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The ON/OFF switching by metal ions of the "Sergeants and Soldiers" chiral amplification effect on helical poly(phenylacetylene)s

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Here we report copolymers where the "Sergeants and Soldiers effect" can be switched ON and OFF by the presence of a metal ion. These copolymers are made by a combination of achiral and chiral monomer units, where the chiral ones are unable to order the chiral amplification unless a small amount of mono- or divalent metal ions is added. In this way, the ions act as promoters, upgrading some of the chiral pendants, initially unable to induce a preferential helical sense, to a higher rank forcing the ordering of the rest of the chain to a specific helical sense. In theses copolymers, the classical "Sergeant" and "Soldier" roles are modified in such a way that the chiral units become "Sergeants" only by the effect of an achiral external stimulus, namely the metal ion. The structure of the metal complex determines its interaction in the helix with the surrounding chiral and achiral "Soldiers" and therefore both the intensity of the amplification and the response of a copolymer to a certain metal. For instance, poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) shows chiral amplification ("Sergeants and Soldiers effect") towards the right-handed helix only with divalent ions, while poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) amplifies the helix to the left-sense with mono- and to the right-handed sense with divalent ions. This behaviour allows, using a single copolymer, to selectively induce any of the two helical senses. The aggregation and encapsulation properties of these copolymers are described too.

Introduction

The "Sergeants and Soldiers effect" in helical copolymers is a chiral amplification phenomenon where a small amount of a chiral monomer in the copolymer is capable to induce a single helical structure. In a pioneering work on chiral amplification, Green and co-workers[1] prepared from achiral monomers, a polyisocyanate that presents a helical skeleton formed by identical proportions of left- and right-handed helical senses, separated by helix reversal points that move along the helical backbone. Interestingly, the introduction of a very small portion of a chiral monomer within the polymer chain generated a copolymer with one-handed helical structure. This phenomenon is the first example of chiral amplification in covalently bonded polymers and is known as the "Sergeants and Soldiers effect", meaning that a small number of chiral units ("Sergeants") order the most abundant achiral units ("Soldiers") to adopt a certain structure.[2] This chiral amplification effect has also been extended to other families of helical polymers such as poly(phenylacetylene)s (PPAs) that in contrast to those polyisocyanates, present a dynamic structure that allows the tuning of their helicity towards the right- or left-handed helical sense by the action of external stimuli.[3]

In this work, we present PPA copolymers with a "Sergeants and Soldiers effect" switchable ON/OFF by the addition of metal ions as external stimulus. These copolymers are made by a combination of chiral and achiral monomers but contrary to Green´s case, the chiral units are unable to order the helical sense on the chain unless a small amount of an achiral agent, namely a metal ion, is added, switching ON the "Sergeants and Soldier effect".

This chiral amplification allows the dual induction on a single copolymer (e.g. with the *R* chiral unit), of either the *M* or the *P* helicity by choosing a mono- or a divalent metal ion as inducer, something that cannot be achieved through the classical "Sergeants and Soldiers effect", where two distinct "enantiomeric" copolymers are necessary in order to obtain the *M* and the *P* helical senses.

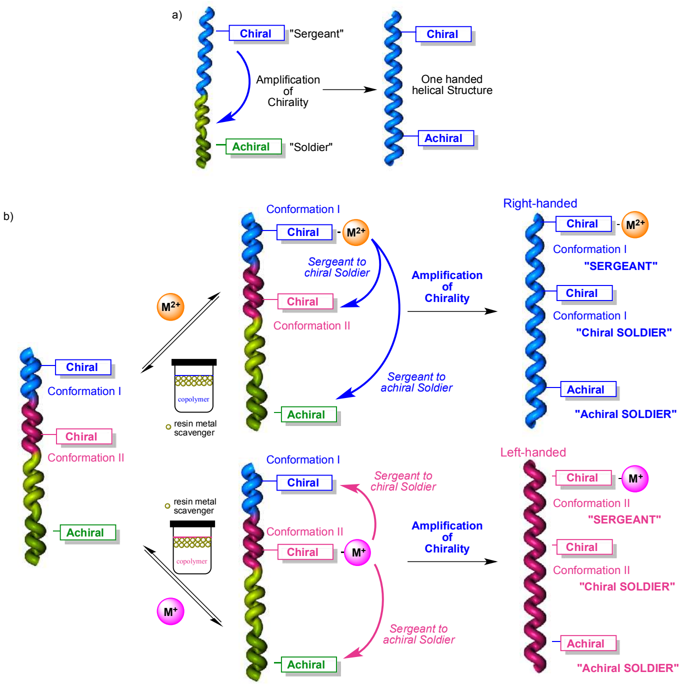

Figure 1. Chiral amplification effects on helical polymers. (a) Conceptual representations of the "Sergeants and Soldiers effect"[1-3]. (b) Idem for the switching ON/OFF "Sergeants and Soldiers effect".

