

Supporting Information

Effect of tactic structure on the chiroptical property of helical vinylbiphenyl polymer

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Materials. N-Bromosuccinimide (99%, Aldrich), triphenylphosphine (PPh₃, 99%, Acros), tetrachloromethane (AR, Beijing Chemical Co.), *S*-(+)-*sec*-butanol (99%, TCI), *R*-(-)-*sec*-butanol (99%, TCI), diethyl azodicarboxylate (DEAD, 99%, J&K Chemical Co.), *n*-butyl lithium (*n*-BuLi, 1.6M in hexane solution, TCI), formaldehyde aqueous solution (40%, AR, Beijing Chemical Co.), chloroform-*d* (CDCl₃, 99.8 atom% D, J&K), *o*-dichlorobenzene-*d*₄ (99.5 atom % D, J&K) and 4-hexyloxyphenylboronic acid (98%, J&K Chemical Co.) were used as purchased. Benzoyl peroxide (BPO, AR, Beijing Chemical Co.) was recrystallized from methanol and dried under vacuum at room temperature. Anisole (AR, Beijing Chemical Co.) was distilled out with calcium hydride. Toluene (HPLC, Fisher) and tetrahydrofuran (THF, HPLC, Fisher) were refluxed with sodium and distilled out just before use. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) was prepared according to the literature procedure and stored under nitrogen atmosphere.¹ All other reagents and solvents were used as obtained unless otherwise specified.

Measurements $^1\text{H-NMR}$ spectra were recorded on a Bruker ARX 300 MHz or 400 MHz NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane as the internal reference. $^{13}\text{C-NMR}$ spectra were recorded on a Bruker ARX 500 MHz with *o*-dichlorobenzene- d_4 as the solvent. Mass spectra were obtained on a Finnigan-MAT ZAB-HS spectrometer. Elementary analyses were run on an Elemental Vario EL instrument. The number-average molar mass (M_n), weight-average molar mass (M_w), and polydispersity (M_w/M_n) of the polymer were estimated with a gel permeation chromatography (GPC) apparatus equipped with a Waters 2410 refractive index detector and a Waters 515 pump. THF was employed as the eluent at a flow rate of 1.0 mL/min at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Optical rotations were measured on a JASCO Model P-1030 digital polarimeter. CD spectra were recorded on a JASCO J-810 spectrometer. The light pathlength of the quartz cell used was 10 mm. The concentration was about 1×10^{-5} mol/L and the solvent was THF. Differential Scanning Calorimetry (DSC) traces were obtained with a TA DSC Q100 instrument. Firstly, heating up to 300 °C at a rate of 20 °C min^{-1} , then cooling down to 0 °C at a rate of 2 °C min^{-1} , finally reheating up to 300 °C at a rate of 20 °C min^{-1} . The DSC curves represented the second heating route. Thermogravimetric analyses (TGA) were performed on a TA SDT 2960 instrument : heating up to 600 °C under nitrogen atmosphere.

Synthesis

(S)-2-(*sec*-Butyloxy)-5-bromotoluene.

To a 250 mL three-necked round-bottom flask containing 4-bromo-2-methylphenol (5.00 g, 26.7 mmol), *R*-(-)-*sec*-butanol (2.03 g, 29.4 mmol), PPh_3 (8.45 g, 32.1 mmol) and THF (60 mL), DEAD (16.37 g, 37.4 mmol) was added dropwise at 0 °C under nitrogen. The solution was then stirred overnight. The solvent was taken away under reduced pressure and the residue was purified by column chromatography (Silica gel, dichloromethane/petroleum ether: 1/5 (v/v) as eluent) to give 5.03 g of product as colorless liquid. Yield: 77%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 7.252~7.192 (dd, 2H, Ar), 6.685~6.663 (d, 1H, Ar), 4.279~4.204 (q, 1H, -OCH), 2.172 (s, 3H, -ArCH₃), 1.785~1.552 (m, 2H, -CH₂),

1.277~1.262 (d, 3H, -CH₃), 0.985~0.948 (t, 3H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 9.68, 16.23, 19.22, 29.18, 75.39, 111.94, 114.26, 129.16, 130.18, 133.32, 155.43. MS (EI, *m/z*) for C₁₁H₁₅BrO: 243.03 (M+H⁺). Anal. Calcd. for C₁₁H₁₅BrO: C, 54.34; H, 6.22; O, 6.58 Found: C, 54.25; H, 6.43; O, 6.45.

