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ARTICLE

## Helical Sense Selective Domains and Enantiomeric Superhelices Generated by Langmuir-Schaefer Deposition of an Axially Racemic Chiral Helical Polymer

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Chiral polymer poly-(*R*)-**1** behaves in solution, despite its chiral pendants, as a dynamic axially racemic (*i.e.*, 1:1) mixture of left- and right-handed helices, but its deposition on graphite by Langmuir-Schaefer (LS) technique leads to helical sense-selective packing that forms separate enantiomeric domains of left- and right-handed helical chains observed by high resolution atomic force microscopy (AFM). The polymer structure within these domains is very uniform, seldom altered by the presence of reversals, grouped always in contiguous pairs maintaining a single helical sense along the polymer chain. The LS deposition technique has shown to be crucial to obtain good quality monolayers from poly-(*R*)-**1** and other poly(phenylacetylene)s (PPAs: poly-**2**, poly-**3** and poly-**4**) with short pendants, where spin coating, drop casting and Langmuir-Blodgett (LB) failed, and suggests that this technique could be the method of choice for the preparation of 2D monolayers for high resolution AFM studies of PPAs with short pendants. Key helical parameters (*i.e.*, sense, pitch, packing angle) are easily measured in this way.

### Introduction

Poly(phenylacetylene)s<sup>1</sup> (PPAs), are dynamic helical polymers,<sup>2</sup> with potential applications in different fields such as sensing,<sup>3</sup> chiral separations,<sup>4</sup> asymmetric synthesis,<sup>5</sup> etc. Their importance as substrates relates to their easy preparation with great variety of functions as pendants, with high stereochemical control, their stimuli-tuneable (pH, T, metal ions, chiral molecules, etc.) helical sense and pitch and their conversion into macroscopically helical supramolecular aggregates.

The elucidation of the helical structure of poly(acetylene)s has been carried out by techniques such as X-ray,<sup>6</sup> NMR,<sup>7</sup> Raman<sup>8</sup> or DSC,<sup>9</sup> that allow to know the conformation around the sigma bond (*cis-cisoidal* or *cis-transoidal*), the diameter of the helix or the columnar assembly (hexagonal, tetragonal) formed, but not the helical sense.

During the last decade, the groups of Percec in USA and Yashima in Japan have been using AFM<sup>10, 11</sup> for this purpose

with poly(phenylacetylene)s with large pendants (e.g., dendrons<sup>10</sup> or long alkyl chains<sup>11</sup>), that are necessary to favour their self-assembly into 2D crystals observable by AFM.

Thus, the high resolution AFM of dendronised PPAs prepared by drop casting and thermal annealing allowed to visualize some parameters of the chains in the monolayer and their packing but the resolution was not enough to distinguish the possible helical sense-preference of the chains in the packing.<sup>10</sup>

In 2006, it was published a report describing the helical parameters of a PPA by high resolution AFM.<sup>11c</sup> The protocol for the preparation of the 2D-crystal involved spin coating a dilute solution of the PPA onto a HOPG or mica substrate, which was leaved overnight under solvent vapour atmosphere to get the 2D-crystal. Following this method, the helical pitch, angle, sense and packing parameters of several achiral and chiral PPAs were obtained.

Thus, racemic PPAs such as the one bearing the achiral pendant aminoisobutyric acid,<sup>11d</sup> produced macroscopically racemic 2D crystals where each individual chain is composed by several helical fragments, some with *P* sense and others with *M* sense, separated rarely occurring reversals.

Among the chiral poly(phenylacetylene)s, one example is represented by a PPA containing *L*-Ala as chiral pendant. This polymer presents a preference for *M* helical sense in solution, and produced macroscopically chiral 2D-crystals composed by chains with *M* helicity sense packed side by side in a helically homogeneous surface.<sup>11c</sup> As expected, the polymer containing

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*D*-Ala (preference for *P* sense in solution), gave the macroscopically enantiomeric 2D assembly by packing of individual chains with *P* helical sense.<sup>11c</sup>

The same group observed an interesting phenomenon when copolymers from a PPA copolymer series [poly (*L*-Ala<sub>x</sub>-co-Aib<sub>1-x</sub>)] formed by a chiral monomer (*L*-Ala) and an achiral one (Aib) were deposited by spin coating forming a well-ordered 2D-crystal. While in solution the “sergeants and soldiers” effect does not take place [null circular dichroism (CD)], the 2D crystals obtained by self-assembly are chiral, indicating that the sergeant and soldiers effect is activated in the solid state. In the 2D-crystal, the copolymer chains adopt a preferred *M* helical sense, although a few fragments with *P* helicity can also be found in the *M* polymer chain separated by a reversal.<sup>12a</sup>

