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New Route to the Introduction of Axial and Helical Chiral Units into Poly(arylene ether)s

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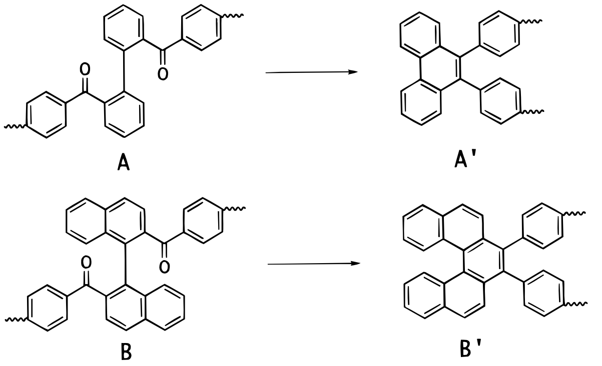
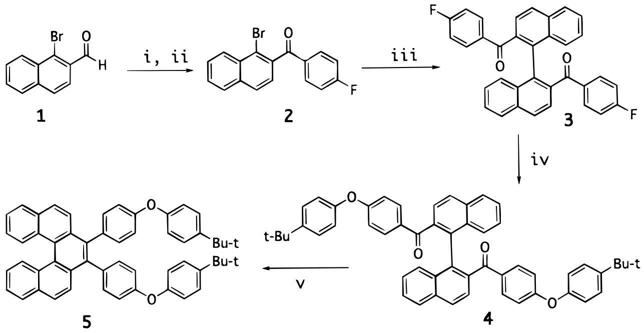
Introduction of a chiral element into the polymer backbone is of synthetic interest and also may lead to a discovery of a new class of chiroptical materials with potential applications in high-tech industries. Among many chiral molecules, *ortho*-substituted 1,1′-binaphthyls[1] and helicenes[2] are particularly notable for their axial and helical chiralities, conjugated π-systems, and fluorescent and chiroptical behaviors. If chiral binaphthyl and helicene are functionalized and polymerized, the resulting polymers are expected to possess some unique properties inherited from these chiral components. A widely used starting material for functionalized chiral binaphthyls is 1,1′-binaphth-2,2′-ol. It can be resolved in large quantities[3] and has been functionalized to yield a variety of monomers such as dibromides for chiral polyarylenes,[4,5] a diamine for polyamides and polyimides,[6] and a dianhydride for aromatic polyimides.[7] In contrast to the chiral binaphthyl system, helicene-based chiral polymers have received less attention, partially due to difficulties in the synthesis and functionalization of helicenes. To date, only a few helicene-based polymers have been synthesized, such as an optically active metallocene polymer derived from a functionalized [6]helicene,[8] the polyimides derived from a [5]helicene dianhydride synthesized by Frimer *et al.* and several [5]helicene AB-type amino anhydride and AA-type diamines reported by us.[9] We have also demonstrated the introduction of the [5]helicene unit into polyimides via chemical transformation of tetrahydro[5]helicene-based precursor polymers.[9d] Generally speaking, helicenes are made in a multistep sequence that usually involves a photochemical cyclization of stilbene-type compounds and are difficult to functionalize with polymerizable groups.[2] Thus, it is desirable to apply the precursor strategy to the synthesis of helicene-containing polymers.

We have previously reported transformation of the 2,2′-dibenzoylbiphenyl unit into a phenanthrene moiety in the backbone of poly(arylene ether)s via a deoxy-olefination reaction using Lawesson's reagent (A to A′, Scheme 1).[10] By analogy, the 2,2′-dibenzoyl-1,1′-binaphthyl unit in a polymer should undergo the same deoxy-olefination reaction, yielding the chiral [5]helicene unit (B to B′, Scheme 1). Thus, this polymer transformation would allow the introduction of helical chiral units into a polymer via a chirality transformation of a precursor polymer containing axial chiral units. To demonstrate the synthetic feasibility and concept of chirality transfer, a novel monomer having an axial chirality, 2,2′-bis(4-fluorobenzoyl)-1,1′-binaphtyl (**3**, Scheme 2), was designed, in which two benzoyl groups should be large enough to hinder the rotation around the axis of the two naphthalene rings.

