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Chiral-Chiral Communication Mechanisms and Modulation of the Helical Sense and the Secondary Structure in PPAs †

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Abstract: Helical Senses are found in important biological macromolecules from living organisms. DNA and proteins are the most representative of the importance of helicity. New and important functions emerge from the helicity control. Different poly(phenylacetylene) copolymers made of chiral monomers are being used for the comprehension of communication effects like Sergeants and Soldiers Effect (SSE), which modulate the helical sense and the secondary structure of PPAs. Copolymers made of two chiral monomers, (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) and (*S*/*R*)-α-methoxy-α-phenylacetic acid (MPA) derivatives, can exhibit complex systems in different solvents following classic or novel effects. Under certain conditions, we can find systems that follow lack of communication, Chiral Conflict and Chiral Accord, that will emerge depending on the helical sense of the two chiral monomers. In relation to this control of *P* and *M* helix preferences, different applications have been discovered and future upgrades in this field are expected for stationary phases in HPLC, sensors, novel materials, etc.

Keywords: helical polymer; copolymer; chiral communication; Chiral Conflict; Sergeants and Soldiers Effect; poly(phenylacetylene)s

1. Introduction

Helical polymers have proven, from early stages, efficacy as stationary phases in HPLC when using the static poly(tert-butyl isocyanide)s [1]. Nowadays, dynamic polymers like poly(phenylacetylene)s (PPAs) have also found applications in this field [2].

The main advantage in dynamic polymers is that they respond to external stimuli, for example, adding chiral molecules, changing the solvent or the pH. This incredible behavior opened the door to discover many new effects by Green and coworkers. In 1988, he was able to command the helix [3] and isolate only one helical sense when the different pendants could communicate across the scaffold following the Sergeants and Soldiers Effect (SSE). They also found that the absence of communication followed a pattern which was dependent on the temperature, Chiral Conflict [4].

In our studies we have applied all the Communication effects to PPA copolymers of MPA and MTPA in order to control the helix and isolate homochiral copolymers. Different interactions between pendants appeared for solvents that stabilize opposite conformations for the monomers.

2. Methods

Monomers and polymers were synthesized at inert atmosphere (Argon), using Schlenk lines and anhydrous high-purity solvents.

UV spectra were obtained using a Jasco V-630 spectrophotometer between a wavelength interval of 240 and 500 nm. Each sample was prepared for a concentration of 0.3 mg of polymer/mL solvent.

CD spectra were obtained using a Jasco V-630 spectrophotometer between a wavelength interval of 240 and 500 nm. Each sample was prepared for a concentration of 0.3 mg of polymer/mL solvent.

3. Results and Discussion

PPA homopolymers made of (*R*)-MTPA [(*R*)-**2**] have a pronounced helical sense, stabilizing different conformations in different solvents and consequently, *M* type or *P* type helices [5]. This strong capability to induce homochirality makes these pendants suitable to be Sergeants. The possible conformations are *cis* or *trans* for the amide group. That being said, non-donor solvents ($CHCl_3$) induce *trans* isomers, (−) CD signal and *M* type helices. On the other hand, donor solvents (THF) produce an inversion in the helicity towards (+) CD signal and *P* type helixes due to the *cis* isomer (Figure 1). Polarity also plays an important role stabilizing: *antiperiplanar* structures in the O=C-C-OMe bonds in less polar solvents like THF; and *synperiplanar* conformations in the presence of polar solvents like DMF or DMSO (Figure 1).