Results and discussion

For the study on the chiral amplification based on "Sergeants and Soldiers effect" trigged by an achiral stimulus, we prepared a series of dynamic copolymers of the PPA type composed by combination of a chiral unit and several achiral units at different ratios. As chiral monomeric component we selected the 4-ethynylphenylamides of (*R*)- and (*S*)-α-methoxy-α-phenylacetic acid (MPA) (**1** and **2** respectively). The MPA group is known to present an equally populated *synperiplanar/antiperiplanar* (*sp*/*ap*) conformational equilibrium [rotation around the (O=)C-C(-O) bond] and consequently, the corresponding highly dynamic homopolymers (poly-**1** and poly-**2**) present a helical structure with the left- and right-handed senses in equal population (null CD) (Figure 2a). Interestingly, addition of a small amount of a monovalent or divalent metal ion to these homopolymers produces a complexation with the chiral units that shifts the 1:1 *sp*/*ap* equilibrium at the pendants. The complex with monovalent ions adopts an *ap* conformation while the complex with divalent ions prefers the *sp* conformer and these changes in the pendants induce a predominant helical sense on the polymer backbone. For instance, poly-**1** adopts a left-handed helix in the presence of monovalent metal ions, while divalent metal ions induce a right-handed helical sense.[4]

This chiral component was combined in the copolymers with the achiral units **3-9** (Figure 2b), selected on the basis of their structural resemblance to the chiral monomers. In this way, a series of PPA copolymers (a total of 63) were prepared by copolymerization with [{Rh(nbd)Cl}$_2$] (nbd= 2,5-norbornadiene) as catalyst, from mixtures of the chiral monomer **1** [derived from (*R*)-MPA] with the achiral monomers **3-9** in different chiral/achiral ratios [poly($\mathbf{1}_r$-*co*-$\mathbf{3}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{4}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{5}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{6}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$), poly($\mathbf{1}_r$-*co*-$\mathbf{9}_{(1-r)}$)$_{,\ r= 0.9\text{-}0.1}$]. Nine homopolymers [poly(**1-9**)] were also prepared (Figure 2c).

All the copolymers showed NMR (vinyl protons, δ= 5.7–5.8 ppm) and Raman resonances (1567, 1335, 1003 cm^{-1}) indicative of an all *cis* polyene backbone,[5] and no preferred helical sense (null CD; 1:1 left- and right-handed helical senses). Their molecular weights (Mn) were estimated by GPC (THF as eluent with polystyrene standards as calibrants; see SI for details) to be between 30,000-40,000 with Mn/Mw values around 1.5-1.8. Their chiral/achiral monomer ratios were determined by NMR and found to be coincident with the feeding mixtures (see SI). Also, their random nature was demonstrated by the Kelen/Tüdös method using varying monomer feed ratios and termination at low conversions (see SI).[3h, 6]

