Synthesis of Helical Polybinaphthyls

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ABSTRACT: Novel helical polybinaphthyls have been designed and synthesized by using an acid-promoted intramolecular cyclization of arylalkynes. The structures of these polymers are characterized by various spectroscopic methods including NMR, UV, FL, and CD. Because of the restricted rotation in their repeat units, these polymers are expected to have a well-defined helical chain structure. The molecular weight effect on the optical properties of such a polymer was studied. Significantly increased fluorescence sensitivity toward an amino alcohol quencher over the parent 1,1′-bi-2-naphthol was also observed.

Introduction

The beauty of the helical structures of proteins and DNAs continues to inspire scientists in many fields. Design and synthesis of unnatural helical polymers for applications in areas such as nonlinear optics, molecular recognition, catalysis, and separation have received ever growing research attention.[1] Examples of synthetic helical polymers include β-amino acid-based oligopepitides,[2a] pyridinyl amide-based double helices,[2b] polyisocyanates,[2c,d] polyisocyanides,[2e] chiral acid-doped polyanilines,[2f,g] polyguanidines,[2h] polytriphenylmethyl methacrylates,[2i] chiral polyacetylenes,[2j] chiral polythiophenes,[2k,l] oligo(*m*-phenyleneethylene)s,[2m] oligomeric aryl amides,[2n] helicences,[2o] and more. Most of these materials have their helicity generated from secondary interactions such as hydrogen bonds and van der Waals forces. The inherently stable helical polymers such as helicences[2o] are less common. Thus, many of the helical polymers undergo conformational change as well as helical reversal easily.

In our laboratory, we have used optically active 1,1′-binaphthyls to build a family of polymers with inherently stable chiral main chains.[3] These materials have shown interesting properties in areas such as nonlinear optics, electroluminescence, and asymmetric catalysis. The chiral binaphthyl units in these polymers are prepared by using conjugated units such as arylenes, ethynylenes, and vinylenes to link them through carbon−carbon *single bonds*. As indicated in polymer **1**,[3c] the single bond linkage allows the aromatic rings in the conjugated units of the polymer to rotate away from the conjugated planar conformation. As a result, we find that polymer **1** does not have a propagating helical chain conformation in solution. The optical rotation and CD spectrum of this polymer are very close to those of its monomeric model compound. That is, each unit in the polymer acts independently without an organized helical chain structure even though the 1,1′-binaphthyl unit itself is helical.

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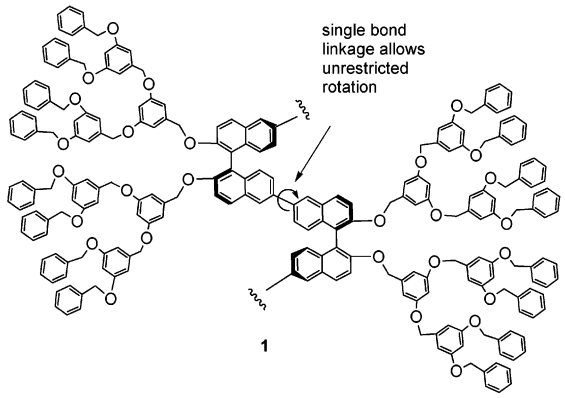

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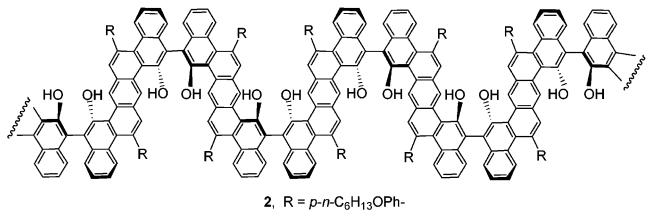
To prepare binaphthyl polymers with propagating stable main-chain helicity, we propose to synthesize the novel 1,1′-binaphthyl-based ladder polymers such as **2**. In **2**, because the chiral binaphthyl units are connected with fused benzene rings, it is expected to have a well-defined helical structure. The 1,1′-binaphthyl units in **2** have a *R* configuration. An energy-minimized molecular modeling structure (PCSpartan-Pro, semiempirical AM1) of a segment of the polybinaphthyl is given in Figure 1 where the R groups of **2** are replaced with H atoms. As shown by the view along the polymer axis, this polymer will have a stable helical chain structure with a helical cavity of ca. 8 Å in diameter. Herein, we report our synthesis and characterization of this class of structurally novel helical polybinathyls.



2, R = *p*-*n*-$C_6H_{13}OPh$-

Results and Discussion

Synthesis of the 1,1′-Binaphthyl Polymer 2 by a Minor-Groove Polymerization. In 1997, Swager and

