

From dense monomer salt crystals to CO₂ selective microporous polyimides *via* solid-state polymerization

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Fully aromatic polyimides are synthesized *via* solid-state polymerization of the corresponding monomer salts. The crystal structure of salts shows strong hydrogen bonding of the reactive groups and thereby paves the way for solid-state transformations. The polycondensation yields copies of the initial salt crystallite habits, accompanied by the development of a porosity especially suited for CO₂.

High performance polymers (HPPs) are an important class of materials, mainly used for technological applications such as microelectronics and aeronautics, but also for gas separation applications.¹ They combine extraordinary mechanical and/or electronic properties with lightweight, solvent resistivity and high temperature stability.^{2–4} These properties arise from molecular features: HPPs consist of stiff, usually aromatic, monomeric units, resulting in highly stable polymers.

Polyimides (PIs), such as the well known poly(4,4'-oxydiphenylene-pyromellitimide) aka Kapton™, are HPPs obtained by step-growth polymerization. Thus, according to Carothers' law,⁵ equimolarity of the comonomers is essential in order to obtain a considerable degree of polymerization and conversion. PIs are usually synthesized in solution from dianhydrides and diamines (*e.g.* **1** and **2**, Scheme 1), typically using toxic solvents and catalysts (*e.g.* *m*-cresol and isoquinoline). Clearly, alternative pathways minimizing environmental danger are highly desirable,^{6,7} and options such as water and supercritical solvents, or entirely solvent-free pathways find increasing use in numerous synthesis fields. We recently investigated the hydrothermal synthesis of PIs and found isolable diamminium dicarboxylic acid-dicarboxylate

intermediates.⁸ These monomer salts (**3** in Scheme 1) are composed of the ionic forms of the comonomers and are fundamentally different from salt-type monomers such as sodium styrene-sulfonate, where only one ion, here styrene-sulfonate, is polymerized. Monomer salts **3** are well-known in polyamide synthesis, where they are often referred to as “nylon-salts”,⁹ but far less investigated in the field of polyimides. Thermogravimetric analysis (TGA),⁸ as well as the promising results presented earlier by Imai *et al.*, indicated that PIs can be synthesized in the solid-state directly from the monomer species.¹⁰ The aim of the present work is to shine more light on the processes involved in such solid-state polymerization (SSP) and to evaluate the potential of the PI materials for application in gas separation.

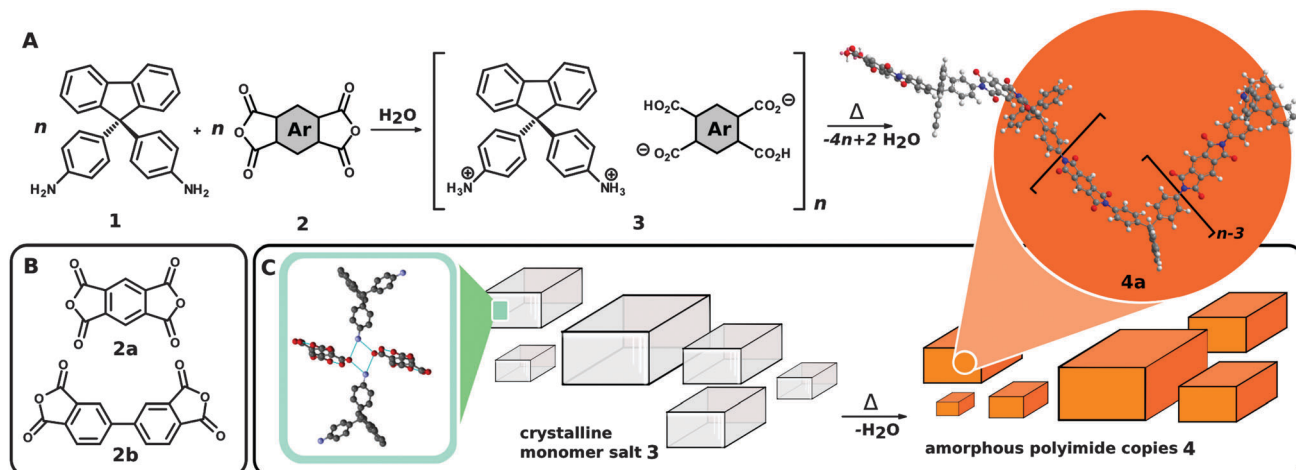
We focused on a monomer system that allows for the synthesis of intrinsically microporous polymers,¹¹ namely a combination of 9,9'-bis(4-aminophenyl)fluorene (BAPF, **1**) with either pyromellitic acid dianhydride (PMDA, **2a**) or 3,3',4,4'-biphenyl-tetracarboxylic acid dianhydride (BPDA, **2b**). Monomer salts **3** were prepared by precipitation from water, as depicted in Scheme 1 (for experimental details see ESI†). The salt **3** is composed of a diamminium cation (denoted H₂BAPF²⁺) and a diacid-dicarboxylate anion (denoted PMA²⁻ and BPTCA²⁻, respectively). SEM images of the salts show cuboid crystallites for **3a** and platelet-like crystallites for **3b**, both are polydisperse (Fig. 1 and ESI†).