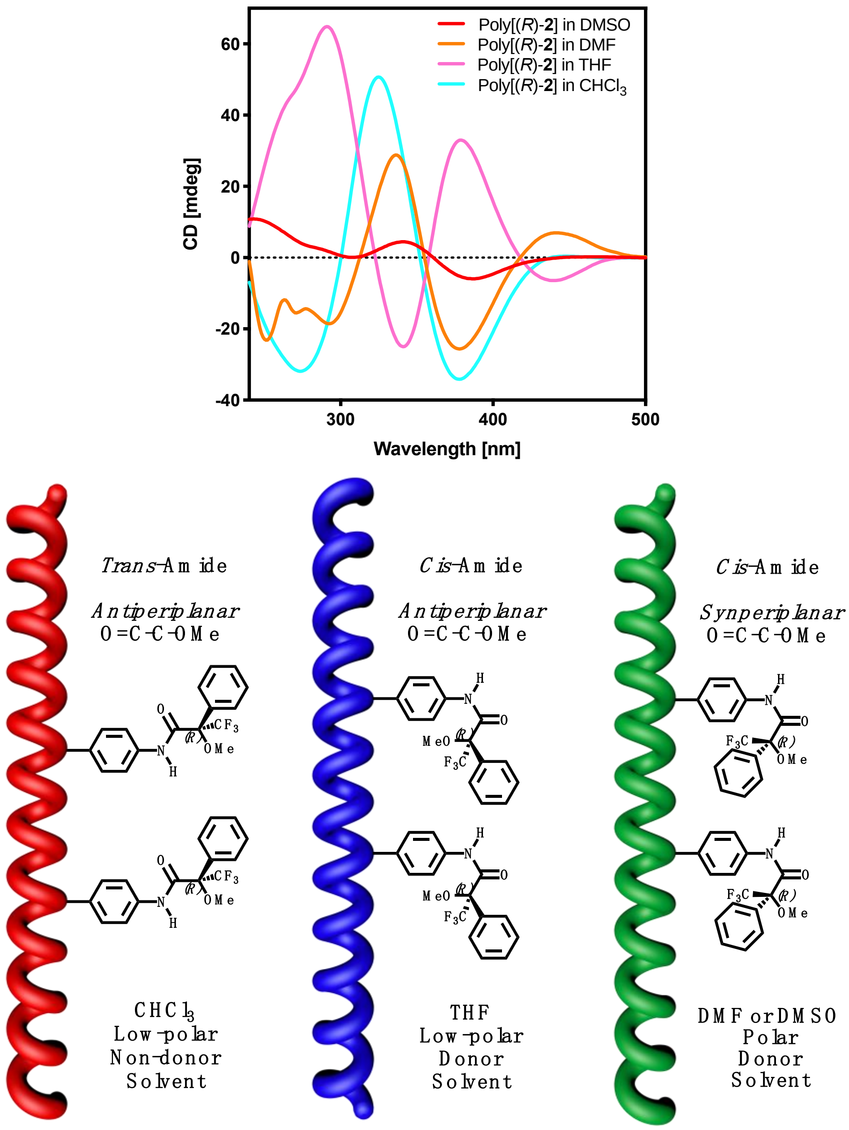
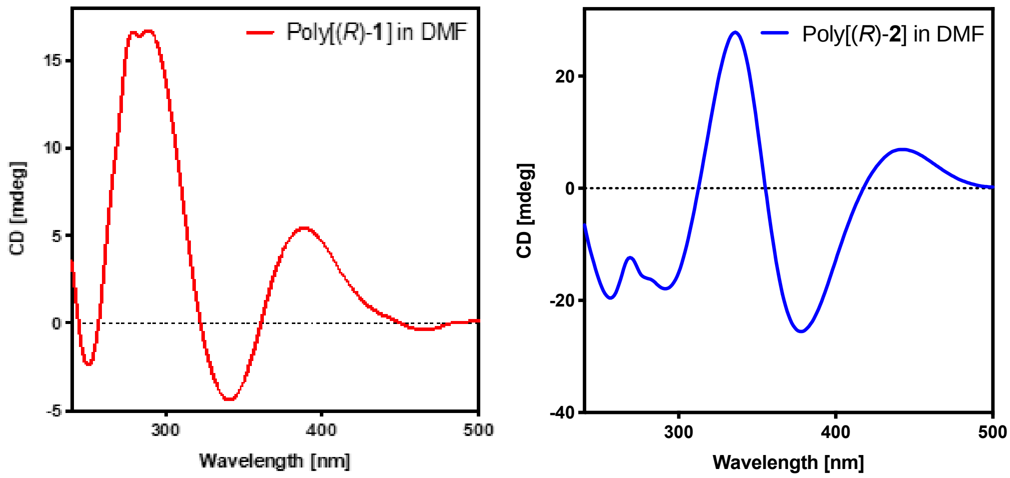
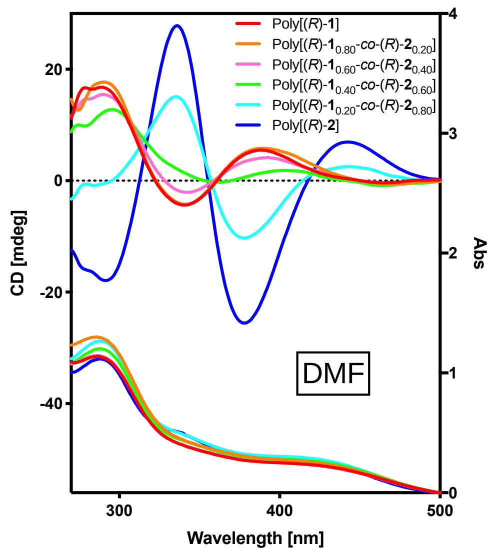