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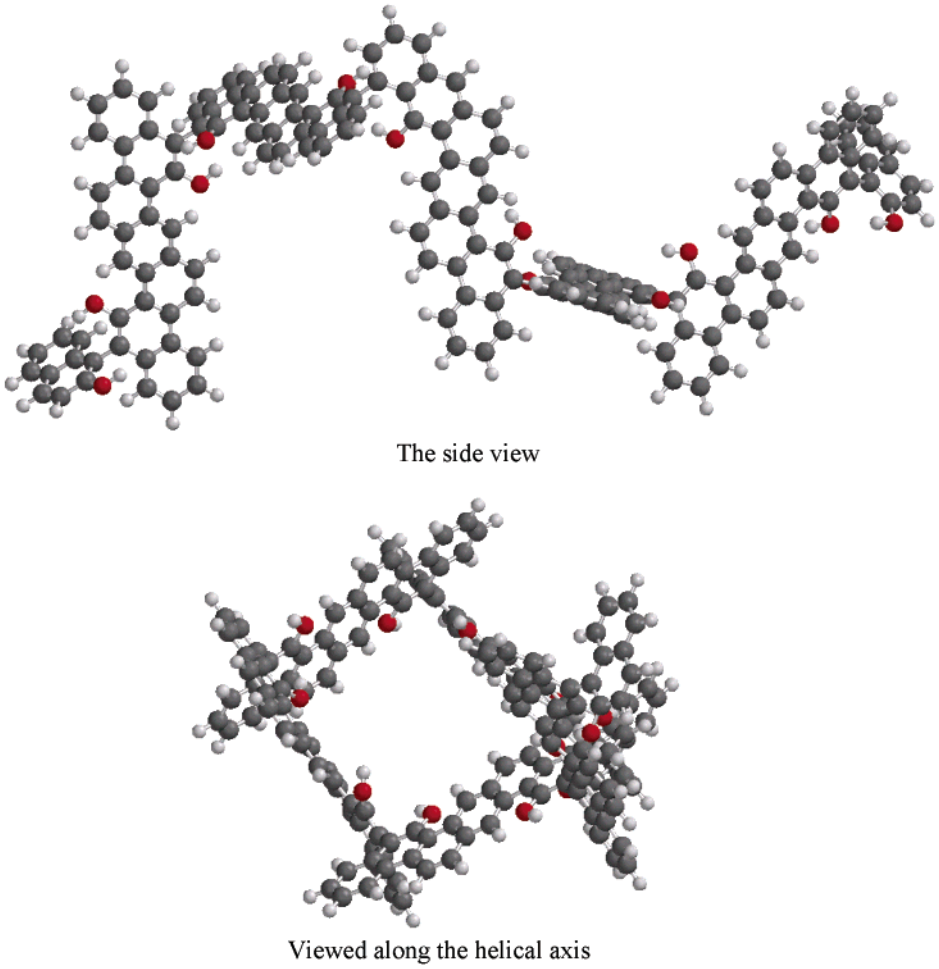
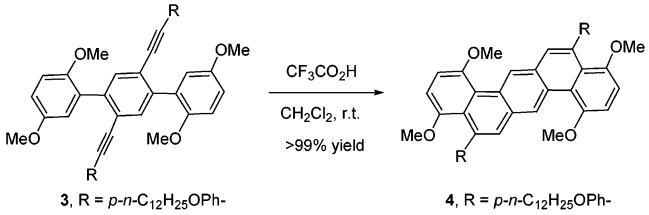


Figure 1. Molecular modeling structure of polymer **2**. The R groups of **2** are replaced with hydrogen atoms.

Scheme 1. Swager's Acid-Catalyzed Cyclization of Arylalkynes to Polyaromatic Compounds



3, R = *p*-*n*-$C_{12}H_{25}$OPh- **4**, R = *p*-*n*-$C_{12}H_{25}$OPh-

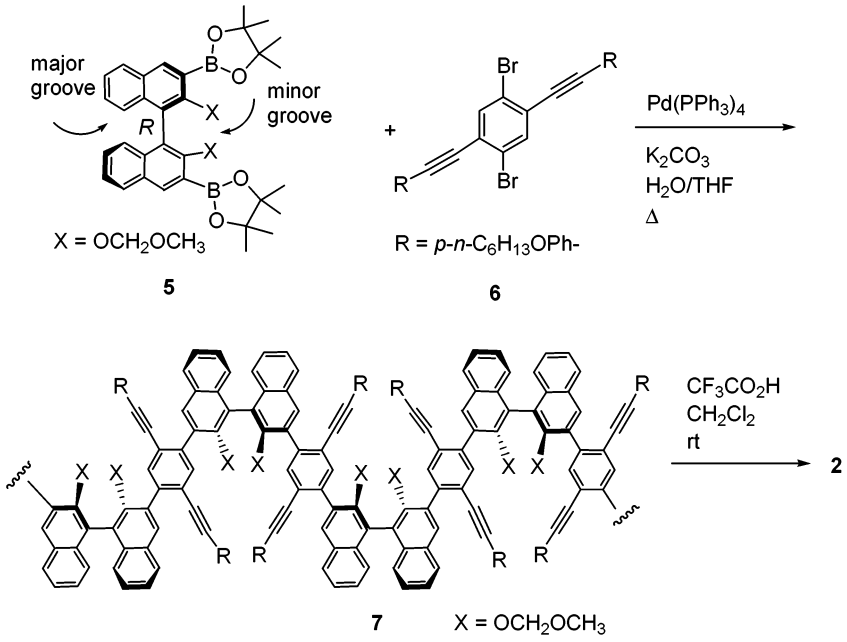
co-workers reported a convenient intramolecular cyclization of arylalkynes to fused polyaromatic compounds.[4] As the example in Scheme 1 shows, treatment of **3** with CF_3CO_2H at room temperature led to a quantitative formation of the fused polyaromatic compound **4**.[4] We have used this method to synthesize the desired helical polybinaphthyls.

Both the optically active binaphthyl compound **5**[5] and the aryl dibromide **6**[4] are readily prepared in two steps from the commercially available starting materials (Scheme 2). A 1,1′-binaphthyl molecule contains a minor groove and a major groove as indicated in Scheme 2. The Suzuki coupling[6] of **5** and **6** led to the polymerization at the minor groove of the 1,1′-binaphthyl monomer to generate polymer **7**. This polymer was soluble in common organic solvent. Gel permeation chromatography (GPC) showed its molecular weight as $M_w = 11\,200$ and $M_n = 7300$ (PDI = 1.54) relative to polystyrene standards. The specific optical rotation of **7**, $[\alpha]_D$, was +36.8 ($c = 0.1$, CH_2Cl_2).

