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“Chiral Conflict” as a New Tool to Create Stimuli-Responsive Materials Based on Dynamic Helical Polymers

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Abstract: A new multi-sensor material based on helical copolymers showing “Chiral Conflict effect” have been prepared, which can successfully detect and identify diverse metal cations in solution. The design of this novel material has taken into account not only the opposite helical senses induced by the two chiral monomers in the copolymer, but also their dynamic behavior. So, the induced helical sense can be enhanced, diminished or inverted by interaction with different stimuli (i.e., metal ions). Thus, depending on both the copolymer compositions (i.e., monomer ratios and absolute configurations) and the nature of the metal ion, the response of these dynamic helical copolymers to adopt a single-handed *P* or *M* helix is unique, making it possible not only to detect their presence, but also to identify them individually. New multi-sensors materials based and inspired on this effect should arise in the future choosing appropriate monomers and stimuli.

The helical structures of dynamic polymers, such as poly(phenylacetylene)s (PPAs), are usually stabilized by supramolecular interactions between monomer repeating units along the polymer chains, with steric effects also playing a role.[1-10]

Controlled conformational changes at the pendant groups modulate these supramolecular and/or steric interactions resulting in variations on the helical structure of the polymer —i.e., elongation[11-13] and/or helical sense[14-15]—. Thus, chiral amplification, helical enhancement or helix inversion can be induced by the action of appropriate external stimuli.[1-10]

In the case of copolymers formed by the combination of chiral and achiral monomers, the modulation of the helical structure may occur through a conformational communication mechanism —going from the chiral to the achiral pendants— that originates a chiral amplification phenomenon denoted as the “Sergeants and Soldiers effect.”[16-28] In such a case, the presence of a small amount of the chiral monomer (minor component, Sergeant) commands the secondary structure of the whole copolymer chain —i.e., either *M* or *P* helices— by inducing a certain spatial orientation in the achiral units (major component, Soldier). Recently, our group extended the concept of "Sergeants and Soldiers effect" to a more complex situation of PPA copolymers —specifically, bipolymers, i.e., copolymers derived from two monomers— in which the two components are chiral.[16-17] In this way, one of them acts as a chiral Sergeant, while the other acts as a chiral Soldier. Hence, while the helical sense of the copolymer (i.e., its *M* or *P* helicity) is commanded by the absolute configuration of the Sergeant (minor component), the chirality at the periphery of the helix depends on the intrinsic chirality of the Soldier (major component).

Those studies showed that this chiral to chiral communication phenomenon —operative along a copolymer chain and responsible of the enhancement of a single-handed helicity— works efficiently when the two participant chiral monomers comprise the following features:

1) The two monomers (Sergeant and Soldier) must promote similar scaffolds in their corresponding homopolymers. For instance, if the homopolymer of the Soldier adopts a cis-cisoidal structure, the homopolymer of the Sergeant must also show a cis-cisoidal backbone.

2) The monomer used as chiral Soldier must display, in the corresponding homopolymer, a conformational equilibrium at least between two conformers providing a highly dynamic polymer with null CD at the vinylic region.

3) The monomer used as chiral Sergeant must show a preferred conformation in the pendant moiety, with a large energy barrier with respect to other conformers, resulting in restricted rotations around its bonds.

In other cases, the communication between chiral monomers is not in force. As a result, both monomers induce —independently of each other— the scaffolds that they previously induced in their corresponding homopolymers which can be of equal (“Chiral Accord”) or opposite (“Chiral Conflict”) helical senses. Green and coworkers described the latter phenomenon in polyisocyanates, where forces favoring left- and right-handed helices arise from structurally different chiral monomers.[29-30] However, as far as we know and despite its potential interest, no practical application of this effect has been reported.

Herein, we show how it is possible to take advantage of this “Chiral Conflict” effect in a dynamic helical copolymer to control its helical sense after interaction with an external stimulus. In this way, the copolymer becomes its sensor.