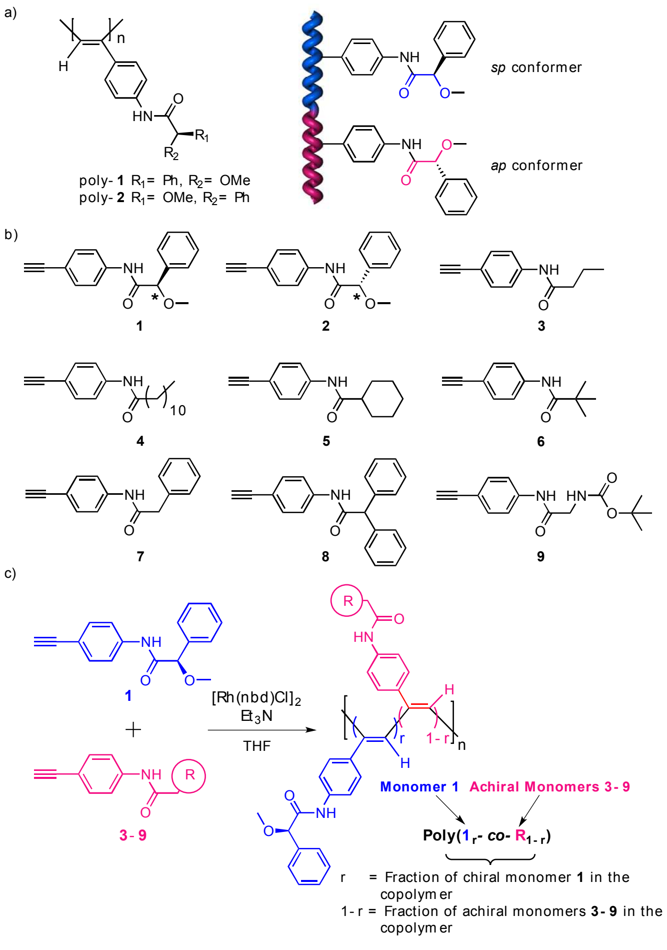

Figure 2. Structures of homopolymers, monomers and copolymer synthesis. a) Structures of poly-**1**, poly-**2** and *sp/ap* conformations. b) Structures of monomers **1-9**. c) Synthesis, structures and notation of copolymers.

In order to evaluate the chiral amplification abilities of these copolymers upon addition of metal ions, different monovalent and divalent metal salts were added to the poly(phenylacetylene)s [poly($\mathbf{1}_r$-*co*-$\mathbf{3\text{-}9}_{(1-r)}$)$_{,\ r= 0.9\text{-}0.1}$] dissolved in