Figure 1. CD spectra of poly[(*R*)-**2**] in DMSO, DMF, THF and $CHCl_3$ solvents. Models for *M* type or *P* type helices changing the conformations between *cis* or *trans* isomers in the amide group and *ap* or *syn* for O=C-C-OMe.

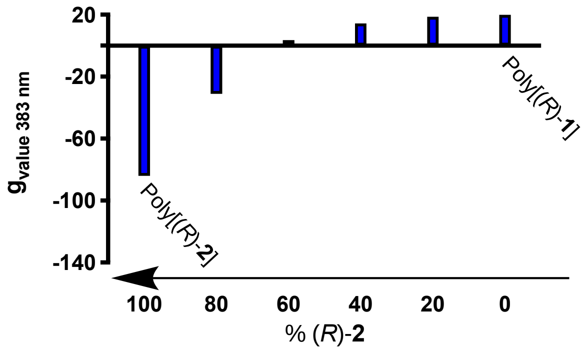
After polymerization, MPA monomers are not able to induce homochirality in the homopolimers because of their racemic conformation. They are called Soldiers as they do not stabilize any of the helical senses. These monomers can be activated to follow the same helical sense of the Sergeants by means of the Sergeants and Soldiers Effect. In contrast, if the Soldiers are commanding the helical sense when activated with low ammounts of Sergeants, the effect will be termed Chiral Coalition [6]. To study these communication effects, copolymers made of the MPA Soldier with the MTPA Sergeant were subjected to solvents with different polarity and donor capability. (*R*)-MPA and (*R*)-MTPA homopolymers stabilize opposite helical senses in DMF. The CD signals of the copolymers follow a linear decrease which is a synonymous of a Chiral communication absence. Their scaffolds are different, *cis*-cisoidal (*c-c)* isomer at the polyenic backbone for MPA and *cis*-transoidal (*c-t)* for MTPA, and they stabilize *P* and *M* helices (Figure 2a), respectively. This absence of communication together with the opposite CD signals of the homopolymers are the main points that classify this effect as Chiral Conflict. Analyzing the g value (Figure 2) we can see that we are not at the conflict temperature because 40% of (*R*)-**2** must have (-) CD signal (Figure 2c). This fenomenum of Chiral Conflict is repeated using the enantiomers in THF (Figure 2d,e).



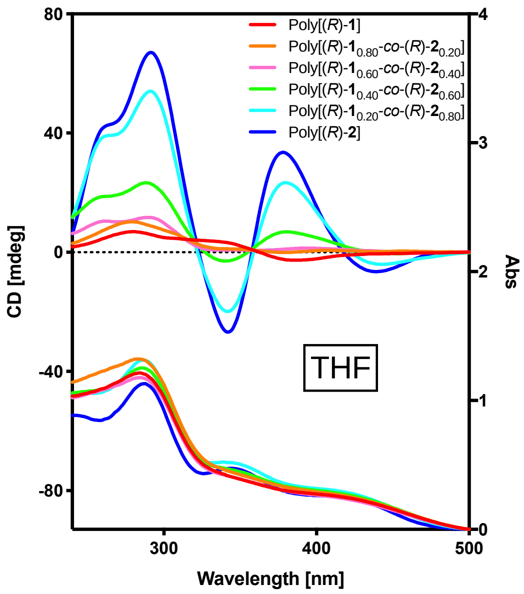
(**a**)