Scheme 1. Intramolecular Deoxy-Olefination of Dibenzoylbiaryls



Scheme 2. Syntheses of Monomer 3 and Model Compounds 4 and 5



The difluoride monomer **3** was synthesized in three steps from 1-bromo-2-naphthaldehyde (**1**, Scheme 2), which was prepared from 1-bromo-2-methylnaphthalene.[11] Aldehyde **1** was reacted with (4-fluorophenyl)-magnesium bromide to yield the corresponding alcohol, which was then oxidized using pyridinium chlorochromate to give ketone **2**.[12] The coupling of **2** using a Ni(0) catalyst[13] afforded the racemic monomer **3** in 45% overall yield based on aldehyde **1**.[14] The FTIR spectrum of monomer **3** showed a carbonyl peak at 1657 cm^{-1}, which is indicative of a conjugated ketone. The structure of monomer **3** was further confirmed by ^{1}H NMR coupled with the 2D COSY experiment.

A model reaction between 4-*tert*-butylphenol and monomer **3** was first carried out under standard nucleophilic displacement conditions (Scheme 2). As expected, the ketone-activated difluoride monomer was reactive enough to undergo quantitative nucleophilic displacement by the phenol to form the corresponding ether **4**.[15] Compound **4** was more soluble than monomer **3** due to the introduction of the flexible ether bonds. Its structure was fully characterized by ^{1}H and ^{13}C NMR, IR, and FAB-MS. Compound **4** absorbs UV radiation with a maximum at 294 nm but does not fluoresce at this wavelength. Chemical transformation using the established method[10] was then performed on compound **4** to obtain the model compound **5** having a chiral [5]-helicene moiety (Scheme 2). The IR spectrum of the [5]-helicene **5** showed the complete disappearance of the carbonyl peak previously found at 1664 cm^{-1} in the spectrum of the precursor **4**. The UV absorption spectrum displayed two peaks centered at 267 and 315 nm. A chloroform solution of the [5]helicene **5** appeared fluorescent to the naked eye and it was blue light emitting with a maximum emission at 435 nm under UV (315 nm) irradiation.[16] In addition, the ^{1}H NMR spectrum of **5** (spectrum a, Figure 1) confirms the

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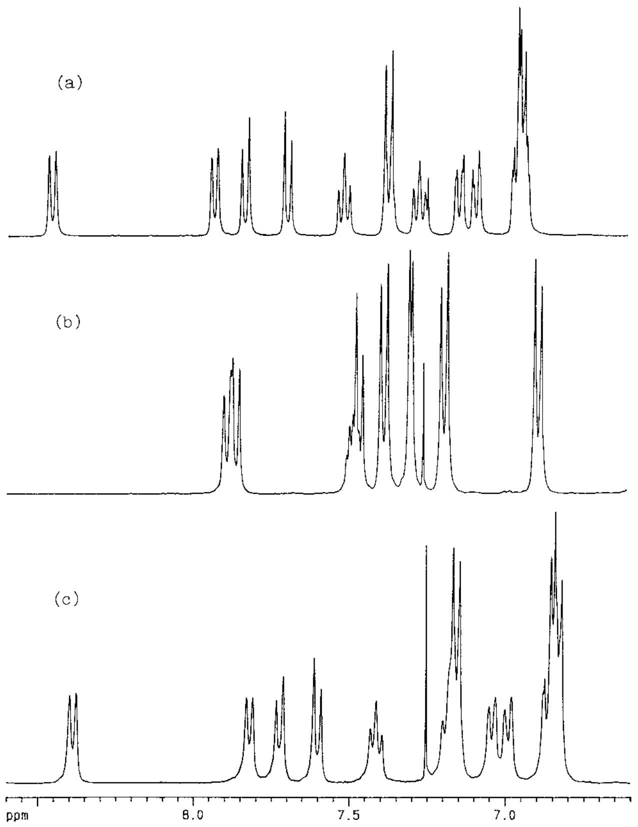


Figure 1. ^{1}H NMR spectra (400 MHz, 6.6−8.6 ppm) of (a) model compound **5**, (b) polymer **6**, and (c) polymer **7**. The singlet peaks at 1.33 ppm for **5** and 1.64 ppm for **6** and **7** and a doublet at 6.59 ppm for **6** are not shown.

helicene structure of the model compound, as indicated by the characteristic “bay” protons at 8.45 ppm.

