

Multistate Chiroptical Switch Triggered by Stimuli-Responsive Chiral Teleinduction

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Multistate Chiroptical Switch Triggered by Chiral Teleinduction

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ABSTRACT: Teleinduction of chirality, from a distant chiral center in the pendant, to the helical backbone of a poly(phenylacetylene) (PPA) was demonstrated by using an achiral, flexible and well-organized spacer originating a multistate chiroptical switch. Two PPA series, with pendants formed by one or two consecutive Gly residues C-attached to the PPA backbone and N-attached to (*R*)- or (*S*)- α -methoxy- α -trifluoromethylacetic acid (MTPA), were prepared and the changes in the helical content upon modification of the MTPA conformation by external stimuli (i.e., polarity of the media, metal cations) were examined. Chiral teleinduction, imposing opposite helicities, was observed in the two polymer series due to the parallel β -sheet arrangements of the Gly residues orienting the chiral groups in specific directions along the external part of the helices. This teleinduction can be tuned inducing either the *P* or *M* helical sense of the polymer by controlled conformational changes on the chiral moiety attached to the achiral β -sheet spacer. This remote control of the helix can be switched On/Off by favoring/disfavoring the β -sheet arrangement of the Gly residues resorting to changes on the temperature and the addition of destabilizing agents (e.g., TFA).

The control of the helical sense of dynamic helical polymers via external stimuli¹⁻¹⁴ has caught the attention of the scientific community due to the potential of these materials as sensors,⁷⁻⁹ chiroptical switches,¹⁰⁻¹² chiral stationary phases¹⁵ or chiral catalysts,¹⁶⁻²¹ among other applications.

In these polymers, the helical sense of the backbone is determined by the chirality of the pendant.¹⁻¹⁴ In this way, *P* or *M* senses can be selectively obtained depending on the *R/S* absolute configuration of the pendant chiral group. Studies by the groups of Nolte²²⁻²³ and Yashima,²⁴ have demonstrated that when the pendant bears more than one chiral center, the helical sense of the polymer, is controlled by the group closer to the backbone. As for the distance between the chiral group and the polymeric backbone, Veciana et al.²⁵⁻²⁶ have shown that the capability for helical induction decreases when the chiral center is shifted away along the pendant chain.

Thus for an effective helical induction, the chiral group should be close to the backbone, limiting very much the structure of the pendants and the applicability of this approach for helical control of the polymer.

In order to demonstrate how chiral teleinduction works in helical polymers, and trying to determine which parameters govern this communication mechanism between the distant chiral center and the helical backbone, Veciana and coworkers performed studies in helical polymers where the distant chiral group is connected to the backbone through quite rigid spacers (e.g., tetrathiafulvalene, TTF), which can self-assemble through π - π interactions.²⁷ Another interesting work in the same field was done by Percec and coworkers introducing connectors with self-assembling properties (e.g., dendrons).^{28,29} All these studies, in combination with the different information obtained from the helical polymer field, allow us now to go deeply into the principles for chiral teleinduction in dynamic helical polymers. Thus, the conformational composition of the chiral element, its distance

to the backbone, the presence of spacers showing self-assembling properties and the need for steric or supramolecular interactions to avoid a helical inversion will dictate principles for transfer the chiral information from the pendant groups to the polymer backbone.

Herein, we decided to test these principles of chiral teleinduction in poly(phenylacetylene)s (PPAs)³⁰⁻⁴¹ using flexible and common linkers such as glycine residues, which are cheap and easy to functionalize offering a straightforward approach to explore chiral teleinduction in a large variety of PPAs, and therefore, the possibility of creating different multistate sensors able to respond to a large variety of external stimuli. As a result of the application of these ideas, new materials possessing novel sensor abilities should arise in the future.

It is known that PPAs bearing amino acid residues as substituents adopt helical structures stabilized by hydrogen bonds between neighboring pendants — n^{th} and $(n+2)^{\text{th}}$ or n^{th} and $(n+3)^{\text{th}}$ — adopting a β -sheet like orientation.¹ Thus, we reasoned that the introduction of an achiral spacer between the distant chiral group and the polymeric backbone able to form a parallel β -sheet structure with the neighboring pendants, would allow us to study the chiral teleinduction to the polyenic backbone when the length of the achiral parallel β -sheet is extended (Figure 1).

