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**Chiral Polymers**

# Tuning the Supramolecular Chirality of Polyaniline by Methyl Substitution**

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The formation of structures that have a controlled helicity continues to be a challenging area in the field of polymer and supramolecular chemistry. Driven by the chirality of the composing unit, one may obtain a specific handedness in a helical conformation (right-handed, *P*, or left-handed, *M*) in biological or synthetic macromolecules,[1] while helical supramolecular structures can be obtained through intermolecular π-stacking interactions.[2] Interestingly, certain macromolecules and supramolecular aggregates can change their helicity between *P* and *M* in a so-called helix–helix transition by introducing an external stimulus such as light,[3] temperature,[4] solvent,[5] and chiral additives.[6] However, the great majority of the studies on helical inversion were carried out in solution. Since device-oriented applications should be based on materials in the solid state,[7] the study of the helical inversion of nanostructures is of great importance for their potential applications.

Polyaniline (PANI) is a typical conducting polymer with multiple applications in electrical, optical, and chemical active materials and devices.[8] A helical conformation of polyaniline was reported to be induced by a chiral dopant.[9] The helical inversion of the conformation of polyaniline was observed by copolymerization with the *o*-toluidine unit in organic solvents.[10] More recently, we have successfully prepared right- and left-handed helical nanofibers of polyaniline, which were induced by D-CSA and L-CSA dopants, respectively (CSA = camphorsulfonic acid).[11] If the helical sense of polyaniline nanofibers could be adjusted by copolymerization with aniline derivatives as in solution, one could easily obtain helical copolyaniline nanofibers with adjustable composition and helicity.

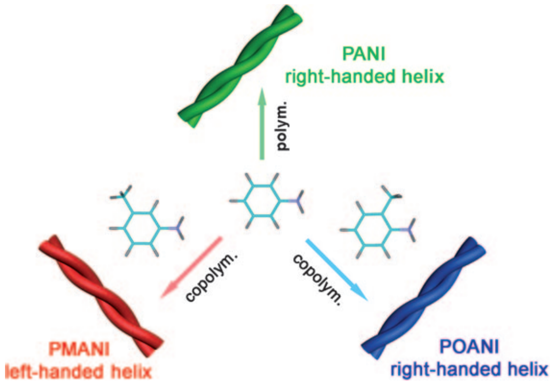

***Figure 1.*** Schematic representation of supramolecular chirality tuning of polyaniline by methyl substitution.

Herein, we report a series of helical copolyaniline nanofibers of formed by copolymerization of aniline with *m*-toluidine or *o*-toluidine, respectively (Figure 1). The helicity of the PANI nanofibers was induced by a chiral D-CSA dopant in the polymerization process, but could be inverted by copolymerization with *m*-toluidine. Copolymerization with *o*-toluidine resulted in a helicity similar to that of PANI. It is of great importance that upon simply introducing a methyl substituent at the *meta* position of the phenyl ring, helical inversions are observed not only for the copolymer conformation but also for their aggregated nanofibers, which provides a subtle method of tuning the induced supramolecular chirality. DFT calculations have been performed to simulate the helical inversion of copolyaniline induced by methyl substitution (see the Supporting Information for computational details), which are highly consistent with our experimental results.

In order to study the influence of the copolymerization process on the polymer conformation, copolymers were prepared by changing the ratio between two monomers—aniline (An) and *m*-toluidine or *o*-toluidine (*m*-An or *o*-An). Copolymers of aniline and *m*-toluidine (PMANI) were synthesized by using D-camphorsulfonic acid (D-CSA) as a dopant. We changed the molar ratio of *m*-toluidine to aniline ([*m*-An]/[An]) while the total monomer concentration and D-CSA concentration were fixed at 0.14 M and 2.8 M respectively, which are optimized synthetic conditions for the preparation of helical polyaniline nanofibers.[11] Pure polyaniline shows a negative CD peak at around 435 nm (Figure 2a), which is induced by the chirality of D-CSA. Since the CD spectrum of D-CSA shows only a positive peak at around 290 nm (see Figure S1 in the Supporting Information), the negative peak at around 435 nm, which could be assigned to the π–π* transition of the polarons, can be ascribed to a right-handed helical conformation of polyaniline. As the [*m*-An]/[An] ratio increased to 1:15, the induced CD peaks of PMANI become positive at 430 nm, which indicates that the conformation of