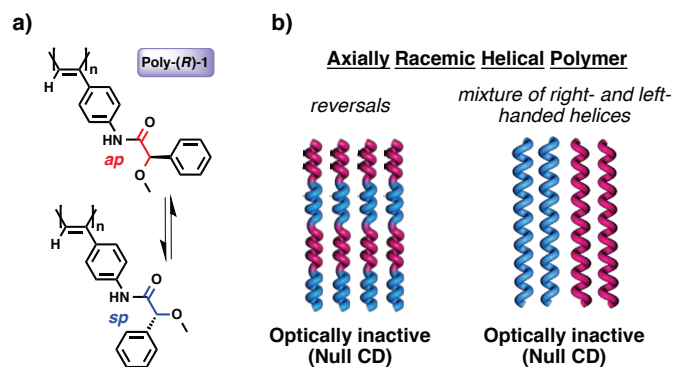
Another example showing chiral amplification in the solid state was reported during the study of the “majority rules” on the PPA copolymer series [poly (*L*-Ala<sub>x</sub>-co-*D*-Ala<sub>1-x</sub>)]. In this case, poly(*L*-Ala<sub>0.55</sub>-co-*D*-Ala<sub>0.45</sub>) containing a very low excess of *L*-Ala, produced 2D-crystals with a 89% excess of *M* helical sense.<sup>12b</sup>

All these studies suggest that the self-assembly of the polymer chains in the 2D-crystal is directly related to the chiral content of the parent monomers. Thus, while achiral homo-PPAs produce assemblies where the two helical senses (*P* and *M*) are present in the polymer chain separated by reversals, in chiral homo-polymers the assembly is formed among chains with homogeneous *P* or *M* helical sense. For their part, in copolymers composed by chiral and achiral fragments, both types of assemblies can be found depending on the chiral content of the copolymer.

In this work, we describe a different, not previously reported arrangement where enantiomeric 2D crystals constituted by *P* helices and by *M* helices, can be obtained from a single an axially racemic chiral PPA.

## Results and discussion

In order to obtain information about the helical structure of an axially racemic helical polymer we studied a poly(phenylacetylene) bearing (*R*)- $\alpha$ -methoxy- $\alpha$ -phenylacetamide pendants [poly-(*R*)-1], which presents a very unique characteristic: in dilute solution it is a dynamic helical polymer, that despite being formed by chiral monomer repeating units, is “axially racemic” from a macroscopic point of view (null CD, equal populations of left- and right-handed helices; Figure 1a),<sup>16a</sup> and does not present a predominant helical sense as usually happens with PPAs bearing chiral side chains. This means that along the chain of the polymer, there should coexist, in a rapid equilibrium, right and left handed fragments, connected by helical reversals (Figure 1b). Moreover, this effect was observed for poly-(*R*)-1 of different molecular weight indicating that there is no relationship between the size of the polymer and its axially racemic behaviour (see ESI).<sup>13a-b</sup>



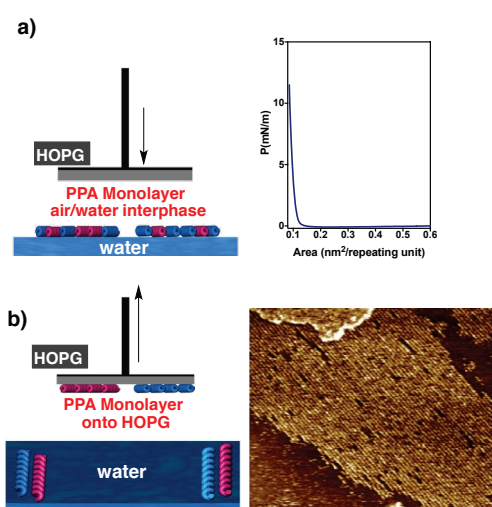
**Figure 1.** a) Preferred conformers at the pendant group for poly-(*R*)-1. b) Possible compositions of the helical structure of an axially racemic helical polymer.

When we tried to prepare 2D-crystals of poly-(*R*)-1 by spin coating on HOPG, the quality of the layer was not good enough to provide high resolution AFM images.

