Supporting Information to the paper

Towards a General Understanding of Hydrothermal Polymerization of Polyimides

By

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1 Experimental details

1.1 Chemicals

*p*-Phenylenediamine (PDA, 97%, Sigma Aldrich) and Benzidine (Bz, 98%, Sigma Aldrich) were purified via sublimation; Benzophenone-3,3’,4,4’-tetracarboxylic dianhydride (BTDA), methanol (Merck, 99%) and ethanol (Sigma Aldrich, 99.5%) were used as received.

1.2 Monomer salt synthesis at room temperature

In a 3-neck-flask under inert atmosphere equipped with a reflux condenser 0.48 g (1.5 mmol) BTDA was hydrolyzed to Benzophenone-3,3’,4,4’-tetracarboxylic acid (BTA) by stirring in 15 mL distilled water at 80 °C for 20 min. The clear solution was cooled down to room temperature and an equimolar amount of diamine (either PDA or Bz) was added. The suspensions were stirred overnight at room temperature. The pale salts were separated by filtration, washed with distilled water and dried in the desiccator over P$_2$O$_5$.

1.3 Monomer salt synthesis at 80 °C

In a 3-neck-flask under inert atmosphere, equipped with a reflux condenser 0.48 g (1.5 mmol) BTDA was hydrolyzed by stirring in 15 mL deionized water at 80 °C for 20 min. To the clear solution an equimolar amount of diamine (either PDA or Bz) was added. The suspensions were stirred overnight at 80 °C. The pale greyish ([H$_2$PDA$^{2+}$BTA$^{2-}$]) and yellowish ([H$_2$Bz$^{2+}$BTA$^{2-}$]) monomer salts were separated by filtration, washed with deionized water and dried in a desiccator over P$_2$O$_5$.

1.4 Monomer salt reflux experiments

In a flask, equipped with a reflux condenser 0.1 g of monomer salt was suspended in 15 mL distilled water and refluxed for 1 h and 12 h, respectively. The resulting suspensions were grey for [H$_2$PDA$^{2+}$BTA$^{2-}$] and yellow-greenish for [H$_2$Bz$^{2+}$BTA$^{2-}$]. The products were separated by filtration, washed with deionized water and dried in the desiccator over P$_2$O$_5$.

1.5 Polymer synthesis

*Hydrothermal polymerization:* The freshly prepared salt dispersion was transferred to a glass liner (V = 27 mL). The liner was then put into PTFE-lined steel autoclave (V = 45 mL). The autoclave was placed in an oven at different temperatures (140 °C, 160 °C, or 200 °C) and kept there for various reaction times (1 – 12 h). At the end of the reaction, the autoclave was quickly cooled back to room temperature. The different PI phases were isolated, washed several times with distilled water and dried *in vacuo* over P$_2$O$_5$. All other hydrothermal polymerizations were carried out accordingly (see Table S1).
TableS1: Overview of HTP-experiments. Given are concentration (in mol/L), reaction temperature (°C), reaction time (h) and pressure (bar). The autogenous pressures were calculated using Wexler’s equation, according to references [S1, S2].

<table>
<thead>
<tr>
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<th>Concentration (mol/L)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Pressure (bar)</th>
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<tr>
<td>p(PDA-BTA)</td>
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<td>200</td>
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<td>16.7</td>
</tr>
<tr>
<td></td>
<td>0.030</td>
<td>200</td>
<td>2</td>
<td>16.7</td>
</tr>
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<td>200</td>
<td>4</td>
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<td></td>
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<td>12</td>
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The aspect of the crude PI products after HTP (exemplarily for t_R = 2 h) is depicted below (Fig.S1).

**Fig.S1: Aspect of crude polyimides after HTP.** A: Schematic of a glass liner illustrating the nomenclature used in this paper (a-phase (bottom), and b-phase (top)). B: p(PDA-BTA); C: p(Bz-BTA), both after HTP (T_R = 200 °C, t_R = 2 h).

**Solid-state polymerization:** 0.2 g of monomer salt was placed in a flask, which was heated to 200 °C in a sandbath, and was kept at this temperature overnight. Yellow to brownish PIs were obtained.

2 Characterization of monomer salts and PIs

2.1 Solubility of monomer salts and PIs

The solubility of a- and b-phase of p(PDA-BTA) and p(Bz-BTA), and their respective monomer salts was tested in various solvents according to the following procedure: 10 mL of the respective solvent was added to 125 mg of the respective solid. The resulting dispersion
was heated up to the boiling temperature of the respective solvent. The dispersion was kept at reflux for several hours. Tables 2 and Table 3 show the used solvents and the outcome of the solubility tests for different monomer salts and PIs.