The simplest example of such a system would be represented by PPAs with a single glycine residue used as spacer C-connected to the PPA backbone through a peptide bond and N-linked to the distant chiral group, constituted by (*R*)- and (*S*)- α -methoxy- α -trifluoromethylphenylacetic acids (MTPA) (Figure 2). In this way, the adoption of a β -sheet like structure by the glycine residues would stabilize the helical structure of the polyene by hydrogen bonding between n^{th} and $(n+2)^{\text{th}}$ or n^{th} and $(n+3)^{\text{th}}$ amide groups transforming the flexible spacer into a rigid one which would facilitate the chiral teleinduction (Figure 1).⁴²

From a previous work it is known that when the MTPA moiety is directly linked to the PPA, the pendant group is sensitive to polarity changes, and therefore helix inversion is observed when going from polar to non-polar solvents and vice versa.⁹ Therefore, changes in polarity should provide us an easy way to test the stimuli-response of the helical backbone to changes in the conformational composition of the chiral center and thus, the effectiveness of the teleinduction.

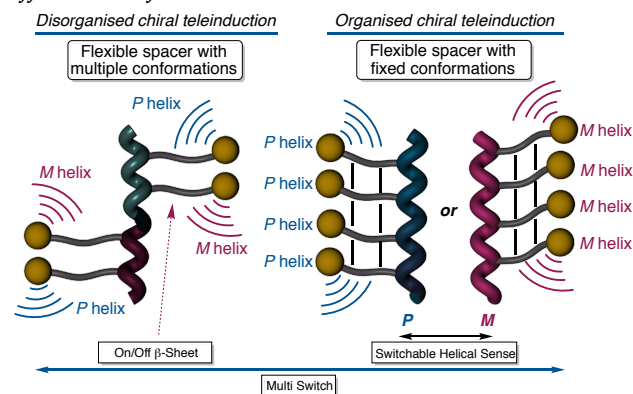


Figure 1. Conceptual representation of the chiral teleinduction produced in a helical polymer when an achiral flexible linker is fixed by internal supramolecular interactions.

Thus, phenylacetylene monomers (*R*)- and (*S*)-MTPA-Gly-4-ethynylanilide [i.e., *m*-(*R*)-**1**, *m*-(*S*)-**1**] were prepared and polymerized using [Rh(*nbd*)Cl]₂ as catalyst (*nbd* = 2,5-norbornadiene), affording PPAs [i.e., poly-(*R*)-**1**, poly-(*S*)-**1**] in good yield (90 %) and with a high content of the *cis* configuration of the double bonds (see SI for full details) (Figure 2).

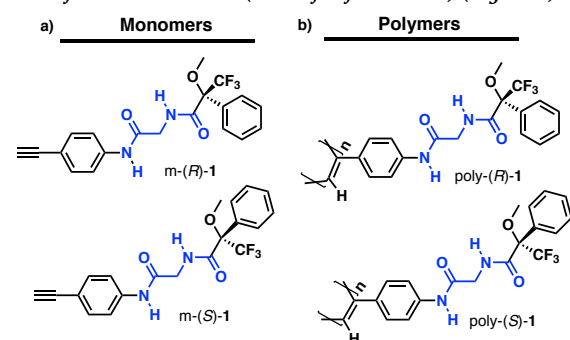


Figure 2. a) Structure of monomers —*m*-(*R*)-**1**, *m*-(*S*)-**1**— and their corresponding polymers —poly-(*R*)-**1**, poly-(*S*)-**1**—. The glycine residues that form the flexible spacers are highlighted in blue.

CD studies of poly-(*R*)-**1** and poly-(*S*)-**1** in several solvents (concn= 0.3 mg/mL) revealed the presence of an induced CD spectra (Figure 3c), indicating that the chirality of the MTPA moiety is transferred via teleinduction to the poly(phenylacetylene) skeleton. In addition, a helix inversion was observed by changing the polarity of the solvent (Figure 3d). This fact demonstrates the efficacy of the glycine residue to act as a well-oriented spacer, allowing the chiral teleinduction from the conformational changes induced on the remote chiral moiety to the helical backbone (Figure 3d).