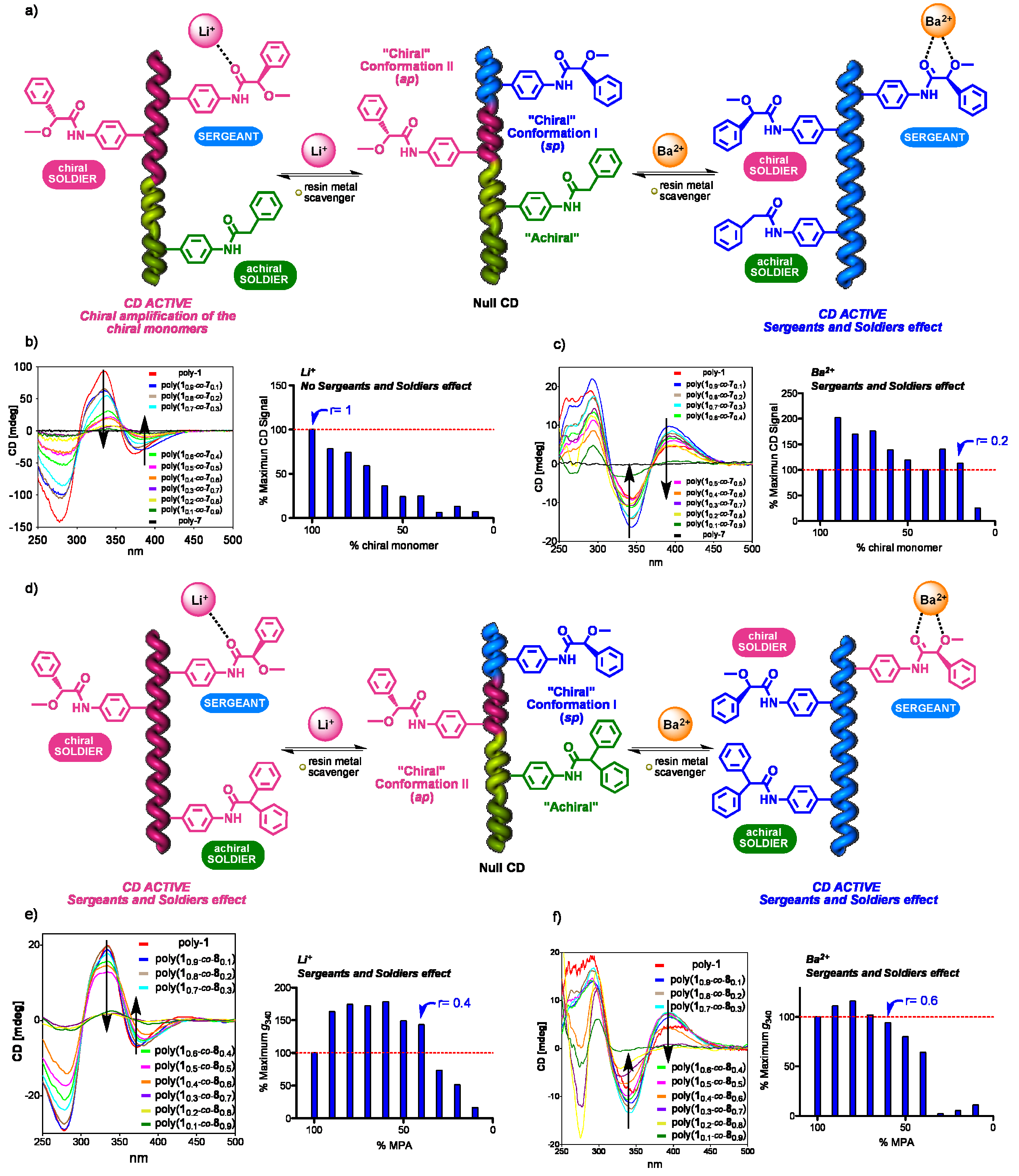

Figure 3. "Sergeants and Soldiers effect". a) "Sergeants and Soldiers effect" (right side) and chiral amplification[28, 29] of the chiral units (left side) of poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) copolymer series in the presence of Ba^{2+} and Li^+ respectively. b) CD spectra and bar graph showing the chiral amplification of the chiral units of poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) series in the presence of Li^+. c) CD spectra and bar graph showing the chiral amplification of the chiral and achiral pendants ("Sergeants and Soldiers effect") of poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) series in the presence of Ba^{2+} (r-values are highlighted). d) "Sergeants and Soldiers effect" of poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) copolymer series in the presence of Ba^{2+} (right) and Li^+ (left). e) CD spectra and bar graph showing the "Sergeants and Soldiers effect" of poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) series in the presence of Li^+. f) Idem in the presence of Ba^{2+} (r-values are highlighted).

$CHCl_3$, and the solutions were examined by IR and CD. A monomer repeating unit (mru)/metal ion ratio of 1.0/0.5 (mol/mol) was used to obtain the highest CD response with the minimum amount of metal (Table 1).[4]

Thus, the IR showed in all cases the bands expected for the distinct coordination of the MPA part of the chiral units with monovalent and divalent metal ions of the copolymers (see SI).[4] For its part, the CD[7] showed that the addition of the ions produced a predominant helical sense determined by the configuration of the chiral component (**1** or **2**) of the copolymers and the valence of the ion. Thus, copolymers poly($\mathbf{1}_r$-*co*-$\mathbf{3}$-$\mathbf{9}_{(1-r)}$) containing the (*R*) isomer (**1**) produce, by addition of monovalent ions, a left-handed helix, while with divalent ions give a right-handed helix as in homopolymer poly-**1**. The opposite results were obtained with copolymers poly($\mathbf{2}_r$-*co*-$\mathbf{3}$-$\mathbf{9}_{(1-r)}$) containing the (*S*) isomer (**2**) as chiral unit. The intensity of the helical sense induction depends on the amount of metal ion added and on the percentage of chiral component in the copolymer but is observed even in copolymers containing just a few chiral units, indicating the existence of "Sergeants and Soldiers effect"[1,4] (Table 1, SI).

Table 1, Figure 3 and additional data at SI show quantitatively the chiral amplifications observed in each case. For simplicity we will concentrate our discussion on copolymers poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) and poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) containing the achiral units **7** and **8**, that serve to explain and understand the results of all the series.

Thus, copolymers containing different ratios of the chiral pendant **1** and the achiral component **7**, showed chiral amplification through the "Sergeants and Soldiers effect" after addition of divalent ions. In the poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) series, the highest amplification by addition of Ba^{2+} was observed from poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{7}_{0.1}$), to poly($\mathbf{1}_{0.2}$-*co*-$\mathbf{7}_{0.8}$). Therefore, just 20% of the chiral unit **1** and 80% of the achiral monomer **7** (Table 1) is enough to promote the right-handed helical structure (Figures 3a and 3c). In fact this solution presents identical CD intensity (helicity) as the homopolymer poly-**1**, composed by 100% (*R*)-MPA, in the same conditions.

In quantitative terms, this amplification presents r= 0.2, where the r-value is the minimum molar ratio of the chiral monomer needed to get the maximum of the CD spectra.

Interestingly, no "Sergeants and Soldiers effect" occurs when monovalent, instead of divalent ions, are added to the solutions of the poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) series. Addition of monovalent ions gives a CD signal whose intensity corresponds exactly to the contribution of the chiral units present in the copolymer —e.g. addition of Li^{+1} to poly($\mathbf{1}_{0.8}$-*co*-$\mathbf{7}_{0.2}$) gives a CD spectrum whose intensity is 80% of the homopolymer poly-**1**—, indicating that there is a chiral amplification through the chiral units without participation of the achiral ones (Figures 3a and 3b).

This effect is surprising because homopolymer poly-**1** amplifies both the right- and left-handed helices by addition of di- and monovalent ions respectively. The different behaviour showed by the copolymers of the poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) series must be ascribed to the role of the achiral component (see below) in this process.