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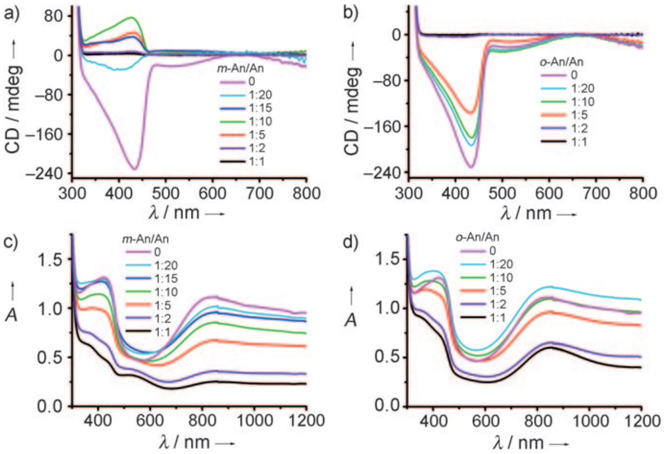

***Figure 2.*** a) CD and c) UV/Vis spectra of PMANI obtained at different [*m*-An]/[An] ratios; b) CD and d) UV/Vis spectra of POANI obtained at different [*o*-An]/[An] ratios. All experiments were carried out at 25 °C with total monomer and D-CSA concentrations of 0.14 M and 2.8 M respectively.

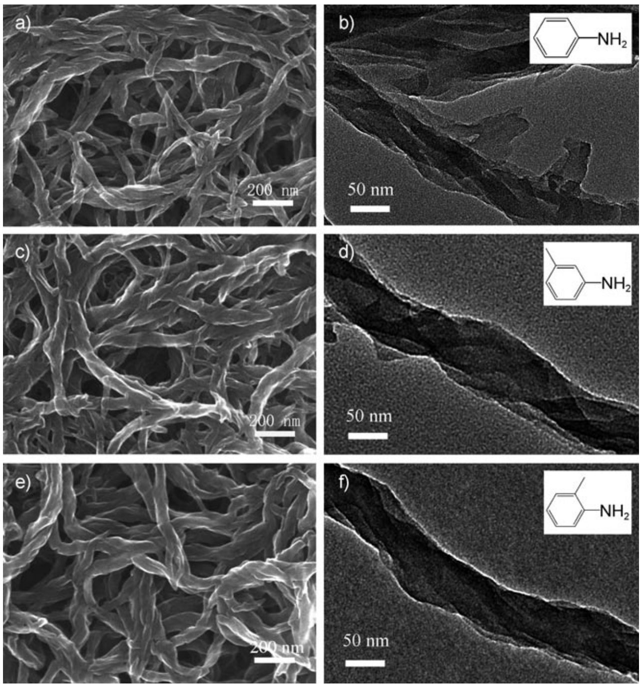

***Figure 3.*** SEM and TEM images of helical nanofibers induced by D-CSA. a, b) pure polyaniline; c, d) PMANI copolymerized at [*m*-An]/[An] = 1:10; and e, f) POANI copolymerized at [*o*-An]/[An] = 1:10. All experiments were carried out at 25 °C with total monomer and D-CSA concentrations of 0.14 M and 2.8 M respectively.

the copolymer is inverted from a predominately right-handed to a left-handed helix. The CD peaks reach a positive maximum at a [*m*-An]/[An] ratio of 1:10, and then decrease slowly as the [*m*-An]/[An] ratio increases further. The decrease in CD intensity is due to the difficulty of copolymerization at high [*m*-An]/[An] ratios, which is proved by a corresponding absorption decrease in the UV/Vis spectra (Figure 2 c). On the other hand, in the case of the copolymer of aniline with *o*-toluidine (POANI), only negative induced CD peaks appeared, which resemble that of pure polyaniline, when the ratio [*o*-An]/[An] increased from 1:20 to 1 as shown in Figure 2 b and the same dopant, D-CSA was used. As shown in the UV/Vis spectra (Figure 2 c,d), all the copolyanilines have two absorption peaks at around 420 nm and 800 nm, which are ascribed to the $\pi$–$\pi^*$ transition of the polarons, thus indicating that the copolyanilines are in a doped state. The UV/Vis spectra of the copolymer POANI (Figure 2 d) are nearly identical to those of PMANI, which suggests that they have similar molecular structures. Moreover, the FTIR spectra of PMANI and POANI are very similar to that of D-CSA-doped PANI (see Figure S2 in the Supporting Information).[12]