Thus, while poly-(*R*)-**1** in THF adopts a right handed (*P*) helix associated to the presence of a synperiplanar conformation (*sp*) at the O=C-C-OMe bond of MTPA (Figure 3b), a left handed (*M*) helix is formed in chloroform due to the adoption of an antiperiplanar (*ap*) conformation at that bond (Figure 3a). Furthermore,

the addition of a Ba(II) salt [i.e., Ba(ClO₄)₂] to a chloroform solution of poly-(*R*)-**1** results in a helix inversion of the PPA (Figure 3e) due to the conformational change—from *ap* to *sp*—produced in the MTPA moiety by chelation to the metal ion.⁴⁴⁻⁴⁹

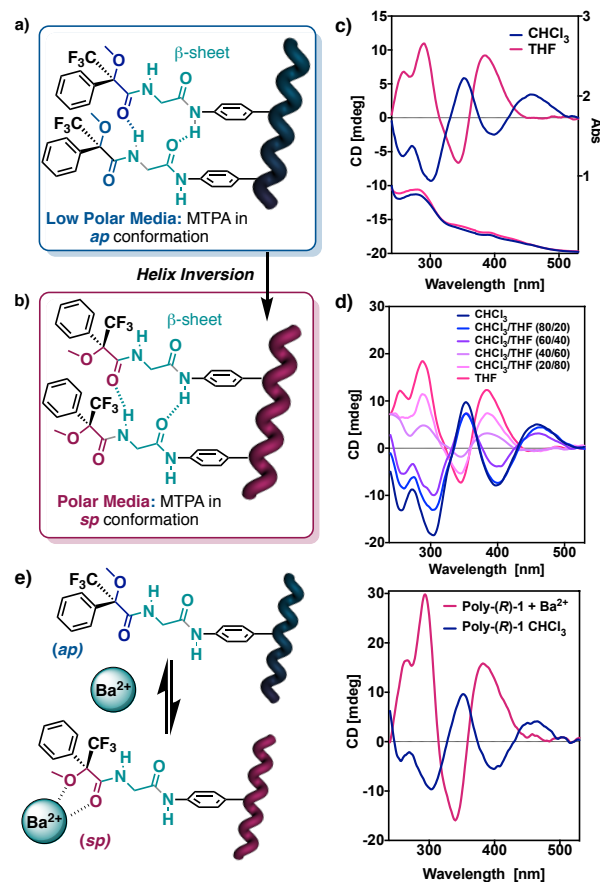


Figure 3. Schematic illustration of the β -sheet pendant array in poly-(*R*)-**1** adopting (a) left- and (b) right-handed helical state due to a polarity-driven conformational *ap/sp* change in the MTPA moiety. c) CD/UV spectra of poly-(*R*)-**1** (0.3 mg/mL) in THF and CHCl₃. Helix inversion of poly-(*R*)-**1** induced by (d) polarity changes and (e) the presence of Ba(ClO₄)₂ as external stimulus (i.e., Ba²⁺).

The key role played by the β -sheet association in the chiral transmission was further confirmed by experiments that activate/deactivate the β -sheet secondary structure, allowing us to create a switch of the chiral teleinduction. In this way, VT-CD experiments revealed that although the helical structure disappears by increasing the temperature, it is recovered unaltered when the solution returns to the starting temperature (Figure 4a) (see SI for VT-CD and VT-NMR experiments).

Similarly, addition of TFA produces the disruption of the β -sheet of poly-(*R*)-**1** and the expected helical decay, effect that can be reversed by addition of Et₃N, regenerating the original helicity (Figure 4b).

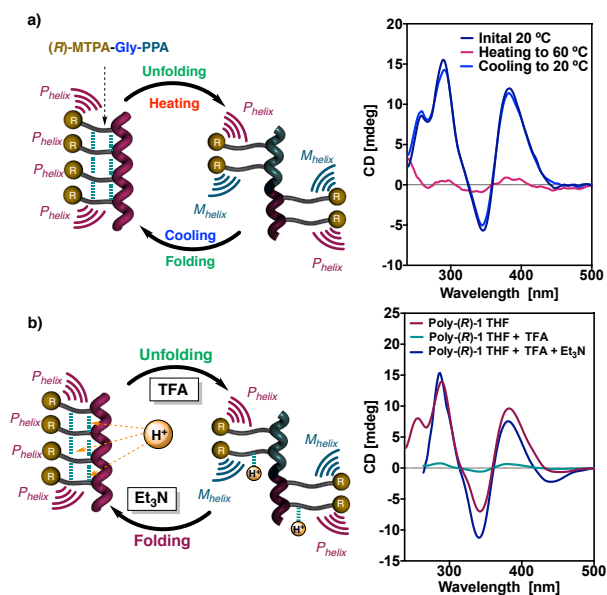


Figure 4. On/Off chiral teleinduction of poly-(*R*)-1 by (a) temperature changes and (b) the presence/absence of acid media (TFA). Poly-(*R*)-1 concn = 0.3 mg/mL THF.