In contrast, similar study of the poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) series (Table 1 and Figures 3d-f) showed that the "Sergeants and Soldiers effect" was operative by addition of both mono- and divalent ions, shifting the helices to one helical sense or to the opposite (Figure 3d). For instance, a minimum 40% of the chiral MPA component is needed [poly($\mathbf{1}_{0.4}$-*co*-$\mathbf{8}_{0.6}$)] with Li^{+} to obtain a predominant helical sense (r= 0.4), while a minimum 60% of the chiral monomer [poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{8}_{0.4}$)] is needed with Ba^{2+} (r= 0.6). Also, it is important to mention that with Ba^{2+}, partial chiral amplification of the achiral fragments was observed until a percentage of 40% [poly($\mathbf{1}_{0.4}$-*co*-$\mathbf{8}_{0.6}$)] (Figures 3d-f), implying that the "Sergeants and Soldiers effect" still took place at that ratio.

Table 1. Chiral amplification r-values obtained for poly($\mathbf{1}_r$-*co*-$\mathbf{R}_{(1-r)}$) interacting with different monovalent and divalent metal ions.

Copolymer	mg/mL copolymer	Metal	Metal/mru (mol/mol)	r-value
poly(1_r-*co*-$3_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.9
poly(1_r-*co*-$3_{(1-r)}$)	0.1	Li^{+}	0.5	0.7
poly(1_r-*co*-$4_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.6
poly(1_r-*co*-$4_{(1-r)}$)	0.1	Li^{+}	0.5	1.0
poly(1_r-*co*-$5_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.8
poly(1_r-*co*-$5_{(1-r)}$)	0.2	Ba^{2+}	0.5	0.8
poly(1_r-*co*-$5_{(1-r)}$)	0.1	Li^{+}	0.5	0.8
poly(1_r-*co*-$6_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.6
poly(1_r-*co*-$6_{(1-r)}$)	0.2	Ba^{2+}	0.5	0.6
poly(1_r-*co*-$6_{(1-r)}$)	0.1	Li^{+}	0.5	1.0
poly(1_r-*co*-$7_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.2
poly(1_r-*co*-$7_{(1-r)}$)	0.2	Ba^{2+}	0.5	0.2
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Ba^{2+}	0.5	0.2
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Li^{+}	0.5	1.0
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Ag^{+}	1.0	0.7
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Ca^{2+}	1.0	0.6
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Co^{2+}	0.3	0.3
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Mn^{2+}	0.5	0.6
poly(1_r-*co*-$7_{(1-r)}$)	0.3	Ni^{2+}	0.5	1.0
poly(1_r-*co*-$8_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.6
poly(1_r-*co*-$8_{(1-r)}$)	0.2	Ba^{2+}	0.5	0.6
poly(1_r-*co*-$8_{(1-r)}$)	0.1	Li^{+}	0.5	0.4
poly(1_r-*co*-$9_{(1-r)}$)	0.1	Ba^{2+}	0.5	0.4
poly(1_r-*co*-$9_{(1-r)}$)	0.2	Ba^{2+}	0.5	0.4
poly(1_r-*co*-$9_{(1-r)}$)	0.1	Li^{+}	0.5	1.0

The other copolymers in Table 1 show different degrees of chiral amplification and varied sensitivity to the particular metal ions responding to the role of the achiral component present in each case (see full description at SI).

From a mechanistic point of view, the copolymers described in this paper show a new class of chiral amplification of the "Sergeants and Soldiers" type where the "Sergeants" need to be activated by the metal ion to trigger the amplification that therefore can be switched ON/OFF by that external stimulus.

Thus, while in the process described by Green et al.,[1] the chiral unit ("Sergeant") forces the whole copolymer to adopt a predominant helical sense, in our copolymers, the chiral units do not act as "Sergeants" until a metal ion is added.

The presence of the metal is essential for the chiral amplification to take place and once installed, it can be inhibit by sequestering the metal. In this way, the macroscopic racemic behaviour of the copolymer, its properties and CD response are recovered (no "memory" is detected) by addition of scavenger resins (see SI). This reversibility allows the copolymer to be reused and the amplification to be switched ON/OFF in a controlled way.

By analogy with homopolymers poly-**1** and poly-**2**, this addition of the metal involves complexation with the oxygen donor atoms in the chiral MPA units that once complexed, shift their 1:1 *sp/ap* conformation towards *sp* with divalent metal ions, or to *ap* with monovalent ions. The interactions of these complexes with the surrounding pendants are obviously different than in the absence of metal and constitute the driven force both for the change in the helical sense of the polyene skeleton and for the chiral amplification.