An alternative to spin coating and drop casting is the Langmuir-Blodgett (LB) method that prepares monolayers in an air/water interface. With this technique, 2D monolayers of poly-(*R*)-1, were prepared but disappointingly, they could not be transferred to the HOPG support due to its high hydrophobicity. Other supports such as mica (hydrophilic) were also tested, but poor results were obtained.<sup>14</sup>

In order to overcome this problem, we reasoned that the Langmuir-Schaefer (LS) methodology, where the monolayer is directly exfoliated from the air/water interphase with the HOPG substrate, could be the solution.<sup>15</sup>

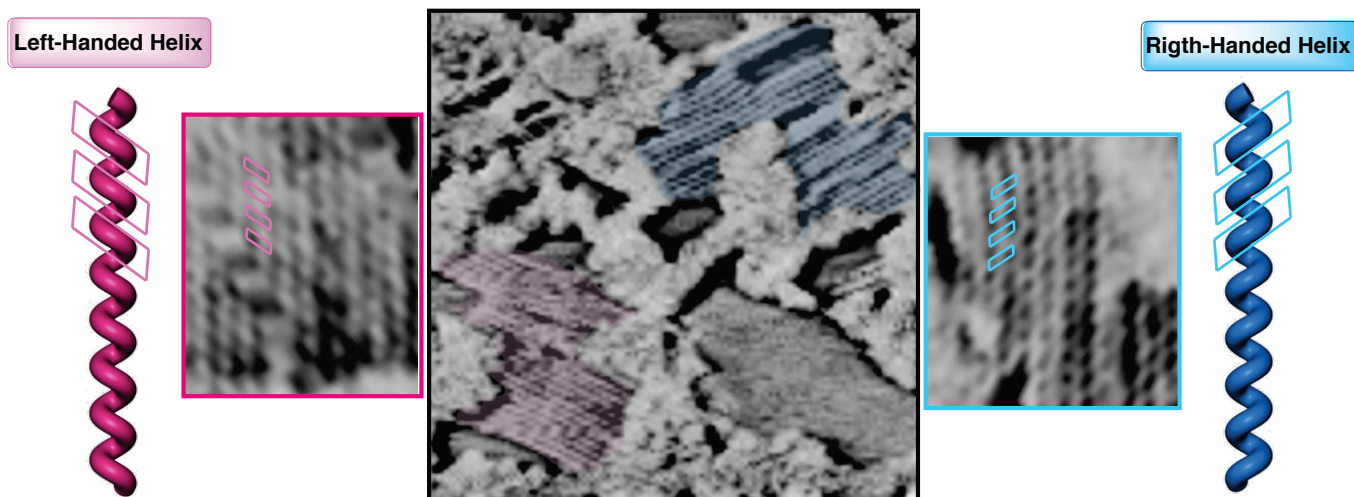
Successful application of the LS method started by careful droplet-by-droplet spreading of 200  $\mu$ L of a chloroform solution of the polymer (0.1 mg/mL) on a water surface at room temperature via syringe (the organic layer remained on the water surface despite its higher density). Then, evaporation of the chloroform took place (5 min approximately), followed by gradual compression of the polymer surface until a compact monolayer of poly-(*R*)-1 was formed (Figure 2 and Figure S12 at ESI).



**Figure 2.** a) Poly-(*R*)-1 monolayer formation at the air/water interphase by the typical Langmuir-Blodgett protocol and its corresponding surface pressure (mN/m) versus the area (nm<sup>2</sup>/repeating unit) graph. b) Exfoliation of poly-(*R*)-1 monolayer by Langmuir-Schaefer and AFM image of the monolayer obtained.

The surface pressure/molecular area ( $\pi$ -A) isotherm of a poly-(R)-1 layer prepared at 0.5 mN (Figure 2a), exhibits two distinct regions with very different slopes: at compressions lower than 0.3 mN/m, the surface region increases gradually with compression, while at compressions higher than 0.3 mN/m, the monolayer surface increases very rapidly with compression. The limiting area for poly-(R)-1 is 0.15 nm<sup>2</sup>. The monolayer of poly-(R)-1, prepared in this way, was transferred from the air/water interface to the surface of newly cleaved HOPG by approximation of the hydrophobic HOPG (1 cm<sup>2</sup>

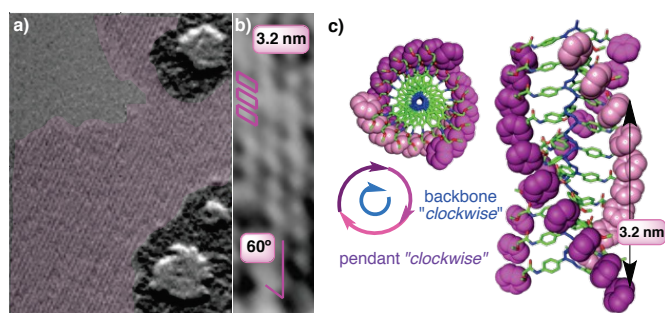
surface) to the polymer monolayer at the air/water interphase. Examination by AFM showed images with resolution enough to provide the parameters defining the helix (helical pitch, helical sense and periodic oblique stripes) as well as the supramolecular arrangements of poly-(R)-1 in the 2D-crystal. Thus, monolayers from poly-(R)-1 present well-defined chiral 2D helix-bundles, with a constant height of 2.5 nm, most of which are clearly resolved into individual right- or left-handed helical fields packed parallel to each other (Figure 3).