Several strategies can be envisaged to make use of this effect. In a simple first approximation, it should be possible to tune the helical sense in a copolymer featuring “Chiral Conflict”, and where one comonomer induces a *P* helix while the other promotes an *M* helix, acting on the conformational composition of one of the comonomers, and thus transforming an axially racemic (or partially racemic) helix into single-handed one after stimulation (Figure 1a).

In a more elaborate application, if each monomer responds in a different and individualized way to the external stimuli in the copolymer showing “Chiral Conflict”, it should be possible, acting selectively on either one or the other, to tune the helical content inducing any of the two helicities (*M* or *P*) (Figures 1a and 1b). Finally, in a borderline case, it should be possible to transform an axially racemic helix (*P*/*M*) into its enantiomeric helix (*M*/*P*), also racemic, acting simultaneously on the two monomers using one or more stimuli (Figure 1c).

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In all these cases, not only the of the stimuli and the structure of the pendants would be main factors in the final results, but the relative composition (% of each comonomer) would also be an important variable to be taken into account due to the different percentage contribution of each pendant to the final structural and optical outcomes.

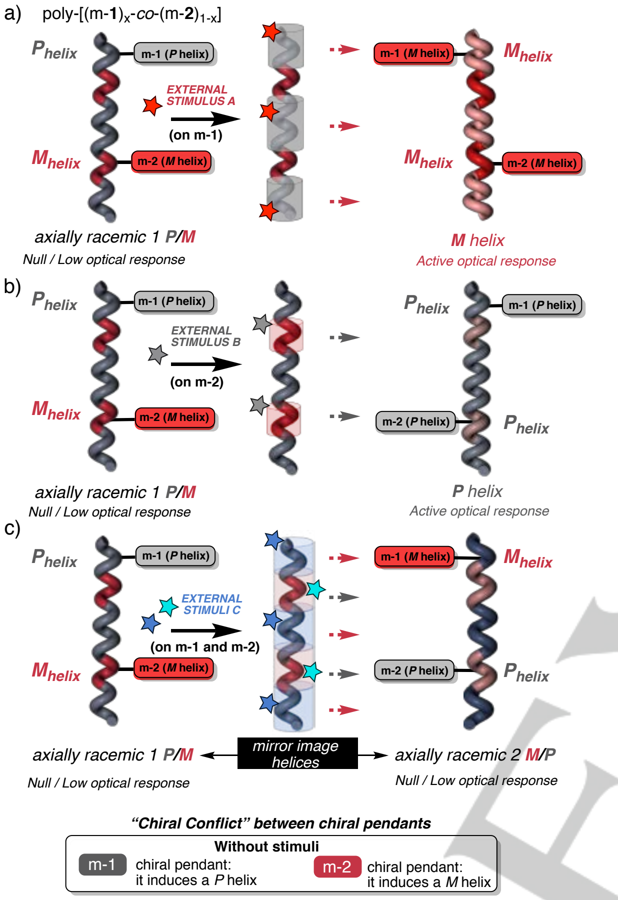

Figure 1. a) Conceptual representation of the "Chiral Conflict" effect in a dynamic helical copolymer and its transformation from an axially racemic helix (*P*/*M*) to an optically active helix (*M*), by means of an appropriate stimulus ("A") acting just on one monomer (m-1). b) Idem to the enantiomeric helix (*P*) by means of a different stimulus ("B") acting just on the other monomer (m-2). c) Idem from an axially racemic helix (*P*/*M*) to another axially racemic helix (*M*/*P*), by means of appropriate stimulus/stimuli ("C") acting simultaneously on both monomers (m-1 and m-2).

As a proof of concept of application of the "Chiral Conflict" effect, we envisioned a number of experiments where different metal ions could be appropriate as external stimuli acting on a series of two-component copolymers with different percentage compositions. As a result, we would expect a set/combination of different and characteristic responses that would allow us to differentiate/identify the diverse stimuli used.

