



# Comment

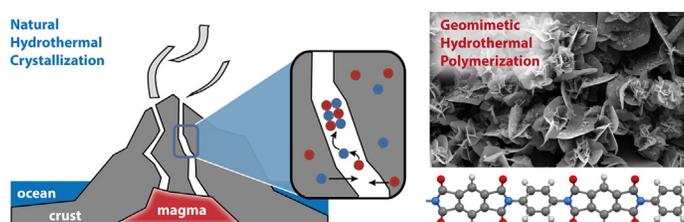
## Creating geomimetic polymers

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### From hydrothermal veins to highly crystalline polymers

Given the importance of silicon microelectronics and computers, the modern era is often referred to as the 'Silicon Age'. This overlooks, however, another crucial class of materials: polymers. In the form of proteins, polymers constitute the very building blocks of life. Artificial polymers, on the other hand, govern many aspects of our everyday life, most prominently in the form of plastic. Our shelves at home, the toys and CDs they are filled with, the floor they stand on and the paint that makes them shine: everything is made out of polymers. As literally every electronic product of our Silicon Age comes wrapped in a shell of polymers, one may in fact say we are living in the 'Plastic Age' in equal measure. Maybe less prominent than these commodity polymers, but by no means less important, are so-called high performance polymers (HPPs). HPPs are organic polymers with outstanding properties, such as high thermal stability and exceptional mechanical performance at very low weight [1]. Initially designed for high-end applications in space ships or power plants, HPPs are steadily progressing into our daily lives, where they replace, for example, various forms of metals. Polyimides are one of the most important classes of HPPs. Their applications range from microelectronics, for example as dielectrics in circuit boards [2], to applications in aeronautics: the sail of the Japanese solar power spacecraft IKAROS, for instance, is a polyimide sheet of 20 m in diameter, yet only 7.5  $\mu\text{m}$  in thickness [3]. The molecular origin of such exceptional properties is the stiffness of their monomeric units: Aromatic rings and other stiff moieties increase the mechanical



Natural hydrothermal crystallization vs. geomimetic hydrothermal polymerization.

performance of polyimides, their glass transition temperature and inertness towards solvents. Unfortunately, these outstanding features come at a high cost: classical synthetic protocols involve high-boiling solvents (e.g. *m*-cresol), toxic catalysts (e.g. isoquinoline) and reaction temperatures of up to 250 °C [1]. Crystallinity is a highly desired feature for these materials, as it strongly enhances several properties, for instance stability. To increase crystallinity, polyimides are typically post-cured at up to 400 °C, which still only yields semicrystalline products at best [4].

A recent discovery in the field of polyimide synthesis provides a solution to yielding high crystallinity and at the same time overcoming the need for harsh polymerization conditions: *the hydrothermal polymerization* (HTP) [5]. The approach is geomimetic, that is inspired by natural ore formation processes taking place in the earth's crust, so-called hydrothermal crystallization. The process takes place in crustal veins that are filled with high-temperature water (see figure, left). As these veins are delimited with solid rock material not giving away to water, autogenous pressures arise. Increased temperature and pressure create a highly dynamic system, in which a plethora of highly crystalline inorganic minerals form. Natural zeolites, for instance, are exclusively of hydrothermal origin. Zeolites form by condensation of silicic acid species, where a stoichiometric amount of water is liberated upon each addition step. Strikingly, polyimides also form by condensation with H<sub>2</sub>O elimination. From a physicochemical point of view, the hydrothermal regime is characterized by  $T > 100\text{ }^\circ\text{C}$  and  $p > 1\text{ bar}$ . To mimic these conditions in the lab, the continuous phase H<sub>2</sub>O and the starting compounds (monomers in the case of HTP) are enclosed in an autoclave and heated to the desired reaction

temperature above 100 °C. Since the autoclave is a closed vessel, autogenous pressures arise: one operates precisely on the liquid–vapor line of water, and thus in a regime where liquid and gaseous H<sub>2</sub>O coexist. The monomers can successively dissolve and polymerize under these conditions and yield highly crystalline products by polymerization in solution [5]. The polymer poly(*p*-phenylene pyromellitimide) that was synthesized *via* HTP possessed quantitative crystallinity without any amorphous fraction. This outstanding crystallinity enabled the determination of the polymer's crystal structure and resulted in highly ordered flower-shaped morphologies (see figure, right).

While the applicability of HTP to other polymer classes is yet to be demonstrated, the potential of hydrothermal polyimide synthesis is certainly enormous, in particular in combination with other materials. Various materials can be synthesized hydrothermally, ranging from inorganic compounds, such as zeolites or numerous metal oxides [6], to carbon materials [7]. A combination of HTP with the hydrothermal synthesis of such materials might

yield a wide range of hybrid materials *via* one-pot reactions. Such approaches do not only minimize energy consumption, but they are also fully 'green' as they are carried out solely in water. In this respect, HTP kills two birds with one stone: obtaining polymer materials of increased performance, and doing so in nothing but hot water.

#### Further reading

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