**Figure 3.** Monolayer obtained at (1mN/m) showing left- and right-handed helical fields (highlighted in pink and blue respectively). In this sample, similar area ratios (i.e., 1:1) for both homochiral domains were obtained. Analogous distribution of domains were found on other regions of the sample (samples showing uniform fields without amorphous domains can be found at ESI). For the sake of clarity, magnifications of both helical fields are shown, indicating the helical sense.

Both types of bundles are originated from the parallel arrangement of individual helical chains of the same helical sense.

The periodic oblique stripes measured in the individual chains forming the bundles tilted counterclockwise ( $M$ ) were determined to be  $-60^\circ$  and the helical pitch 3.2 nm (Figure 4).

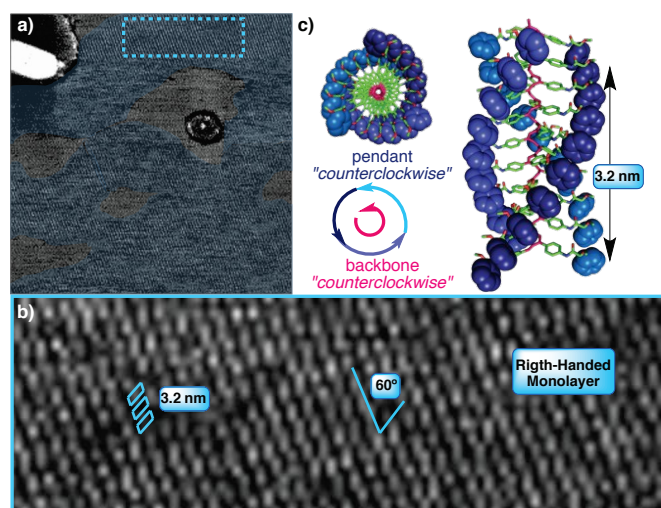


**Figure 4.** a) Left-handed monolayer field [obtained at (1mN/m)] b) Magnification of a left-handed monolayer, highlighting the helical sense, pitch and packing angle. c) Molecular model of the left-handed structure of poly-(R)-1.

The clockwise bundles ( $P$ ) showed analogous values of  $60^\circ$  and 3.2 nm (Figure 5), in accordance with a *cis-cisoidal* skeleton in both cases.

In fact, those values for periodic oblique stripes and pitch are virtually identical to those obtained in solution when poly-(R)-1 undergoes chiral amplification by complexation with mono- or divalent metal ions.<sup>19</sup> The parameters obtained after LS

deposition, indicate the presence of helices with the pendants properly oriented to form hydrogen bonds between  $n^{\text{th}}$  and  $(n+3)^{\text{th}}$  units (Figures 4c and 5c).



**Figure 5.** a) AFM image of a right-handed monolayer obtained at (1mN/m). b) Magnification of the highlighted area in Figure 5a, showing the helical sense, pitch and packing angle. c) Molecular model of the right-handed helical structure of poly-(R)-1.

Interestingly, comparison of the DSC trace due to the LS monolayer with the one obtained for the film prepared by spin coating demonstrates that the LS technique does not modify



the helical scaffold of the polymer. In both cases, there is an exothermic peak around 192 °C, corresponding to the *cis-cisoidal* to *trans-transoidal* isomerization of the backbone (See SI).<sup>9b-c</sup>

The high-resolution AFM images of the chiral poly-(*R*)-1 2D-crystals also showed that the average chain-to-chain distance in the right-handed *PP*, and in the left-handed *MM* helical blocks is virtually the same (See ESI). This value (4.5 nm) is in good agreement with those found for other helical polymers with short non-associative<sup>20</sup> pendants and larger than those reported for PPAs bearing long alkyl groups, where interdigitation of those pendants favour a tighter parallel packing.<sup>11b-d</sup>