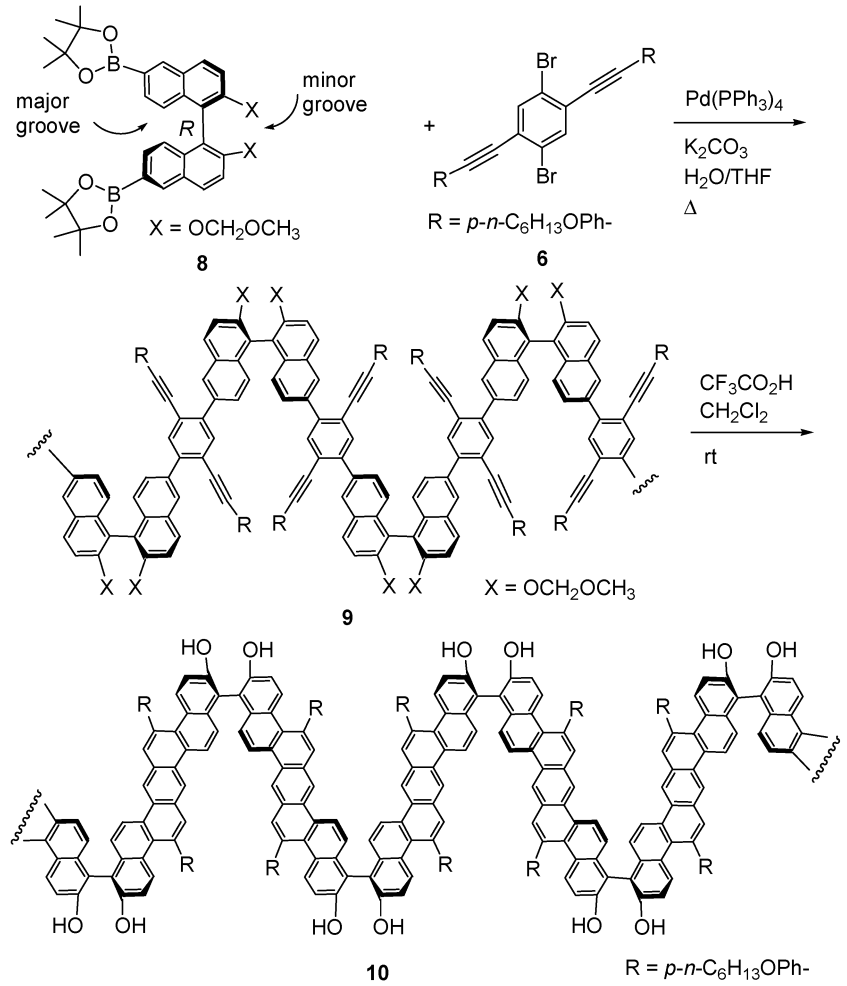
We then applied the Swager method to convert **7** to the helical polymer **2**. Polymer **7** was reacted with CF_3CO_2H in methylene chloride at room temperature during which the yellow solution turned dark green in 1 h. After stirred for ca. 12 h followed by aqueous work up, polymer **2** was obtained. Purification by precipitation with hexane from methylene chloride multiple times gave **2** as a dark brown solid in 95% yield. Polymer **2** was completely soluble in common solvents such as THF, methylene chloride, and chloroform. Because of its dark color in solution, its specific optical rotation fluctuated at around −531 ($c = 0.1$, CH_2Cl_2), the opposite sign of that of polymer **7** with greatly increased value. GPC showed its molecular weight as $M_w = 17\,900$ and $M_n = 10\,500$ (PDI = 1.70).

Synthesis of the 1,1′-Binaphthyl Polymers 10 and 13 by the Major-Groove Polymerization. Another 1,1′-binaphthyl monomer **8** was also synthesized. The Suzuki coupling of **8** with **6** led to polymerization at the major groove of the binaphthyl unit to generate polymer **9** (Scheme 3). The molecular weight of this polymer as measured by GPC was $M_w = 14\,300$ and $M_n = 8700$ (PDI = 1.64). Its specific optical rotation was $[\alpha]_D = -115.7$ ($c = 0.1$, CH_2Cl_2). Treatment of this polymer with CF_3CO_2H in methylene chloride at room temperature gave polymer **10** as a dark brown solid in 97% yield. This polymer was soluble in common organic solvents. GPC analysis gave its molecular weight as $M_w = 17\,400$ and $M_n = 10\,200$ (PDI = 1.71). The dark color of the polymer solution gave a fluctuating specific optical

Scheme 2. Synthesis of the Minor-Groove Helical Polybinaphthyl 2



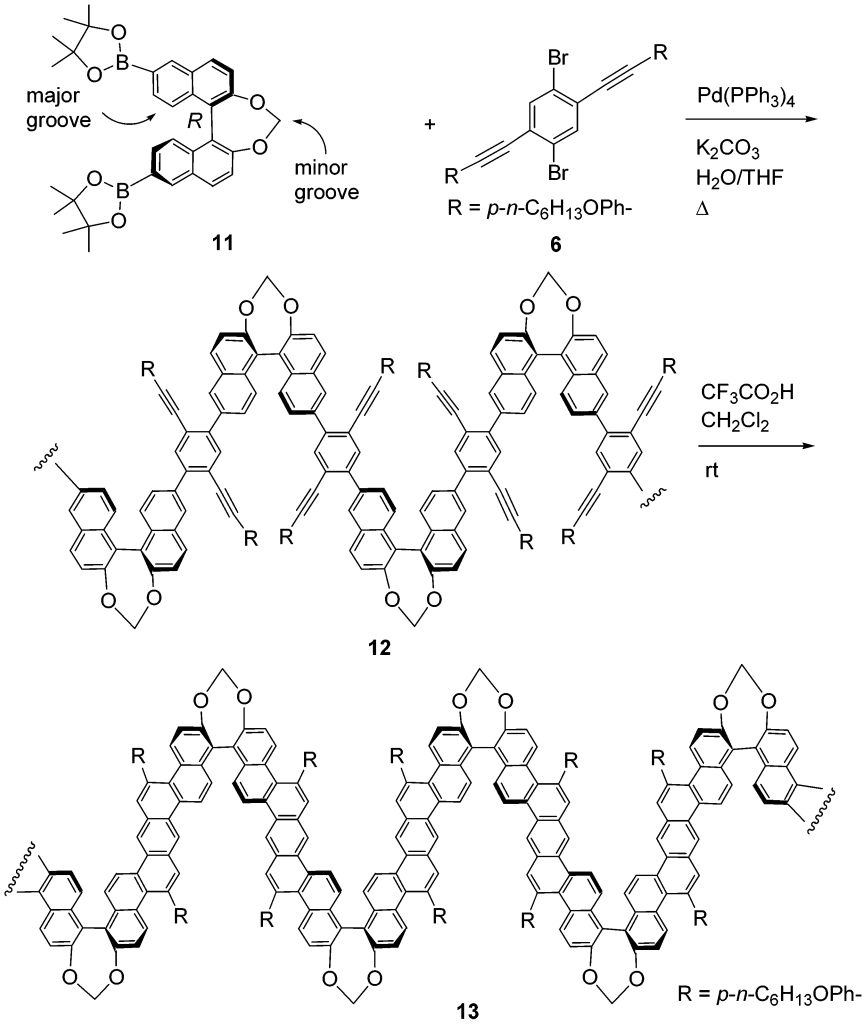
Scheme 3. Synthesis of the Major-Groove Helical Polybinaphthyl 10



rotation at around $[\alpha]_D \approx -708$ (c = 0.1, CH_2Cl_2), a much larger value than that of **9**. The intramolecular cyclization of **9** could occur by the electrophilic attack on either the α or β positions of the naphthyl rings. Although at this stage, we are not able to determine the actual pathway spectroscopically, it is proposed that the generally more reactive α-positions of the naphthyl rings might have participated to form **10**.

