

# ENVIRONMENTALLY FRIENDLY GENERATION OF HIGH-PERFORMANCE POLYIMIDE FOAMS USING MONOMER SALTS

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## INTRODUCTION

Polyimides (PIs) are polymers whose backbones comprise mostly aromatic and heteroaromatic moieties connected by typically cyclic imide functions. They are materials of the utmost thermal, chemical and mechanical stability [1], and hence they are applied in high-performance sectors such as aeronautics and microelectronics. Unfortunately, the superior materials properties of PIs come at the high cost of being conventionally synthesized under harsh and demanding conditions [2]. In classical syntheses (Figure 1 A) the comonomers diamine and dianhydride are employed and first reacted to poly(amic acid) intermediates, which are subsequently converted to the final PI by thermally induced condensation cyclizations (typically referred to as “baking” or “curing”). These classical syntheses use high-boiling and 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.

## FUNDAMENTAL OF THE PROBLEM

Alternatively, one can prepare a salt-type single-source precursor, which contains both necessary comonomers of PIs. These so-called monomer salts, *i.e.* ammonium carboxylate salts (Figure 1 B) are highly advantageous as starting materials. First, they intrinsically provide ideal stoichiometry of the comonomers, which is of the utmost importance in order to obtain high-molecular weight polymers according to Carothers' law. Second, the fact that the comonomers are bound in the form of a salt increases storability. In contrast, the pristine diamine comonomers require storage with special precautions such as the absence of oxygen.

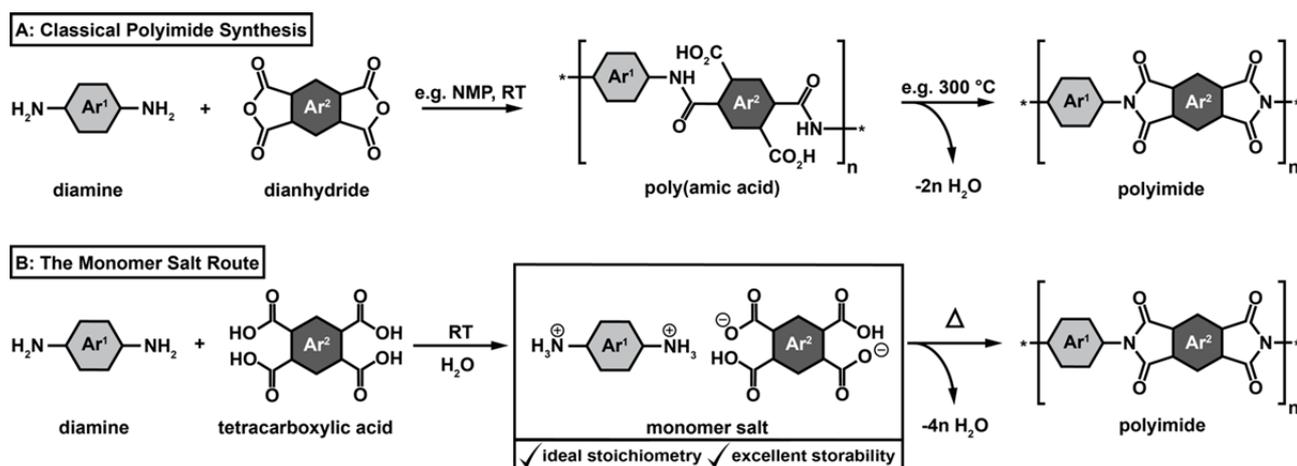


Figure 1: A – Classical two-step procedure towards PIs from an aromatic dianhydride and an aromatic diamine *via* a poly(amic acid) intermediate. B – The monomer salt route in which a single-source salt precursor is first generated by acid-base reaction, and subsequently thermally imidized.

The preparation of monomer salts is straightforward: They are simply obtained by an acid-base reaction between the comonomers (Figure 1 B, first step) and can be transformed to PIs by

subsequent heat treatment (Figure 1 B, second step). This transformation process is called solid-state polycondensation (SSP). As SSP is a solvent-free route, it can be classified as a “green” method and is therefore of great scientific, ecological and economic interest. Polyimides from SSP often show intriguing properties that are a direct consequence of the polymerization process, such as increased porosity [3], and conservation of the initial monomer salt’s shape [4].

## RESULTS AND DISCUSSION

We discovered a novel monomer salt as precursor for polyimides that upon heating does not conserve its initial shape, but instead goes through a liquid-like state prior to polymerization. Such softening has only rarely been observed in PI syntheses employing the monomer salt route: these syntheses typically take place in the solid-state. This liquefaction enables the formation of a continuous PI phase, which appears to have a foam-like form. The foaming behavior is partially due to the water vapor arising from the polycondensation reaction (*cf.* Fig. 1). Additionally, the foaming process is promoted by a peculiar and to date unreported demixing of the condensation byproduct water from short-chain oligomers forming at the beginning of the thermally induced polymerization. We herewith present this unique monomer salt, including its crystal structure as determined from single crystal X-ray diffraction (SC-XRD). Furthermore, the system was characterized using powder X-Ray diffraction (PXRD), scanning electron microscopy (SEM), infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The fact that this monomer salt allows for generating high-performance polyimide foams without the need for any organic solvents or foaming agents makes the route intrinsically green. Moreover, the novel monomer salt is easily synthesizable and easily storable under ambient conditions and all that at a very low cost of all involved compounds.

## CONCLUSION

With this contribution, we present a novel monomer salt as precursor for polyimides, which is perfectly suitable for producing high-performance polymer foams. The novel monomer salt shows unusual behavior upon thermally induced polymerization. Most importantly, the peculiar combination of the monomer salt’s softening with phase separation of freshly formed oligomers from the condensation byproduct allows for generating PI foams without the need to add foaming agents or organic solvents. Hence, the presented monomer salt lays the basis for the environmentally friendly generation high-performance polyimide foams.

## REFERENCES

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