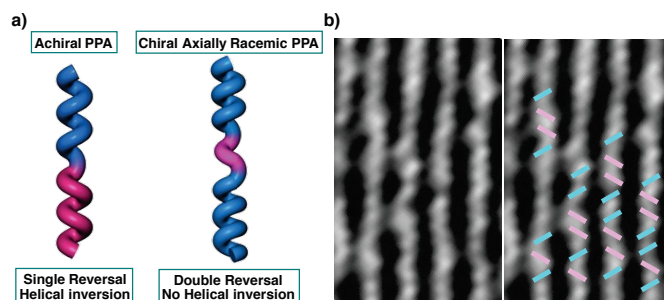
These results complement those described by Yashima *et al.* for optically inactive PPAs bearing achiral long chain pendants, that formed blocks constituted by helices of both *P* and *M* senses,<sup>11d</sup> and with those found in optically inactive copolymers bearing mixtures of chiral and achiral monomers, that form single handed 2D-crystals identical to those obtained for the parent chiral homopolymer.<sup>12a</sup>

In our case, although the polymer in solution is “axially achiral” (equilibrium of equally populated *M*- and *P*-helical backbones), the 2D monolayer generated shows a packing pattern where the helices prefer to aggregate with others of the same helical sense leading to separate fields, one for polymer chains uniformly left-handed and others formed by chains uniformly right-handed. Therefore, these results resemble chiral amplification effects —*i.e.*, “sergeants and soldiers”, “majority rule”— previously reported in the solid state,<sup>12</sup> but in our case, outstandingly, poly-(*R*)-1 produces a brand new scenario: an equal number of *P* and *M* 2D-crystals through a chiral amplification effect. This fact differs from the systems reported by Yashima *et al.* where only a single chiral 2D crystal was obtained (*P* or *M*) defined by the chirality of the chiral monomer.

From the thermodynamic point of view, this suggests that different energies are associated to the packing of axially homochiral (*e.g.*, *PPP*, *MMM*) and heterochiral helices (*e.g.*, *PMP*, *MPM*), being the homochiral chain–chain interactions favoured in poly-(*R*)-1 over the heterochiral counterparts.

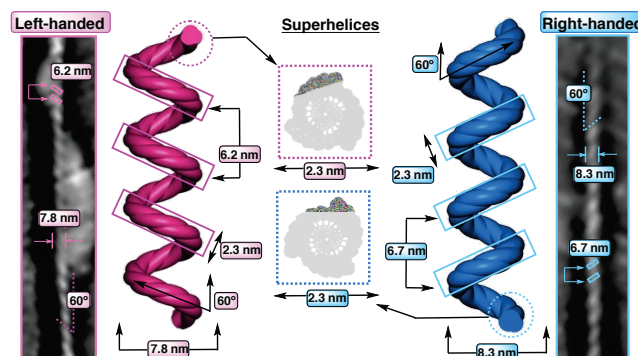
Also, the uniform height measured (*i.e.*, 2.5 nm) indicates the effectiveness of the LS method to obtain homogeneous monolayers without accumulation of polymeric chains one on top of the other (see SI). Furthermore, by this method the chains do not present the oblate or flattened shapes observed in other PPAs on HOPG.<sup>9</sup>

It is relevant to point out that although the domains are uniformly formed by all left- or by all right-handed helices, some helical reversals are distinguished along the polymer chains. Interestingly, the reversals are always present as contiguous pairs in the chain, allowing in that way to maintain both the same helical sense along the complete chain of the polymer (Figure 6) and the final chiral content of the monolayer.



**Figure 6.** a) Schematic illustration of the effects of the different types of reversals in a helical structure. b) AFM image of a right-handed monolayer showing reversals along the polymer chains (left), and the same image with double helical reversals highlighted for the sake of clarity.

In addition to the right and left handed- well-ordered domains, AFM images also showed the presence of separate enantiomeric superhelices, left- and right-handed oriented. Their measured helical pitches are 6.7 nm for the left-handed and 6.2 nm for the right-handed superhelix, the packing angles being 60° in both cases. Figure 7 shows plausible coiled-coil structures formed from the 3/1 helical scaffolds that match the observed experimental values. To our knowledge, this is the first report of a chiral helical polymer that generates superhelices of both helical senses.<sup>21,22</sup>



**Figure 7.** Left- and right-handed superhelices originated from poly-(*R*)-1 and visualized by AFM and a plausible model based on the AFM observation.

Finally, it is worth mentioning the effectiveness of the Langmuir-Schaefer deposition technique to generate 2D monolayers useful for high resolution AFM of polyphenylacetylenes with short pendants, has been also proven with other PPAs where spin coating, drop casting and Langmuir-Blodgett failed [*e.g.*, *para*- and *meta*-phenyl substituted (*S*)-phenylglycine methyl ester (poly-2 and poly-3) and *meta*-phenyl substituted (*S*)-*α*-methoxy-*α*-phenylacetic acid (poly-4) as pendant groups, see SI], suggesting that LS could be the method of choice for the preparation of good quality 2D monolayers for high resolution AFM studies of PPAs lacking long chain pendants.

