Reaction Kinetic Modeling of the Synthesis of Polymers of Intrinsic Microporosity

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Introduction

- **P**olymers of **I**ntrinsic **M**icroporosity (PIM) is a class of polymers with a high microporosity due to their highly rigid ladder structure
- PIM-1 was first synthesized by polycondensation more than 20 years ago. [1]
- While the synthesis procedure was optimized in many studies since than, it was never the investigated by using reaction kinetic modeling.
- This study presents a reaction kinetic modeling approach (with the software PREDICI) in combination with experimental methods such as reaction calorimetry, GPC and MALDI-TOF. [2]

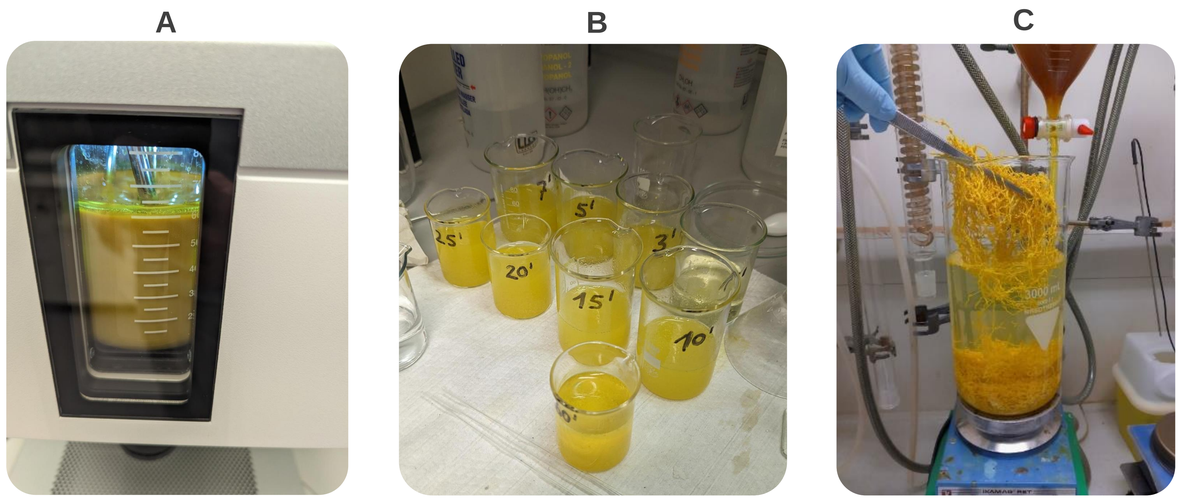


Figure 1: Synthesis in the calorimeter (A), samples taken after precipitation in water (B), and final product (C).

The synthesis process consists of two major steps, the activation of the spirobisendane comonomer $P_{AA}(1)$ with K_2CO_3 (deprotonation) followed by the typical polycondensation reactions steps with 2,3,5,6-tetrafluoroterephtalonitrile (TFTPN) $P_{BB}(1)$ forming the growing PIM-1 polymer P_{AB} (n). (Fig. 2)

