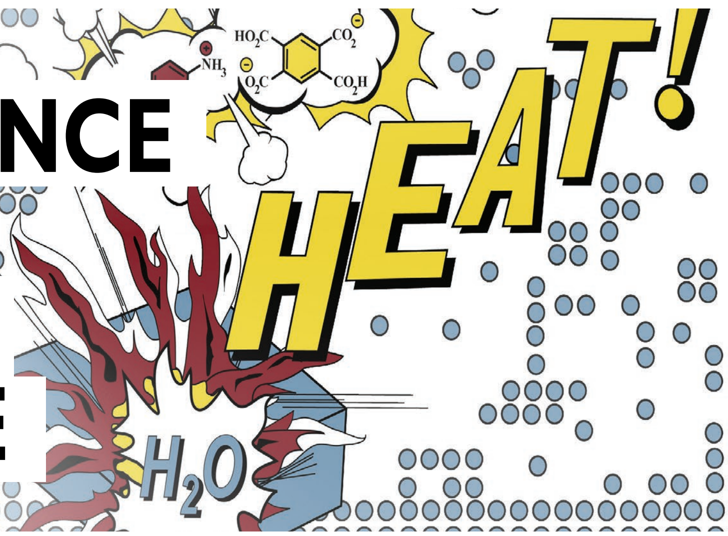
HIGH-PERFORMANCE POLYIMIDE PARTICLES WITH ANGULAR SHAPE

Poliimidas de alto rendimiento con forma angular



Alonso Cerrón-Infantes and Miriam M. Unterlass

High-performance polymers (HPPs) play an important role in modern technology. Many efforts aim to develop cost-effective pathways to synthesize polymers without causing any harm to health and the environment. Polyimides (PIs) belong to the class of HPPs and they show outstanding features e.g. high-temperature stability, resistance to aggressive chemicals and radiation, as well as insulating properties. PI synthesis, however, present yet major challenges. We herein present an alternative approach to PIs of intriguing shape and of impressive size.

Los polímeros de alto rendimiento (HPP) desempeñan un rol importante en la actualidad. El desarrollo de métodos más económicos para sintetizar estos polímeros minimizando el impacto tanto en la salud como en el medio ambiente es una prioridad. Las poliimidas (PI) pertenecen al grupo de los HPP y presentan características excepcionales como una gran estabilidad ante elevadas temperaturas, alta resistencia a los productos químicos agresivos y a la radiación, así como propiedades de aislamiento. Sin embargo, la síntesis de las PI presenta aún retos importantes. En este artículo presentamos un enfoque alternativo para sintetizar PI de forma y tamaño impresionante.

Keywords: Polyimides, monomer salts, shape-anisotropic particles, solid-state polycondensation, gel-crystallization.

Palabras claves: Poliimidas, sal de monómeros, partículas de forma anisotrópica, policondensación en estado sólido, cristalización en gel.

Polymers are omnipresent in our lives. These “plastics”, in layman’s terms, surround us in every aspect of modern live, from packaging to transportation or electronic devices. Chemically, they are composed of many repetitive covalently bonded smaller subunits, so-called monomeric units.

Less visible, but by no means less important than commodity polymers are the high-performance polymers (HPPs), due to their extreme chemical and thermal stability as well as their light weight. HPPs find applications in different areas among which are aeronautics, automotive and even microelectronics; however, their design depends principally on the range of functions of the final product. Most HPPs are produced *via* polycondensation reactions (*i.e.* step-growth polymerizations accompanied by the liberation of a low molecular weight byproduct upon each monomer addition), where stoichiometry plays a crucial role to attain high average molecular weights. HPP production is mostly carried out using high process temperatures, harsh and hazardous solvents, catalysts and long reaction times. Overall these processes are hence extremely expensive.