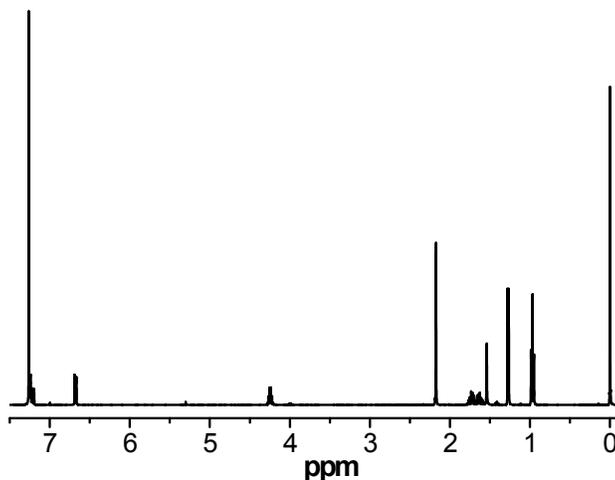


Figure S1 ¹H NMR spectrum of (S)-2-(*sec*-Butyloxy)-5-bromotoluene

(S)-2-(*sec*-Butoxy)-5-(4'-hexyloxyphenyl)toluene

To a 250 mL three-necked round-bottom flask were added (S)-2-(*sec*-butoxy)-5-bromotoluene (5.03 g, 20.7 mmol), 4-hexyloxyphenylboronic acid (5.56 g, 24.8 mmol), Pd(PPh₃)₄ (0.48 g, 0.41 mmol), benzene (50 mL), ethanol (30 mL), and 2.0 M Na₂CO₃ aqueous solution (40 mL). The reaction mixture was vigorously stirred and refluxed for 6 h under argon atmosphere. After the reaction was completed, the reaction mixture was extracted with CH₂Cl₂ (100 mL × 3). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Silica gel, dichloromethane/petroleum ether: 1/10 (v/v) as eluent) to yield 4.58 g of white solid. Yield: 65%. ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.462~7.441 (d, 2H, Ar), 7.332~7.238 (m, 2H, Ar), 6.938~6.916 (dd, 2H, Ar), 6.863~6.842 (d, 1H, Ar), 4.333~4.288 (m, 1H, -OCH), 3.990~3.928 (t, 2H, -OCH₂), 2.261 (s, 3H, -ArCH₃), 1.825~1.719 (m, 3H, -CH₃), 1.671~1.619 (m, 1H, -CH₂), 1.505~1.432 (m, 2H, -CH₂), 1.380~1.303 (m, 7H, -CH₂), 1.014~0.976 (t, 3H, -CH₃), 0.926~0.891 (t, 3H, -CH₃), ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 9.79, 14.03, 16.59, 19.44, 22.61, 25.74, 29.29, 29.35, 31.60, 68.05, 75.15, 112.89, 114.64, 124.73, 127.64, 127.94, 129.21, 129.37, 132.78,

133.55, 155.47, 158.10. MS (EI, m/z) for $C_{23}H_{32}O_2$: 341.24 ($M+H^+$). Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47; O, 9.40. Found: C, 81.15; H, 9.30; O, 9.55.

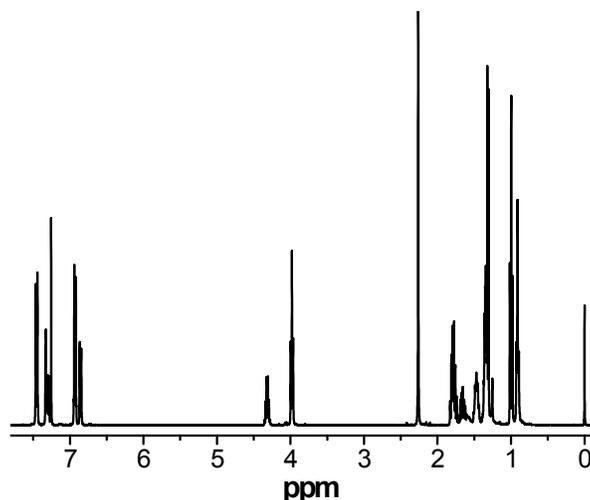


Figure S2 1H NMR spectrum of (S)-2-(*sec*-Butoxy)-5-(4'-hexyloxyphenyl)toluene

(S)-2-(*sec*-Butoxy)-5-(4'-hexyloxyphenyl)styrene (S-M)