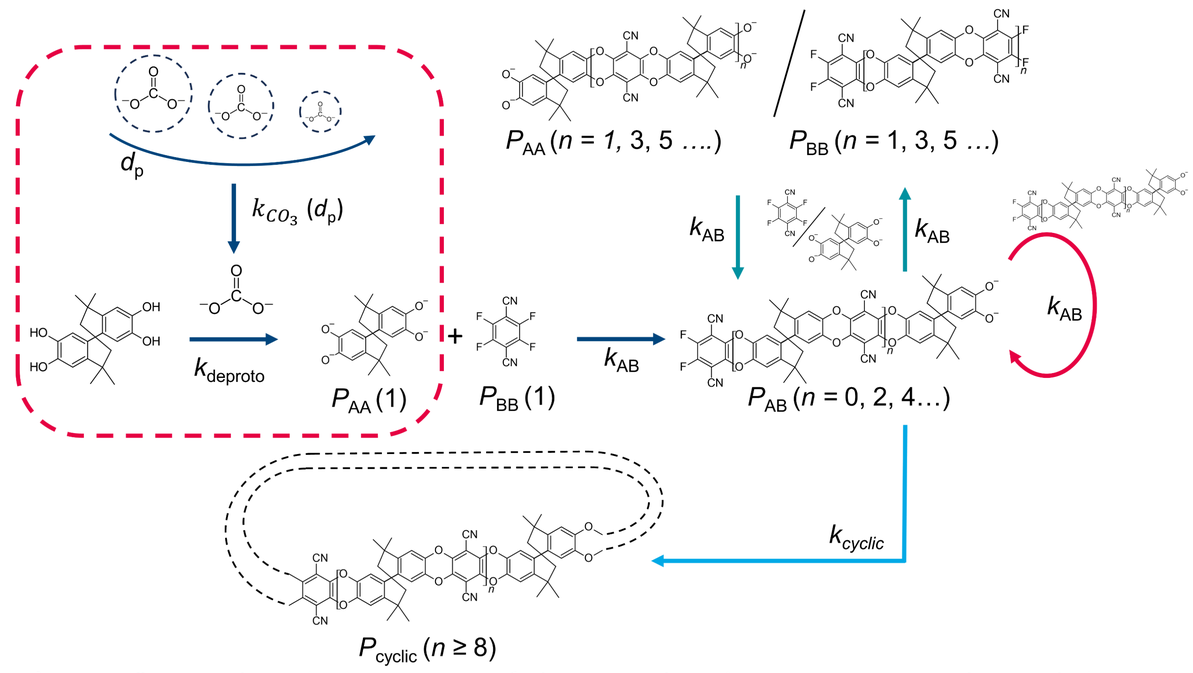


Figure 2: Mechanistic steps of the synthesis process and model structure. [2]

Model Performance

- **Model includes the deprotonation step and the polycondensation kinetics including the formation of cyclic species.**
- **Parameter estimation of two reactions (Fig. 3A) coefficients [2]:**
  - **$k_{AB} = 1.05 \cdot 10^{-2}$ L mol^{-1} s^{-1}**
  - **$k_{cyclic} = 8.00 \cdot 10^{-2}$ s^{-1}**
- **The model can predict the evolution of the molar mass distribution over the course of the reaction (Fig. 3B).**

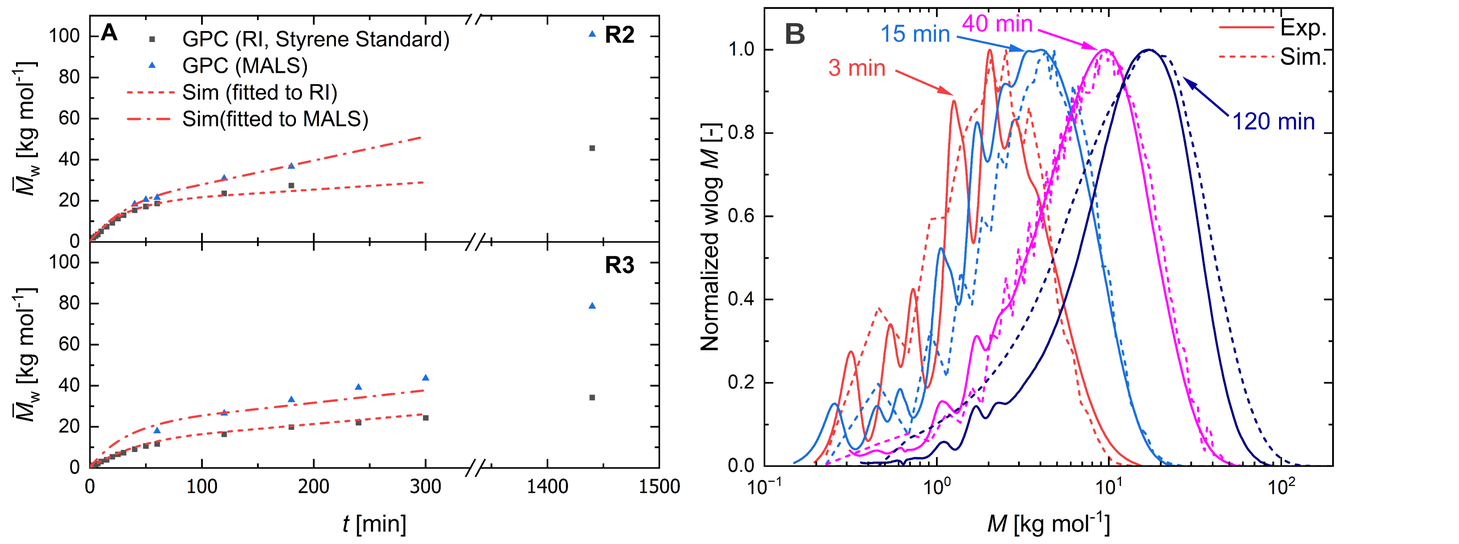
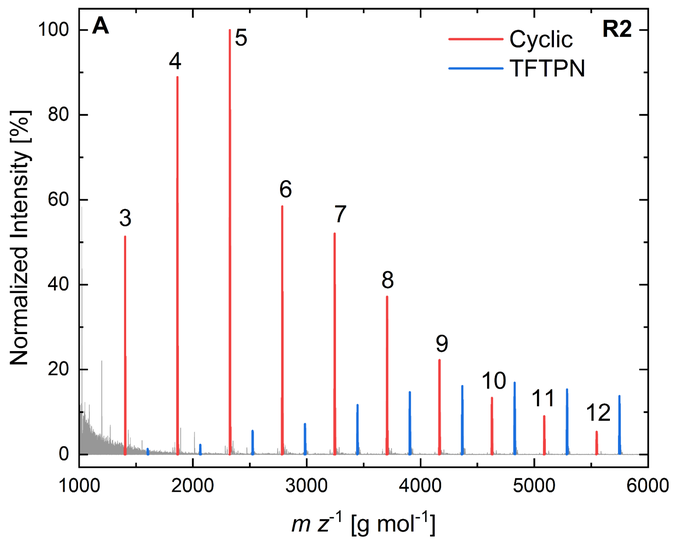