Polyimides (PIs) are amongst the toughest HPPs on the market, because aside high-temperature stability, they feature extraordinary mechanical properties, resistance against aggressive chemicals and radiation, as well as insulating properties. PIs enclose a vast field of applications, for example as part of gas separation membranes, as insulating materials on printed circuit boards of cameras (**Figure 1a**), and even in space ships and satellites, like the James Webb Telescope (**Figure 1b**) or the IKAROS solar sail (**Figure 1c**).

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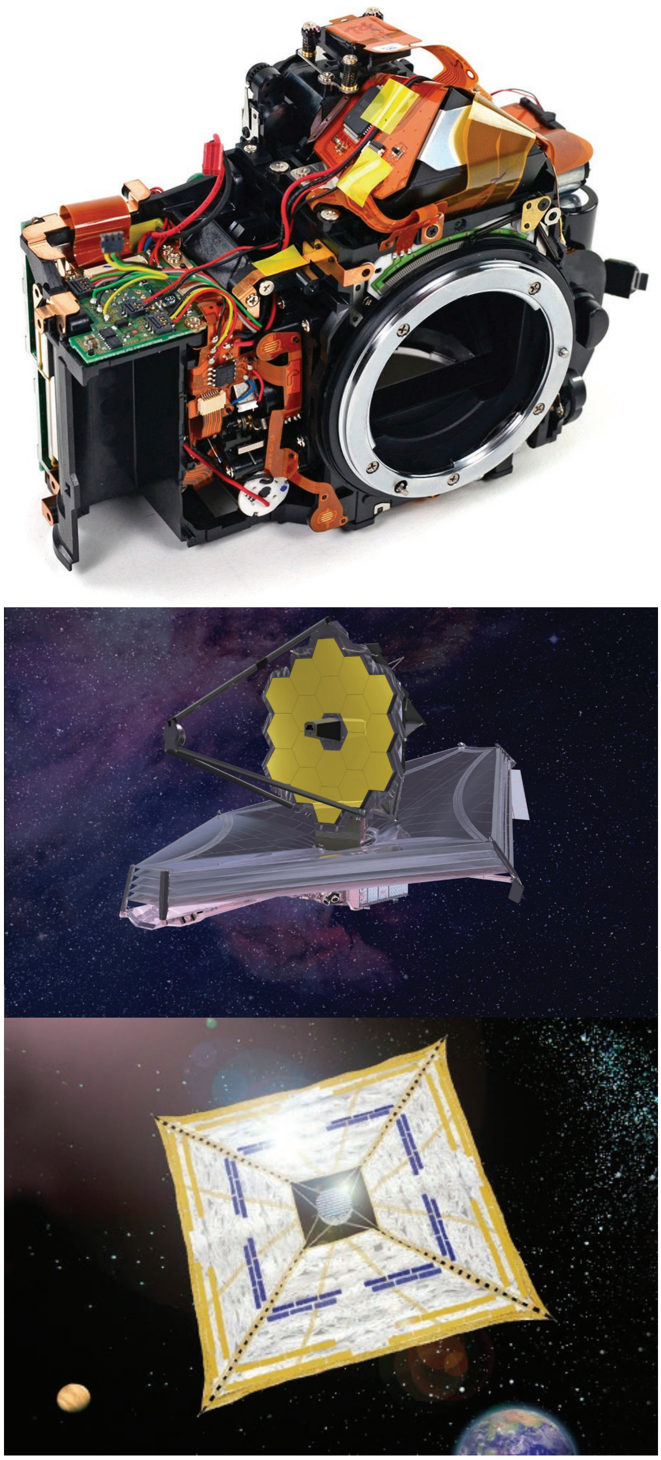