Following successful model reactions, monomer **3** was then polymerized with Bisphenol A under the same conditions as the model reaction, yielding high molecular weight poly(ether ketone) **6**. Gel permeation chromatography indicated the apparent weight-average molecular weight (M_w) of 101 000 and a polydispersity index (M_w/M_n) of 2.2, relative to polystyrene standards. The inherent viscosity seemed unusually low (0.36 dL/g, $CHCl_3$, 25 °C) in comparison with other naphthalene-containing poly(ether ketone)s[17] but could be justified by its coiled and nonlinear shape. Polymer **6** was soluble in chloroform and could be cast into a tough flexible film. A glass transition temperature (T_g) was 225 °C by differential scanning calorimetry and the onset temperature for 5% weight loss in nitrogen was found to be 485 °C, as assessed by thermogravimetry. In its IR spectrum, a carbonyl peak was clearly identified at 1664 cm^{-1} (spectrum a, Figure 2). The ^{1}H and ^{13}C NMR spectra of polymer **6** resemble those of model compound **4**. The UV spectrum showed a maximum absorbance at 294 nm.

Chemical transformation of poly(ether ketone) **6** was then carried out using Lawesson’s reagent in TCE at 120 °C. The resulting poly(arylene ether) **7** had molecular weight ($M_w = 82\ 000$, $M_w/M_n = 2.0$) similar to that of the precursor polymer **6** and remained soluble in chloroform. The carbonyl absorption at 1664 cm^{-1} (spectrum a, Figure 2) of the precursor **6** completely disappeared in the IR spectrum (spectrum b, Figure 2) of the [5]helicene polymer **7**. The ^{1}H NMR spectrum of polymer **7** (spectrum c, Figure 1) was similar to that of the model compound **5** (spectrum a) but quite different from that of the precursor **6** (spectrum b). Again, there is a characteristic doublet at 8.40 ppm attributed to the internal “bay” protons of the [5]helicene moiety. Furthermore, two separate doublets at about 7.0 ppm in both spectra a and b are due to a case of magnetic nonequivalence of the two protons of the pendent benzene ring, which implies the restricted rotation of the pendent benzene rings attached on the [5]helicene core. Polymer **7** had UV absorbances at 268 and 315 nm and a maximum fluorescent emission at 435 nm when excited at 315 nm. The onset temperature for 5% weight loss in nitrogen was found to be 459 °C for polymer **7**. Introduction of the rigid [5]helicene unit into the polymer backbone resulted in an increase in the chain rigidity, as indicated by an increase in the T_g for polymer **7** to 265 °C.

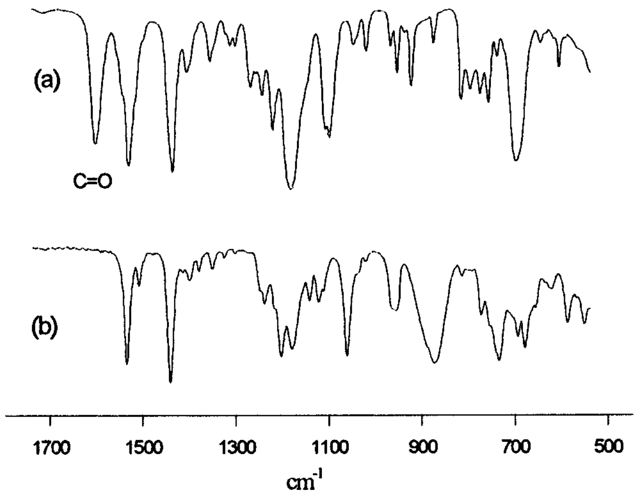
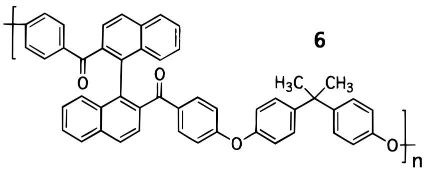


Figure 2. IR spectra of (a) binaphthyl poly(ether ketone) **6** and (b) [5]helicene poly(arylene ether) **7**.