## Conclusions

In summary, we present an axially racemic chiral polymer with high selectivity for homochiral packing in the 2D crystal, producing uniform fields composed by either left-handed or right-handed helical chains, but no fields of mixed helicity. This preference for the assembly of chains with identical helical sense is also operative in the formation of separate left- and right-handed superhelices and the absence of aggregates with mixed-sense chains.

To our knowledge, this is the first report of a chiral, dynamic polymer that forms separated macroscopically enantiomeric left- and right-handed domains and superhelices.

These results with axially racemic chiral PPAs complement those of Yashima *et al.* and allow to get the whole picture of how macroscopically optically inactive PPAs behave when forming monolayers:

a) Axially racemic achiral PPAs give monolayers where the individual polymer chains contain fragments with either *P* or *M* helical senses, separated by reversals.

b) Axially racemic copolymers —made by chiral and achiral monomers or mixtures of enantiomeric monomers— give monolayers with amplification of chirality (*sergeants and soldiers* or *majority rule* effects) making the copolymer to adopt mainly a single helical sense with the rarely presence of reversals.

c) Finally, axially racemic chiral PPAs produce mixtures of macroscopically homogeneous chiral monolayers formed by polymer chains with either *P* or *M* helical sense. In these chains some reversals may occur, but they are always present in contiguous pairs that allow maintaining the homogeneity of the helical sense.

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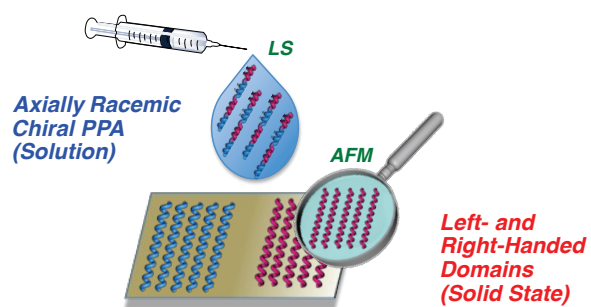
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## Notes and references

