Fabiana Ciocchetti, 10/03/2022

Competition between chiral solvents and chiral monomers in the helical bias of supramolecular polymers

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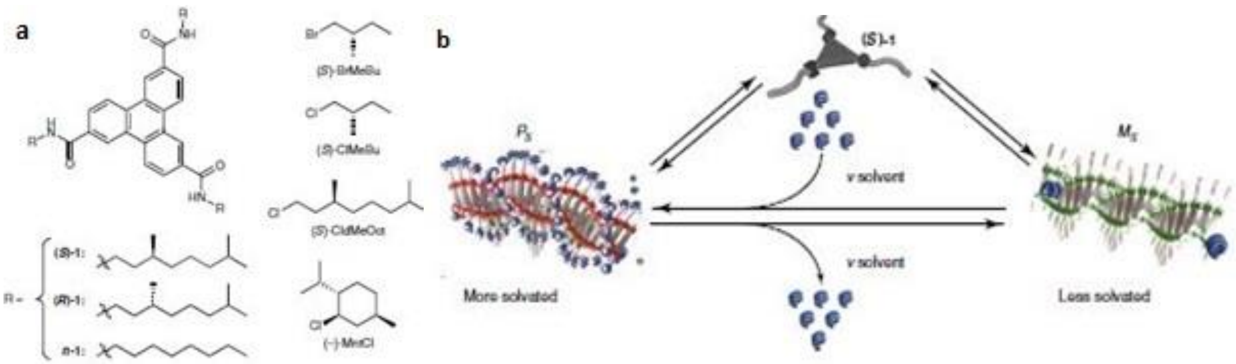

***Figure 1: Fig. 1 | TTAs form supramolecular polymers of left- and right-handed helicities in chlorinated solvents**. a, Structures of 1 and the optically active solvents used in this study. b, Cartoon depicting the role of solvent in the thermodynamic equilibrium between two competing helical aggregates for a single enantiomer.*

Who are the corresponding authors and what are their research areas?

Bert Meijer (Eindhoven University of Technology, The Netherlands), Anja R. A. Palmans (Eindhoven University of Technology, The Netherlands).

Meijer is a prolific author, sought-after academic lecturer and recipient of multiple awards in the fields of organic and polymer chemistry. His group conducts research in various fields associated to supramolecular polymers, materials and systems. The group focuses on different organic approaches to make nanomaterials and functional biomaterials, and they also explore novel concepts where excellent polymer properties are combined with dynamic supramolecular interactions.

Palmans joined the group of Prof. Meijer as a PhD student and obtained her doctorate in 1997. Since 2019 she is full professor in the field of Supramolecular Chemistry and Catalysis. The research of Anja Palmans develops along two lines. The first is aimed at mimicking multistep synthesis as it occurs in Nature. This allows for reduction of the need for purification procedures, and limits costs and waste in the production of complex organic molecules. The second line concerns the control of the dynamic behavior of supramolecular copolymerizations, especially the exchange dynamics that represent the equilibrium between the monomer and the polymer.

What is the main claim of the article?

Competition between the preferences induced by the stereocenters of the assembled monomers and those present in the solvent molecules results in unforeseen temperature-dependent solvation effects. When the energetic difference between the P- and M-helical aggregates is close to the energetic contribution of the chiral solvent, the dissymmetry introduced by the solvent can be amplified by the additive cooperativity of these effects along the polymer backbone. Majority-rules and 'sergeants-and-soldiers' experiments show that the sensitivity of the polymers to the difference in solvation can be exploited to overrule the helical preference of chiral monomers in copolymers.

How is it demonstrated?

By using a combination of spectroscopy, calorimetric experiments, and mathematical modelling, they showed that optically active solvents induced helical conformation in achiral monomers and that the chiral solvent can bias the copolymer helicity and thereby overrule the helical preference of the monomers.
With Variable-temperature circular dichroism spectroscopy they discovered that the enantiomers of the monomer present a helix inversion at certain temperature. The helix inversion temperature is independent from the concentration of monomers, but it's solvent dependent and in particular is caused by different solvation at different temperatures. They also showed that, below the inversion temperature the enantiomer S gives P helical aggregate and the enantiomer R give M helical aggregate. After preliminary studies about the interactions between chiral solvents and achiral monomers, chiral monomers and achiral solvents, they investigated the copolymerization. In the key experiment of copolymerization between achiral monomers and R-monomers, the initial addition of achiral monomers to the R ones, results in a gradual shift of the helix inversion temperature. When the concentration of achiral monomers is 60% the transition to M helix does not occur and only P helices are observed. They therefore conclude that chiral solvent and achiral monomer can cooperate to overrule the preference of the chiral monomer.

What are the typical experimental conditions?

Apolar chlorinated solvents, micromolar concentration range, temperature range from 20 to 100 °C.

Which are the key related papers?

1. Green, M. M., Khatri, C. & Peterson, N. C.. *J. Am. Chem. Soc.* **115**, 4941–4942 (1993).
2. Cantekin, S., de Greef, T. F. A. & Palmans, A. R. A. *Chem. Soc. Rev.* **41**, 6125–6137 (2012).