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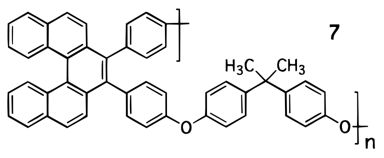

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In conclusion, a synthetic approach to the synthesis of a soluble, fluorescent, high molecular weight [5]-helicene poly(arylene ether) has been established using a chiral binaphthyl poly(ether ketone) as a precursor derived from novel monomer **3**. The synthetic sequence shown herein demonstrates the successful introduction of axial and helical chiral units into poly(arylene ether)s.

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References and Notes

(1) (a) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley and Sons, Inc.: Toronto, 1994; Chapter 14. (b) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977.

(2) (a) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649. (b) Meurer, K. P.; Vögtle, F. Helical Molecules in Organic Chemistry. In *Topics in Current Chemistry*; Dewar, M. J. S., Dunitz, J. D., Hafner, K., Heilbronner, E., Ito, S., Lehn, L.-M., Niedenzuk, N., Raymond, K. N., Rees, C. W., Vögtle, F., Wittig, G., Eds.; Springer-Verlag: New York, 1985; Vol. 127, pp 32−53.

(3) Hu, Q.-S.; Vitharana, D.; Pu, L. *Tetrahedron Asym.* **1995**, *6*, 2123 and references cited therein.

(4) (a) Hu, Q.-S.; Vitharana, D.; Liu, G.-Y.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082. (b) Hu, Q.-S.; Vitharana, D.; Liu, G.-Y.; Jain, V.; Pu, L. *Macromolecules* **1996**, *29*, 5075. (c) Ma, L.; Hu, Q.-S.; Musick, K. Y.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083. (d) Ma, L.; Hu, Q.-S.; Pu, L. *Tetrahedron Asym.* **1996**, *7* (11), 3103. (e) Pu, L. *Acta Polym.* **1997**, *48*, 116.

(5) Bedworth, P. V.; Tour, J. M. *Macromolecules* **1994**, *27*, 622.

(6) (a) Liou, G.-S.; Kakimoto, M.-A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3265. (b) Liou, G.-S.; Maruyama, M.; Kakimoto, M.-A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2499.

(7) Mi, Q.; Gao, L.-X.; Ding, M.-X. *Macromolecules* **1996**, *29*, 5758.

(8) Dai, Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2109.

(9) (a) Frimer, A. A.; Kender, J. D.; Youngs, W. J.; Meador, M. A. B. *J. Org. Chem.* **1995**, *60*, 1658. (b) Frimer, A. A.; Cavano, P. J.; Alston, W. B. *High Perform. Polym.* **1995**, *7*, 93. (c) Wang, Z. Y.; Qi, Y.; Bender, T. P.; Gao, J. P. *Macromolecules* **1997**, *30*, 764. (d) Bender, T. P.; Qi, Y.; Gao, J. P.; Wang, Z. Y. *Macromolecules* **1997**, *30*, 6001.

(10) (a) Zhang, C.; Wang, Z. Y. *Macromolecules* **1993**, *26*, 3330. (b) Wang, Z. Y.; Zhang, C.; Arnoux, F. *Macromolecules* **1994**, *27*, 4415.

(11) Aldehyde **1** was prepared in 63% overall yield according to reported procedures involving (i) bromination of 1-bromo-2-methylnaphthalene with *N*-bromosuccinimide,[11a] (ii) hydrolysis in aqueous 1,4-dioxane with $CaCO_3$,[11b] and (iii) oxidation by pyridinium chlorochromate (PCC).[11c] (a) Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Org. Chem.* **1986**, *51*, 3762. (b) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242. (c) Corey, E.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(12) Mp 134−136 °C; IR (KBr) 1672 (C═O), 1596 (C═C aromatic) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10−7.17 (t, 2H), 7.35−7.39 (d, 1H), 7.60−7.72 (m, 2H), 7.83−7.95 (m, 4H), 8.37−8.39 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.8, 116.1, 119.8, 124.5, 126.8, 127.8, 128.2, 128.3, 128.4, 131.9, 132.6, 132.8, 132.9, 134.6, 138.5, 164.9, 167.5, 194.9; MS (EI, *m/e*, relative intensity) 328 ($M^{\bullet+}$, 52.1), 249 ($M^{\bullet+} - {}^{\bullet}Br$, 11.4), 233 ($M^{\bullet+} - {}^{\bullet}PhF$, 32.9), 123 ($COPhF^+$,100).