As deduced from the CD spectra, the conformation of copolyaniline PMANI changed from a predominantly right-handed helix to a left-handed helix as the ratio of [*m*-An]/[An] increased. Therefore, it was expected that the morphologies of the PMANI nanofibers also experienced helical transitions. For pure PANI nanofibers, only right-handed helical nanofibers are observed (Figure 3 a, b). Interestingly, nanofibers of copolymer PMANI with a left-handed helicity are obtained when *m*-An and the same enantiomeric dopant (D-CSA) are used. When the [*m*-An]/[An] ratio is between 1:20 and 1:10, both left-handed and right-handed helical nanofibers of PMANI are observed. When the [*m*-An]/[An] ratio is higher than 1:10, left-handed helical nanofibers become predominant, and almost no right-handed helical nanofibers are observed (Figure 3 c, d). Conversely, copolymerization of aniline with *o*-toluidine led to POANI nanofibers with the same helicity (right-handed) as that of PANI (Figure 3 e, f). The helicity of the nanofibers could be clearly observed in the SEM and TEM images. To the best of our knowledge, this is the first report of helical inversion in conducting polymer nanofibers that arises by merely changing the position of a methyl substituent in one of the monomers.

As reported previously, the interaction between D-CSA and PANI results in the right-handed helix as the more stable conformation for D-CSA-doped PANI.[11] We set out to rationalize why the helical conformation of PMANI is the inverse of that of PANI and POANI.

Copolymers PMANI and POANI have exactly the same molecular composition, which indicates that helical inversion does not originate from any structural differences in the polymers. Furthermore, solutions of PANI, PMANI, and POANI doped with D-CSA in DMF showed a uniform right-handed helical conformation (see Figure S3 in the Supporting Information).[13] Therefore, the position of the methyl group must play a dominant role in the polymerization process. The polymerization of aniline is a redox polymerization process, in which amino groups of one aniline molecule react with the *para* position of a second aniline molecule.[14] We performed theoretical simulations to investigate the inversion process of helical conformations of PMANI with respect to that of PANI and POANI.

For our simulations, we assume that the right-handed (or left-handed) helical conformation of PANI with the corresponding D-CSA (or L-CSA) dopant reported previously[9,11] is the preferred conformation. In the initial redox polymerization, one N−H group of aniline reacts with the *para* position of the aniline derivatives (An, *o*-An, or *m*-An). The benzyl plane of the second monomer should rotate through a certain angle compared to that of the first aniline derivative to leave another N−H bond free for interaction (for example, the N−H bond on the right-hand side). During the process, a D-CSA dopant molecule approaches the dimer. The D-CSA molecule blocks both the N−H bonds on the right-hand side of the dimer through the $(NH)^+(SO_3)^-$ ionic interaction and the hydrogen bond N−H···O=C (Figure 4a). Thus, the third aniline molecule can only react with the N−H terminus on the left-hand side of the dimer. Further dynamic simulations reveal that the aniline molecules react with the N−H terminus on the left-hand side all along the polymer, thus a right-handed chiral helix is formed for the An–An/D-CSA (Figure 4a and Figure S4 in the Supporting Information). Most interestingly, we find the chirality of the N atom near the reacting position is an important characteristic of the helical conformation. For An–An/D-CSA, we define a left-handed chirality of the N atom (see the Supporting Information).

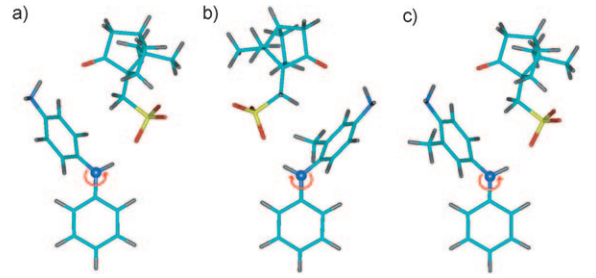

***Figure 4.*** Theoretical model for the stable forms of dimers of a) An–An, b) An–*m*-An, and c) An–*o*-An with D-CSA dopant in the polymerization process. The N atom near the reacting position is represented as a purple ball. The N atoms in (a) and (c) are both of left-handed chirality, while the N atom in (b) is of right-handed chirality.