(S)-2-(*sec*-Butoxy)-5-(4'-hexyloxyphenyl)toluene (1.30 g, 3.8 mmol), N-bromosuccinimide (0.77 g, 3.8 mmol) and BPO (30.00 mg, 0.12 mmol) were dissolved in tetrachloromethane (25 mL). The solution was refluxed for 3 h with rapid stirring and then cooled to room temperature. The suspended solids were separated by filtration. After evaporation of solvent, the residue was mixed with 25 mL of acetone and 1.10 g (3.8 mmol) of triphenylphosphine. The mixture was refluxed for about 2 h and then cooled to room temperature. The quaternary phosphonium bromide were purified by silica gel column using dichloromethane and methanol as eluents sequentially.

The above prepared phosphonium bromide salts were dissolved in 20 mL formaldehyde aqueous solution (40 wt%). With constant stirring, 5 mL of K_2CO_3 aqueous solution (40 wt%) was added dropwise to the solution at 0 °C, and the reaction was allowed to continue for 12 h. The reaction mixture was extracted with dichloromethane, washed with water and dried over sodium sulfate. The crude product was obtained after evaporation of solvent and purified by column chromatography (Silica gel, dichloromethane/petroleum ether: 1/3 (v/v) as eluent) to yield 0.99 g of white solid. Yield:

58%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 7.655~7.649 (d, 1H, Ar), 7.491~7.455 (d, 2H, Ar), 7.382~7.355 (dd, 1H, Ar), 7.147~7.074 (dd, 1H, =CH), 6.961~6.924 (d, 2H, Ar), 6.914~6.892 (d, 1H, Ar) 5.817~5.769 (dd, 1H, =CH), 5.278~5.248 (dd, 1H, =CH), 4.361~4.316 (m, 1H, -OCH), 3.994~3.961 (dd, 2H, -OCH₂), 1.828~1.756 (m, 3H, -CH₃), 1.697~1.629 (m, 1H, -CH₂), 1.489~1.434 (m, 2H, -CH₂), 1.369~1.312 (m, 7H, -CH₂), 1.016~0.979 (t, 3H, -CH₃), 0.928~0.893 (t, 3H, -CH₃). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ ppm): 9.79, 14.03, 19.37, 22.61, 25.74, 29.27, 31.59, 68.07, 75.85, 114.09, 114.11, 114.71, 124.85, 126.93, 127.70, 127.87, 132.06, 133.23, 133.35, 154.52, 158.28. MS (EI, m/z) for $\text{C}_{24}\text{H}_{32}\text{O}_2$: 353.51 ($\text{M}+\text{H}^+$). Anal. Calcd. for $\text{C}_{25}\text{H}_{34}\text{O}_2$: C, 81.77; H, 9.15; O, 9.08. Found: C, 81.75; H, 9.30; O, 8.95.

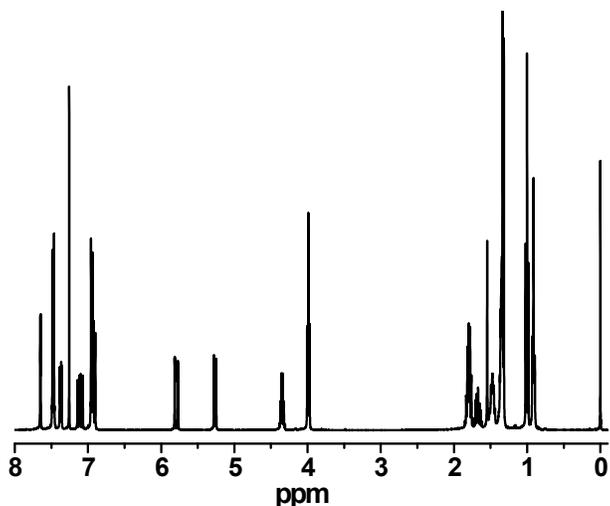


Figure S3 $^1\text{H NMR}$ spectrum of (*S*)-2-(*sec*-Butoxy)-5-(4'-hexyloxyphenyl)styrene (**S-M**)

