Article 11 - Solvent-free autocatalytic supramolecular polymerization

Chen, Z.; Suzuki, Y.; Ayumi Imayoshi; Ji, X.; Kotagiri Venkata Rao; Omata, Y.; Miyajima, D.; Sato, E.; Atsuko Nihonyanagi; Aida, T. Solvent-Free Autocatalytic Supramolecular Polymerization. Nature Materials 2021, 21 (2), 253–261. https://doi.org/10.1038/s41563-021-01122-z.

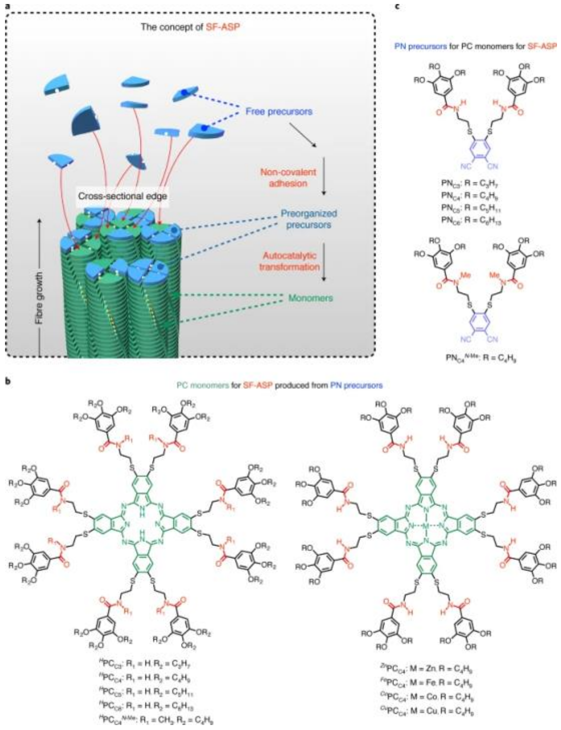

Figure 1:

a. The schematic shows how the solvent-free autocatalytic supramolecular polymerization (SF-ASP) process works. The target product, once formed, starts the polymerization process via noncovalent interactions, creating single-crystalline fibers. These fibers help organize the precursor molecules for the reaction, speeding up the chemical transformation autocatalytically. Fiber growth slows down terminal coupling due to limited diffusion in the absence of solvents.

b. The chemical structures of phthalocyanine (HPCCn) derivatives and their metal complexes (MPCC4) with Zn, Fe, Co, and Cu are shown. These are produced via SF-ASP using the precursor PNC4.

c. The chemical structures of fan-shaped dithioalkylphthalonitrile (PNCn) derivatives are shown. These serve as monomer precursors for the SF-ASP process.

Synopsis:

The 2021 study Solvent-Free Autocatalytic Supramolecular Polymerization by Chen et al. presents an innovative approach to creating polymers without the need for solvents. Traditional methods of polymerization often rely on solvents to dissolve reactants and facilitate chemical reactions. However, using solvents can lead to environmental pollution and requires energy-intensive purification processes to remove leftover solvents. To address these challenges, this study introduces a method that does not require solvents, offering a greener, more sustainable way to produce high-performance polymers.

The researchers focused on a specific chemical compound known as phthalonitrile, which was modified to include hydrogen-bonding side chains. These modifications allowed the compound to transform phthalocyanine, a large, stable molecule with a unique ring structure. What sets this process apart is its autocatalytic nature, meaning that as phthalocyanine molecules are created, they serve as templates to speed up the creation of more phthalocyanine. In other words, the newly formed molecules help guide the process, leading to a fast and efficient buildup of the polymer without the need for external catalysts or solvents.

The reaction takes place under solvent-free conditions, and the researchers achieved an impressive yield of over 80%. This high yield demonstrates the effectiveness of the method in producing the desired material. The resulting phthalocyanine units naturally arrange themselves into supramolecular polymers, which are held together by non-covalent interactions, such as hydrogen bonding. These interactions allow the polymers to form well-ordered crystalline fibers. Interestingly, these fibers have mechanical properties similar to conventional polymers like poly(alkyl methacrylates), which are commonly used in industrial applications.

A key figure in the article helps explain the process visually. The first part of the figure shows the chemical structure of the modified phthalonitrile monomer, which includes the hydrogen-bonding side chains. The next part illustrates how this monomer transforms into phthalocyanine molecules, with the product serving as a template for further transformation. Finally, the figure shows how the phthalocyanine molecules organize into supramolecular polymers, forming structured crystalline fibers.

This solvent-free method of polymerization has significant implications for sustainable materials science. By eliminating the need for solvents, the process reduces environmental impact, making it more eco-friendly and cost-effective. Furthermore, because the process is self-driving—thanks to its autocatalytic nature—it is simpler and requires fewer external chemicals and catalysts. The resulting supramolecular polymers have desirable mechanical properties, making them suitable for a variety of applications, such as in electronics, coatings, and nanotechnology.

Additionally, the study opens up the possibility of creating more complex polymers in the future. For instance, the researchers suggest that by introducing different monomers at specific stages of the reaction, they could create block copolymers—polymers made from two or more different types of monomers, which could lead to even more specialized materials. This flexibility in polymer design could lead to new materials with tailored properties for specific uses.

In conclusion, Chen et al.'s research presents a significant advancement in the field of polymer chemistry. By demonstrating a solvent-free, autocatalytic method for creating supramolecular polymers, the study offers a more sustainable and efficient way to produce high-performance materials. This method not only reduces environmental impact but also provides a platform for the development of advanced polymers in a variety of industries, making it a key step forward in the pursuit of greener, more adaptable materials.