Figure 1. Applications of polyimides. **(1a, top)** Photograph of a Nikon D600 teared-down camera, where PIs are used as insulating support of flexible circuits (orange ribbons) throughout the device. http://www.cameraegg.org/tag/ifixit/ (🖳). **(1b, centre)** James Webb Telescope, NASA's large infrared telescope for observatory purposes. The sunshield, seen in yellow colour, is covered with a coating layer film of polyimide, aluminium and doped-silicon in order to reflect the sun back to the space. http://jwst.nasa.gov/images.html (🖳). **(1c, down)** IKAROS (**I**nterplanetary **K**ite-craft **A**ccelerated by **R**adiation **O**f the **S**un) is a project of the Japan aerospace exploration agency (JAXA). The main goal of IKAROS is the evaluation of the solar power sails employing photon propulsion and thin film solar power generation for interplanetary cruise. The solar sail is made of the polyimide Kapton™ and has the extraordinary dimensions of 20m (diagonal) x 7.5 μm. http://www.jspec.jaxa.jp/e/activity/ikaros.html (🖳).

How are polyimides prepared?

To date, the most representative PI synthesis involves a two-step polymerization of the co-monomers diamine (an organic base) and dianhydride (anhydrides of organic acids). As depicted in **Figure 2**, the first step takes place in hazardous solvents (*e.g.* N-methyl-pyrrolidone, NMP) and toxic catalysts (*e.g.* Isoquinoline) leading to a soluble intermediate poly(amic acid), PAA. PAAs are indeed useful, as they are still processable and can be manufactured into films, which are the common form of PIs. The main representative of PI film is Kapton™ developed by DuPont in the late 1960s.

The second step requires long reaction times and high reaction temperatures, where water is eliminated as PIs are formed in a so-called dehydration or condensation reaction. Since solvents are expensive and toxicity is nowadays considered a major drawback, current research on polyimides aims at replacing these harsh and costly conditions, while – at best – even generating better materials properties. Also, PAAs can be processed into films, but other more advanced forms are still inaccessible.

In general small plastic polymer particles are obtained as spherical objects by the vast majority of polymerization techniques. The reason for that is that a freshly formed polymer is physicochemically different from the solution and thus tries to minimize its interfacial area with the surrounding. However, roundish particles are poorly suited for many applications. Particle-containing liquids are extensively used as paints and protective coatings. The geometric shape of the particles then determines how the particles are arranged and move within the liquid. Many of such dispersions do not dry uniformly because an unfavourable current is produced during evaporation, which transports the particles in a particular direction. Clearly, one would prefer paints to dry homogeneously. Nonetheless, the few existing approaches to non-spherical homopolymer particles are limited to polymerizations through photolithographic masks and deformation of spherical particles.[1,2]

First steps towards a new pathway to synthetize polyimides

As an alternative to the classical synthesis, PIs are as well produced as non-spherical polymer particles *via* gel crystallization and its subsequent solid-state polymerization (SSP). Here, the co-monomers diamine and dianhydride are first reacted to a so-called monomer salt (**Figure 3**).