It is known from previous studies that homopolymers from (*R*)- and (*S*)-*N*-(4-ethynylphenyl)-2-methoxy-2-phenylacetamide [m-(*R*)-**1** and m-(*S*)-**1**; enantiomers] and methyl (*R*)-2-(4-ethynylbenzamido)-2-phenylacetate [m-(*R*)-**2**] (Figure 2), adopt different types of polyene scaffolds —poly-(*R*)-**1** and poly-(*S*)-**1** *cis-cisoidal;* poly-(*R*)-**2** *cis-transoidal*— and therefore, no chiral communication (neither Chiral Coalition nor Chiral to Chiral Sergeants and Soldiers effects) should occur.[17] Moreover, these two types of homopolymers respond in different ways to monovalent and divalent metal ions.[31-38] Hence, if each monomer retains independently its ability to respond to these stimuli within the copolymer without being affected by the presence of the other chiral monomer, a novel sensor material with better properties than the parent homopolymers could be generated based on the "Chiral Conflict" effect depicted above.

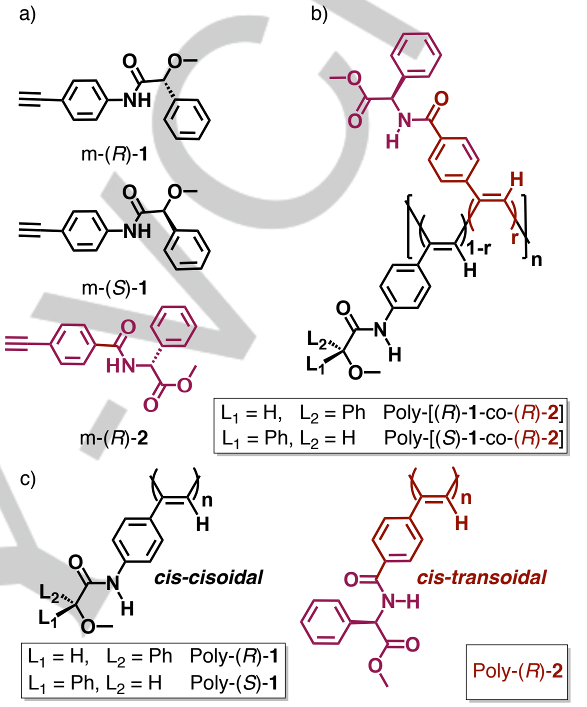

Figure 2. Chemical structure of (a) monomers, (b) copolymer series and (c) homopolymers used in these studies.

Thus, homopolymers poly-(*R*)-**1** and poly-(*R*)-**2** and the copolymer series poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] (x= 0.1-0.9) were prepared by using a Rh(I) catalyst, $[\{Rh(nbd)Cl\}_2]$ (nbd=2,5-norbonadiene)]. All the copolymers showed by NMR (vinyl protons, δ= 5.7–5.8 ppm) and Raman (1580, 1343, 1006 cm^{-1}) to possess a *cis* polyene backbone.[39-45] Their molecular weights were estimated by GPC (THF as eluent with polystyrene standards as calibrants; see SI for details) to be between Mn= 7832 and 20325 with Mn/Mw values around 1.58-1.68. The monomer ratios [(*R*)-**1**/(*R*)-**2**] in the copolymers were shown by NMR to be coincident with the feeding mixtures (see SI). Also, the Kelen-Tüdos method using varied monomer feed ratios and termination at low conversions[46-47] demonstrated their random distribution along the polymer chain (see SI).