(S)-4-(*sec*-Butoxy)-3-ethyl-4'-(hexyloxy)-1,1'-biphenyl (Model compound)

The mixture containing 0.20 g of **S-M**, 20.00 mg (10 wt%) of Pd/C and 2.0 mL ethyl acetate was stirred under H_2 for 24 h at room temperature. Then the suspended solids were separated by filtration. 0.99 g white solids were obtained by removing the solvent. Yield: 99%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 7.595~7.569 (d, 1H, Ar), 7.481~7.445 (d, 2H, Ar), 7.362~7.335 (dd, 1H, Ar), 6.958~6.922 (d, 2H, Ar), 6.908~6.884 (d, 1H, Ar), 4.351~4.309 (m, 1H, -OCH), 3.989~3.957 (dd, 2H, -OCH₂), 2.589~2.490 (m, 2H, -CH₂), 1.815~1.743 (m, 3H, -CH₃), 1.679~1.613 (m, 1H, -CH₂), 1.478~1.426 (m, 2H, -CH₂), 1.358~1.308 (m, 7H, -CH₂), 1.256~1.186 (s, 3H, -CH₃), 1.014~0.970 (t, 3H,

-CH₃), 0.919~0.886 (t, 3H, -CH₃). $[\alpha]_{365}^{25}$ (in THF, c = 2 g/dL) = +103°

Radical Polymerization

S-M (0.20 g, 0.59 mmol) and BPO (1.40 mg, 5.8×10^{-3} mmol) were added into a reaction tube containing 1.0 mL of anisole. After three freeze-pump-thaw cycles, the tube was sealed under vacuum and put into an oil-bath thermostated at 90 °C for 24 h. After being cooled to room temperature, the tube was opened and the reaction was diluted with THF (10 mL) and dropped into methanol (200 mL). The precipitates were collected by filtration and washed by methanol. After drying under vacuum at 50 °C for 24 h, 0.18 g of white solids were obtained. Yield: 90%.

Anionic polymerization

The anionic polymerization was manipulated under high-vacuum line in an all-glass apparatus by breakseal techniques. Taking the anionic polymerization in toluene at -40 °C as the example to describe the reaction manipulation. The monomer (0.20 g, 0.57 mmol) and *n*-BuLi (0.01 mmol) were encapsulated in ampoule by toluene (2 mL) and hexane (0.2 mL) respectively. Toluene (2 mL) was vacuum distilled into reaction apparatus. After the addition of *n*-BuLi by breaking the breakseal, the solution was stirred at -40 °C for at least 10 min. The monomer was finally added to the reactor one time by breaking the breakseal. The reaction mixture turned from light yellow to jacinth gradually and the final color of the mixture was maintained during the reaction. After the reaction was continued for 48 h, it was terminated with methanol. The solution was diluted with THF and then dropped into methanol (200 mL). The polymer was collected by filtration and washed by methanol. After drying under vacuum at 50 °C for 24 h, 0.12 g of white powders was obtained. Yield: 60%.

Coordination polymerization

In a glovebox, a toluene solution (1.0 mL) of (2,3,4,5,6-Me₅-4*H*-cyclopenta[b]thiophenyl)Sc(CH₂SiMe₃)₂THF **I** (4.80 mg, 0.01 mmol) was added into a 25 mL flask. Then, 10 equiv of Al/*i*Bu₃ (0.2 mL, 0.5 mol/L), 1 equiv of [Ph₃C][B(C₆F₅)₄] (9.20 mg, 0.01 mmol) dissolved in toluene (1.0 mL), and **S-M** (0.35 g, 1.0 mmol) were introduced into the flask. After

stirring for 2 h, methanol (0.2 mL) was injected to terminate the polymerization. The viscous mixture was dropped into a large quantity of methanol. The obtained white solids were collected by filtration, washing with methanol, and then dried under vacuum at 50 °C for 24 h as white powers (0.19 g). Yield: 55%.

