

SOLID-STATE POLYMERIZATION OF HAIRY-ROD POLYIMIDES

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INTRODUCTION

Fully aromatic polyimides (PIs), such as poly(*p*-phenylene pyromellitimide) (PPPI; chemical structure see Figure 1 right), show outstanding mechanical, thermal and chemical properties.^[1] As a matter of fact, most PIs are practically insoluble in all common solvents and do not melt when heated. Instead, they simply decompose at very high temperatures. These features impart their use *e.g.* in gas separation membranes or aeronautics applications. All of the just mentioned extraordinary properties can be traced back to PIs' molecular structure: Their polymer backbone is entirely stiff. Therefore, PIs belong to the family of rigid-rod polymers.

EXPERIMENTAL PART

However, the aforementioned superior properties of PIs come hand in hand with their major drawback: difficult processability and synthesis under harsh and demanding conditions.^[2] Classically, usually stepwise procedures (Figure 1 A) employ high-boiling, toxic solvents, such as dimethylformamide (DMF), and toxic catalysts, such as isoquinoline. Furthermore, long reaction times ($t > 8$ h) at elevated temperatures (T up to 450 °C) are necessary. In a first step an aromatic dianhydride and an aromatic diamine, *e.g.* pyromellitic dianhydride and *p*-phenylene diamine, are converted into a high-molecular weight polymeric intermediate. This soluble poly(amic acid) species allows for processing *e.g.* into fibers, films or coatings. In a subsequent curing step the desired insoluble, infusible PI product (here PPPI) is obtained.

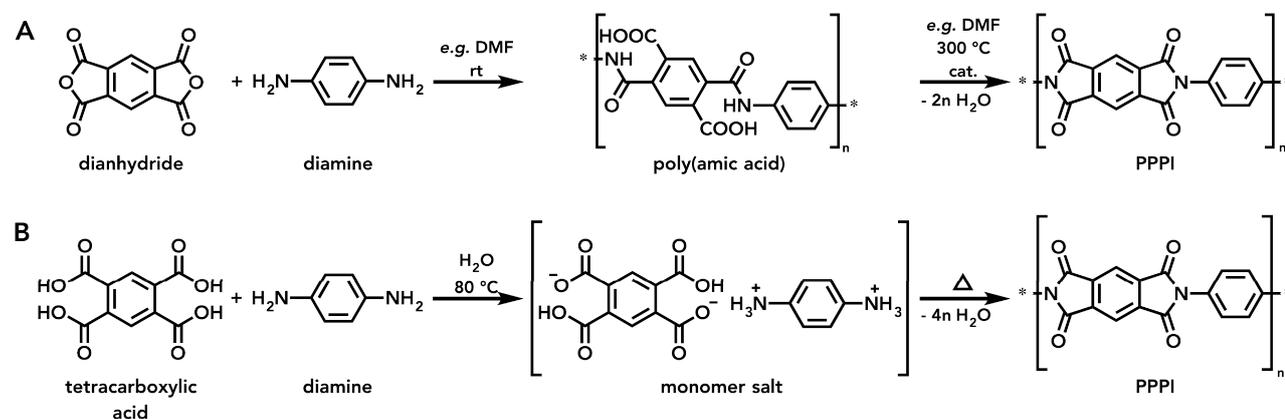


Figure 1: A - Classical two-step procedure to PPPI from pyromellitic dianhydride and *p*-phenylene diamine comonomers. Poly(amic acid) intermediate is soluble and hence solution-processable. B - Solid-state polymerization of PPPI *via* a monomer salt.

In contrast to conventional PI syntheses there are a number of non-classical approaches that avoid the utilization of toxic solvents and catalysts. Hence, such methods can be classified as “green” and are therefore of great scientific, ecological and economic interest. Among these alternative procedures a rather simple one is solid-state polymerization (SSP).^[3,4] SSP is a solvent-free polymerization technique that involves heat treatment of appropriate starting materials at temperatures below their melting point. For the SSP of PIs it is advantageous to use monomer salts as starting materials, as they intrinsically provide ideal stoichiometry of comonomers, which is of

the utmost importance in order to obtain high-molecular weight polymers. Furthermore, in contrast to aromatic diamines monomer salts are completely stable under ambient conditions and can be stored without special precautions. Such monomer salts are simply prepared by an acid-base reaction between the comonomers (Figure 1 B, first step). Subsequent heat treatment (Figure 1 B, second step) directly yields the final PI product (in this case PPPI), which is hardly soluble or fusible. In further consequence, this leads to severe processing issues. The goal of the presented project is to improve the processability of PIs by developing a family of potentially malleable monomer salt systems by introducing flexible side chains.

RESULTS AND DISCUSSION

In order to design processable PIs, we attached flexible side chains to PPPI's backbone (Figure 2, R = *n*-alkyl side chain, respectively), so that the rigid-rod nature and hence the high-performance properties are potentially retained. Such a macromolecule - which has a rigid polymer backbone with pendent, flexible side chains - is commonly termed hairy-rod polymer.

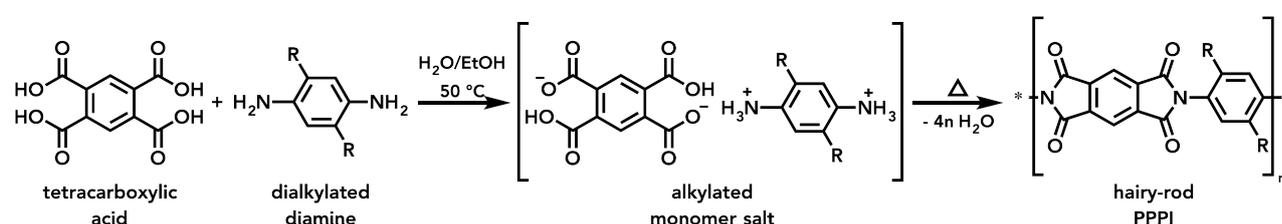


Figure 2: Reaction of pyromellitic acid and a dialkylated aromatic diamine to yield a monomer salt (first step) and subsequent SSP to obtain a hairy-rod polymer (second step). R = *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl side chain.

In this contribution we present our investigation of the influence of aliphatic side chains on (i) salt-formation, (ii) the ease of SSP, (iii) the mechanism of SSP and (iv) the resulting hairy-rod PIs' properties and processability. All studied systems were characterized using scanning electron microscopy (SEM), infrared spectroscopy (IR), powder X-Ray diffraction (XRD), *in situ* high temperature XRD (HT-XRD), nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In contrast to SSPs of all PIs studied to date, it was possible for the first time to observe softening phenomena prior to or during SSP.^[4] These phenomena lead to enormous changes in morphology of the polymers as compared to the monomer salts. DSC and HT-XRD measurements reveal several thermal events during elevating the temperature, which might explain these softening phenomena.

CONCLUSION

The hairy-rod PIs' physicochemical properties differ from regular, non-alkylated PPPI. Aside the achieved easier processing, the synthesized hairy-rod PIs are highly interesting for applications in which PIs can conventionally not be applied.

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