Therefore, the interaction of the M^{+} or M^{2+} complexed MPA units with the neighbour chiral and achiral "Soldiers" is the key factor to explain the different response to mono- and divalent ions shown by the copolymers of Table 1, exemplified by poly($\mathbf{1}_{r}$-*co*-$\mathbf{7}_{(1-r)}$) that responds with "Sergeants and Soldiers effect" only to divalent ions while poly($\mathbf{1}_{r}$-*co*-$\mathbf{8}_{(1-r)}$) responds with that effect to both mono- and divalent ones.

In order to find a mechanistic explanation to the role played by the metals and achiral "Soldiers" in the chiral amplification of poly($\mathbf{1}_{r}$-*co*-$\mathbf{7}_{(1-r)}$) and poly($\mathbf{1}_{r}$-*co*-$\mathbf{8}_{(1-r)}$), we decided to compare the helical structures formed by homopolymer poly-**1** [100% (*R*)-MPA] and those copolymers, when the mono- and divalent ions are added, by a combination of experimental data and geometry calculations.

Secondary Structure of Copolymers: the role of the achiral "Soldier" units

Addition of mono- and divalent metal ions to poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{7}_{0.4}$) in $CHCl_3$ generates CD and UV spectra practically identical to those of poly-**1**, indicating that in solution their helical sense and backbone are virtually the same (see Figure 3 and SI). In the solid state, films of poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{7}_{0.4}$) complexed with Ba^{2+} [(mru)/Ba^{2+} ratio of 1.0/0.5 (mol/mol) in $CHCl_3$; copolymer concentration= 0.03 mg/mL], showed AFM[8] images and helical parameters practically identical to those of poly-**1**[4] and indicative of a 3/1 helical structure (Figure 4a). This coincidence, both in solution and film, indicates that the presence in the copolymer of the achiral unit **7** does not block the ability of the chiral unit **1** to be complexed with both mono- and divalent ions shifting the 3/1 helix to the left- and the right-handed helices respectively (as in poly-**1**),[9] but interferes in some way with the "Sergeants and Soldiers effect", that is produced with divalent ions only.

Using the 3/1 helical structure as template and locking the chiral MPA units (**1**) of the copolymer in *ap* and *sp* conformations (as simplified models of the complexation with mono- and divalent metal ions respectively), we evaluated by geometry calculations how the different conformations of the achiral unit **7** could fit into the left- and the right-handed helices that should be obtained with mono- and divalent ions.

