

PRF # 56721-ND7: Supramolecular Polymerization Approach to the Synthesis and Dynamic Self-Assembly and Disassembly of Rod-Coil Block Copolymers

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This proposal explores a new pathway to synthesizing conjugate-coil block copolymers using supramolecular polymerization for the conjugated block. Supramolecular polymerization is a powerful tool to build in a dynamic and reversible assembly/disassembly function into hierarchically assembled structures. This proposal is based on using a monodispersed coil block synthesized by anionic polymerization and end functionalized with quadruple hydrogen bonding units to grow a conjugated block by supramolecular polymerization of a difunctional monomer. However, very little is known about methods to control the dispersity of the chains which are inherently polydispersed, methods to characterize the molecular weights and dispersity, and if the confinement between the coil blocks affects the dynamics of supramolecular polymerization. We propose the synthesis of these conjugated-coil block copolymers and the study of their dynamic assembly/disassembly using dynamic light scattering, diffusion coefficient measurements and their morphology by Transmission Electron Microscopy, and X-ray scattering. By exploiting the temperature and concentration effects we propose to study the “self-correction” of chain lengths due to dynamic assembly/disassembly process induced by confinement of a monodispersed coil blocks. We have made significant progress towards the two goals in the proposal namely:

- 1) Synthesis of the conjugated-coil diblocks and triblocks using supramolecular polymerization of fluorene oligomers as the conjugated block.

Progress: Synthesis was completed last year. Mainly worked on the scaling up of the rod-monomers to have enough material for characterization this year.

- 2) Characterization of the molecular weight, dispersity and the supramolecular polymerization behavior of the conjugated block through a combination of studies.

Progress: See below.

Our main achievements in the last year towards these goals are:

- Initial studies on self-assembly or aggregation state of the rod-monomer in various solvents that either promote or inhibit H-bonding was undertaken (Figure 1).
 - These solvents were chloroform (promotes H-bonding), THF (disrupts H-bonding) and methyl cyclohexane (MCH which is a non-polar solvent). A solution of 0.1 mM UPy-FO-UPy in chloroform is already aggregated with a λ_{\max} of 384 nm which further blue shifts over a one week time frame as the H-aggregates grow. Upon addition of TFA H-bonding is disrupted to achieve isolated rod-monomer with a λ_{\max} of 397 nm.
 - In THF where the hydrogen bonding is inhibited enhanced monomeric peak at λ_{\max} of 396 nm, along with co-existence of H-aggregate (λ_{\max} of 384 nm) as well as J-aggregate (a λ_{\max} of 416 nm) is observed. This suggests that cooperative mechanism can be incited by proper choice of solvent.
 - In MCH, higher order H-aggregates (a λ_{\max} of 384 nm, 360nm) is observed along with a relatively small J-aggregate (a λ_{\max} of 416 nm). Upon addition of TFA to this solution the peak distribution becomes identical to that observed in THF. This suggests that the formation of H-aggregate is driven by hydrogen bonding between the UPy groups.
- To control the polymerization kinetics we explored the role of temperature during the assembly. By using hot solvent to dissolve the rod-monomer followed by slow cooling, equilibrium was achieved much faster and in a reproducible manner. At higher temperatures we believe we are essentially slowing down the nucleation step to achieve a more narrowly dispersed sample (data not shown here)

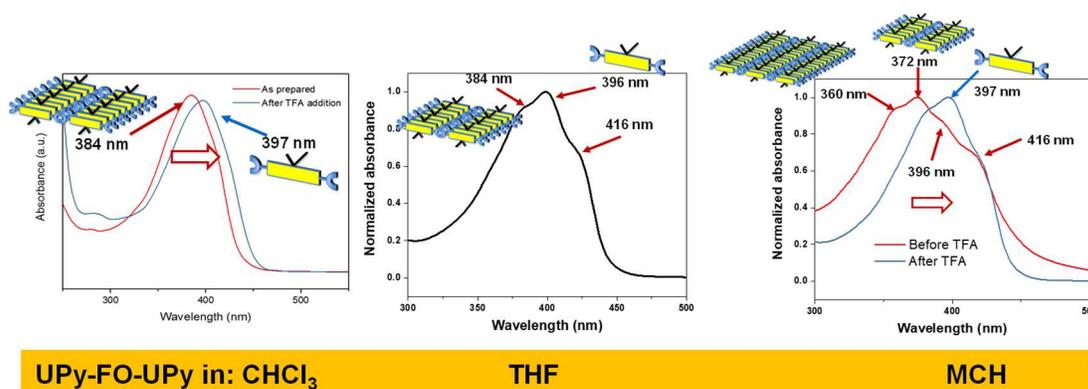
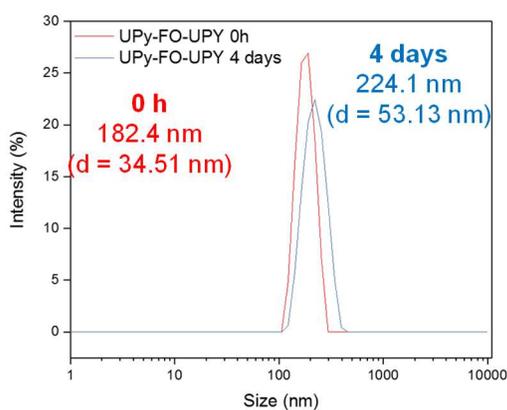


Figure 1: Aggregation behavior of the rod-monomer in chloroform, THF and MCH showing the role of hydrogen bonding on the formation of H-aggregates. The data above is UV-Vis spectroscopy based characterization of the aggregates and the monomeric form.

UPy-FO-UPy **without** PMMA-UPy



UPy-FO-UPy **with** PMMA-UPy

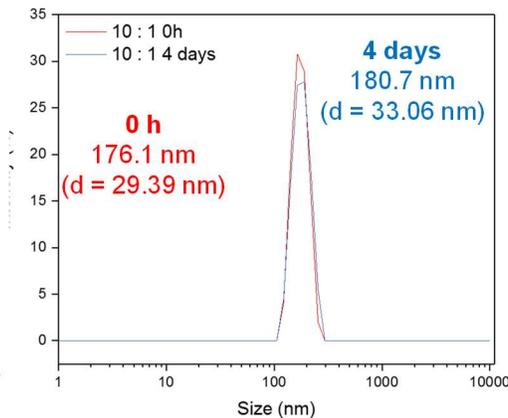


Figure 2: DLS studies on the rod monomer UPy-FO-UPy showing the stabilization of the size of the aggregates formed upon addition of the macromolecular chain stopper.

- Based on these optimized conditions of temperature, concentration and solvents we are currently studying the role of the macromolecular chain stopper. Initial results show that in fact the coil block seems to stabilize and reduce the H-aggregate formation by the rod-block. This indicates the potential for using the coil block to influence the morphology and size of the assembled structures (Figure 2).

Impact on Students: Students have learned not only the synthesis of these materials but the basics of supramolecular polymerization, solution characterization of the assembled structures and developing a theoretical understanding of the mechanistic aspects. These are all new techniques and tools for the PI's group.