(13) Colon, I.; Kelsey, R. R. *J. Org. Chem.* **1986**, *51*, 2627.

(14) A 250 mL, three-necked, round-bottomed flask was charged with zinc (2.900 g, 0.046 mol) and flame dried under argon flow. Triphenylphosphine (3.200 g, 0.012 mol), $NiCl_2$ (0.400 g, 0.0012 mol), and anhydrous DMAc (40 mL) were added to the flask, and the resulting mixture was stirred at 80 °C for 15 min to generate the blood red catalyst. After 1 h of stirring, a solution of 1-bromo-2-(4-fluorobenzoyl)naphthalene (10.00 g, 0.031 mol) in DMAc (40 mL) was added slowly to the reaction flask. The reaction continued at 80 °C overnight. DMAc was then removed by vacuum distillation. The residue was recrystallized from 1,2-dichlorobenzene to give monomer **3** as a white solid; 4.63 g (61%); mp 298 °C; IR (KBr) 1657 cm^{-1}; UV ($CHCl_3$) λ_{max} 255 nm; ^1H NMR (400 MHz, 1:1 $CF_3COOD/CDCl_3$) δ 6.75−6.84 (t, 4H), 7.37−7.43 (m, 4H), 7.52−7.66 (m, 8H), 7.95−7.99 (d, 2H), 8.01−8.25 (d, 2H); MS (EI, *m/e*, relative intensity) 498 ($M^{\bullet+}$, 6.6), 375 ($M^{\bullet+}$ − COPhF, 100.0). Anal. Calcd for $C_{34}H_{20}O_2F_2$: C, 81.92; H, 4.04; F, 7.62. Found: C, 81.57; H, 4.06; F, 7.89.

(15) Mp 125−135 °C; IR (KBr) 1664 (C═O) cm^{-1}; UV ($CHCl_3$) λ_{max} 295 nm; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 6.55−6.62 (d, 2H), 6.94−6.99 (d, 2H), 7.30−7.40 (m, 6H), 7.47−7.56 (m, 2H), 7.89−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 161.9, 152.7, 147.6, 136.5, 136.0, 134.3, 133.5, 132.5, 131.4, 128.3, 128.0, 127.3, 127.2, 126.9, 126.8, 125.4, 119.9, 116.0, 31.6, 31.5; MS (FAB, *m/e*, relative intensity) 759 ($M + H^+$, 8.1).

(16) In a 50 mL round-bottomed flask, compound **4** (0.400 g, 0.530 mmol) was dissolved in 15 mL of 1,1,2,2-tetrachloroethane (TCE) under argon. Upon the addition of Lawesson's reagent (0.43 g, 1.06 mmol), the reaction mixture was heated to 120 °C and turned from a light lime green to a dark aquamarine color within 30 min. The reaction mixture was stirred at 120 °C overnight, after which IR showed the complete disappearance of the ketone peak at 1664 cm^{-1}. TCE was distilled from the reaction mixture. The remaining solid was washed several times with methanol and stirred in boiling methanol for 3 h. Compound **5** was obtained as a white solid: 0.27g (70.2%); mp 283−285 °C; UV ($CHCl_3$) λ_{max} 268, 315 nm; fluorescence ($CHCl_3$) λ_{em} 435 (excitation: 315 nm); ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 9H), 6.95−7.00 (m, 4H), 7.06−7.12 (d, 1H), 7.12−7.18 (d, 1H), 7.24−7.30 (t, 1H), 7.35−7.40 (d, 2H), 7.49−7.55 (t, 1H), 7.67−7.72 (d, 1H), 7.80−7.85 (d, 1H), 7.91−7.96 (d, 1H), 8.44−8.48 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.9, 146.0, 137.7, 134.2, 133.0, 132.1, 132.0, 131.1, 130.6, 129.5, 127.6, 127.2, 126.7, 126.5, 126.4, 124.7, 124.6, 118.2, 118.1, 34.3, 31.6.

(17) (a) Wang, Z. Y.; Le Guen, A. *Macromolecules* **1995**, *28*, 3728. (b) Douglas, J. E.; Wang, Z. Y. *Macromolecules* **1995**, *28*, 5970.

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