Once teletransmission —through a well-organized flexible spacer formed by a glycine residue— was demonstrated, we decided to explore if a similar process could occur even at a longer distance, introducing a spacer formed by two consecutive glycine residues. Thus, phenylacetylene monomers, (*R*)- and (*S*)-MTPA-Gly-Gly-4-ethynylanilide [i.e., *m*-(*R*)-2, *m*-(*S*)-2], were prepared and polymerized as above affording poly-(*R*)-2 and poly-(*S*)-2 in good yields (90 %) and with a high content of the *cis* configuration of the double bonds (see SI for details) (Figure 5).

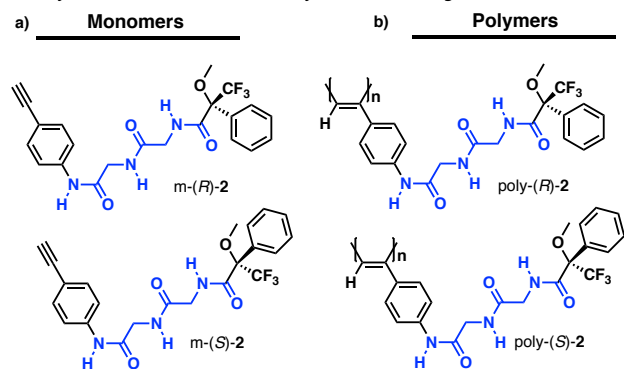


Figure 5. a) Structure of monomers *m*-(*R*)-2, *m*-(*S*)-2. b) Structure of polymers poly-(*R*)-2, poly-(*S*)-2. The glycine residues that form the flexible spacers are highlighted in blue.

CD studies of poly-(*R*)-2 and poly-(*S*)-2 in dioxane or acetone (concn= 1 mg/mL) revealed the presence of an induced CD spectra, and therefore the existence of an efficient chiral transmission (Figure 6a). In other solvents, the chiral teleinduction is very weak or null indicating that the arrangement of the flexible spacer is poor.

Interestingly, comparison of the CD spectra of both polymer series —i.e., poly-(*R*)-1 and poly-(*R*)-2— prepared in dioxane reveals the presence of opposite helical senses, although the chirality and conformational composition at the chiral MTPA unit is the same. This opposite helical sense induction for the same chirality in both polymer series can be easily explained by

the parallel β -sheet orientation of the Gly and Gly-Gly spacers within the helical structure of the PPAs. It is known that the side chain orientation of peptide residues forming a parallel β -sheet depend on the odd/even number of residues forming the secondary structure.⁵⁰ In poly-(*R*)-1 the spacer is made by a single glycine (odd number), while poly-(*R*)-2 has two glycines (even number) (Figure 6c). Thus, these different spacer geometries will place the chiral MTPA moiety in different orientations, and therefore teletransmission of the geometrical elements from the chiral group to the polyene backbone commands opposite helical senses (Figure 6c).

For its part, the smaller CD intensity of poly-(*R*)-2 regarding poly-(*R*)-1 illustrates the chiral teleinduction/distance relationship. In fact, a 3D model of both polymers shows that the chiral inductor —aryl ring of the MTPA moiety— is in poly-(*R*)-2, around 0.5 nm further away from the backbone than in poly-(*R*)-1, explaining the lower chiral teleinduction (Figures 3 d-e).

Tuning the helical sense of the polymer by external stimulus acting on the MTPA was also possible in the poly-2 series. Thus, when Ba(ClO₄)₂ is added to a dioxane solution of poly-(*R*)-2, helical sense enhancement is observed due to the increase of the native *sp* conformation of MTPA by chelation (see SI).