Monomer **11** containing a bridging methylene at the minor groove was prepared. The Suzuki coupling of **11** with **6** gave the major groove polymer **12** (Scheme 4). This polymer was obtained as a light-yellow solid in 90%

Scheme 4. Synthesis of the Major-Groove Helical Polybinaphthyl 13



yield. GPC gave its molecular weight as M_w = 38 800 and M_n = 12 100 (PDI = 3.22). Its specific optical rotation was $[\alpha]_D = -466.7$ ($c = 0.1$, CH_2Cl_2). Treatment of this polymer with CF_3CO_2H in methylene chloride at room temperature gave polymer **13** as a dark brown solid in 95% yield. This polymer was soluble in common organic solvents. GPC analysis gave its molecular weight as M_w = 29 800 and M_n = 11 400 (PDI = 2.61).

Spectroscopic Study of the Chiral Polybinaphthyls. In the ^{1}H NMR spectra of polymer **7**, the CH_3OCH_2O protons are observed at δ 2.48 (brs, 6 H), and 4.55 (brs, 4H). Its ^{13}C NMR spectrum shows two alkyne carbon signals at δ 94.69 and 98.49. After treatment of **7** with CF_3CO_2H, the ^{1}H and ^{13}C NMR spectra of the resulting polymer **2** show the disappearance of both the CH_3OCH_2O groups and the alkyne carbons. The same is observed in the conversion of **9** to **10**. That is, both the intramolecular cyclization and deprotection took place under the acidic condition. However, in the reaction of **12** with CF_3CO_2H, the ^{1}H NMR spectrum of the resulting polymer **13** showed that the bridging methylene protons were still present while the alkyne carbon signals disappeared. The bridging methylene groups of **13** were found to be very stable toward hydrolysis. The ^{13}C NMR signals of polymers **2**, **10**, and **13** are significantly weaker than their precursor polymers because of the much more rigid ladder structures of their repeating units.

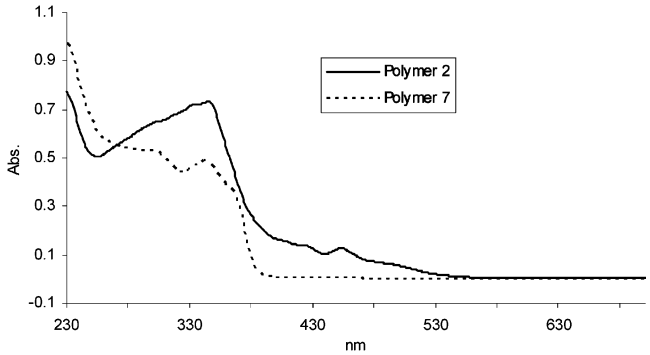


Figure 2. UV spectra of polymers **2** and **7** in methylene chloride.

The optical properties of these polymers were studied. Figure 2 compares the UV spectrum of polymer **7** with that of **2**. It shows new absorptions at the long wavelength between 390 and 560 nm after polymer **7** is converted to **2**. In the fluorescence spectra, a very large red shift ($\Delta\lambda$ = 123 nm) is observed going from **7** to **2** (Figure 3). The large red shifts observed for the absorption and emission of polymer **2** indicate a greatly increased conjugation in this polymer. These observations are similar to what was observed by Swager in the conversion of **3** to **4** (see Scheme 1). Large red shifts in the UV and fluorescence spectra are also observed from polymers **9** and **12** to polymers **10** and **13**,

Table 1. Spectral Data of the Polymers 7, 2, 9, 10, 12, and 13 in Methylene Chloride Solution

polymer	**7**	**2**	**9**	**10**	**12**	**13**
UV λ_{max} (ϵ) nm	366 (sh, 3.58×10^4) 341 (4.86×10^4)	453 (1.26×10^4) 344 (7.33×10^4)	320 (6.28×10^4) 281 (5.53×10^4)	411 (1.03×10^4) 339 (6.06×10^4)	372 (sh, 3.47×10^4) 315 (7.23×10^4) 268 (5.28×10^4)	410 (1.28×10^4) 330 (7.14×10^4)
fluorescence λ_{emi} (nm)	398	521	408	450 476 (sh)	408	455 484 (sh)
CD [θ] (λ_{max}, nm, 1.0×10^{-5} M)	5.86×10^4 (365) -1.17×10^5 (292) 1.90×10^5 (258)	-6.98×10^4 (360) 7.49×10^4 (330) 1.23×10^5 (268)	-4.06×10^3 (359) 8.07×10^3 (341) -1.64×10^5 (284)	-2.86×10^5 (351) 1.62×10^5 (320) -3.54×10^3 (273)	2.80×10^4 (337) -1.75×10^5 (289) 3.90×10^4 (252)	-2.49×10^5 (350) 6.05×10^4 (324) -4.76×10^4 (303) -8.19×10^4 (277) 1.56×10^5 (241)

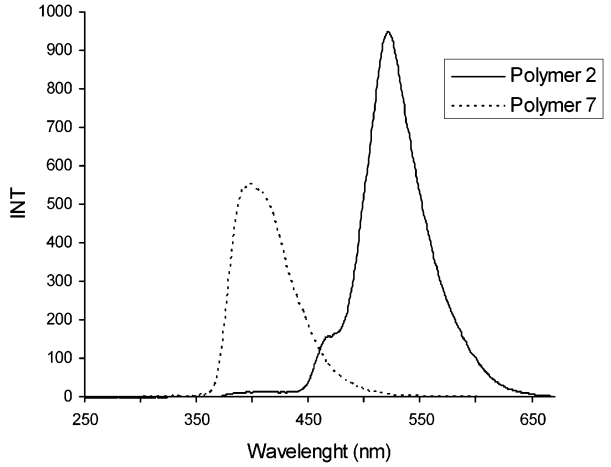


Figure 3. Fluorescence spectra of polymers **2** and **7** in methylene chloride.

