Supporting Information

Photostability and Dynamic Helical Behavior in Chiral Poly(phenylacetylene)s with a Preferred Screw-Sense

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Materials and Methods

ECD measurements were done in a Jasco-720 and VT-ECD measurements in a Jasco-1100 with a 1 mm quartz cuvette. The amount of polymer used for ECD and VT-ECD measurements was 0.3 mg/mL.

UV spectra were registered in a Jasco V-630 with a 1 mm quartz cuvette. The amount of polymer used for UV measurements was 0.3 mg/mL.

Optical rotation was measured in a Jasco-P2000.

NMR experiments were measured in a Varian 300 operating at 300 MHz for proton NMR and 75 MHz for carbon. CDCl₃ signal (δ= 77.2ppm) was used as standard for ¹H or ¹³C experiments.

Crystallographic data was obtained with a Bruker D8 Venture.

ATR/FT-IR spectra were recorded in a Perkin Elmer FT-IR ATR Spectrum Two

Raman spectra were done in a Renishaw confocal Raman spectrometer (Invia Reflex model), equipped with two lasers (diode laser 785 nm and Ar laser 514 nm).

Vibrational CD (VCD) experiments were measured in a 150 μm BaF₂ cell with a JASCO FVS-6000 spectrometer. The amount of polymer used was 50 mg/mL in CDCl₃ and d₈-THF.

GPC studies were carried out in a Waters Alliance 2695 HPLC with a UV-2489 detector (Waters) and three Phenomenex GPC columns. The amount of polymer used for GPC measurements was 0.3 mg/mL.

DSC traces were obtained in a DSC Q200 Tzero Technology (TA Instruments, New Castle, UK), equipped with a refrigerated cooling system RCS90 (TA Instruments, New Castle, UK), using a Tzero low-mass aluminum pan.

TGA traces were obtained in a TGA Q5000 (TA Instruments, New Castle, UK) using a platinum pan.

AFM measurements were performed in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air at rt with standard silicon cantilevers and supersharp cantilevers in tapping mode using 12 μm and 1 μm scanners Nanoscope processing software and WSxM 4.0 Beta 1.0 [4] (Nanotec Electronica, S.L.) were used for image analysis. All measurements were performed at CACTI (Vigo University, Spain).

Irradiation experiments were done in an Asahi Spectra Xenon light model MAX-303.
Synthesis of Monomer

mono-(R)-1 was prepared according to the procedure described in the Reference S1.

\[ \alpha \]_D^{20} = -2.3820 (c = 5.0 mg/mL, CHCl₃)

\(^1\)H NMR (300 MHz, CDCl₃) δ (ppm): 2.35 (s, 3H), 3.36 (s, 1H), 3.71 (s, 3H), 3.96 (s, 3H), 6.92 (s, 1H), 7.12-7.23 (d, 2H) 7.47-7.58 (m, 3H)

\(^{13}\)C NMR (75 MHz, CDCl₃) δ (ppm): 21.6, 56.5, 57.0, 79.6, 83.0, 107.1, 114.2, 117.1, 125.7, 130.0, 135.8, 141.9, 142.3, 149.1, 156.3.

HRMS (ESI) m/z calcd for C₁₇H₁₇O₃S [M+H]^+: 301.0898, found: 301.0896

Figure S1. \(^1\)H and \(^{13}\)C NMR spectra of mono-(R)-1 (CDCl₃, 300 and 75 MHz respectively).
The reaction flask (sealed ampoule) was dried under vacuum and argon flushed for three times before monomer was added as a solid (80 mg, 0.27 mmol). Dry THF (0.5 mL) was added with a syringe. A solution of rhodium norbornadiene chloride dimer, [Rh(nbd)Cl]$_2$ (1.23 mg) and Et$_3$N (7.1 μL) in dry THF (0.1 mL) was added at 50 °C. The reaction mixture was stirring at 50 °C for 12 h. Then, the resulting polymer was diluted in CH$_2$Cl$_2$ and it was precipitated in a large amount of methanol:diethyl ether (2:8), centrifuged (2 times), reprecipitated in hexane and centrifuged again obtaining 53 mg of poly-(R)-1 (66%).