**Table 2:** Solubility experiments of the monomer salts [H$_2$PDA$^{2+}$BTA$^{-2}$] and [H$_2$Bz$^{2+}$BTA$^{-2}$]. Used solvents and boiling points: acetone (bp = 56 °C), MeOH = methanol (bp = 65 °C), EtOH = ethanol (bp = 78 °C), THF = tetrahydrofuran (bp = 66 °C), i-PrOH = isopropanol (bp = 83 °C), DMSO = dimethylsulfoxide (bp = 189 °C), DMF = dimethylformamide (bp = 152 °C).

<table>
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<th>[H$_2$Bz$^{2+}$BTA$^{-2}$]</th>
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<tr>
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<td>DMF</td>
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</table>

**Table 3:** Solubility experiments of PIs p(PDA-BTA) and p(Bz-BTA). Used solvents and boiling points: acetone (bp = 56 °C), MeOH = methanol (bp = 65 °C), EtOH = ethanol (bp = 78 °C), THF = tetrahydrofuran (bp = 66 °C), i-PrOH = isopropanol (bp = 83 °C), NMP = N-methyl-2-pyrrolidone (bp = 202 °C), DMSO = dimethylsulfoxide (bp = 189 °C), DMF = dimethylformamide (bp = 152 °C), H$_2$SO$_4$, conc. = concentrated sulfuric acid (heated to 200°C as it decomposes at bp).

<table>
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<tr>
<th></th>
<th>p(PDA-BTA)$_a$</th>
<th>p(PDA-BTA)$_b$</th>
<th>p(Bz-BTA)$_a$</th>
<th>p(Bz-BTA)$_b$</th>
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<tbody>
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<tr>
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<td>no</td>
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<td>i-PrOH</td>
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2.2 FT-IR-ATR analysis of monomer salts and PIs

FT-IR-ATR spectra were recorded on a Bruker Tensor 27 working in ATR MicroFocusing MVP-QL with a diamond crystal, using OPUS (version 4.0) software for data analysis. Resolution was set to 2-4 cm$^{-1}$, and spectra were recorded from 4000 to 600 cm$^{-1}$.

FT-IR-ATR spectra of dried monomer salts [H$_2$PDA$^{2+}$BTA$^{-2}$] and [H$_2$Bz$^{2+}$BTA$^{-2}$] synthesized at 80 °C for 2 h are shown in Fig. S2. The spectra depict the typical monomer salt modes ($\tilde{\nu}_{as}$(Ar-NH$_3^+$) $\approx$ 2830 cm$^{-1}$, $\tilde{\nu}_s$(Ar-NH$_3^+$) $\approx$ 2580 cm$^{-1}$, $\tilde{\nu}$(C=O, Ar-COOH) $\approx$ 1680 cm$^{-1}$, $\tilde{\nu}_{as}$(C=O, Ar-COO$'$) $\approx$ 1605 cm$^{-1}$ and $\tilde{\nu}_s$(C=O, Ar-COO$'$) $\approx$ 1570 cm$^{-1}$) but also the characteristic imide modes ($\tilde{\nu}_{as}$(C=O) $\approx$ 1775 cm$^{-1}$, $\tilde{\nu}_s$(C=O) $\approx$ 1720 cm$^{-1}$ and $\tilde{\nu}$(C-N) $\approx$ 1365 cm$^{-1}$).
cm$^{-1}$). Both systems show the coexistence of monomer salt and imide modes, as they had already started to polymerize/oligomerize.

![Graph A](image1.png)

![Graph B](image2.png)

**Fig.S2:** FT-IR-ATR spectra of monomer salt [H$_2$PDA$^{2+}$BTA$^{2-}$] (A) and [H$_2$Bz$^{2+}$BTA$^{2-}$] (B) synthesized by stirring for 2 h at 80 °C. ●= typical monomer salt modes ($\tilde{\nu}$(Ar-NH$^{3+}$) $\approx$ 2830 cm$^{-1}$, $\tilde{\nu}$(Ar-NH$^{3+}$) $\approx$ 2580 cm$^{-1}$, $\tilde{\nu}$(C=O, Ar-COOH) $\approx$ 1680 cm$^{-1}$, $\tilde{\nu}$(C=O, Ar-COO$^-$) $\approx$ 1605 cm$^{-1}$ and $\tilde{\nu}$(C=O, Ar-COO$^-$) $\approx$ 1570 cm$^{-1}$). ▲= characteristic imide modes ($\tilde{\nu}$(C=O) $\approx$ 1775 cm$^{-1}$, $\tilde{\nu}$(C=O) $\approx$ 1720 cm$^{-1}$ and $\tilde{\nu}$(C-N) $\approx$ 1365 cm$^{-1}$). *=tracing CO$_2$.