- (a) E. Yashima, K. Maeda, *Macromolecules* **2008**, *41*, 3-12. (b) J. G. Rudick, V. Percec, *Acc. Chem. Res.*, **2008**, *41*, 1641-1652. (c) E. Yashima, K. Maeda, Y. Furusho, *Acc. Chem. Res.*, **2008**, *41*, 1166-1180. (d) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Iman, V. Percec, *Chem. Rev.*, **2009**, *109*, 6275-6540. (e) E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai, *Chem. Rev.*, **2009**, *109*, 6102-6211. (f) W.-S. Li, T. Aida, *Chem. Rev.*, **2009**, *109*, 6047-6076; (g) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Adv. Polym. Sci.*, **2013**, *262*, 123-140. (h) J. Rudick, *Adv. Polym. Sci.*, **2013**, *262*, 345-362.
- (a) T. Nakano, Y. Okamoto *Chem. Rev.*, **2001**, *101*, 4013-4038. (b) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, *Chem. Rev.*, **2001**, *101*, 4039-4070. (c) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.*, **2001**, *101*, 3893-4012. (d) M. Sugimone, Y. Ito, *Adv. Polym. Sci.*, **2004**, *171*, 77-136. (e) J. W. Y. Lam, B. Z. Tang, *Acc. Chem. Res.*, **2005**, *38*, 745-754. (f) E. Yashima, K. Maeda, in *Foldamers: Structure, Properties, and Applications*, ed. S. Hecht and I. Huc, Wiley-VCH, Weinheim, **2007**, pp. 331-366; (g) R. J. M. Nolte, A. E. Rowan, *Polym. Chem.*, **2011**, *2*, 33-47.
- (a) E. Anger, H. Iida, T. Yamaguchi, K. Hayashi, D. Kumano, D. Crassous, N. Vanthuyne, C. Rouselc, E. Yashima, *Polym. Chem.*, **2014**, *5*, 4909-4914. (b) H. Iida, M. Miki, S. Iwahana, E. Yashima, *Chem. Eur. J.*, **2014**, *20*, 4257-4262.
- (a) K. Shimomura, T. Ikai, S. Kanoh, E. Yashima, K. Maeda, *Nat. Chem.*, **2014**, *6*, 429-434.
- (a) R. P. Megens, G. Roelfes, *Chem. Eur. J.*, **2011**, *17*, 8514-8523. (b) Z. Tang, H. Iida, H.-Y. Hu, E. Yashima, *ACS Macro Lett.*, **2012**, *1*, 261-265. (c) H. Iida, Z. Tang, E. Yashima, *J. Polym. Sci., Part A: Polym. Chem.*, **2013**, *51*, 2869-2879.
- (a) V. Percec, E. Aqad, M. Peterca, J. G. Rudick, L. Lemon, J. C. Ronda, B. B. De, P. A. Heiney, E. W. Meijer, *J. Am. Chem. Soc.*, **2006**, *128*, 16365-16372. (b) V. Percec, M. Peterca, J. G. Rudick, E. Aqad, M. R. Imam, P. A. Heiney, *Chem. Eur. J.*, **2007**, *13*, 9572-9581. (c) V. Percec, J. G. Rudick, M. Peterca, E. Aqad, M. R. Imam, P. A. J. Heiney, *J. Polym. Sci., Part A: Polym. Chem.*, **2007**, *45*, 4974-4987. (d) J. G. Rudick, V. Percec, *Macromol. Chem. Phys.*, **2008**, *209*, 1759-1768. (e) M. Asahi, Y. Mawatari, R. Motoshige, Y. Yoshida, M. Tabata, *J. Polym. Sci., Part A: Polym. Chem.*, **2013**, *51*, 5177-5183. (f) X-Q. Liu, J. Wang, Sh. Yang, E-Q. Chen, *ACS Macro Lett.*, **2014**, *3*, 834-838.
- (a) R. Motoshige, Y. Mawatari, A. Motoshige, Y. Yoshida, T. Sasaki, H. Yoshimizu, T. Suzuki, T. Yoshiharu, M. Tabata, *J. Polym. Sci., Part A: Polym. Chem.*, **2013**, *52*, 752-759. (b) Y. Yoshida, Y. Mawatari, A. Motoshige, R. Motoshige, T. Hiraokib, M. Tabata, *Polym. Chem.*, **2013**, *4*, 2982-2988. (c) Y. Yoshiaki, Y. Mawatari, A. Motoshige, R. Motoshige, T. Hiraoki, M. Wagner, K. Müllen, M. Tabata, *J. Am. Chem. Soc.*, **2013**, *135*, 4110-4116.
- (a) K. K. L. Cheuk, J. W. Y. Lam, J. Chen, M. L. Lai, B. Z. Tang, *Macromolecules*, **2003**, *36*, 5947-5959. (b) B. S. Li, K. K. L. Cheuk, L. Ling, J. Chen, X. Xiao, C. Bai, B. Z. Tang, *Macromolecules*, **2003**, *36*, 77 - 85. (c) J. W. Y. Lam, B. Z. Tang, *Acc. Chem. Res.*, **2005**, *38*, 745 - 754. (d) M. G. Mayershofer, O. J. Nuyken, *Polym. Sci. Part A*, **2005**, *43*, 5723-5747. (e) K. K. L. Cheuk, B. S. Li, J. W. Y. Lam, B. Z. Tang, *Macromolecules*, **2008**, *41*, 5997-6005.
- (a) L. Liu, T. Namikoshi, Y. Zang, T. Aoki, S. Hadano, Y. Abe, I. Wasuzu, T. Tsutsuba, M. Teraguchi, T. J. Kaneko, *J. Am. Chem. Soc.*, **2013**, *135*, 602-605. (b) S. Leiras, F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Sci.*, **2013**, *4*, 2735-2743. (c) S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.*, **2014**, *53*, 13720-13724. (d) S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Polym. Chem.*, **2015**, *6*, 4725-4733.
- (a) V. Percec, J. G. Rudick, M. Wagner, M. Obata, C. M. Mitchell, W.-D. Cho, S. N. Magonov, *Macromolecules*, **2006**, *39*, 7342-7351. (b) V. Percec, J. G. Rudick, M. Peterca, S. R. Staley, M. Wagner, M. Obata, C. M. Mitchell, W.-D. Cho, V. S. K. Balagurusamy, J. N. Lowe, M. Glodde, O. Weichold, K. J. Chung, N. Ghionni, S. N. Magonov, P. A. Heiney, *Chem. Eur. J.*, **2006**, *12*, 5731-5746.
- (a) T. Nishimura, K. Takatani, S. Sakurai, K. Maeda, E. Yashima, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3602-3604. (b) S.-I. Sakurai, K. Okoshi, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.*, **2006**, *128*, 5650-5651. (c) K. Okoshi, S. Sakurai, J. K. Ohsawa, E. Yashima, *Angew. Chem. Int. Ed.*, **2006**, *45*, 1245-1248. (d) S.-I. Sakurai, K. Ohsawa, K. Nagai, K. Okoshi, J. Kumaki, E. Yashima, *Angew. Chem. Int. Ed.*, **2007**, *46*, 7605-7608. (e) E. Yashima, *Polym. J.* **2010**, *42*, 3-16 (f) S. Ohsawa, S.-I. Sakurai,