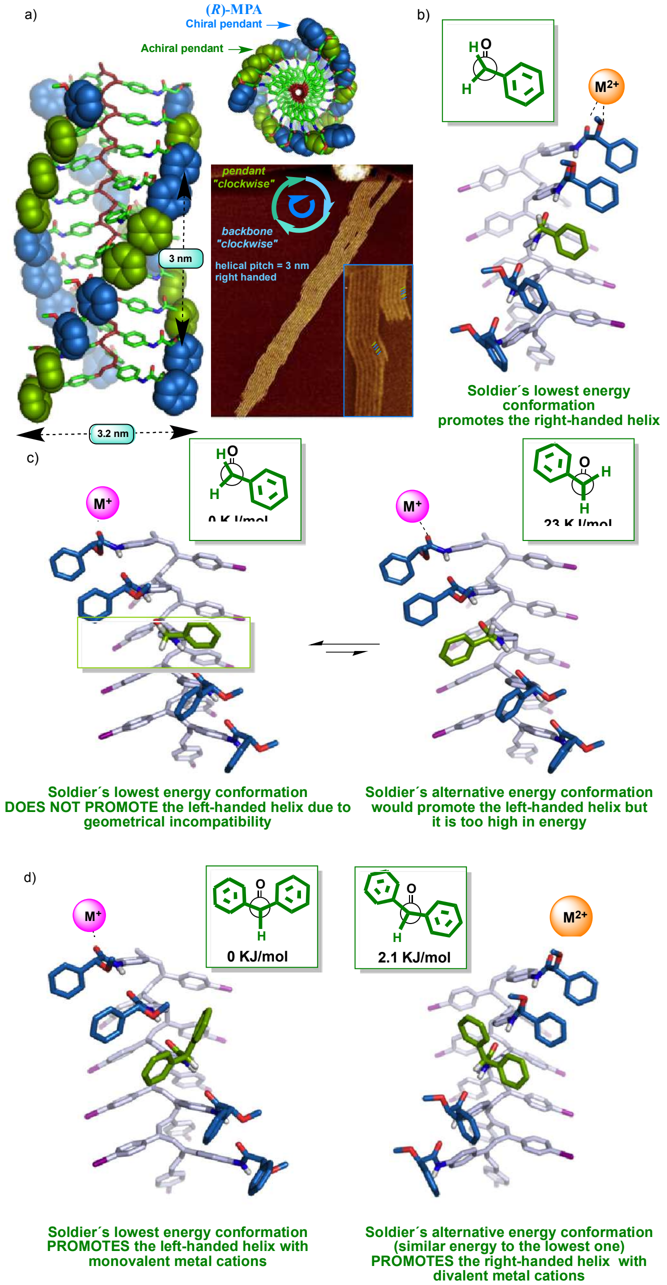

Figure 4. Secondary structure of copolymers and mechanism of chiral amplification. a) AFM image and helical structure adopted by poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{7}_{0.4}$) copolymer after the addition of $Ba(ClO_4)_2$ in a (mru)/Ba^{2+} ratio of 1.0/0.5 (mol/mol) in $CHCl_3$. b) Helical structure adopted by poly($\mathbf{1}_{r}$-*co*-$\mathbf{7}_{(1-r)}$) in the presence of divalent metal ions. (c) Idem in the presence of monovalent metal ions. d) Left- and right-handed helical structures adopted by poly($\mathbf{1}_{r}$-*co*-$\mathbf{8}_{(1-r)}$) in the presence of mono- and divalent metal ions.

Thus, DFT calculations[10] on the achiral monomer **7** in combination with modelling studies[11] showed that the lowest energy conformation of monomer **7** fits perfectly, without any disturbance, into the right-handed 3/1 helical structure that corresponds to complexation with divalent ions (*sp* conformation of the chiral pendants). In this way, poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) can generate a "Sergeants and Soldiers effect" by addition of divalent metals (Figure 4b) because the achiral units **7** can accommodate perfectly, without steric interference to that structure.

In contrast, when the MPA units are blocked in the *ap* conformation as corresponds to complexation with monovalent ions, the conformation of monomer **7** that best fits into the 3/1 left-handed helix is 23 KJ/monomer mol higher than the lowest energy conformation for that monomer (Figure 4c). In these conditions, there is an important energy penalty for the accommodation of the achiral units **7** on a left-handed helix (Figure 4c) and therefore, no amplification is observed.

Similar studies with the poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) series served to explain the existence of amplification ("Sergeants and Soldiers effect") both with mono- and with divalent ions.

Thus, the CD, UV and AFM of poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$) copolymers indicated, as before, a 3/1 helix skeleton (Figures 3e,f). DFT calculations[10] and modeling[11] showed that the two conformations of monomer **8** that best fit the right- and the left-handed 3/1 helices, differ in just 2 KJ/monomer mol one from the other (Figure 4d). This fact explains the compatibility of monomer **8** with both helical senses and the positive response of these copolymers [e.g. poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{8}_{0.4}$)] to both mono- and divalent ions following the "Sergeants and Soldiers" principle. The slight energy gap between both conformations also justifies the different r-values (0.4 and 0.6) reached by the two chiral amplification processes (Figures 3e,f).

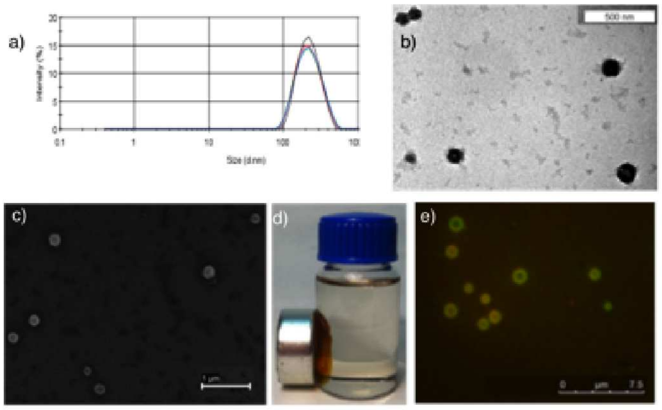

Figure 5. Copolymer nanospheres and encapsulating properties. a) DLS trace. b) TEM image of copolymer-Ba^{2+} metal complex nanospheres. c) SEM images of the nanospheres. d) Vial showing the nanospheres encapsulating iron oxide magnetic nanoparticles placed close to a magnet. e) Confocal images of the nanospheres encapsulating rhodamine B.

Methods

The amount of polymers and copolymers used for CD measurements were 0.1 mg/mL. CD measurements were done in a Jasco-720. The CD intensity was reported based on the *G* value (symmetric factor), which takes into account the different concentration effects when different solutions are compared.