Figure S2. $^1$H NMR spectra of poly-(R)-1 (CHCl$_3$, 300 MHz).
General Protocol for PPA Irradiation

Poly-(R)-1 was solubilized at room temperature by stirring in the correspondent solvent for prepare a solution of 2.1 mg in 7 mL. After this, irradiation experiments were performed using a collimator Lens (x1.0) of a MAX-303 (Asahi Spectra) equipped with a UV-VIS mirror module (300-600 nm) and a shortpass filter (VIS 550nm 25 dia.) applying the general protocol for PPA irradiation described in the reference S2 for measures in a 1 mm cuvette.

Crystallographic Data

For X-ray analysis, crystals of mono-(R)-1 was grown by slow evaporation from a CHCl₃ solution. The obtained crystal was collected in a total of 4451 frames for 3.51 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 32926 reflections to a maximum θ angle of 28.35° (0.75 Å resolution), of which 3514 were independent (average redundancy 9.370, completeness = 99.8 %, R_int = 6.69%, R_sig = 3.30 %) and 3292 (93.68 %) were greater than 2σ (F2). The final cell constants are a = 5.5842(4) Å, b = 6.8897(4) Å, c = 9.4917(6) Å, α = 93.865(3)°, β = 92.971(3)°, γ = 94.308(3)°, volume = 362.72(4) Å³, that are based upon the refinement of the XYZ-centroids of 9896 reflections above 20 σ(I) with 5.945° < 2θ < 56.66°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9470 and 0.9620.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1, with Z = 1 for the formula unit, C₁₇H₁₆O₃S. The final anisotropic full-matrix least-squares refinement on F² with 193 variables converged at R1 = 3.35 %, for the observed data and wR2 = 8.65 % for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.423 e.-/Å³ and the largest hole was -0.243 e.-/Å³ with an RMS deviation of 0.053 e.-/Å³. On the basis of the final model, the calculated density was 1.375 g/cm³ and F(000), 158 e.-.
Spectroscopy Studies

Raman

Samples were prepared by drop casting 0.5 mg/mL solutions of poly-(R)-1 in CHCl₃ and THF over a microscope slide. After solvent evaporation, the spectra were recovered in a Renishaw confocal Raman spectrometer.

Figure S3. (a) Raman spectra of poly-(R)-1 in compressed (CHCl₃) and stretched (THF) helices.

ATR/FT-IR

Figure S4. (a) ATR/FT-IR spectra of poly-(R)-1 in compressed (CHCl₃) and stretched (THF) helices.
Thermal Studies

DSC studies

A polymer sample, pre-dried in the correspondent solvent, was introduced in an aluminum pan and heated from 40 °C to 350 °C with a heating rate of 10 °C/min (Figure S5). The thermograms of the polymers show traces of a cis-transoidal backbone, where two exothermal peaks corresponding to the c-t to c-c and the c-c to t-t were observed. The exothermal peak corresponding to c-t to c-c transition show strong variations in intensity and broad of the peak in comparison with the standard PPAs for the stiffness of the polymer.

![Figure S5. DSC thermograms of a polymer sample dried in (a) CHCl₃ and (b) THF of poly-(R)-1.](image)

TGA studies

A solid polymer sample was remained under vacuum for 12 hours. After this, was introduced in an platinum pan and heated from 40 °C to 800 °C with a heating rate of 10 °C/min (Figure S6).

![Figure S6. TGA thermogram of poly-(R)-1.](image)
GPC Studies

GPC results were obtained in an Alliance 2695 HPLC with a UV-2489 detector (Waters). The samples were eluted in THF by three Phenogel columns connected to each other with stationary phases of 103, 104 and 105 Armstrong and packed with a solid support of a cross-linked styrene and p-divinylbenzene copolymer. For GPC data of poly-\((R)\)-1 see the table below.

| Mn (Daltons) | Mw (Daltons) | Mp (Daltons) | Mz (Daltons) | Mw/Mn |
|-------------|-------------|-------------|-------------|-------|
| 88701       | 191229      | 160973      | 37351       | 2.15  |

AFM Studies

Monolayers was prepared from 0.1 mg/mL solutions in CHCl₃ and THF spin-coated over HOPG and kept under the corresponding solvent vapor 12 hours. After this, AFM measurements were performed at CACTI (Vigo University, Spain) in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air and room temperature. Also, Standard silicon cantilevers and supersharp cantilevers in tapping mode was selected using 12 μm and 1 μm scanners. Nanoscope processing software and WSxM 4.0 Beta 1.0 (Nanotec Electronica, S.L.) were used for image analysis.

