Chiral recognition in D-, L-arginine derived polyamidoamino acids and sodium deoxycholate solutions

Federica Lazzari,[1] Amedea Manfredi,[1] Jenny Alongi,[1] Elisabetta Ranucci,[1] Paolo Ferruti,[1,2] Peter Griffiths[3]

[1]Department of chemistry, University of Milan, via Golgi 19, 20133, Milan, Italy;
[2]National Interuniversity Consortium of Materials Science and Technology (INSTM), via Giusti 9, 50121, Florence, Italy;
[3]Department of Pharmaceutical, Chemical and Environmental Science, University of Greenwich, Central Avenue, ME4 4TB, Chatham, United Kingdom;
E-mail: federica.lazzari@unimi.it.

Nowadays the spontaneous self-organization of a polymer into an ordered structure is a sought-after property of many smart materials, whose applications might range from catalysis[1] to drug-delivery[2]. However, literature regarding the role played by these specific conformations in chiral recognition remains scarce. In this context, polyamidoamino acids (PAACs) are an emerging class of stimuli-responsive bioinspired synthetic polymers able to self-assemble into pH depend conformations.[3,4] Arginine based PAACs, named ARGO7, were obtained in water at pH 8-9 from the stepwise polyaddition of *L*- or *D*-arginine to *N,N'*-methylenebisacrylamide. Results indicated M_n 8500, PDI 1.4 and R_h of 1.2 nm.[3]

Molecular dynamics (MD) and circular dichroism (CD) showed ARGO7 folded into a rigid structure, reminiscent of the hairpin conformation, solely driven by the polymer main chain. Due to its ability to self-assemble in solution forming chiral structures, *L*- and *D*-ARGO7 may selectively interact with biological components.

To assess chiral recognition, sodium deoxycholate (NaDC), one of the components of bile salts, was chosen as a chiral model surface. In aqueous solution, NaDC showed three different pH dependent behaviour: homogeneous solution (pH>8), gel phase (pH 7-8) and aggregation/flocculation (pH<6.5).

Notwithstanding the ability of NaDC to self-assemble into different conformations at each pH interval, signs of chiral recognition were found in NaDC gel phase only. Conformational modifications were probed by circular dichroism spectroscopy: both *D*- and *L*-ARGO7 changed shape and magnitude of the CD pattern, whereas *D,L*-ARGO7 did not modify the CD spectra of NaDC. After 8 days, NaDC compact structure loosened, ended up being fluid and the CD pattern were completely modified due to NaDC and *D*- or *L*-ARGO7 interactions. Incoming SANS studies will probably highlight the mechanisms and dynamics of the chiral interactions in these polyelectrolyte-micelle systems.

(1) Luo, R.; Zhu, M.; Shen, X.; Li, S. *J. Catal.* **2015**, 331, 49.
(2) Quiñones, J. P.; Peniche, H.; Peniche, C. *Polymers.* **2018**, 10, *3*, 235.
(3) Manfredi, A.; Mauro, N.; Terenzi, A.; Alongi, J.; Lazzari, F.; Ganazzoli, F.; Raffaini, G.; Ranucci, E.; Ferruti, P. *ACS Macro Lett.* **2017**, *6*, 987.
(4) Lazzari, F.; Manfredi, A.; Alongi, J.; Mendichi, R.; Ganazzoli, F.; Raffaini, G.; Ferruti, P.; Ranucci, E. *Polymers* **2018**, *10*, 1261.