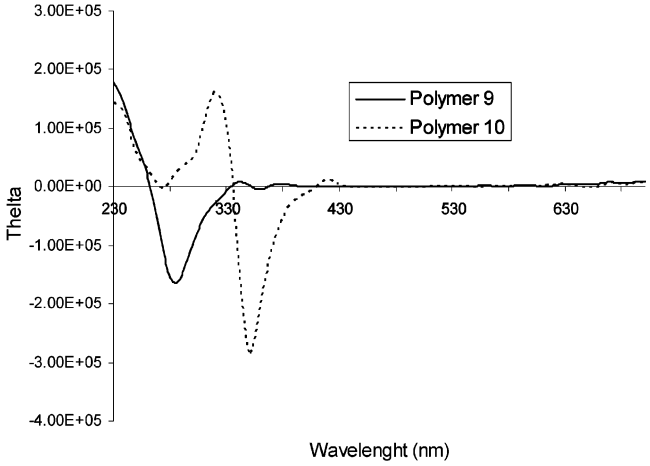


Figure 4. CD spectra of polymers **9** and **10** in methylene chloride.

respectively. These data are summarized in Table 1.

In our previous studies,[3b,d,e] we have demonstrated that the conjugation of the polybinaphthyls is determined by the nature of their repeating units, and there is no extended conjugation across the 1,1′-bond of the binaphthyl units. Therefore, on the basis of both the UV absorption and fluorescence studies, we conclude that the acid-promoted intramolecular cycloaromatization has proceeded smoothly from polymers **7**, **9**, and **12** to polymers **2**, **10**, and **13**, respectively, and the resulting polymers have much better conjugated repeating units because of the formation of the planar and fused polyaromatic systems.

Dramatic changes are also observed in the CD spectra of the chiral polymers after cyclization. The CD spectra of polymer **9** and **10** are displayed in Figure 4. As shown in the figure, new positive and negative CD signals centered at ca. 340 nm, probably due to the exciton coupling of the helical aromatic units, appeared when polymer **9** was converted to polymer **10**. Large differences are also observed going from polymers **7** and **12** to polymers **2** and **13**, respectively (Table 1).

Effect of the Molecular Weight of Polymer 10 on Its Spectroscopic Properties. To study how the molecular weight of the new polymers influences their optical properties, we have prepared polymer **10** of various molecular weights by quenching the coupling of **6** and **8** at 24, 10, 6, and 4 h followed by treating the isolated polymers with CF_3CO_2H. This process gave polymers **10a** (M_n = 10 200, PDI = 1.71), **10b** (M_n = 5600, PDI = 1.38), **10c** (M_n = 4200, PDI = 1.31), and **10d** (M_n = 3300, PDI = 1.27).

The UV spectra of these materials show that the absorbance at the long wavelength region increases with the increase of the molecular weight of the polymer (Figure 5). This is consistent with the increased number

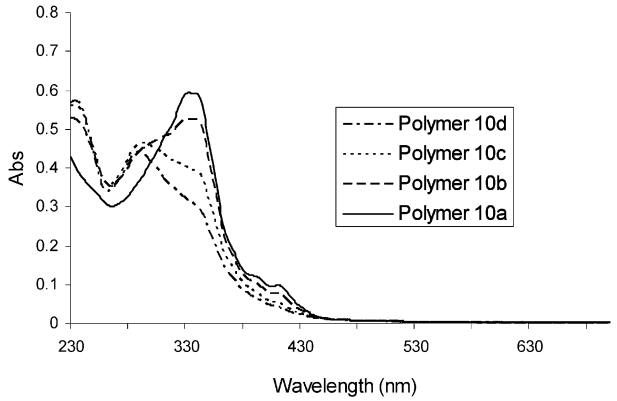


Figure 5. UV spectra of polymers **10a**−**d**.

of the planar polycyclic aromatic repeat units in the polymer chain at high molecular weights. The fluorescence spectra of these polymers demonstrate that there is almost no change in the emission wavelengths at the different molecular weights (Figure 6). This indicates that the emission of the polymers is due to their better conjugated internal repeating unit, and there is no emission from the less conjugated terminal units. An efficient energy transfer from the less conjugated terminal units to the more conjugated internal repeat units can be proposed.

The CD spectra of these polymers are shown in Figure 7. As the molecular weight increases from polymer **10d** to **10a**, there is a large increase for the CD effects centered at ca. 340 nm. The formation of the planar conjugated repeat unit in polymer **10** is expected to force the polymer to adopt a propagating helical chain structure. The large changes in the CD signals of **10** with respect to the increasing molecular weights indicates the formation of more of the planar polycyclic

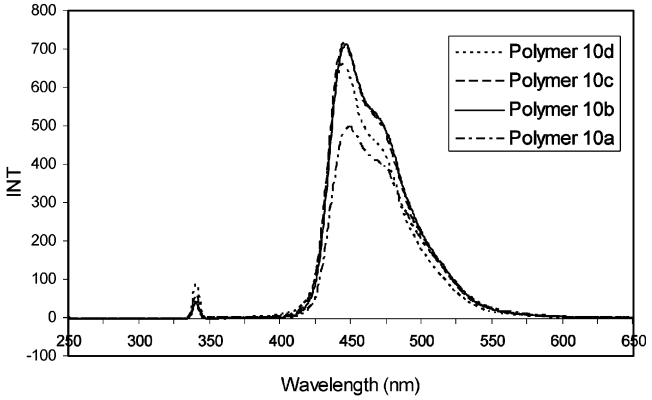


Figure 6. Fluorescence spectra of polymers **10a**−**d**.