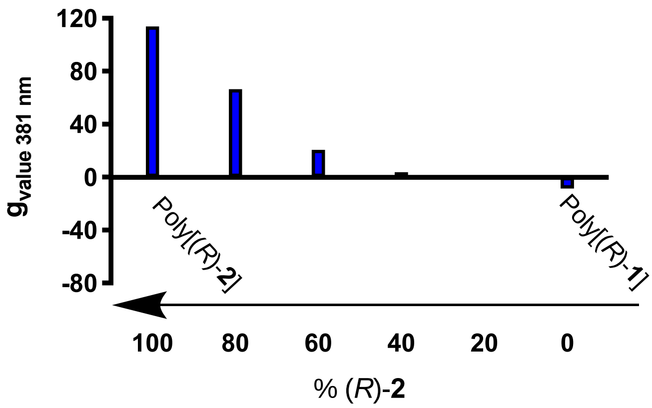
(**b**)



(**c**)



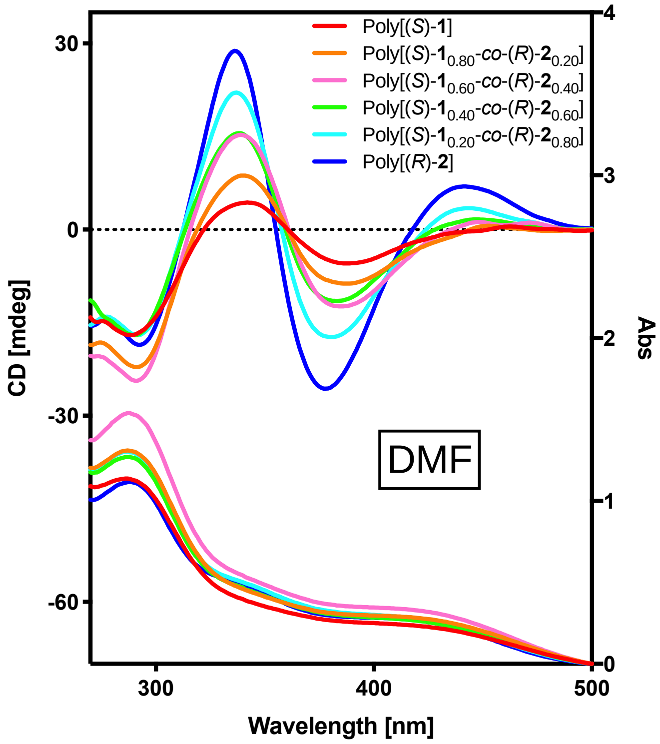
(**d**)



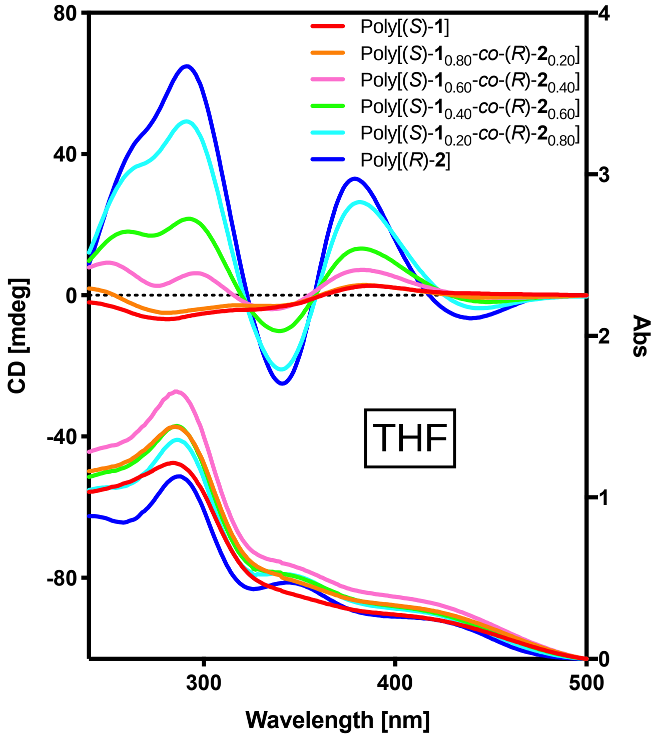
(**e**)

Figure 2. (**a**) CD spectra for the homopolymers poly[(*R*)-**1**] and poly[(*R*)-**2**] with opposite signals in DMF. CD, UV spectra and g values for (*R*)-**1** and (*R*)-**2** copolymers (**b**,**c**) in DMF. (**d**,**e**) in THF.

