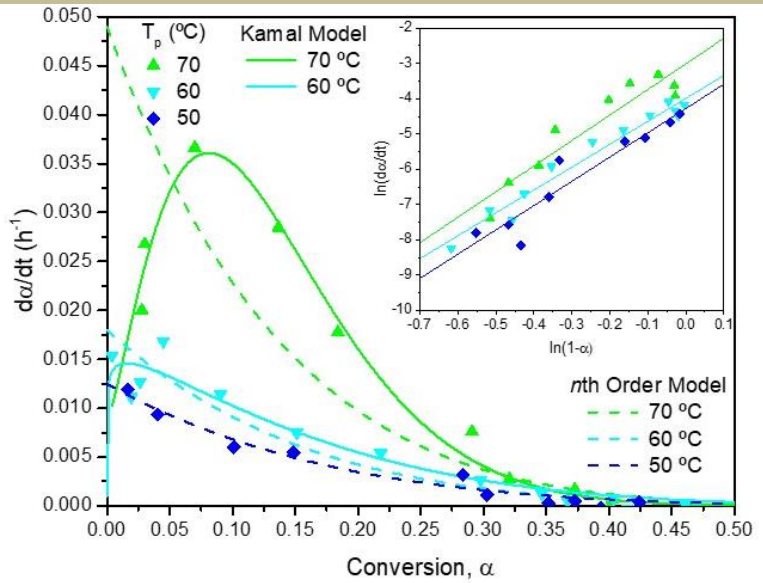
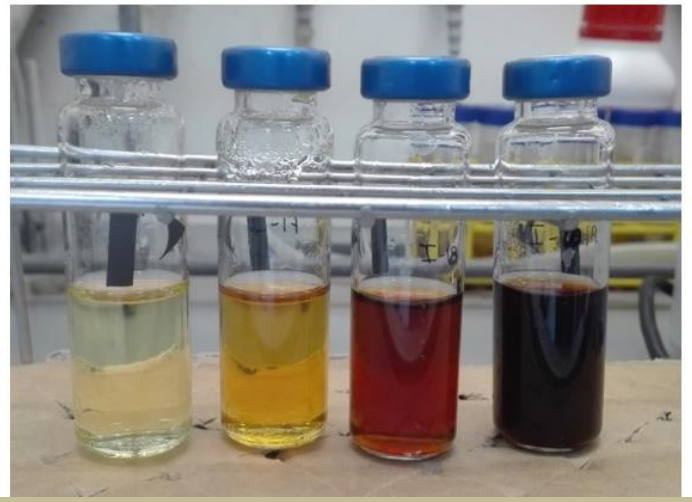
Temperature effect on aqueous NH_4CN polymerization: Relationship between kinetic behaviour and structural properties





Herein, a kinetic analysis for aqueous NH_4CN polymerizations is presented, which is consistent with an autocatalytic model when polymerizations are performed at relatively high temperatures, 80–90 °C. Further experiments at lower polymerization temperatures, approximately 50 °C, have demonstrated that this relevant prebiotic reaction follows *n*th-order kinetics rather than an autocatalytic mechanism. In addition, the sol fractions of these precipitation polymerizations have been evaluated by UV–Vis measurements, which also show a mechanistic shift with the reaction temperature. This change in the kinetic behaviour led to the proposal of a simple empirical methodology to describe both chemical- and diffusion-controlled regions. Despite the simplicity of the approach based on the Hill equation, fundamental kinetic parameters, such as the activation energy, can be determined in the diffusion-free zone. These results motivated a systematic structural characterization study of the respective insoluble polymers by means of elemental analysis, FT-IR and NMR spectroscopies and XRD. All these kinetic and structural analyses confirmed that the temperature has a significant effect on the polymerization kinetic of the system, on the macrostructural features and properties of the HCN-based polymers, and presumably also on the polymerization pathways. These data increase our knowledge about the chemistry of this particular family of HCN polymers, which is currently of interest both in the field of materials science and in prebiotic chemistry and astrobiology.

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