FT-IR-ATR spectra of dried monomer salts [H$_2$PDA$^{2+}$BTA$^{2-}$] and [H$_2$Bz$^{2+}$BTA$^{2-}$] synthesized at RT for 1 d are shown in **Fig.S3**. The spectra depict the typical monomer salt modes ($\tilde{\nu}$(Ar-NH$^{3+}$) $\approx$ 2830 cm$^{-1}$, $\tilde{\nu}$(Ar-NH$^{3+}$) $\approx$ 2580 cm$^{-1}$, $\tilde{\nu}$(C=O, Ar-COOH) $\approx$ 1680 cm$^{-1}$, $\tilde{\nu}$(C=O, Ar-COO$^-$) $\approx$ 1605 cm$^{-1}$ and $\tilde{\nu}$(C=O, Ar-COO$^-$) $\approx$ 1570 cm$^{-1}$ and no characteristic imide modes.
Fig. S3: FT-IR-ATR spectra of the monomer salts synthesized at RT for 1 d. A: [H₂PDA₂⁺BTA⁻]; B: [H₂Bz₂⁺BTA⁻]. ● = typical monomer salt modes ($\tilde{\nu}_{as}(Ar\text{-}NH^3+) \approx 2830$ cm$^{-1}$, $\tilde{\nu}_{s}(Ar\text{-}NH^3+) \approx 2580$ cm$^{-1}$, $\tilde{\nu}(C=O, Ar\text{-}COOH) \approx 1680$ cm$^{-1}$, $\tilde{\nu}_{as}(C=O, Ar\text{-}COO^-) \approx 1605$ cm$^{-1}$ and $\tilde{\nu}_{s}(C=O, Ar\text{-}COO^-) \approx 1570$ cm$^{-1}$.

The superimpositions of FT-IR-ATR spectra of the PIs $p$(PDA-BTA) and $p$(Bz-BTA) synthesized via HTP at different reaction times ($t_R = 1$ h, 2 h, 4 h and 12 h) at 200 °C are depicted in Fig. S4. The spectra of $p$(PDA-BTA) and $p$(Bz-BTA) obtained after 1 h do not show monomer salt modes at all, and are fully imidized: the classical cyclic imide modes are present.
**Fig S4: FT-IR-ATR spectra of PIs synthesized via HTP at 200°C for different reaction times.** In all panels: light blue for $t_R=1$ h, blue $t_R=2$ h, dark blue $t_R=4$ h and black for $t_R=12$ h. **A:** $\rho$(PDA-BTA) $a$-phases; **B:** $\rho$(PDA-BTA) $b$-phases; **C:** $\rho$(Bz-BTA) $a$-phases; **D:** $\rho$(Bz-BTA) $b$-phases. The relevant modes are emphasized by a yellow triangle ($\bullet$=characteristic imide modes ($\tilde{\nu}_{as}(C=O) \approx 1775$ cm$^{-1}$, $\tilde{\nu}_{s}(C=O) \approx 1720$ cm$^{-1}$ and $\tilde{\nu}_{s}(C-N) \approx 1365$ cm$^{-1}$)). We find no typical monomer salt modes, which would occur at $\tilde{\nu}_{ad}(Ar-NH^+) \approx 2830$ cm$^{-1}$ and $\tilde{\nu}_{d}(Ar-NH^+) \approx 2580$ cm$^{-1}$. $*$=atmospheric CO$_2$.

