *Fed. Am. Soc. Exp. Biol.* **1968**, *27*, 1305.

MA941180Y

CORRECTIONS

P. Van der Schoot: Nematic Transition in Solutions of Semiflexible Chains: Influence of an Annealed Size Distribution. Volume 27, Number 22, October 24, 1994, pp 6473–6475.

The expression under eq 2 should read $\sigma_1 \propto x = l/P$.

MA941139V