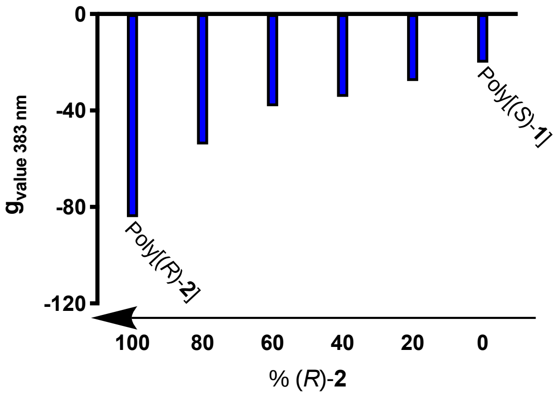
On the other hand, if we use the (*S*)-MPA enantiomer in the same solvents (DMF and THF), the helical senses of the homopolymers are inverted. In this case, the two monomers stabilize the same helical sense for the homopolymers poly[(*S*)-**1**] and poly[*R*)-**2**], anticlockwise in DMF and clockwise in THF. In copolymers poly[(*S*)-**1**$_{x}$-*co*-(*R*)-**2**$_{x-1}$] the absence of communication does not dissappear due to the same structural difference as before in copolymers poly[(*R*)-**1**$_{x}$-*co*-(*R*)-**2**$_{x-1}$]. This lack of communication with the stabilization of the same type of helices deffines a system dominated by the Chiral Accord (Figure 3).



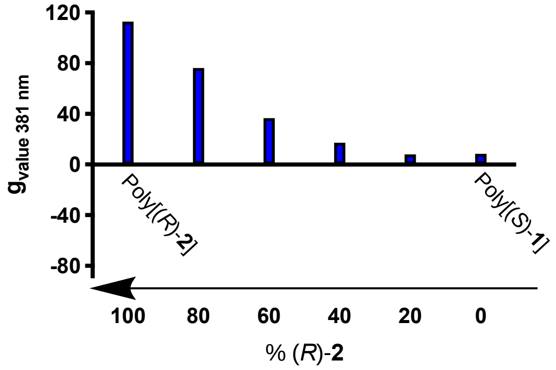
(**a**)



(**b**)



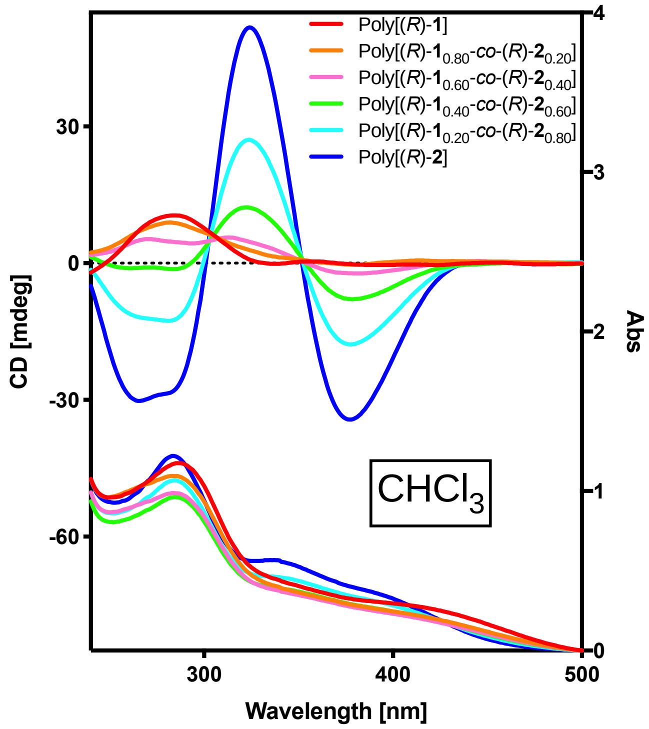
(**c**)