Stretched helix (CHCl₃)

![Figure S7. AFM images of stretched helical monolayers of poly-(R)-1 from CHCl₃ solution.](image)

Compressed helix (THF)

![Figure S8. AFM images of helical monolayers of poly-(R)-1 from THF solution.](image)
VT-ECD Experiments

Variable temperature circular dichroism (VT-ECD) experiments were measured in a 1 mm quartz cell in a Jasco-1100. The amount of sample used was 0.3 mg/mL in the solvents analysed.

Figure S9. Heating/cooling ECD curves of poly-(R)-1 in (a) CHCl₃, (b) THF and (c) DMF.
ECD and UV Experiments

ECD and UV experiments were measured in a 1 mm quartz cell in a Jasco-720 and a Jasco V-630 respectively. The amount of sample used was 0.3 mg/mL in the solvents analysed.

Poly-(R)-1

![Graph](image1.png)

**Figure S10.** Mixture of poly-(R)-1 at 0.3 mg/mL in different percentages of CHCl₃ and THF monitored by (a) ECD and (b) UV spectra.

m-(R)-1

![Graph](image2.png)

**Figure S11.** Mono-(R)-1 at 0.3 mg/mL in different solvents monitored by (a) ECD and (b) UV spectra.
Monomer calculations

Calculated ECD spectra reveals a $S_0$ to $S_1$ transition experimentally absent. As result, $S_0$ to $S_7$ transition is bathochromically displaced of its expected maximum (this displacement is negligible due to the lambda factor applied as result of the difference between the theoretical and experimental wavelengths). Finally, last ECD signal (experimentally around 275 nm) corresponds mainly to $S_0$ to $S_{17}$ transition.

**Figure S12.** Main HOMO and LUMO of the transition assign to each calculated natural transition orbitals (NTO).
**Enantiomeric Studies**

Using the same protocol described for preparation of poly-(R)-1, its enantiomer (poly-(S)-1) was polymerized in a 63 % of yield. Applying the same experimental conditions, mono-(S)-1 and poly-(S)-1 was submitted to ECD and UV experiments to confirm that their chirality transfers properties can promote the formation of its corresponding right-handed helices instead the left-handed observed in poly-(R)-1.

**Figure S13.** ECD and UV comparison between (a) m-(R)-1 and m-(S)-1 and (b) poly-(R)-1 and poly-(S)-1.
Computational Details

Considering the difficulties to carry out theoretical calculations on large polymers, we apply the methodology reported in the reference S3. Thus, oligomers constituted by 8 monomer repeating units was build using Spartan 18. The generated structure was adjusted according to the information obtained from several techniques such as Raman, IR, ECD and AFM. Moreover, this experimentally supported structure was refined through Molecular Mechanics (MMFF94) before being submitted for ECD calculations. Finally, the time-dependent density functional theory (TD-DFT, Ref. S4) was used together with the rCAM-B3LYP density functional (Ref. S5) and the 3-21G* basis set (Ref. S6). We included 100 excitation energies in the calculation for the stretched scaffold (CHCl₃) and 110 excitation energies for the compressed scaffold (THF). The resulting ECD spectrums were selected with a full width at half height (FWHM) of 0.4 eV. Moreover, we evaluated a correction factor for lambda as the difference between the theoretical and experimental wavelengths, and we shifted the rest of the theoretical spectra accordingly. In a similar way, the intensity, was rescaled for the theoretical values to get the experimental intensity at the first Cotton effect band.

For monomer calculations, optimization of the geometry was applied using the density functional theory (DFT) together with the rCAM-B3LYP functional and the 6-31G* basis set. Thus, the theoretical ECD spectrum was calculated since the optimized geometry using the time-dependent density functional theory (TD-DFT) together the rCAM-B3LYP density functional and the 6-31G* basis set. The resulting ECD spectrum was selected with a full width at half height (FWHM) of 0.45 eV. Moreover, we evaluated a correction factor for lambda as the difference between the theoretical and experimental wavelengths, and we shifted the rest of the theoretical spectrum accordingly. Similarly, the ECD intensity was rescaled in the theoretical values.
Supporting References

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