1. S. Sacanna y D. J. Pine, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 96 – 105.

2. K. J. Lee, *y col.*, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 195 – 202.

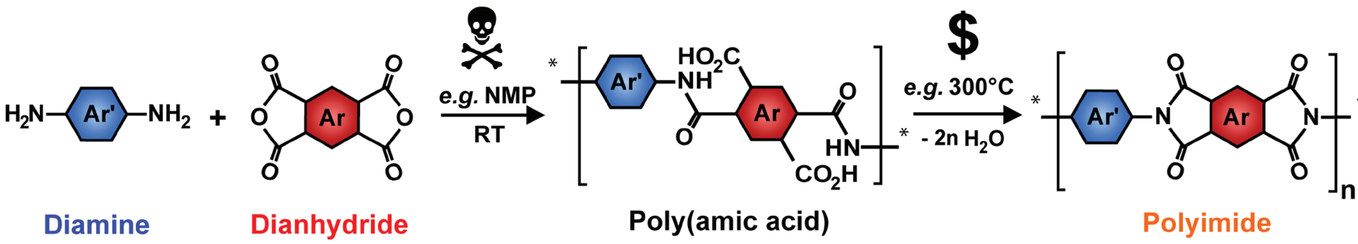

Figure 2. Classical polyimide synthesis: The typical co-monomers for polyimides, diamines and dianhydrides are first reacted to poly(amic acids), PAAs. This step takes places at room temperature (RT) in toxic, high-boiling solvents such as N-methyl-pyrrolidone (NMP). PAAs are still soluble, and can thus be processed into *e.g.* films. The PAA object is then thermally transformed to the polyimide at high temperatures (>300 °C) by a dehydration reaction, a so-called condensation . (Ar = aromatic ring).

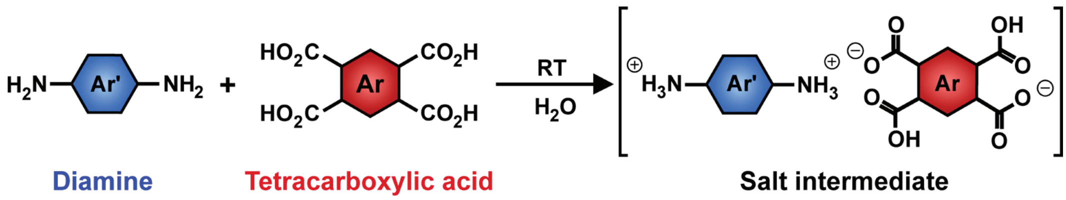

Figure 3. Monomer salts: Diamine and tetracarboxylic acid (the hydrolyzed form of a dianhydride) react in an acid-base reaction to a monomer salt species that is basically a diammonium dicarboxylate dicarboxylic acid.

This is possible due to the acid (dianhydride) and base (diamine) characters of the co-monomers.[3,4] These monomer salts present several advantages: first, they provide higher stability than the co-monomers (organic diamines are for instance prone to oxidation), and second, they intrinsically provide a perfect 1:1 stoichiometry of the co-monomers.

If the two co-monomers were brought in contact in solution, they would combine in a rather disorganized manner and a polycrystalline salt would form. However, we could show that if the reaction was carried out in a gel of particular viscosity, the diffusion of the molecules would slow down, therefore decelerating the reaction. Furthermore, the molecules 'have the time' to slowly produce a highly ordered salt, which results in high-quality single crystals of anisotropic (*i.e.* non-spherical) shape of impressive size as can be seen in **Figure 4**.

This groundbreaking method serves as an alternative to the classical synthesis, because it allows us to produce anisotropic polymers *via* gel crystallization of the two starting co-monomers and further its solid-state polymerization. In order to accomplish this goal, it is indispensable that the salt intermediates are heated above 200° C, after which we end up with identical copies without any physical changes: neither dissolution nor melting.