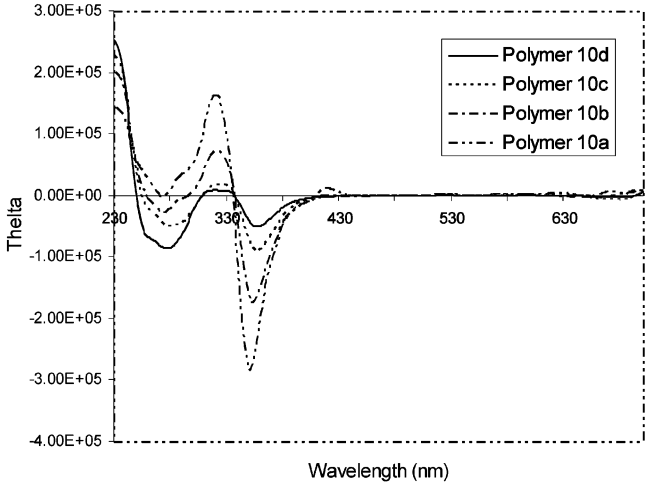


Figure 7. CD spectra of polymers **10a**−**d**.

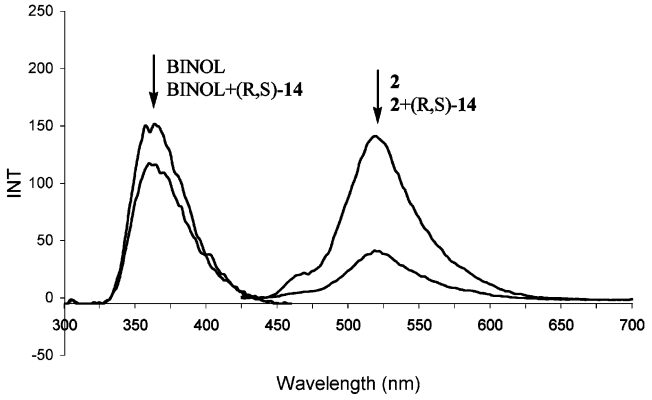


Figure 8. Fluorescence spectra of BINOL and polymer **2** with and without the amino alcohol (*R*,*S*)-**14**.

aromatic repeating units at the high molecular weights.

Study of the Fluorescence Spectrum of the Minor Groove Polymer 2 in the Presence of an Amino Alcohol. A preliminary study on the use of the helical polymers for the fluorescent sensing of amino alcohols was conducted. Previously, it was reported that the fluorescence of the parent 1,1′-bi-2-naphthol (BINOL) can be quenched by amines and amino alcohols.[7] We found that polymer **2** was a much more efficient fluorescent sensor than BINOL when interacting with an amino alcohol quencher. Figure 8 compares the fluorescence spectra of (*R*)-BINOL with that of **2** both at 1.0×10^{-5} M in CH_2Cl_2/hexane (1:1) for interaction with (1*R*,2*S*)-(−)-*N*-methylephedrine (**14**, 3.0×10^{-2} M). The I_0/I is 1.3 for BINOL but 3.4 for **2**. This significantly increased fluorescence sensitivity of the polymer over BINOL toward the amino alcohol may be due to an energy migration along the helical conjugated polymer chain.[8] This could also be attributed to the lower $\pi-\pi^*$ band gap of the polymer which may facilitate the photoinduced electron-transfer quenching by the amino alcohol. We further found that the fluorescence quenching of **2** by the two enantiomers of **14** was different with an *ef* (*ef* = $|I_0 - I_{RS}|/|I_0 - I_{SR}|$, the enantiomeric fluorescence difference ratio) value of 1.12 ± 0.01. Although this enantioselectivity is small, it is larger than using (*R*)-BINOL, which showed no difference at all in the fluorescence quenching when treated with the two enantiomers of **14**.

Summary

In summary, we have applied the acid-catalyzed intramolecular cyclization of electron-rich aromatic alkynes to convert the polybinaphthyls to novel helical polymers. The UV, fluorescence, and CD spectra support the formation of polycyclic aromatic repeating units in these polymers. The molecular weight effect on the optical properties of such a helical polymer was also studied. One of the polymers has shown significantly increased fluorescence sensitivity toward an amino alcohol quencher over the parent BINOL. Polymers of such a novel helical and conjugated structure may find applications in areas such as chiral sensing, polarized light emission, nonlinear optics, and asymmetric catalysis.

Experimental Section

General Data. Unless otherwise noted, all the reagents were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl immediately prior to use. Hexane was distilled over calcium chloride. Toluene was distilled from sodium, and dichloromethane was distilled over calcium hydride. Thin-layer chromatography was performed on precoated silica gel plates. Silica gel (70−230 and 230−400 mesh) was used for column chromatography. 4-(Hexyloxy)phenylacetylene was purchased from Maybridge Chemical Co.

The NMR spectra were recorded on a Varian-300 MHz spectrometer. Mass spectra were recorded either at atmospheric pressure chemical ionization (APCI) or at electrospray ionization (ESI) mode. Gel permeation chromatography (GPC) utilized a Waters 510 HPLC pump, a Waters 410 differential refractometer, and a Ultrastyragel linear GPC column. THF was used as the eluting solvent in the GPC analysis, and polystyene standards were used. The UV−vis spectra were recorded with a Cary 5E UV−vis−NIR spectrophotometer. The CD spectra were recorded with JASCO J-720 spectropolarimeter. Elemental analyses were performed by Atlantic Microlab, Inc. High-resolution mass analyses were performed by University of California Riverside Mass Spectrometry Facility.

Preparation and Characterization of 1,4-Dibromo-2,5-bis((4-(hexyloxy)phenyl)ethynyl)benzene, 6. A solution of 4-(hexyloxy)phenylacetylene (3.48 g, 17.2 mmol) in THF (15 mL) was cannulated dropwise into a mixture of 1,4-dibromo-2,5-diiodobenzene (4.0 g, 8.2 mmol), $(PPh_3)_2PdCl_2$ (115 mg, 0.16 mmol), CuI (156 mg, 0.82 mmol), $(C_4H_9)_4NBr$ (158 mg, 0.49 mmol), toluene (35 mL), diisopropylamine (35 mL), and THF (20 mL) at room temperature under nitrogen. The reaction mixture was stirred for 6 h to afford a gray suspension. After removal of solvent, the residue was dissolved in $CHCl_3$ (120 mL) and washed with 5% HCl (3 × 30 mL), H_2O (30 mL), 5% NH_4OH (3 × 30 mL), and H_2O (2 × 30 mL). After concentration by rotary evaporator to about 50 mL, MeOH was added to precipitate the compounds out as a light yellow solid. Recrystallization from THF/MeOH gave compound **6** as white granu-

lar crystals in 80% yield (4.2 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 6H, J = 6.6 Hz), 1.35−1.47 (m, 12H), 1.80 (m, 4H), 3.99 (t, 4H, J = 6.6 Hz), 6.89 (d, 4H, J = 8.7 Hz), 7.50 (d, 4H, J = 8.7 Hz), 7.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.56, 25.65, 29.08, 31.52, 68.11, 85.78, 96.90, 114.10, 114.61, 123.41, 126.32, 133.29, 135.68, 159.87. MS(EI): *m*/*z* (relative intensity) 636 (M^+, 100), 468 (45). HRMS (EI): *m*/*z* calcd for $C_{34}H_{36}Br_2O_2$: 634.1082; found: 634.1094.