IR spectra

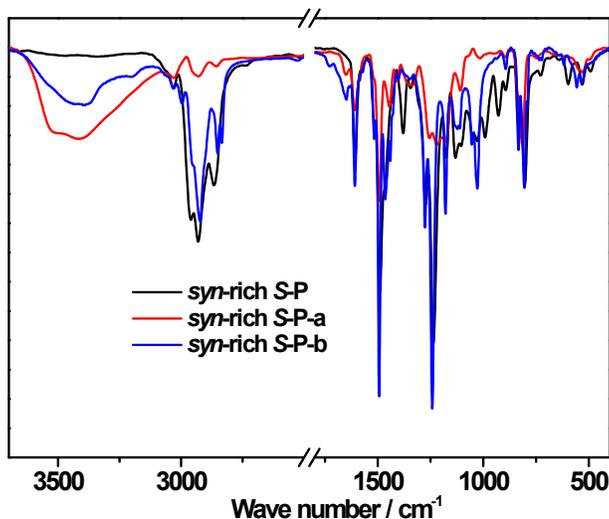


Figure S4 IR spectra of *syn-rich S-P*, *syn-rich S-P-a* and *syn-rich S-P-b*

Computer Simulation

The molecular modeling and molecular mechanics calculations were carried out in the Materials Studio software (version 5.0; Accelrys Software Inc.) by using the COMPASS force field. Firstly, the repeated units were built and their structures were optimized continuously through the geometry optimization of the Force module until the root-mean-square value became less than 0.1 kcal mol⁻¹ Å⁻¹. In order to establish different kinds of main chain backbone structures of polymers, the backbone dihedral angles of the repeating units, hereafter named ϑ_1 and ϑ_2 , were varied systematically in steps of 30°. The isotactic and syndiotactic polymers with 50 repeating units were then built up in head to tail manner by using Polymer Builder in the Material Studio, in which the dihedral angles were constrained to specific degrees. According to the different dihedral angles of the main chain, two types of polymers contained 144 different structures of conformations

respectively. Firstly, all the established structures were subjected to energy minimization with the Smart Minimizer of the Discover module. Secondly, Atomistic MD simulations were performed with the Dynamics of Discover module with a NVT ensemble at 298 K for all the conformations. The total simulation time was 0.1 ns, and time step was 5 fs. Energy deviation was 5000 kcal/mol. After the tentative simulation, the energies of the 144 conformations were ranked and the 50 conformations with relative low energies were screened to proceed further dynamic simulation. Compared with the former simulation, the simulation time was prolonged to 1ns. Finally, the 50 conformations were also ranked in terms of energies and the ten optimized conformations with relative low energies were chosen to carry out the structural analysis. The results were summarized in Table S1 and S2, the screw sense of main chain and side groups were figured out separately. Besides, the directions and angles of all the 50 repeating units in both two optimized conformations were counted and summarized in Table S3.

Table S1 Computer simulation results of isotactic S-P

	$\vartheta_1 / ^\circ$	$\vartheta_2 / ^\circ$	Energy/kcal·mol ⁻¹	Main chain	Side group
1	180	-120	7955.74	right	straight
2	-150	-120	8050.293	right	left
3	60	-150	8057.213	left	right
4	0	180	8089.354	zig-zag	
5	-150	-90	8116.144	right	left
6	-120	-120	8118.535	right	right
7	-60	-60	8127.654	left	right
8	-120	-30	8152.979	straight	left
9	30	90	8156.945	right	left
10	60	30	8234.787	right	left

Table S2 Computer simulation results of syndiotactic S-P

	$\vartheta_1 / ^\circ$	$\vartheta_2 / ^\circ$	Energy/kcal·mol ⁻¹	Main chain	Side group
1	-120	-30	7960.736	left	left
2	180	180	7991.896	zig-zag	
3	-60	-90	8017.022	left	left
4	-30	-120	8024.98	straight	left
5	-60	-60	8036.011	left	Zig-zag
6	-90	-60	8043.585	left	left
7	30	120	8059.68	right	right
8	0	180	8065.42	zig-zag	
9	180	0	8075.848	zig-zag	
10	120	30	8087.743	right	right