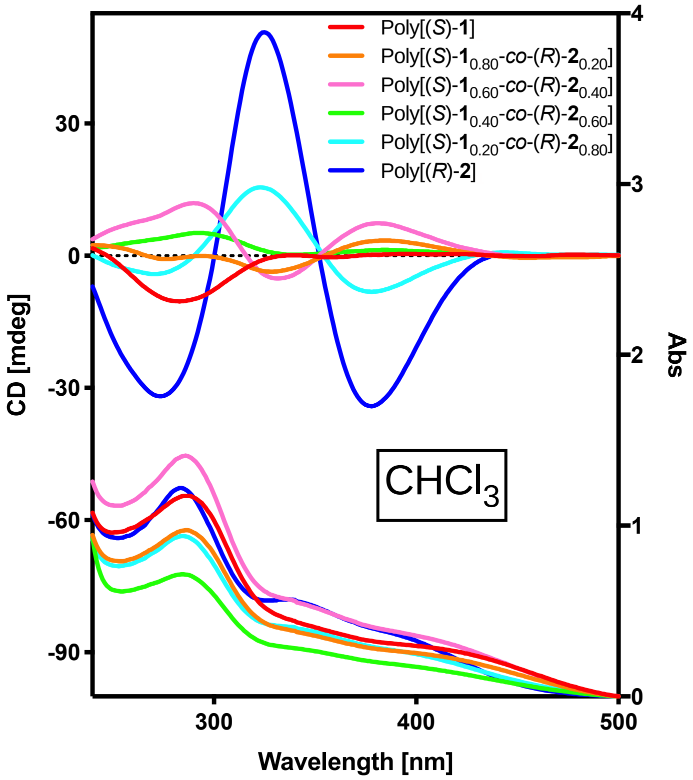
(**d**)

Figure 3. CD, UV spectra and g values for (*S*)-**1** and (*R*)-**2** copolymers (**a**,**b**) in DMF. (**c**,**d**) in THF.

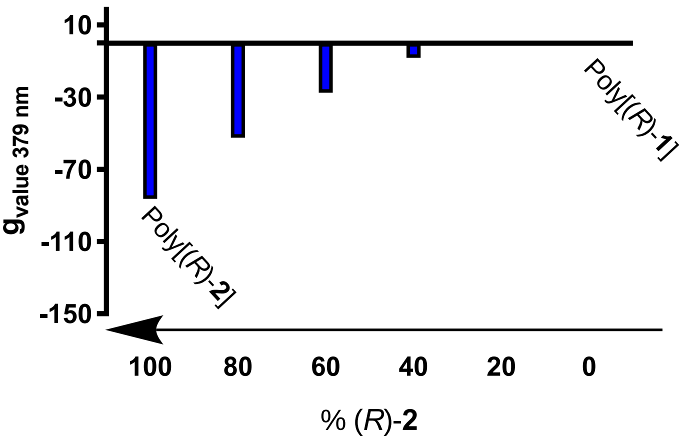
Using $CHCl_3$ as solvent, the scaffolds for the two of the monomers are *c-c* at the polyenic backbone. Chiral communication effects arise when the two pendants stabilize the same isomer at the inner hellix. In the case of copolymers poly[(*R*)-**1**$_x$-*co*-(*R*)-**2**$_{x-1}$], we can see communication between the pendants due to the non-linear decrease of the CD signal (Figure 4a,b). In copolymers poly[(*S*)-**1**$_x$-*co*-(*R*)-**2**$_{x-1}$] the communication is more percetible with opposite CD signals for poly[(*S*)-**1**$_{80}$-*co*-(*R*)-**2**$_{20}$] and poly[(*S*)-**1**$_{60}$-*co*-(*R*)-**2**$_{40}$] to that of the Sergeant homopolymer poly[(*R*)-**2**]. This is a clear example of an abnormal Sergeant and Soldiers Effect in which the MTPA Sergeant is inducing a *P* helix in the (*S*)-MPA Soldier (Figure 4c,d).