The purity and composition of the studied monomer salts were ensured by FTIR spectroscopy, elemental analysis (EA) and TGA, as reported previously.⁸ Both monomer salts were polycrystalline and of high crystallinity, as verified by powder X-ray diffraction (PXRD) under ambient conditions (see ESI†). Crystallite densities were determined *via* analytical density-gradient ultra-centrifugation (AUC).¹² A binary solvent mixture of toluene and bromoform (ratio 0.71/0.29) was used in combination with absorption optics. The density gradient of the pure solvent mixture upon ultracentrifugation over the cell radius was calculated according to a conventional protocol.¹³ In both cases we find a single sharp peak, allowing for the exclusion of eventual polymorphism (see ESI†). The obtained densities (1.39 g cm⁻³ for **3a** and 1.41 g cm⁻³ for **3b**) are in the typical range for organic crystals.¹⁴ The structure of **3a** (PMA-H₂BAPF) was elucidated from

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Scheme 1 Solid state synthesis of PIs. (A) The diamine BAPF **1** forms a monomer salt **3** with an aromatic dianhydride **2** in water. Upon heating, solid state polycondensation takes place and the aromatic PI **4** is obtained (depicted as **4a**). (B) Dianhydrides used in this study; pyromellitic acid dianhydride (PMDA) **2a** and 3,3',4,4' biphenyltetracarboxylic acid dianhydride (BPDA) **2b**. (C) Solid state polymerization: monomer salt crystallites **3** are transformed to PI copies **4** by heating, undergoing amorphization. Green inset: tetrameric arrangement of comonomers within the crystal structure of **3**; orange inset: chain structure of the resulting PI **4a**.

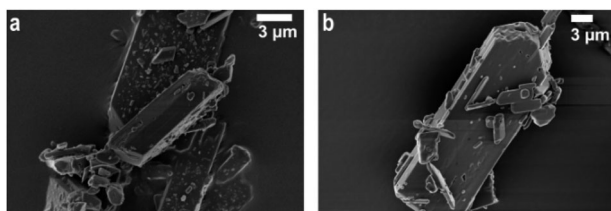


Fig. 1 Exemplary SEM images of **3a** (PMA·H₂BAPF) and the corresponding polymer **4a** (PMDA·BAPF).

PXRD data as no monocrystals could be grown, using the program FOX.¹⁵ To reduce the total number of degrees of freedom, the phenyl rings were refined as a rigid group. The crystal structure of **3a** was solved by a simulated annealing procedure and further subjected to a Rietveld refinement, which converged to $R_{wp} = 5.873\%$ ($R_{Bragg} = 4.658\%$) and agrees well with the measured powder patterns (Fig. 2a). **3a** crystallizes in the triclinic space group $P\bar{1}$. PMA²⁻ and H₂BAPF²⁺ molecules form tetramers (Fig. 2c) connected *via* two hydrogen bonds between the ammonium group and the carboxylate group (N–H···O, 2.8125 Å, 117°, N–H···O, 2.9832 Å, 106°). The tetramers are arranged parallel to the *a*–*b* plane and form stacks along the *c*-axis (Fig. 2b). The solution confirms the ammonium–dicarboxylate dicarboxylic acid structure suggested by FTIR spectroscopy (see ESI[†]), and reveals a complex hydrogen-bonding pattern. Similar hydrogen bonding motifs have been reported for ammonium carboxylate salts of fumaric and succinic acid.¹⁶ Unfortunately, the structure of **3b** could not be solved, as the simulation did not converge to a minimum. However, we expect equally complex H-bonding. Clearly, the comonomers arranged within this tetramer have to move considerably to form the final PI chain (*cf.* **4a** in Scheme 1).

