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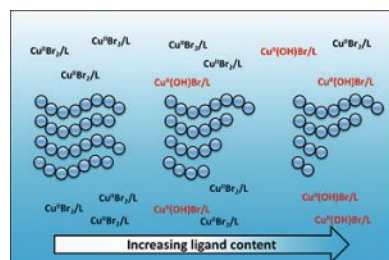
Controlling dispersity in aqueous atom transfer radical polymerization: rapid and quantitative synthesis of one-pot block copolymers

Hyun Suk Wang, Kostas Parkatzidis, Simon Harrison, Nghia P. Truong*, Athina Anastasaki*, *Chem. Sci.* **2021**, *12*, 14376, <https://doi.org/10.1039/d1sc04241f>
ETH Zurich

A rapid and quantitative method to tailor the dispersity (D) of both homo and block copolymers has been developed for aqueous atom transfer radical polymerization (ATRP). This is the first reported strategy that can control D in aqueous media since all the previous methods operate exclusively in organic solvents, giving slow polymerization rates, moderate conversions, and loss of initiator efficiency. This new method allows for very high monomer conversion (~99%) in a very short time (within 10 min) while maintaining very high end-group fidelity. Moreover, *in situ* diblock copolymers can be synthesized with absolute control over their dispersity, while maintaining monomodal molecular weight distributions.

Authors' comments:

“One of the highlights of this work is its simplicity: By just altering the ligand concentration we can control polymer dispersity in a variety of materials.”



Living supramolecular polymerization of fluorinated cyclohexanes

Oleksandr Shyshov, Shyamkumar Vadakket Haridas, Luca Pesce, Hhayuan Qi, Andrea Gardin, Davide Bochicchio, Ute Kaiser, Giovanni M. Pavan,* Max von Delius*, *Nat. Comm.* **2021**, *12*, 3134, <https://doi.org/10.1038/s41467-021-23370-y>
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Living supramolecular polymerization (LSP) is a method of interest for the synthesis of artificial macromolecules. Although the narrow monomer scope and fine-tuning LSP characteristics is a challenge, an innovative minimalistic molecular platform based on all-*cis*-1,2,3,4,5,6-hexafluorocyclohexane was developed. Its large dipole moment was used to thermodynamically drive the self-assembly of supramolecular polymers and to trap metastable monomeric states due to folding. The dormant monomers engage in a kinetically controlled polymerization upon addition of well-defined seeds initiating LSP. Results revealed self-assembled nanofibers of controlled length possessing a peculiar double helical structure. Overall, this study provides a new type of building block for LSP and demonstrates the versatility of the approach by the successful preparation of supramolecular A-B-A block copolymers with variable side chains.

Authors' comments:

“This work got really interesting, when PhD student Oleksandr Shyshov followed up on some really ‘funny’ behaviour of the monomer shown below. A Swiss-German-Italian collaboration was crucial to understand the structure of the nanofibers.”