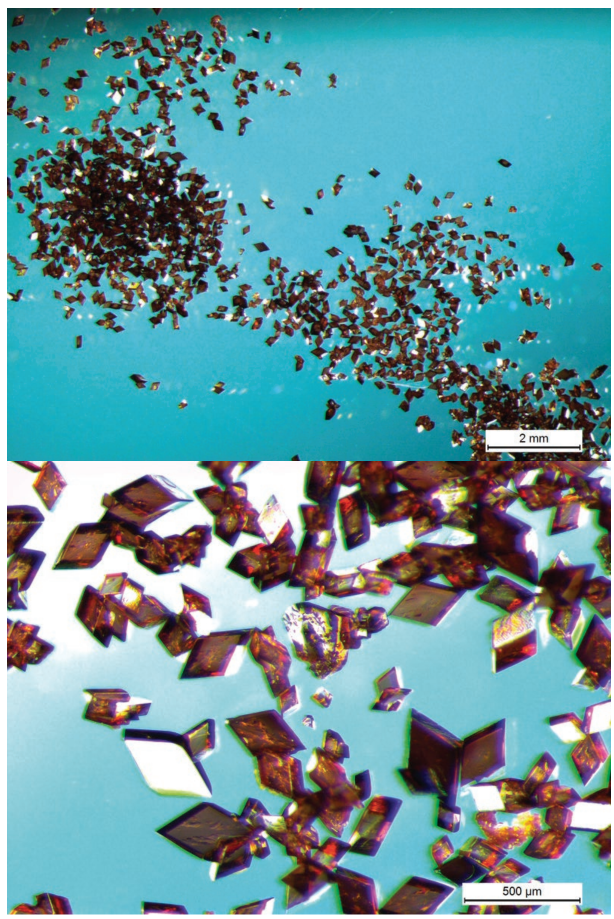

Figure 4. Salt intermediates of rhombohedral shape: optical microscopy images illustrate the high number of high-quality single crystals of angular shape that can be obtained by gel crystallization.[5]

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4. M. M. Unterlass *y col.*, *Chem. Commun.* **2014**, *50*, 430 – 432.

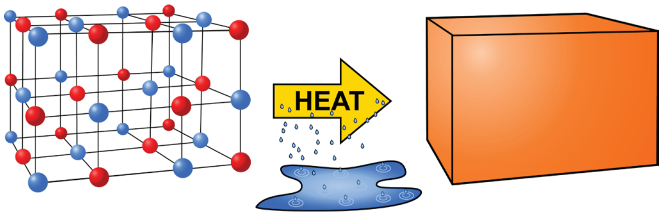

Figure 5. Illustration of polyimide formation by thermal solid-state reaction of monomer salts accompanied by the elimination of water.

As it can be seen in **Figure 5**, water is eliminated and the salt intermediate reacts towards polyimides without any change on their morphology or dimension. The anisotropic shape of the original salt is thus retained and rhombohedral PI particles are formed as 'copies' of the initial crystals of the monomeric salt. The final PIs show a particular yellow-orange colour, which is typical for PIs.

Figure 6 depicts the reaction equation of PI formation *via* solid-state polymerization (SSP) with water as the only byproduct. The resulting high-performance polymer withstands almost any solvent and remains stable up to 700° C.

What have we accomplished and what is to be done?

Our results are the first example of the preparation of polyimide particles of defined, angular shape. Moreover, as they are prepared without any toxic solvents, the preparation pathway itself is less harmful than classical techniques *via* PAAs.

Since the monomer salt crystals were of impressive size and quality, we were able to perform profound mechanistic analysis of the transformation by X-ray diffraction[5] – a result that was only possible because the salt crystals were prepared by gel crystallization.

Such PI particles are highly promising as particulate additives for advanced coatings or high-performance formulations. We are currently working on implementing these particles for such advanced applications.

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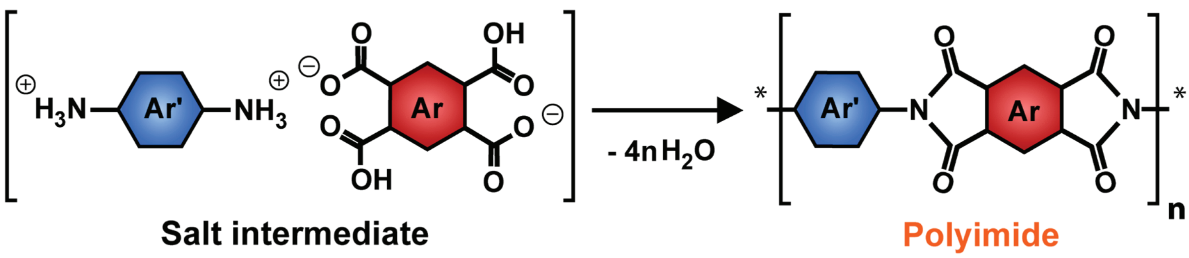

Figure 6. Reaction equation of the solid-state polycondensation (SSP) of the monomer salts.

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ESSENTIAL LITERATURE

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