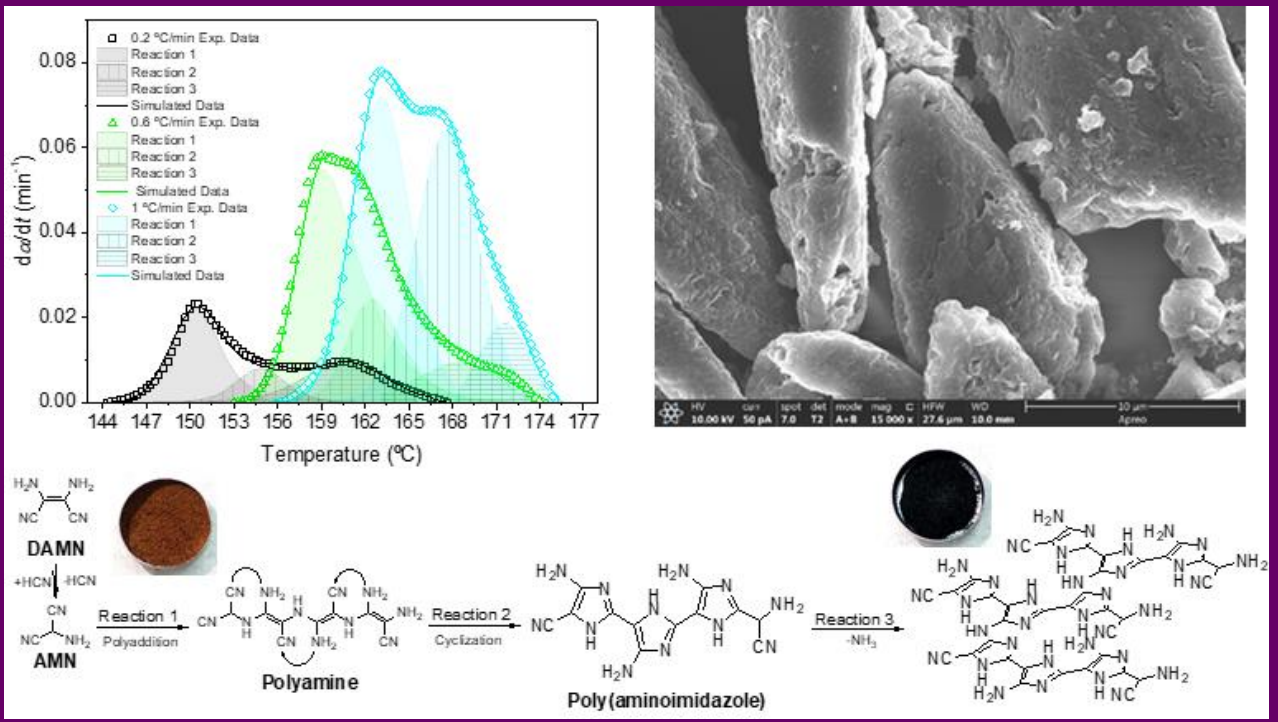
Solid-state polymerization of diaminomaleonitrile: Toward a new generation of conjugated functional materials



The solid-state polymerization (SSP) of organic molecules to form two dimensional (2D) materials remains a challenge, especially when these reactions are performed in one pot using a single reagent. As will be shown, the SSP of the HCN tetramer diaminomaleonitrile (DAMN) may be an excellent example of these reactions. Dynamic experiments by differential scanning calorimetry (DSC) allow the analysis of the thermally initiated bulk polymerization of DAMN. Under nonisothermal measurements at low heating rates, a multiple-step polymerization reaction takes place. The SSP of DAMN is highly efficient, possibly due to the autocatalytic nature of its kinetics, which are consistent with the two-parameter Šesták-Berggren (SB) model and describe the three stages found in its complicated mechanism, confirmed also from an analysis of the variation in the apparent activation energy with the conversion degree. Relevant mechanistic aspects, such as the dehydrocyanation and deamination processes during SSP, are extracted by thermogravimetry-mass spectrometry (TG-MS). Moreover, some structural and morphological properties of these materials are characterized by Fourier-transform infrared (FTIR) spectroscopy and microscopy. All this information allows us to propose hypothetical pathways for the production of a complex conjugated system, predominantly constituted by a 2D macrostructure based on imidazole rings. This work opens up new possibilities for the synthesis of functional poly(heterocycle) systems, expanding our view of a plausible prebiotic chemical reaction space and providing the foundation for systematic studies of the structure-property relationships of novel HCN-derived polymers, which are currently of great interest in the fields of materials and surface science.

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