The CD spectra of poly-(*R*)-**1** and poly-(*R*)-**2** (0.3 mg/mL in THF) at room temperature showed the presence of opposite helical senses —*M* helix for poly-(*R*)-**1** (CD negative at 370 nm, Figure 3a)[35] and *P* helix for poly-(*R*)-**2** (CD positive at 380 nm, Figure 3b)[38]—. In the poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] copolymer series, the CD signature is cancelled when the ratio between monomers reach a value close to 50% (Figure 3c). This fact indicates that a "Chiral Conflict" effect is taking place, and therefore, while the pendants from m-(*R*)-**1** induce a *M* helix, those from m-(*R*)-**2** induce the opposite *P* helical sense (Figure 3c). In THF, the "strengths" (i.e., the capacities to induce a certain helical sense) of the pendants from m-(*R*)-**1** and m-(*R*)-**2** are similar, being this the reason for a null CD in a copolymer with a monomer ratio of approximately 50% —i.e., poly-[(*R*)-**1**$_{0.5}$-*co*-(*R*)-**2**$_{0.5}$]—.

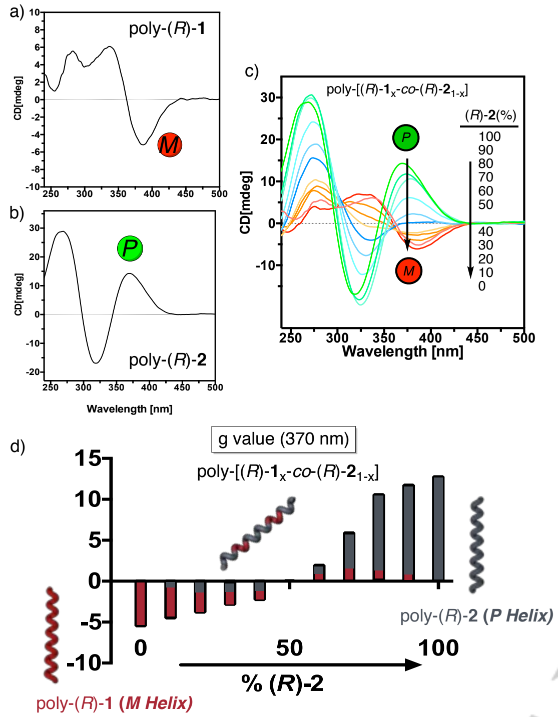

Figure 3. CD spectra of (a) poly-(*R*)-**1**, (b) poly-(*R*)-**2** and (c) poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] copolymer series, including (d) g values. [copolymers] = 0.3 mg/mL in THF.

Therefore, once the presence of the "Chiral Conflict" was established, we decided to explore the dynamic behavior of these copolymers by studying their interaction with metal ions (i.e., external stimuli) in THF. In literature, it is found that poly-(*R*)-**1** adopts an *M* helix in the presence of monovalent metal ions, while a *P* helix is induced by divalent ones (Figure 4a).[33-37] On the other hand, poly-(*R*)-**2** stabilizes an *M* helix in the presence of both types of ions (Figure 4b).[38-39]

Due to the active "Chiral Conflict" in the copolymer, it was expected that the different interactions of the comonomers with the ions could either enhance a certain helical sense —e.g., m-(*R*)-**2** inverts its helical sense from P_2 to M_2, while m-(*R*)-**1** keeps its M_1 helical structure; i.e., an excess of *M* helicity (Figure 4c)— or generate another axially racemic copolymer mirror image of the original one —e.g., m-(*R*)-**1** goes from M_1 to P_1 and m-(*R*)-**2** from P_2 to M_2; i.e., from axially racemic 1 to axially racemic 2 (Figure 4c)— through the mechanisms shown in Figure 1.

To test this hypothesis, we studied the interaction between the copolymer series —poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] (x= 0.1-0.9); a total of 9 copolymers—, with different metal perchlorates —M^{n+}= Li$^+$, Na$^+$, Ag$^+$, Ba^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}—. These metal ions were added to THF solutions of the above copolymers (0.3 mg/mL) in M^{n+}/mru (monomer repeating unit) ratios= 10 mol/mol.