In An–*m*-An/D-CSA, the methyl group directly affects the direction of approach of the monomers and the chirality of the N atom near the reacting position is inverted (Figure 4b). As a result, the accessible reactive group for the third monomer becomes the N−H terminus on the right-hand side of the dimer, and the chirality of the helix inverts to be left-handed, while in An–*o*-An/D-CSA, the methyl group is far from the approaching monomer. Theoretical results show that the chirality of the N atom near the reacting position is not changed (Figure 4c). It is clear that helical inversion arises from the steric hindrance of the methyl group at the *meta* position that affects the accessibility of the N−H group. Such a polymerization process has been simulated with four An (or *o*-An or *m*-An) repeating units with two D-CSA dopants, and also for the process with L-CSA dopants (see Figure S4 in the Supporting Information). The dynamic simulations show that the hindrance of the methyl group at the *meta* position of the phenyl ring plays a dominant role in the helical inversion.

In order to further prove that methyl group at the *meta* position of polyaniline plays a key role in forming inverted helical nanofibers, polymerization was carried out in the presence of either D- or L-CSA. Left-handed helical nanofibers of PMANI were produced using D-CSA as dopant (Figure 5a), while right-handed helical nanofibers of PMANI are obtained using L-CSA as the dopant under the same synthetic conditions (Figure 5c).

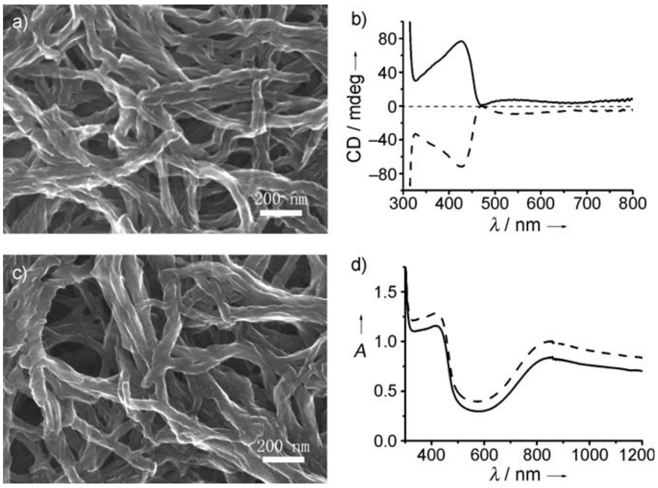

***Figure 5.*** SEM images of helical PMANI nanofibers obtained using D-CSA (a) and L-CSA (c) as the dopant. The corresponding CD (b) and UV/Vis (d) spectra are also shown for the D-CSA dopant (solid line) and the L-CSA dopant (dashed line). All experiments were carried out at 25 °C with total monomer and D-CSA concentrations of 0.14 M and 2.8 M respectively. [*m*-An]/[An] = 1:10.

The CD spectra of PMANI with right- and left-handed helical nanofibers are mirror-images, which indicates that they have opposite helical conformations (Figure 5b). The UV/Vis spectra of right- and left-handed helical nanofibers of PMANI are exactly the same (Figure 5d), which proves that they have similar molecular structures. Therefore, the helical inversions of PMANI to that of PANI are observed in both cases by using different enantiomers of CSA.

In summary, by copolymerization of aniline with *m*-toluidine, the helicity of the conformation and aggregated nanofibers were totally inverted with respect to that of polyaniline, while copolymers with aniline and *o*-toluidine were of the same helicity as polyaniline. Theoretical simulations revealed that the steric hindrance of the methyl group at the *meta* position of the phenyl ring played a dominant role in the helical inversion. Therefore, besides the helicity induced by chiral dopants, we find that changing a simple subunit, such as the methyl group at the *meta* position can also tune the helical sense of helical nanofibers, which may help to control the helicity and composition of functional supramolecular materials for future applications.

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