Figure 3: Model performance. (A) Experimental and simulated evolution of $\bar{M}_W$. (B) Experimental and simulated evolution of the full molar mass distribution of R2. [2]

Analysis of the Polymer Formation



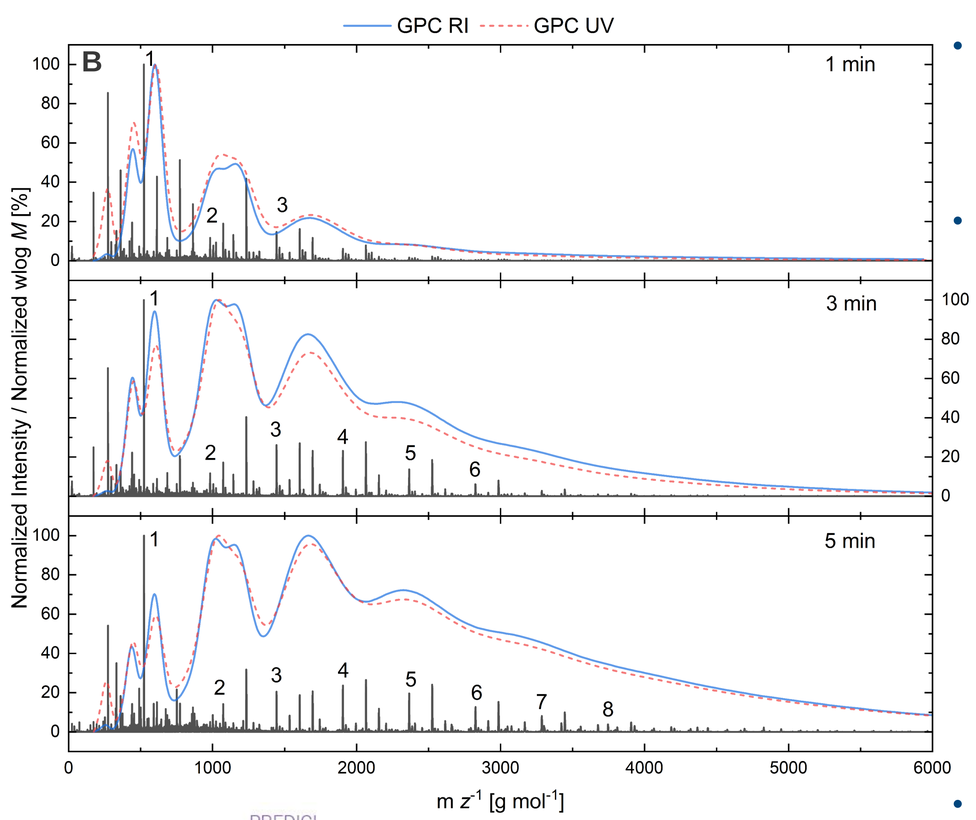
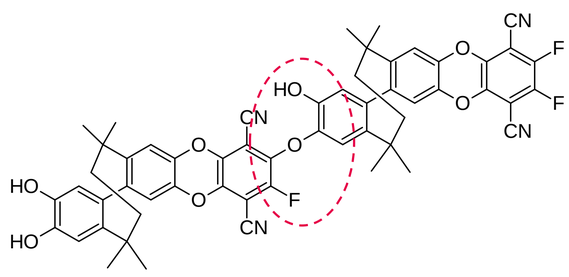


Figure 4: Polymer Formation over time. (A) MALDI-TOF of the product. (B) MALDI-TOF and GPC distributions of samples taken in the starting phase of the polymerization. [2]

- **The product contains a low molar mass fraction consisting of mostly cyclic species (Fig. 4A).**
- **At the beginning of the reaction the product is a complex mixture of different species including underreacted ones (Fig. 4B).**



- **The formation of cyclic species starts at later phases of the reaction.**

Literature:

[1] P. M. Budd et al., *Chem. Comm.*, **2004**, 2, 230-231.
[2] F. Kandelhard et al., *Adv. Funct. Mater.* , under review.

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