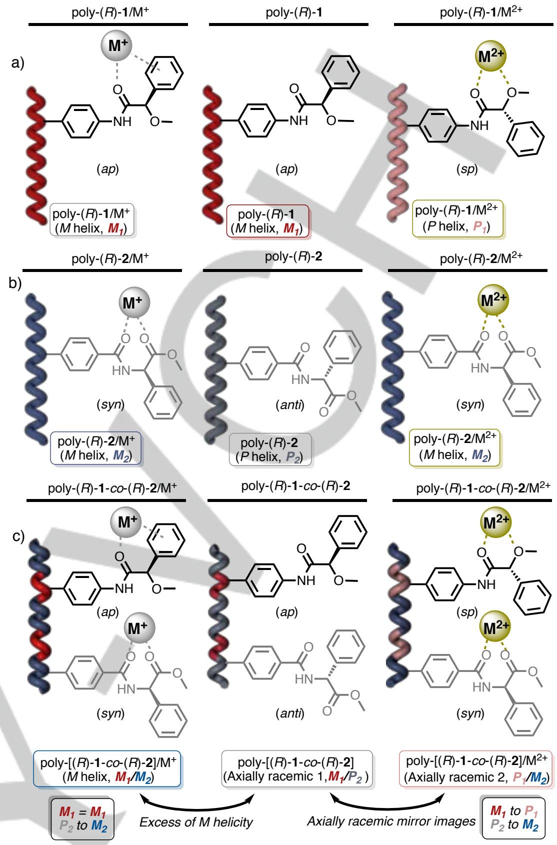

Figure 4. Established helical senses in (a) poly-(*R*)-**1**/M$^+$ complex, poly-(*R*)-**1** and poly-(*R*)-**1**/M^{2+} complex. (b) Idem in poly-(*R*)-**2**/M$^+$ complex, poly-(*R*)-**2** and poly-(*R*)-**2** /M^{2+} complex. (c) Expected helical senses in poly-[(*R*)-**1**-*co*-(*R*)-**2**]/M$^+$ complex, poly-[(*R*)-**1**-*co*-(*R*)-**2**] and poly-[(*R*)-**1**-*co*-(*R*)-**2**]/M^{2+} complex.

We found, as expected, that the two components responded to the different ions independently, just as they did in the parent homopolymers. Therefore, depending on the nature of the metal ion and the copolymer composition, it was possible to play with the content of a helical sense excess in the copolymer. For instance, Ba^{2+} induced an excess of a *P* helix in poly-[(*R*)-**1**$_{0.8}$-*co*-(*R*)-**2**$_{0.2}$] (CD$_{380nm}$> 0), while an excess of an *M* helix was obtained in poly-[(*R*)-**1**$_{0.3}$-*co*-(*R*)-**2**$_{0.7}$] (CD$_{380nm}$< 0) with the same ion (Figure 5a). On the contrary, when Li$^+$ is used, the opposite helical sense excess is induced in both copolymers: *M* helix for poly-[(*R*)-**1**$_{0.8}$-*co*-(*R*)-**2**$_{0.2}$] (CD$_{380nm}$< 0) and *P* helix for poly-[(*R*)-**1**$_{0.3}$-*co*-(*R*)-**2**$_{0.7}$] (CD$_{380nm}$> 0) (Figure 5b).

The CD data from the titration of the nine copolymers —poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] (x= 0.1-0.9)— with the different perchlorates showed that five metals —Li$^+$, Na$^+$, Ag$^+$, Fe^{2+} and Ba^{2+}— control the helical content inducing specific combinations of *P* and *M* helices —detected as positive, negative or null CD responses— along the series. The other divalent ions tested induce always a *P* helix (SI).