Polyreactions were carried out by heating **3a** and **3b** to 270 °C and 250 °C, respectively, for 2 hours; neither an inert atmosphere nor reduced pressure was necessary, since the elimination byproduct H₂O phase separated and was further removed by evaporation. The polymerization points of **3a** and **3b** are at 260 °C and 245 °C, respectively, as determined by TGA.⁸ FT-IR analysis confirms the

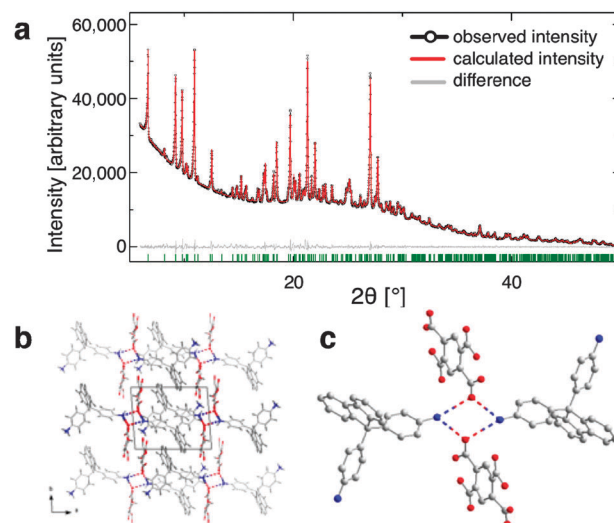


Fig. 2 Crystal structure of PMA·H₂BAPF. (a) Superposition of observed (grey) and calculated patterns (red); their difference in light grey. (b) Packing of PMA²⁻ and H₂BAPF²⁺ molecules viewed along the *c* axis; (c) detailed view of a hydrogen bonded tetramer. (b and c) Colour code: C atoms: grey, O atoms: red; N atom: blue; H atom: omitted for visibility (see ESI[†] for larger representation).

complete transformation of both monomer salts: –NH₃⁺, –CO₂H and –CO₂[–] modes disappear entirely, and imide modes appear (see ESI[†]). Additional indication of the successful transition into PIs is provided by the products' aspect: in both cases, the colour changes from white (**3a** and **3b**) to bright orange PI **4a** and greenish yellow PI **4b**, respectively. SEM images (Fig. 1) of monomer salt **3a** and PI **4a** clearly show that the external crystal habit is preserved without melting phenomena: identical copies are obtained. Additionally, the density of **4a** decreases to 1.274 g cm^{–3} (obtained by buoyancy measurements, see ESI[†]). The mass loss corresponds very well to 4 equivalents of water per monomeric unit, for a constant volume given by the obtained external copies. The obtained polymers are soluble in NMP after stirring at 80 °C for 2 hours (see ESI[†] for SEC analysis), and rather high weight average molecular weights are observed.

The solubility is expected to be a consequence of the fluorenyl units within the polymer backbone, *i.e.* the *cardo* principle.¹⁷

The thermal transformation of the salts into PIs was monitored by HT-XRD using synchrotron irradiation. The recorded patterns (see ESI†) reflect a transition from highly crystalline salts to amorphous products. The overall amorphization occurs in both cases between 250 °C and 275 °C, and has three main reasons. First, from the initial arrangement of the two monomers in the salt's crystal structure (*cf.* Scheme 1 and Fig. 2b and c) a considerable molecular movement is necessary to react to the cyclic imide. Second, two equivalents of water are liberated per imide ring formation. As water molecules move considerably at these temperatures and also tend to phase separate from the formed PI chains, we believe that they play a major role in the global amorphization. Third, the kinked structure of BAPF **1** should allow for a variety of energetically comparable conformations, additionally disturbing chain-to-chain packing. While the internal structure amorphizes, the macroscopic crystal habit persists, emphasizing the solid-state nature of the transformation. The amorphization goes along with the development of a special type of microporosity, as evidenced by CO₂ adsorption experiments conducted at 273.15 K and 298.15 K. The porosity of the PIs synthesized *via* SSP shows almost equal gas uptake (~1.2 mmol g⁻¹ at 273.15 K; see ESI†) as chemically equivalent PIs that have been synthesized using solution-based routines previously, proving the intrinsic nature of the micropores.^{11,18} Note that the PI particles are apparently non-porous in nitrogen adsorption experiments at 77.4 K, *i.e.* the developing intrinsic porosity is very specifically suited for CO₂. Consequently, we explored the versatility of the materials for gas separation applications. We calculated the separation selectivity α for the gas pair CO₂/N₂ based on CO₂ and N₂ single gas adsorption isotherms obtained at 273.15 K and 298.15 K, respectively, using the ideal adsorbed solution theory (IAST) methodology (see ESI†).¹⁹ The PIs showed a high α (CO₂/N₂) of >1000 at 273.15 K, and a α (CO₂/N₂) of >300 at 298.15 K (gas composition of 15/85 vol%; Fig. 3).