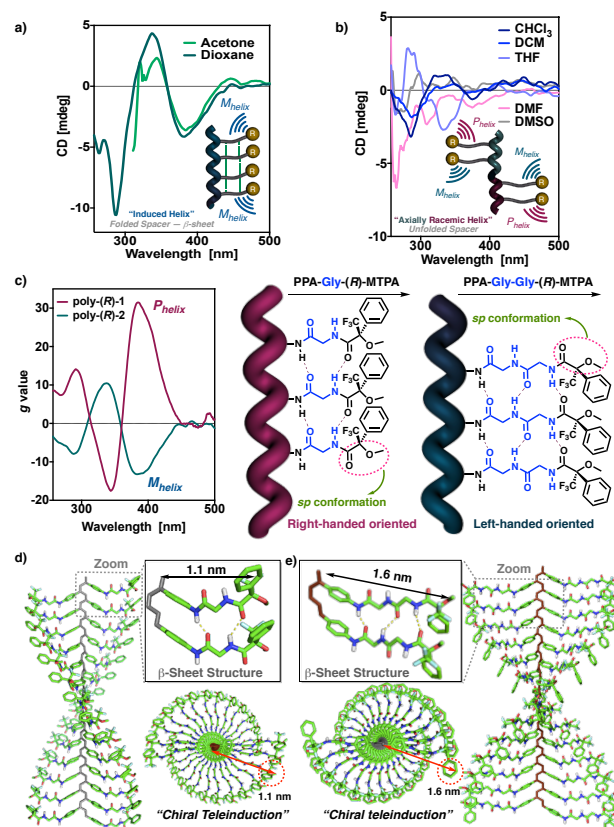


Figure 6. CD spectra of poly-(*R*)-2 (a) in acetone, dioxane and (b) in DCM, THF, CHCl₃; poly-(*R*)-2 concn= 1 mg/mL. c) CD spectra of poly-(*R*)-1 and poly-(*R*)-2 in dioxane indicating the presence of enantiomeric helices as a consequence of an even/odd number of residues in the β -sheet spacer. d) 3D-model of poly-(*R*)-1 and poly-(*R*)-2 highlighting the β -sheet orientation between pendants and the distance between the chiral MTPA moiety and the polymer skeleton.

Finally, different methodologies to switch the helical sense of poly-(*R*)-2 based on the activation/deactivation of the well-

organized β -sheet orientation of the spacer were tested. Thus, VT-CD experiments showed that the helical structure is unfolded above 70°C when the hydrogen bonds that stabilized the parallel beta sheet are disrupted. Folding of the helical structure can be recovered by decreasing temperature (Figure 7a). Moreover, addition of TFA disrupts the β -sheet and deactivates the chiral teleinduction, which is recovered once triethylamine is added (Figure 7b).

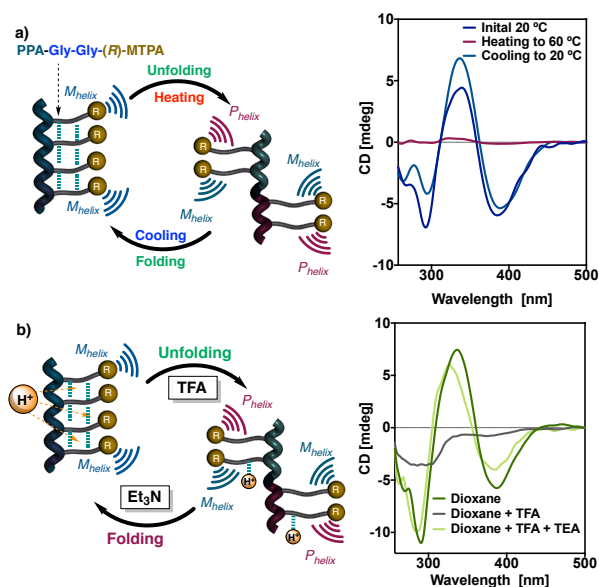


Figure 7. On/Off chiral teleinduction of poly-(R)-2 by (a) temperature changes and (b) the presence/absence of acid media. Poly-(R)-2 concn = 1 mg/mL in dioxane.

In conclusion, we have demonstrated that effective chiral teleinduction from a distant chiral group in the pendant to the helical skeleton of a PPA is possible if the chiral inducer is linked to the polymer backbone through a flexible and well-organized spacer. In our examples, the spacer is made by one (poly-1 series) or two (poly-2 series) glycine residues, and demonstrate that selective teleinduction towards a left or right handed helix can be tuned even at distances as long as 1.6 nm. Moreover, this chiral teleinduction can be switched On/Off by acting on the folding of the flexible achiral spacer.

The key role played by the β -sheet motif generated from flexible achiral spacers —e.g., glycine residues— opens a new way to design switches based on chiral teleinduction. An additional advantage derived from this work is that poorly dynamic PPAs, bearing bulky groups, can be transformed into a more dynamic helix if these large substituents are placed in a position farther from the polyene backbone.

ASSOCIATED CONTENT

Supporting Information

Materials and methods, synthesis and characterization of monomers, synthesis and characterization of polymers and supporting references.

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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