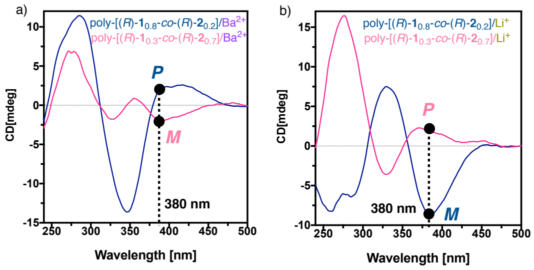

Figure 5. CD traces for poly-[(*R*)-**1**$_{0.8}$-*co*-(*R*)-**2**$_{0.2}$] and poly-[(*R*)-**1**$_{0.3}$-*co*-(*R*)-**2**$_{0.7}$] after the addition of (a) $Ba(ClO_4)_2$ and (b) $LiClO_4$. M^{n+}/mru ratios= 10 mol/mol. [copolymers]= 0.3 mg/mL in THF, $[M(ClO_4)_n]$ = 10 mg/mL in THF.

So, those five metal ions can be identified from their unambiguous CD patterns. For instance, Fe^{2+} produces a null CD in all the copolymer series (Table 1 and SI). The other four —Li^+, Na^+, Ag^+ and Ba^{2+}— induce an *M* helix in poly-[(*R*)-**1**$_{0.7/0.6/0.5}$-*co*-(*R*)-**2**$_{0.3/0.4/0.5}$] and a *P* helix in poly-[(*R*)-**1**$_{0.1}$-*co*-(*R*)-**2**$_{0.9}$]. However, they induce specific patterns in the CD spectra of other copolymers that allow distinguishing among them (Table 1 and SI). Thus:

1) Na^+ is the only metal that induces a null CD in the vinylic region of poly-[(*R*)-**1**$_{0.4}$-*co*-(*R*)-**2**$_{0.6}$]. Consequently, it is possible to identify Na^+ from the other monovalent ions.

2) Ba^{2+} is the only one from these five metals that induce a *P* helix in poly-[(*R*)-**1**$_{0.9/0.8}$-*co*-(*R*)-**2**$_{0.1/0.2}$].

3) Ag^+ is the only metal that induces an *M* helix in poly-[(*R*)-**1**$_{0.2}$-*co*-(*R*)-**2**$_{0.8}$].

4) Li^+ is the only one that induces a *P* helix in poly-[(*R*)-**1**$_{0.3}$-*co*-(*R*)-**2**$_{0.7}$] and an *M* helix in poly-[(*R*)-**1**$_{0.4}$-*co*-(*R*)-**2**$_{0.6}$].

In summary, the signature combinations of these 5 cations using nine copolymers are different and allow their identification (Table 1).

Similar studies were carried out with mixtures of the two homopolymers —poly-[(*R*)-**1** and poly-[(*R*)-**2**— in ratios ranging from 0.9/0.1 to 0.1/0.9 to compare their behavior with the poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] series. It was found that the responses of the homopolymer mixtures to the metal ions were different to those from the copolymers, being the latter more sensitive to a larger number of metal ions (see full description in the SI).

A different and complementary copolymer series can be obtained from other diastereomeric combination of monomers —e.g., poly-[(*S*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$]—, which can help to discriminate more metals.

Thus, stimuli-responsive studies on the poly-[(*S*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] series indicated, as in the previous case, that those copolymers are dynamic and respond to the presence of metal ions as external stimuli (see SI). The results obtained reveal that in this series is also possible to control the folding of the copolymers according to both the nature of the metal ion and the composition ratio of the two constituent monomers. As a result, and together with the five ions also identified by the poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] series —Li^+, Na^+, Ag^+, Fe^{2+}, Ba^{2+}—, three other divalent cations can be individually recognized —Ca^{2+}, Hg^{2+}, Cu^{2+}— (see SI).

The other two possible series based on the combination of other stereoisomers —i.e., poly-[(*R*)-**1**$_x$-*co*-(*S*)-**2**$_{1-x}$] and poly-[(*S*)-**1**$_x$-*co*-(*S*)-**2**$_{1-x}$]— present the enantiomeric composition of the two series described in this article, and therefore "mirror image" results must be obtained —i.e., opposite helicities and CD responses—.