The capacity and selectivity drop might be explained by the less pronounced condensation tendency of confined CO₂ at higher *T*, which is itself connected to the overall uptake. However, the predicted capacity for CO₂ adsorption from the mixed gas is in a comparable regime to the pure gas adsorption, and thus is highly interesting for practical applications, where a significant drop in the capacity is often reported. The scientific literature regarding selectivity and capacity of a gas is still rather inhomogeneous, but it can be stated that outstanding gas uptake does not necessarily suggest high selectivities.²⁰ Such high

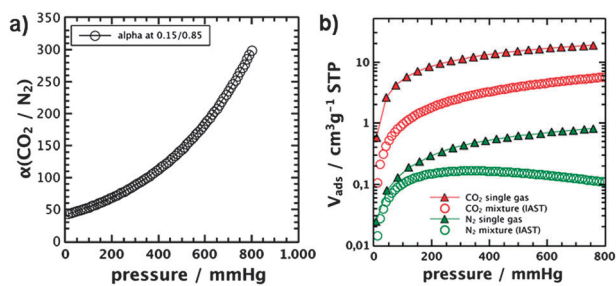


Fig. 3 (a) IAST selectivity of **4a** for a gas mixture (0.15/0.85 of CO₂/N₂) at 298.15 K; (b) single gas adsorption isotherms of CO₂ and N₂ on **4a** together with predicted uptakes from a 0.15/0.85 gas mixture of CO₂/N₂ (open symbols).

selectivities could arise as a consequence of a “molecular sieving effect” due to very small pore sizes as observed previously in modified zeolites.²¹ To see whether the as-made microporous polyimides are indeed capable of separating CO₂ and N₂, column breakthrough tests were conducted. A gas mixture composed of CO₂/N₂ was allowed to flow through a column filled with **4a** particles. The gas composition was analyzed by mass-spectrometry straight after the gas left the column (see ESI†). We found evidence for the successful separation of CO₂/N₂ gas mixtures, *i.e.* pure N₂ left the column before the elution of CO₂. Desorption of N₂ and CO₂ by He purge could be achieved proving the physisorptive nature of the process.

In summary, the successful solid-state transformations of monomer salts to aromatic microporous PIs at ambient pressure have been evidenced. The crystal structure of **3a** has been solved for the very first time. The polymerization yields structural amorphization. The necessary internal structural rearrangements do not affect the external crystal habit and identical copies of the monomer salt crystallites can be obtained. The obtained microporous PIs are able to separate CO₂ from N₂, indicating that these amorphous polymeric materials are an interesting addition to the field of classic crystalline microporous materials. It can be expected that the presented synthesis routine will have an impact on the sustainable synthesis of a variety of functional HPPs opening thereby new possibilities in the area of science and technology.

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Notes and references

- W. Volksen, R. D. Miller and G. Dubois, *Chem. Rev.*, 2010, **110**, 56.
- P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3.
- D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, *Polyimides*, Blackie & Son Ltd., Glasgow, London, 1990.
- Polyimides Thermally Stable Polymers*, ed. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev and L. A. Laius, Consultants Bureau, N.Y., New York, 1987, vol. 4.
- W. H. Carothers, *J. Chem. Soc., Faraday Trans.*, 1936, **32**, 39.
- M. Antonietti, *Nachr. Chem.*, 2011, **59**, 1027.
- R. Noyori, *Chem. Commun.*, 2005, 1807.
- M. M. Unterlass, D. Kopetzki, M. Antonietti and J. Weber, *Polym. Chem.*, 2011, **2**, 1744.
- C. D. Papaspyrides, *Polymer*, 1988, **29**, 114.
- Y. Imai, *Progress in Polyimide Chemistry*, Springer Verlag, Berlin Heidelberg, 1999, vol. 140, p. 1.
- N. Ritter, I. Senkowska, S. Kaskel and J. Weber, *Macromolecules*, 2011, **44**, 2025.
- J. Dirks, *Analytical Density Gradient Ultracentrifugation*, Beckman Instruments GmbH, Munich, 1964.
- W. Mächtle and L. Börger, *Analytical Ultracentrifugation of Polymers and Nanoparticles*, Springer Verlag, Berlin Heidelberg, 2006.
- S. K. Bhattacharjee and H. L. Ammon, *Acta Crystallogr., Sect. B*, 1981, **37**, 2082.
- V. Favre Nicolin and R. Cerny, *J. Appl. Crystallogr.*, 2002, **35**, 734.
- D. A. Haynes and L. K. Pietersen, *CrystEngComm*, 2008, **10**, 518.
- V. V. Korshak, *et al.*, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1974, **C11**, 45.
- A. Thomas, *Angew. Chem., Int. Ed.*, 2010, **49**, 8328.
- A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
- R. Dawson, A. I. Cooper and D. J. Adams, *Polym. Int.*, 2013, **62**, 345.
- F. Akhtar, Q. Liu, N. Hedin and L. Bergstrom, *Energy Environ. Sci.*, 2012, **5**, 7664.