AFM measurements were performed in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air at RT with standard silicon cantilevers and super-sharp 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. The samples were prepared from stock solutions of poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{7}_{0.4}$) (1 mg/mL) in $CHCl_3$ that were diluted until 0.03 mg/mL. A solution of 10 mg/mL of $Ba(ClO_4)_2$ in THF was prepared and 0.2 equiv of Ba^{2+} were added to a 0.03 mg/mL solution of poly($\mathbf{1}_{0.6}$-*co*-$\mathbf{7}_{0.4}$) in $CHCl_3$. One drop of this mixture (10 μL) was placed on freshly cleaved HOPG (Telstar Instrumat, ZYH grade) and was spin coated at 900 and/or 1800 rpm at rt.

DLS measurements were performed on a Malvern Nano ZS (Malvern Instruments, U.K.), operating at 633 nm with a 173º scattering angle. Samples were measured at a final concentration of 0.1 mg/mL diluted with THF. These studies indicate that the HPMCs (helical polymer-metal complexes) form aggregates with a defined structure.

SEM measurements were performed on a LEO-435VP electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer. A drop of a solution of different copolymers with different equivalents of a selected perchlorate (0.1 mg/mL) was settled on a silicon wafer chip (Ted Pella, Inc), and allowed to dry at rt for 12 h.

TEM measurements were carried out on Philips CM-12 electron microscope. In this case a drop of the copolymer solution (0.1 mg/mL) was placed onto a carbon grid (Ted Pella, Inc).

Conclusions

We present here a family of copolymers where the chiral amplification based on the "Sergeants and Soldiers effect" can be switched ON/OFF by the presence/absence of metal ions. In these copolymers, the chiral component (**1** or **2**) does not trigger by itself the chiral amplification —it does not act as a "Sergeant"— until a small amount of a metal ion is added. The structure of the metal complex determines its interaction in the helix with the surrounding "Soldiers" and therefore the intensity of the amplification and the response of a copolymer to a certain metal.

This response is especially interesting in poly($\mathbf{1}_r$-*co*-$\mathbf{7}_{(1-r)}$) that shows amplification by "Sergeants and Soldiers effect" with divalent ions to the right sense but not with monovalent ones, and in poly($\mathbf{1}_r$-*co*-$\mathbf{8}_{(1-r)}$), that amplifies the helix to the left-handed sense with mono- and to the right-handed sense with divalent ions by "Sergeants and Soldiers effect". This allows inducing selectively on a single copolymer, and through chiral amplification, any of the two helical senses (*M* or *P*) just by selecting the type of ion.

The structural and functional analogy of these copolymers with the parent homopolymers poly-**1** and poly-**2** is not limited to the existence of chiral amplification based on the presence of a "dormant Sergeant" selectively ON/OFF activated by addition of metal ion. It also attains to the aggregation and encapsulation properties reported for the homopolymers as a result of the cross-linking role played by the metal cations that does not affect the "Sergeants and Soldiers effect" here reported.[4b]

In fact, addition of increasing amounts of a Ba^{2+} salt to $CHCl_3$ solutions of the copolymers produce stable nanospheres (see Figures 5a-c), similar to those obtained from Ba^{2+}/poly-**1**, whose size and helical sense can be tuned to shrink or to grow by manipulation of the metal/polymer ratio as with the homopolymer.[4b] These helically controlled nanospheres can also be employed to encapsulate materials such as iron oxide magnetic nanoparticles, quantum dots and organic molecules (e.g. fluorescent dyes) (Figures 5d,e).

Overall, our results indicate that the most interesting properties of the helical PPAs can be reproduced by copolymers with low content of chiral monomer.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Structures, synthesis and spectral data of monomers, homopolymers and copolymers; monomer reactivity ratios; CD/UV studies and chiral amplification mechanism; aggregation, encapsulation, AFM and thermal studies (97 pages). See DOI: 10.1039/b000000x/

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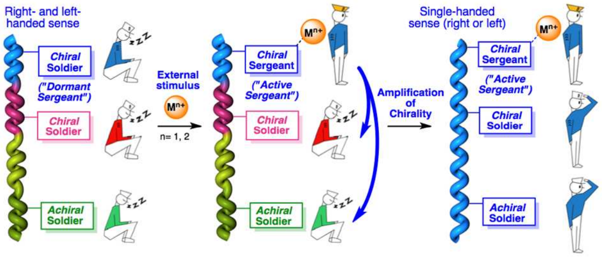
TOC



Chiral amplification can be switched ON/OFF to both helical senses by the presence/absence of metal ions in copolymers of poly(phenylacetylene)s