Preparation and Characterization of Polymer 7. In drybox, THF (6.0 mL) and degassed aqueous K_2CO_3 (2.0 mL, 1.0 M, 2.0 mmol) were added to a mixture of (*R*)-**5** (188 mg, 0.3 mmol), **6** (191 mg, 0.30 mmol), and $Pd(PPh_3)_4$ (21 mg, 0.018 mmol). The reaction mixture was heated at reflux for 90 h. The solvent was then removed under vacuum, and the residue was redissovled in CH_2Cl_2 (30 mL). The solution was washed with H_2O (3 × 30 mL) and brine and dried over Na_2SO_4. After filtration and removal of solvent, the sticky residue was dissolved in a minimum amount of CH_2Cl_2. The polymer was precipitated out with the addition of hexane. This procedure was repeated two more times to afford polymer **7** as an orange solid in 91% yield (230 mg). $[\alpha]_D$ = +36.8 (c = 0.1, CH_2Cl_2). GPC: M_n = 7300, M_w = 11 200 (PDI = 1.54). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (br, m, 6H), 1.31 (br, 12H), 1.70 (br, 4H), 2.48 (br, 6H), 3.87 (br, 4H), 4.55 (br, m, 4H), 6.72 (br, 4H), 7.18−7.42 (br, 10H), 7.94 (br, 4H), 8.17 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.54, 25.63, 29.06, 31.52, 55.80, 67.97, 87.70, 94.69, 98.49, 114.40, 123.08, 125.10, 126.14, 126.53, 127.82, 129.63−134.84 (m), 139.94, 151.79, 159.20. Anal. Calcd for $C_{58}H_{56}O_6$ + H_2O: C, 80.40; H, 6.75. Found: C, 80.71; H, 6.54.

Preparation and Characterization of Polymer 2. Under nitrogen, trifluoroacetic acid (0.69 mL, 8.9 mmol) was added to a solution of polymer **7** (150 mg, 0.18 mmol) in CH_2Cl_2 (20 mL) at room temperature. The color of the solution changed from yellow to dark green within 1 h. After stirred for overnight, the solution was washed with 10% $NaHCO_3$ (3 × 20 mL) and H_2O (2 × 20 mL) and dried over Na_2SO_4. After filtration and removal of solvent, the sticky residue was dissolved in a minimum amount of CH_2Cl_2. The polymer was precipitated out with the addition of hexane. This procedure was repeated two more times to afford polymer as a dark brown solid in 95% yield (128 mg). $[\alpha]_D$ = −531.2 (c = 0.1, CH_2Cl_2). GPC: M_n = 10 500, M_w = 17 900 (PDI = 1.70). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92−1.87 (br, m, 22H), 4.09 (br, 4H), 7.06−8.11 (br, m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.03, 22.60, 25.76 (m), 29.30, 31.55, 68.12, 114.97, 122.56−137.76 (br, m), 158.25 (br, m). Anal. Calcd for $C_{54}H_{48}O_4$ + H_2O: C, 83.33; H, 6.48. Found: C, 81.67; H, 6.17.

Preparation and Characterization of Monomer 8. Under nitrogen, ^{n}BuLi (6.25 mL, 1.6 M in hexane, 10 mmol) was added to a solution of (*R*)-6,6′-dibromo-2,2′-bis(methoxymethoxy)-[1,1′]binaphthalenyl (2.17 g, 4.0 mmol) in THF (40 mL) at −78 °C. After the reaction mixture was stirred for 6 h at the same temperature, it was then cannulated dropwise into a solution of 2-isopropoxy-4,4′,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 mL, 20 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered, and the solid was washed with CH_2Cl_2. The combined solution was concentrated. The residue was purified by column chromatography on silica gel to give monomer **8** as a white solid in 47% yield (1.21 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (s, 24 H), 3.14 (s, 6H), 4.97 (dd, 2 H, J_1 = 3.9 Hz, J_2 = 0.6 Hz), 5.07 (dd, 2 H, J_1 = 3.9 Hz, J_2 = 0.6 Hz), 7.10 (d, 2 H, J = 5.1 Hz), 7.56 (m, 4 H), 8.00 (d, 2 H, J = 5.4 Hz), 8.40 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.90, 55.83, 83.74, 94.91, 116.89, 120.86, 124.54, 129.17, 130.26, 130.83, 135.70, 136.37, 153.55. Anal. Calcd for $C_{36}H_{44}B_2O_8$: C, 69.03; H, 7.08. Found: C, 68.96; H, 7.30.

Preparation and Characterization of Polymer 9. The preparation procedure for polymer **9** was the same as polymer **7** except that monomer **8** was used, and the reaction mixture was refluxed for 24 h under nitrogen. Polymer **9** was obtained as an orange solid in 97% yield. $[\alpha]_D$ = −115.7 (c = 0.1, CH_2Cl_2). GPC: M_n = 8700, M_w = 14 300 (PDI = 1.64). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (m, 6 H), 1.31 (m, 12 H), 1.68 (m, 4 H), 3.16 (s, 6 H), 3.82 (t, 4H, J = 6.3 Hz), 5.05 (d, 2H, J = 6.6 Hz), 5.15 (d, 2H, J = 6.6 Hz), 6.67 (d, 4H, J = 9.0 Hz), 7.16 (d, 4H, J = 9.0 Hz), 7.38 (d, 2H, J = 8.4 Hz), 7.66 (d, 2H, J = 9.3 Hz), 7.74 (d, 2H, J = 8.7 Hz), 7.81 (s, 2H), 8.07 (d, 2H, J = 9.0 Hz), 8.31 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.99, 22.55, 25.68, 29.10, 31.53, 55.88, 67.95, 88.09, 94.36, 95.43, 114.43, 117.76, 121.33, 121.88, 125.09, 128.01, 129.83, 132.77, 133.49, 135.31, 141.68, 153.15, 159.28. Anal. Calcd for $C_{58}H_{56}O_6$ + H_2O: C, 80.40; H, 6.75. Found: C, 80.00; H, 6.47.