Table S3 Dihedral angles statistics of isotactic and syndiotactic S-P

Sequence No	Dihedral angle of biphenyl pedants in isotactic polymer (°)	Dihedral angle of biphenyl pedants in syndiotactic polymer (°)
1	34.4	-36.1
2	17.6	-51.6
3	35.1	22.9
4	35.6	-50.6
5	12.6	22.4
6	15.6	2.9
7	6.2	15.2
8	22.4	23.8
9	7.6	-20.2
10	24.1	91.3
11	27.9	60.7
12	26.4	71.1
13	4.3	42.1
14	42.7	94.7
15	30.5	46.1
16	28.4	79.4
17	14.0	-107.1
18	27.8	62.3
19	17.4	47.3
20	25.8	6.7
21	30.6	42.9
22	45.7	24.6

23	51.9	-1.0
24	51.8	-70.0
25	23.0	40.9
26	26.6	52.6
27	13.6	71.9
28	27.7	84.2
29	11.7	55.3
30	9.8	53.8
31	4.8	69.5
32	21.4	79.3
33	-3.7	75.8
34	48.7	65.4
35	31.1	66.8
36	18.9	68.4
37	25.6	-90.0
38	33.1	16.0
39	32.9	81.0
40	34.8	33.7
41	23.9	-1.3
42	17.5	-59.0
43	30.2	37.2
44	-34.6	51.6
45	46.1	68.0
46	-16.4	25.3
47	28.2	-50.7
48	14.1	22.2
49	22.3	-8.1
50	51.0	-24.5

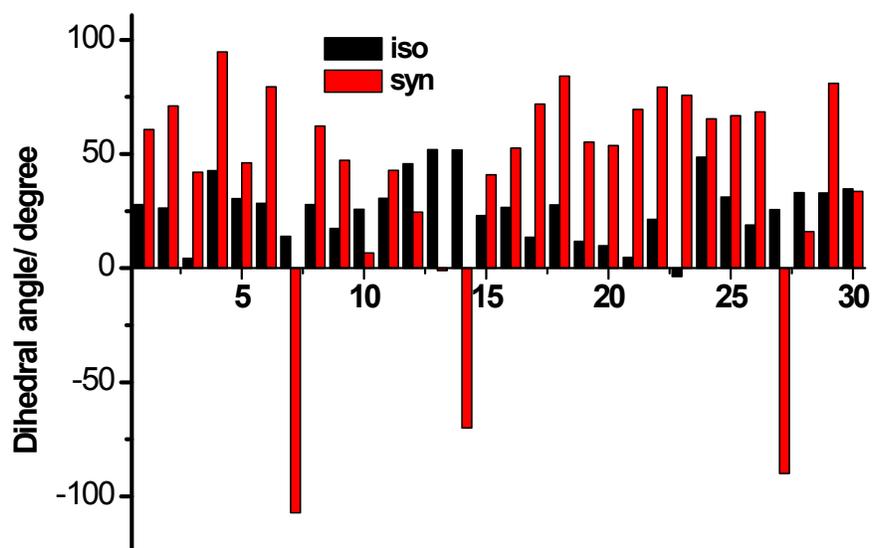


Figure S5 Dihedral angles statistics of biphenyl groups in isotactic S-P (black) and syndiotactic S-P

(red)

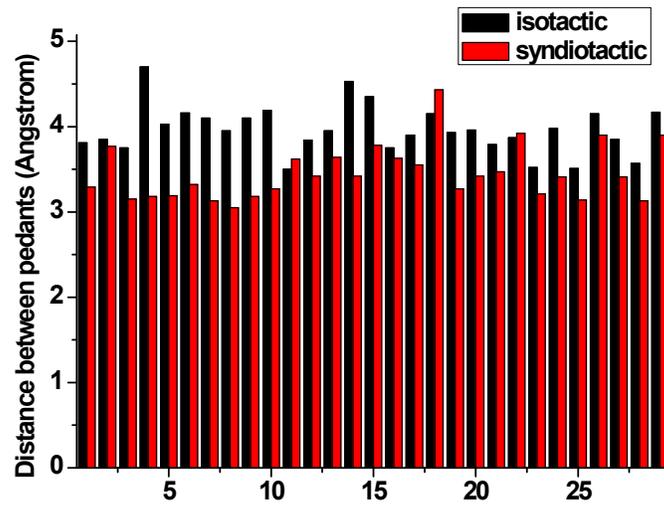


Figure S6 Distance between neighboring pendants in isotactic and syndiotactic S-P

Reference

1. L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, *Springer: New York*, 1995; p 5.