The monomer salts were refluxed for 1 h and 12 h, respectively, in water to mimic the subhydrothermal conditions. The obtained spectra for all systems are depicted in **Fig S5**. The spectra show the typical monomer salt modes ($\tilde{\nu}_{as}(Ar-NH^+) \approx 2830$ cm$^{-1}$, $\tilde{\nu}_{d}(Ar-NH^+) \approx 2580$ cm$^{-1}$, $\tilde{\nu}(C=O, Ar-COOH) \approx 1680$ cm$^{-1}$, $\tilde{\nu}_{ad}(C=O, Ar-COO^-) \approx 1605$ cm$^{-1}$ and $\tilde{\nu}_{d}(C=O, Ar-COO^-) \approx 1570$ cm$^{-1}$ $\tilde{\nu}_{d}(C=O, Ar-COO^-) \approx 1570$ cm$^{-1}$) and also the characteristic imide modes ($\tilde{\nu}_{as}(C=O) \approx 1775$ cm$^{-1}$, $\tilde{\nu}_{d}(C=O) \approx 1720$ cm$^{-1}$ and $\tilde{\nu}_{d}(C-N) \approx 1365$ cm$^{-1}$). Thus, both systems had already started to oligo-/polymerize in the subhydrothermal regime.
Fig. S5: FT-IR-ATR spectra of the two monomer salts refluxed for 1 h and 12 h in H₂O. A: [H₂PDA²⁺BTA⁻] refluxed for 1 h, B: [H₂PDA²⁺BTA⁻] refluxed for 12 h, C: [H₂Bz²⁺BTA⁻] refluxed for 1 h, D: [H₂Bz²⁺BTA⁻] refluxed for 12 h. The relevant modes are emphasized as follows: ● = typical monomer salt modes (v_\text{as}(\text{Ar-NH₃⁺}) \approx 2830 \text{ cm}^{-1}, v_\text{s}(\text{Ar-NH₃⁺}) \approx 2580 \text{ cm}^{-1}), ▲ = characteristic imide modes (v_\text{as}(\text{C=O}) \approx 1775 \text{ cm}^{-1}, v_\text{s}(\text{C=O}) \approx 1720 \text{ cm}^{-1} and v_\text{s}(\text{C-N}) \approx 1365 \text{ cm}^{-1}). * = atmospheric CO₂.

2.3 ^1H-NMR analysis of monomer salts

Since the monomere salts were soluble in a number of protic and aprotic polar solvents, solution NMR could be carried out.

^1H and ^13C solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz) and a Bruker AVANCE DPX 300 spectrometer (300.13 MHz) equipped with a 5 mm inverse-broad probe head and z-gradient unit.

The ^1H spectra of dried monomer salts are shown in Fig. S6. Both spectra show broad singlets between 3 and 4 ppm, which correspond to the protons of the ammonium group. Furthermore, the peaks of the ionized monomers are shifted to higher ppm values compared to the neutral BTA and diamines. Very broad and weak singlets between 8 and 11 ppm correspond to the acidic proton of BTA⁻, in both cases. The two protonated acidic BTA groups are hardly visible in the spectra due to rapid proton exchange processes (with nondeuterated solvent impurities, traces of H₂O, and between the species themselves) which broaden peaks extremely.

Since there are no amine-groups (singlet between 4 and 6 ppm) visible, we conclude a stoichiometric ratio of 1:1, of BTA: to each diamine (see Fig. S6). The ratio of integrals related to BTA⁻ and each respective ammonium fits reasonably well, the deviations from the expected ratios are related to the proton exchange processes.
Integral ratios: Expected ratio for \([\text{H}_2\text{PDA}^{2+}\text{BTA}^{2-}]\) is \((\int \text{H}_d) : (\int \text{H}_a + \int \text{H}_b + \int \text{H}_c) = 4:6\) obtained ratio = 3.77:6. Expected ratio for \([\text{H}_2\text{Bz}^{2+}\text{BTA}^{2-}]\) is \((\int \text{H}_a + \int \text{H}_c) : (\int \text{H}_a + \int \text{H}_b + \int \text{H}_c) = 6:8\) obtained ratio = 5.3:7.96.

**Fig.S6:** \(^1\text{H}-\text{NMR spectra of the monomer salts.} \) A: \([\text{H}_2\text{PDA}^{2+}\text{BTA}^{2-}]\); B: \([\text{H}_2\text{Bz}^{2+}\text{BTA}^{2-}]\). The assignment of all signals is included in panels A and B.

The \(^{13}\text{C}-\text{APT} \) (Attached Proton Test) spectra of the two monomer salts are depicted in **Fig.S7** and **S8**, respectively. All signals are attributed as insets in the figures.
Fig S7: $^{13}$C-NMR spectra of the monomer salt $[H_2PDA^{2+}BTA^{2-}]$. All signals are attributed in the figure (see molecule drawings). Quaternary carbon atoms and carbon atoms bearing two protons are pointing downwards, carbon atoms connected to one (CH) and three protons (CH$_3$) are pointing upwards.