Preparation and Characterization of Polymer 10. The preparation procedure for polymer **10** was the same as polymer **2** except that polymer **9** was used. Polymer **10** was obtained as a dark brown solid in 95% yield. $[\alpha]_D$ = −708.4 (c = 0.1, CH_2Cl_2). GPC: M_n = 10 200, M_w = 17 400 (PDI = 1.71). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95−1.87 (br, m, 22 H), 4.10 (br, m, 4H), 5.16 (br, 2H), 7.11−9.10 (br, m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.08, 22.64, 25.82, 29.34, 31.65, 68.21, 115.1, 122.9−158.5 (m). Anal. Calcd for $C_{54}H_{48}O_4$ + H_2O: C, 83.33; H, 6.48. Found: C, 80.39; H, 6.18.

Preparation and Characterization of Monomer 11. (a) (*R*)-9,14-Dibromo-3,5-dioxacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (**A**) was prepared from the reaction of (*R*)-6,6′-dibromo-[1,1′]binaphthyl-2,2′-diol with CH_2I_2 and K_2CO_3 in DMF.[9] (b) Conversion of **A** to monomer **11**. Under nitrogen, ^{n}BuLi (3.0 mL, 2.5 M in hexane, 7.5 mmol) was added to a solution of **A** (1.37 g, 3.0 mmol) in THF (50 mL) at −78 °C. After the reaction mixture was stirred for 6 h at the same temperature, it was then cannulated dropwise into a solution of 2-isopropoxy-4,4′,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 mL, 15 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered, and the solid was washed with CH_2Cl_2. The combined solution was concentrated and then passed through a short silica gel column with the ethyl acetate as the elute to give a light-yellow solid. Recrystallization from ether/hexane gave **11** as colorless crystals in 76% yield (1.25 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (s, 24 H), 5.72 (s, 2 H), 7.44 (d, 2 H, J = 8.4 Hz), 7.48 (d, 2 H, J = 8.7 Hz), 7.64 (dd, 2H, J_1 = 8.7 Hz, J_2 = 1.2 Hz), 8.03 (d, 2 H, J = 8.4 Hz), 8.46 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.90, 83.93, 103.16, 120.88, 125.89, 125.99, 130.64, 131.11, 133.78, 136.63, 151.13. MS (APCI): *m*/*z* (relative intensity) 551 (M^+ + 1, 100). Anal. Calcd for $C_{33}H_{36}B_2O_6$: C, 72.03; H, 6.59. Found: C, 71.82; H, 6.63.

Preparation and Characterization of Polymer 12. The preparation procedure for polymer **12** was the same as polymer **7** except that monomer **11** was used, and the reaction mixture was refluxed for 24 h under nitrogen. Polymer **12** was obtained as a light-yellow solid in 90% yield. $[\alpha]_D$ = −466.7 (c = 0.1, CH_2Cl_2). GPC: M_n = 12 100, M_w = 38 800 (PDI = 3.22). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (brs, 6 H), 1.17 (brs, 8 H), 1.28 (brs, 4 H), 1.61 (brs, 4 H), 3.78 (brs, 4H), 5.80 (brs, 2H), 6.69 (d, 4H, J = 6.9 Hz), 7.23 (d, 4H, J = 7.8 Hz), 7.57 (m, 2H), 7.70−7.90 (m, 6H), 8.10 (m, 2H), 8.35 (brs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.96, 22.50, 25.64, 29.09, 31.48, 67.92, 87.78, 94.65, 103.29, 114.51, 114.72, 121.36, 121.98, 126.12, 126.46, 127.71, 128.82, 130.77, 131.58, 131.81, 132.88, 134.20, 136.38, 141.50, 151.65, 159.40. Anal. Calcd for $C_{55}H_{48}O_4$ + H_2O: C, 83.58; H, 6.38. Found: C, 83.86; H, 6.19.

Preparation and Characterization of Polymer 13. The preparation procedure for polymer **13** was the same as polymer **2** except that polymer **12** was used. Polymer **13** was obtained as a dark brown solid in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90−1.87 (br, m, 22H), 4.10 (br, 4H), 5.72 (br, 2H), 7.20−9.18 (br, m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.11, 22.64, 25.82, 29.34, 31.66, 68.19, 103.3 9w), 114.9−158.4 (br, m). GPC: M_n = 11 400, M_w = 29 800 (PDI = 2.61). Anal. Calcd for $C_{55}H_{48}O_4$ + H_2O: C, 83.58; H, 6.38. Found: C, 83.04; H, 6.25.

Fluorescence Measurement for the Interaction of 2 and (*R*)-BINOL with the Amino Alcohol *N*-Methylephedrine, 14. Spectroscopic grade CH_2Cl_2 and hexane were used. The CH_2Cl_2 stock solutions of polymer **2** (1.9 mg/25 mL, 1.0 × 10^{-4} M), (1*R*,2*S*)-(−)-**14** (53.8 mg/10 mL, 0.30 M), and (*R*)-BINOL (2.9 mg/100 mL, 1.0 × 10^{-4} M) were prepared. In a 10 mL volumetric flask, 1 mL of the stock solution of polymer **2**

was diluted with CH_2Cl_2/hexane (1:1) to 10 mL. The fluorescence spectrum of the resulting solution of **2** (1.0×10^{-5} M) gave $\lambda_{emi} = 519$ nm ($\lambda_{exc} = 355$ nm). Similarly, in a 10 mL volumetric flask, 1 mL of the stock solution of polymer **2** was mixed with 1 mL of the stock solution of (1*R*,2*S*)-(−)-*N*-methylephedrine, which was then diluted with CH_2Cl_2/hexane (1:1) to 10 mL for fluorescence measurement. In the same way, the interaction of (*R*)-BINOL with the amino alcohol was studied. For (*R*)-BINOL, the λ_{exc} and λ_{emi} are 280 and 364 nm, respectively.

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