FROM RIGID-ROD TO HAIRY-ROD POLYIMIDES

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Fully-aromatic polyimides (PIs; product in Fig. 1, R = H) are rigid-rod polymers, *i.e.* they comprise an entirely stiff polymer backbone. Therefore, they belong to the class of high-performance polymers. Due to their molecular structure they exhibit outstanding mechanical, thermal and chemical stability.

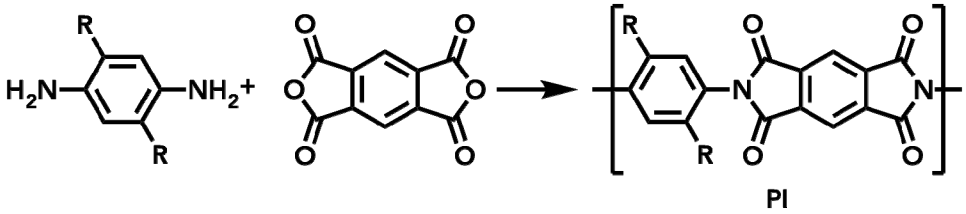

Fig. 1: Synthesis of PIs: If R = H rigid-rod PIs are obtained. Introduction of flexible, aliphatic side chains (R = alkyl chain) leads to hairy-rod PIs.

Typical synthetic procedures utilize a soluble polymeric intermediate, a so-called poly(amic acid), PAA, which is processable. Classically, PAA solutions in toxic solvents are processed - *e.g.* cast into a film - and further converted to the PI at high temperatures (T > 300 °C). Given increasing environmental regulations, green techniques for PI synthesis and processing are highly desirable. Two such techniques are: hydrothermal polymerization (HTP) and solid-state-polymerization (SSP).[1,2] In HTP PIs are formed under high-pressure at elevated temperatures in an autoclave using solely water as reaction medium. SSP is a solvent-free thermal polymerization method, where appropriate starting compounds are heated to temperatures below their melting point. However, both of these methods directly lead to rigid-rod PI products. In further consequence their infusibility and insolubility hampers processing.

In general an improvement in processability of such rigid-rod polymers can be achieved by (*i*) introduction of flexible spacers, (*ii*) introduction of kinks into the backbone or (*iii*) by attaching flexible side chains to the still stiff backbone. However, mechanical properties and high crystallinity can only be retained by method (*iii*), leading to so called “hairy-rod” polymers (product in Fig. 1, R = alkyl chain).

With this contribution we address the following points: influence of the side chains on (*i*) polymerization behavior, (*ii*) processability (solubility, fusibility) and (*iii*) polymer properties (morphology, thermal stability, crystallinity).

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[1] B. Baumgartner; M. J. Bojdys; M. M. Unterlass; Polym. Chem. **2014**, 5 (12), 3771.

[2] K. Kriechbaum; D. A. Cerrón-Infantes et al.; Macromolecules **2015**, 48, 8773–8780.