Poly[(R)-1]
Poly[(R)-1$_{0.80}$-co-(R)-2$_{0.20}$]
Poly[(R)-1$_{0.60}$-co-(R)-2$_{0.40}$]
Poly[(R)-1$_{0.40}$-co-(R)-2$_{0.60}$]
Poly[(R)-1$_{0.20}$-co-(R)-2$_{0.80}$]
Poly[(R)-2]
CD [mdeg]
Abs
CHCl$_3$
Wavelength [nm]
30
0
-30
-60
4
3
2
1
0
300
400
500

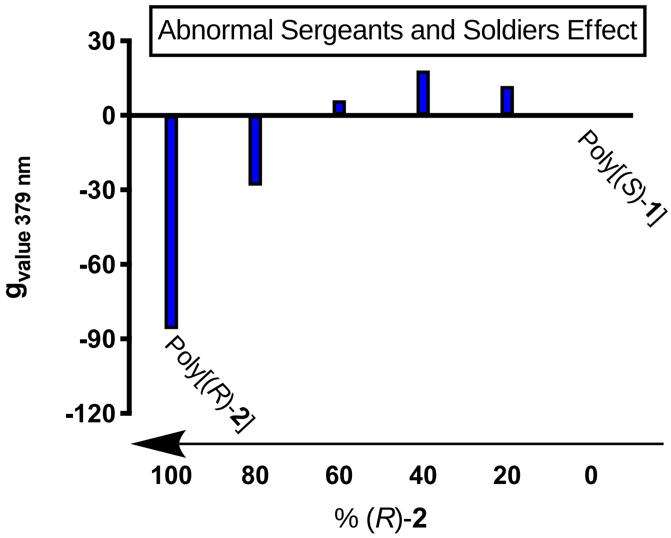
(**a**)


Poly[(S)-1]
Poly[(S)-1$_{0.80}$-co-(R)-2$_{0.20}$]
Poly[(S)-1$_{0.60}$-co-(R)-2$_{0.40}$]
Poly[(S)-1$_{0.40}$-co-(R)-2$_{0.60}$]
Poly[(S)-1$_{0.20}$-co-(R)-2$_{0.80}$]
Poly[(R)-2]
CD [mdeg]
Abs
CHCl$_3$
Wavelength [nm]
30
0
-30
-60
-90
4
3
2
1
0
300
400
500

(**b**)



(**c**)

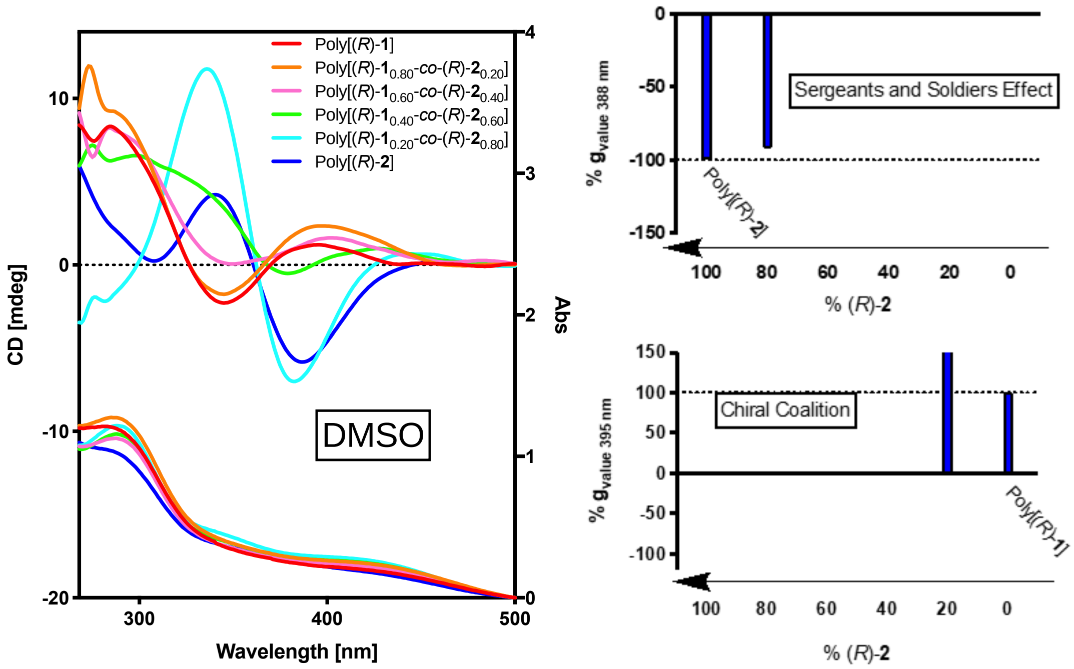


(**d**)