- K. Nagai, M. Banno, K. Maeda, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.*, **2011**, *133*, 108-114.
- 12 For chiral amplification of PPA on surface see: (a) S. Ohsawa, S. Sakurai, K. Nagai, M. Banno, K. Maeda, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.*, **2011**, *133*, 108-114. (b) S. Ohsawa, S. Sakurai, K. Nagai, K. Maeda, J. Kumaki, E. Yashima, *Polym J.*, **2011**, *44*, 42-50.
- 13 For helical polymers with helical sense depending on molecular weight see (a) H. Onuchi, K. Okoshi, T. Kajitani, S.-I. Sakurai, K. Nagai, J. Kumaki, K. Onitsuka, E. Yashima, *J. Am. Chem. Soc.*, **2008**, *130*, 229-236 (b) Z.-Q. Wu, K. Nagai, M. Banno, K. Okoshi, K. Onitsuka, E. Yashima, *J. Am. Chem. Soc.*, **2009**, *131*, 6708-6718.
- 14 (a) B. S. Li, S. Z. Kang, K. K. L. Cheuk, L. Wan, L. Ling, C. Bai, B. Z. Tang, *Langmuir*, **2004**, *20*, 7598-7603. (b) B. S. Li, J. W. Y. Lam, Z.-Q. Yu, B. Z. Tang, *Langmuir*, **2012**, *28*, 5770-5774.
- 15 Ulman, A. *An Introduction to Ultrathin, Organic Films—From Langmuir–Blodgett to Self-Assembly*, Academic Press, New York, **1991**.
- 16 (a) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.* **2011**, *50*, 11692-11696. (b) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *J. Am. Chem. Soc.*, **2012**, *134*, 19374-19383. (c) J. Bergueiro, F. Freire, E. P. Wendler, J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Sci.*, **2014**, *5*, 2170-2176. (d) S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.*, **2014**, *53*, 13720-13724.
- 17 S. Sakurai, K. Kuroyanagi, R. Nunokawa, E. Yashima, *J. Polym. Sci. Part A.*, **2004**, *42*, 5838-5844.
- 18 For helical polymers with helical sense depending on the molecular weight see: (a) H. Onuchi, K. Okoshi, T. Kajitani, S.-I., S. Sakurai, K. Nagai, J. Kumaki, K. Onitsuka, E. Yashima, *J. Am. Chem. Soc.*, **2008**, *130*, 229-236. (b) Z.-Q. Wu, K. Nagai, M. Banno, K. Okoshi, K. Onitsuka, E. Yashima, *J. Am. Chem. Soc.*, **2009**, *131*, 6708-6718.
- 19 AFM of the helical polymer-metal complexes (HPMCs) of poly-(*R*)-**1** with mono- and divalent cations were carried out on polymer chains already biased towards a predominant helical sense due to complexation with the metals and not on “axially racemic” chains, as it is now the case. See ref. 14a.
- 20 The lack of groups in the pendants favouring the self-assembly justifies this disposition. This is a larger distance than the one found in PPAs bearing long alkyl chains, where tighter packings have been observed. See ref. 11b-11d. However, values around 4.5 nm were observed in AFM images of polymers with short pendants lacking the presence of groups that can favour the aggregation of the helical chains. See ref. 9b, and 16.
- 21 The existence of this type of superhelices has been postulated in 2/1 helical PPAs bearing aza-18-crown-6 ether pendants associated to amino acids on mica surfaces. See ref. 17.
- 22 For superhelices based on PPA see: (a) S. Matsushita, K. Azagi, *J. Am. Chem. Soc.*, **2015**, *137*, 9077-9087. (b) T. Mori, M. Kyotani, K. Azagi, *Chem. Sci.*, **2011**, *2*, 1389-1395. (c) K. Akagi, *Chem. Rev.*, **2011**, *109*, 5354-5401. (d) T. Mori, M. Kyotani, K. Azagi, *Macromolecules*, **2010**, *43*, 8363-8372.
- 23 For helical nanoribbons generated by self-assembly of achiral bolaamphiphiles see: (a) B. Song, B. Liu, Y. Jin, X. He, D. Tang, G. Wu, S. Yin, *Nanoscale*, **2015**, *7*, 930-935. (b) Y. Jin, Y. Xia, S. Wang, L. Yan, Y. Zhou, J. Fan, B. Song, *Soft Matter*, **2015**, *11*, 798-805.

## TOC



An axially racemic chiral helical polymer generates left- and right-handed monolayers and enantiomeric superhelices by LS deposition