Table 1. *P*, *M* and null helical sense induction by different metal perchlorates in the poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$] series.

Copolymer series	**Metal perchlorates**				
poly-[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{1-x}$]	Li^+	Na^+	Ag^+	Ba^{2+}	Fe^{2+}
poly-[(*R*)-**1**$_{0.9}$-*co*-(*R*)-**2**$_{0.1}$]	*M*	*M*	*M*	*P*	- -
poly-[(*R*)-**1**$_{0.8}$-*co*-(*R*)-**2**$_{0.2}$]	*M*	*M*	*M*	*P*	- -
poly-[(*R*)-**1**$_{0.7}$-*co*-(*R*)-**2**$_{0.3}$]	*M*	*M*	*M*	*M*	- -
poly-[(*R*)-**1**$_{0.6}$-*co*-(*R*)-**2**$_{0.4}$]	*M*	*M*	*M*	*M*	- -
poly-[(*R*)-**1**$_{0.5}$-*co*-(*R*)-**2**$_{0.5}$]	*M*	*M*	*M*	*M*	- -
poly-[(*R*)-**1**$_{0.4}$-*co*-(*R*)-**2**$_{0.6}$]	*M*	- -	*M*	*M*	- -
poly-[(*R*)-**1**$_{0.3}$-*co*-(*R*)-**2**$_{0.7}$]	*P*	*P*	*M*	*M*	- -
poly-[(*R*)-**1**$_{0.2}$-*co*-(*R*)-**2**$_{0.8}$]	*P*	*P*	*M*	*P*	- -
poly-[(*R*)-**1**$_{0.1}$-*co*-(*R*)-**2**$_{0.9}$]	*P*	*P*	*P*	*P*	- -

In conclusion, the work presented here constitutes the proof of concept that establishes that copolymers showing “Chiral Conflict” —where their helical structure is cancelled by appropriate chiral comonomers— can adopt an excess of a single-handed helix by acting, through an appropriate external stimulus, on the conformational composition of the constituting comonomers. In this way it is possible to tune the excess of the helical content by playing with the nature of the external stimulus (e.g., metal ion) and the copolymer composition. Another interesting phenomenon is observed when the external stimuli act on the conformational composition of the two comonomers at the same time. In this case, an axially mirror image structure is generated, where the helical structure is again cancelled by the two opposite helicities induced by the constituent monomers.

This control in the helical content of copolymers based on “Chiral Conflict” effect opens new horizons to inspire the design of new polymeric sensor materials based on chiral recognition ability —choosing appropriate comonomers and stimuli— and to deepen the knowledge of the role of the secondary structure in applications such as asymmetric catalyst, chiral recognition, chiral chromatography or sensory devices among others.

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Keywords: “Chiral Conflict” • external stimuli • dynamic helical polymer • poly(phenylacetylene) • circular dichroism

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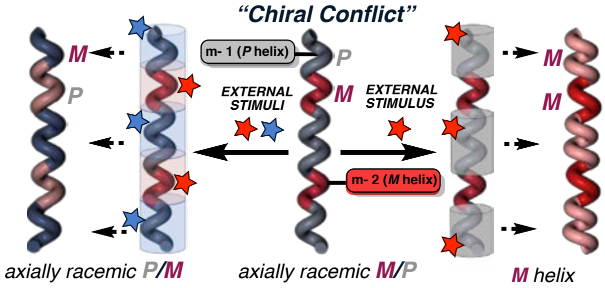
COMMUNICATION

“Chiral Conflict effect” in chiral helical copolymers becomes a new instrument for the development of multi-sensor materials and demonstrates its potential identifying monovalent and divalent metal ions



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“Chiral Conflict” as a Tool to Create Stimuli-Responsive Materials from Dynamic Helical Polymers