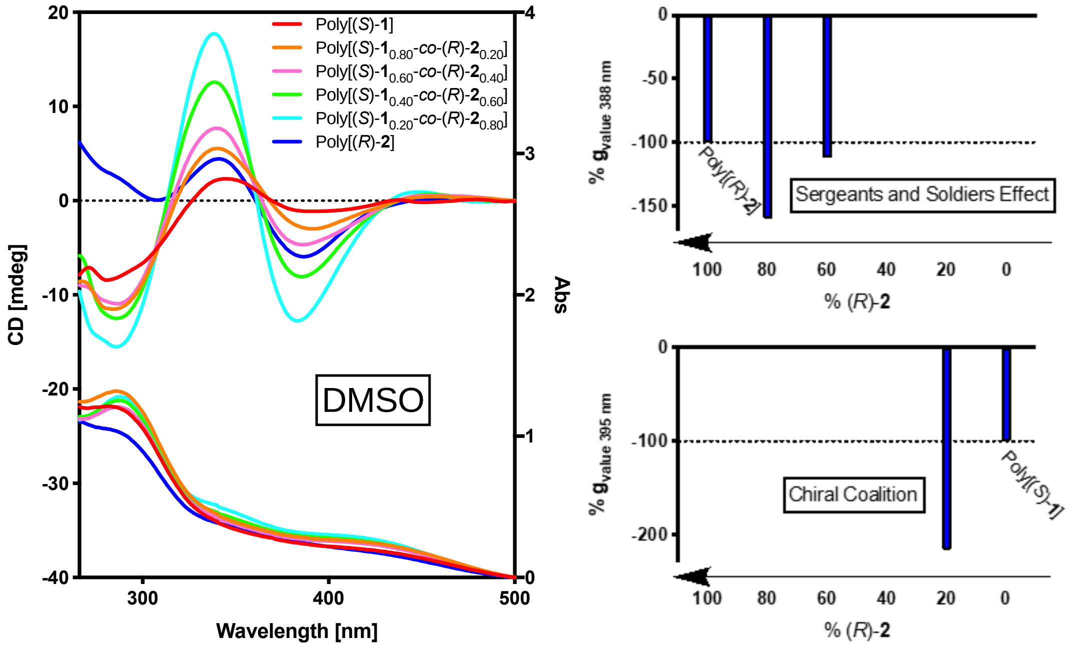
Figure 3. CD, UV spectra and g values in $CHCl_3$ (**a**,**b**) for (*R*)-**1** and (*R*)-**2** copolymers (**c**,**d**) for (*S*)-**1** and (*R*)-**2** copolymers.

Despite the fact that DMSO stabilizes *c-t* scaffolds for MTPA and *c-c* for MPA, we can find many communication effects in this solvent. The monomers have a prefered helical sense. (*S*)-**1** and (*R*)-**2** stabilize *M* type helices, while (*R*)-**1** has a prefered *P* type helix. MPA Soldiers show a bathocromic effect due to the formation of more elongated structures than MTPA Sergeants. When we have an excess of the Soldier in the copolymer, we are in the presence of Chiral Coalition. A low ammount of Sergeant is able to activate the Soldier to stabilize only one helical sense, (+) CD signal and *P* type helices in (*R*) configuration and (−) CD signal and *M* type helices for (*S*) configuration. They absorbe at same wavelenght (395 nm).

However, if the ammount of Sergeant in the copolymer is increased, the copolymers will stabilize the poly[(*R*)-**2**] type of helix at 388 nm and will suffer Chiral amplification through Sergeants and Soldiers Effect. The Sergeant commands the helix and stabilize (−) CD signal and *M* type helices with the two enantiomers of the Soldier.



(**a**)



(**b**)

Figure 4. CD, UV spectra and normalized g values in DMSO (**a**) (*R*)-**1** and (*R*)-**2** copolymers (**b**) (*S*)-**1** and (*R*)-**2** copolymers.

4. Conclusions

To summarize, we have been able to induce chiral communication between the pendants of MPA and MTPA PPAs in DMSO through Sergeants and Soldiers effect and Chiral coalition. In the presence of $CHCl_3$ that stabilized *c-c* isomers for the two monomers, the helix was commanded by the Sergeant through Abnormal Sergeants and Soldiers effect. In THF and DMF that stabilized different helical structures for MPA (*c-c*) and MTPA (*c-t*), copolymers did not show communication following Chiral Conflict or Chiral Accord.

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