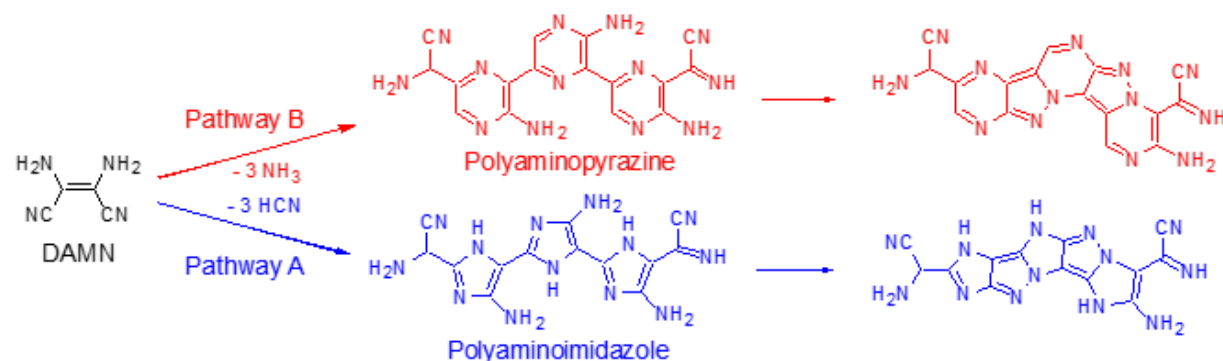
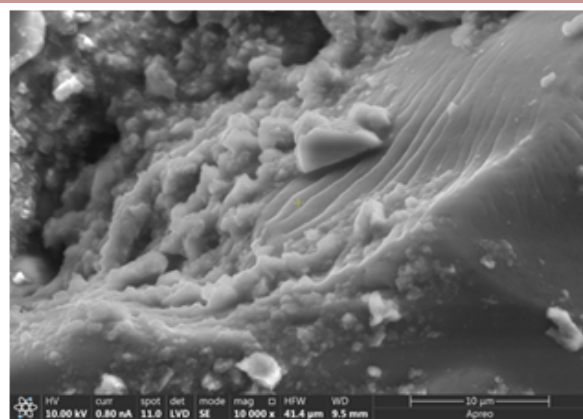
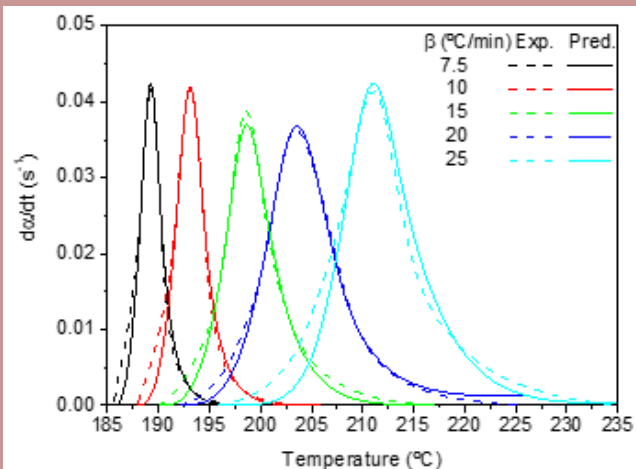


Highly efficient melt polymerization of diaminomaleonitrile



HCN polymers are of great interest in research on the origin of life and, currently, in materials science because they have shown potential for the design of electrical devices, (photo)catalysts and biomedicine. Herein, calorimetric measurements have successfully described the bulk polymerization of HCN tetramer, diaminomaleonitrile (DAMN). Two series of nonisothermal experiments were carried out by differential scanning calorimetry (DSC), and low-heating rate (β) the thermograms ($\beta \leq 5$ °C/min) indicated that the polymerization is initiated at temperatures lower than the DAMN meltingpoint, ~ 180 °C; while higher heating rates results in a rapid polymerization reaction, which occurs entirely in the liquid phase. The DSC data were analysed using model-free linear iso-conversional methods to estimate kinetic parameters, such as activation energy, and a suitable kinetic model was proposed for these thermal polymerizations in the melt. A preliminary structural and morphological characterization by means of Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) was also completed. This study demonstrated the autocatalytic, highly efficient and straightforward character of this stimulated thermal polymerization of DAMN and, to the best of our knowledge, describes for the first time a systematic and extended kinetic analysis to gain mechanistic insights into this process. The latter was done through the help of simultaneous thermogravimetry (TG)-DSC and in situ mass spectrometry (MS) technique to investigate the gas products generated during these melt polymerizations. These analyses revealed that deamination and dehydrocyanation processes are two relevant reactions involved in DAMN polymerization mechanism.