Fig S8: $^{13}$C-NMR spectra of monomer salts $[H_2Bz^{2+}BTA^{2-}]$. All signals are attributed in the figure (see molecule drawings). Quaternary carbon atoms and carbon atoms bearing two protons are pointing downwards, carbon atoms connected to one (CH) and three protons (CH$_3$) are pointing upwards.
2.4 Powder X-ray diffraction

Powder X-ray diffraction data was collected with a PANalytical X’Pert Pro multi-purpose diffractometer (MPD) in Bragg Brentano geometry operating with a Cu anode at 40 kV, 40 mA, and an X-Celerator multichannel detector was used. Samples were ground and mounted as loose powders on silicon single crystal sample holders. The diffraction patterns were recorded between 5 and 60° or 5 and 50° (2θ) with 69.215 s/step and a step size of 0.0050134°, sample holders where rotated during the measurement with 4 s/turn.

Superimpositions of the XRD patterns of a- and b-phases of $p$(PDA-BTA) and $p$(Bz-BTA), respectively, obtained after different $t_R$ (1 h, 2 h, 4 h and 12 h) are shown in Fig.S9. The diffractograms of the monomer salts $[H_2PDA^{2+}BTA^{2-}]$ and $[H_2Bz^{2+}BTA^{2-}]$ are depicted in Fig.S10. The a- and b-phases of each PI - for the same $t_R$ - show identical major reflexes. However, the b-phases are typically of higher crystallinity and show a few additional reflexes (highlighted with grey arrows in Fig.S9). In XRD, we still find reflexes related to non-reacted monomer salt after $t_R = 1$ h, however only in the b-phases (highlighted with orange arrows in Fig.S9 B and D).

**Fig.S9.** Diffractograms of $p$(PDA-BTA) and $p$(Bz-BTA) synthesized via HTP at 200 °C for different reaction times. For all all panels: $t_R = 1$ h (light blue), $t_R = 2$ h (blue), $t_R = 4$ h (dark blue), and $t_R = 12$ h (black). A: a-phases of $p$(PDA-BTA); B: b-phase of $p$(PDA-BTA); C: a-phases of $p$(Bz-BTA), and D: b-phases of $p$(Bz-BTA).
The diffractograms of the products of reflux experiments carried out for 1 h and 12 h, respectively, in water are superimposed with the diffractograms of the pure monomer salts (Fig.S11.) For both systems we observe amorphous halos from the prepolymerized/-oligomerized species, in coexistence with monomer salt reflexes.
**Fig.S11**: Diffractograms of the two systems after reflux for 1 h and 12 h superimposed with the corresponding monomer salt patterns. A-B: [H₂PDA²⁺BTA⁻] (grey) and the product after 1 h (A, light blue) and 12 h (B, dark blue) of reflux in H₂O; C-D: [H₂Bz²⁺BTA⁻] (grey) and the product after 1 h (C, light blue) and 12 h (D, dark blue) of reflux in H₂O.

Solid-state polymerizations (SSPs) have been carried out for comparison (200 °C, 12 h). The diffractograms of PIs obtained by SSP are depicted **Fig.S12**. The amorphous halos in **Fig.S12** are qualitatively emphasized as colored areas, and their centers are emphasized by dotted lines: the pattern of p(PDA-BTA) showing amorphous halos centered at around 18° (2θ), 21° (2θ) and a very broad and week halo around 43° (2θ). The diffractogram of p(Bz-BTA) shows a semicrystalline product featuring amorphous halos centered at around 20°, 26° and 38° (2θ).
Fig.S12: Diffractograms of PIs obtained by solid-state polycondensation of monomer salt \([\text{H}_2\text{PDA}^{2+}\text{BTA}^2\text{]}\) (A) and \([\text{H}_2\text{Bz}^{2+}\text{BTA}^2\text{]}\) (B) polymerized by solid-state polymerization at 200°C for 12 h.

### 2.5 Thermogravimetric analysis of monomer salts

Thermogravimetric analysis was carried out using a Netzsch TG 209 analyzer at a heating rate of 10 K min\(^{-1}\) under nitrogen atmosphere, equipped with NETZSCH Proteus (Version 4.3) software.

The TGA curves of the dried monomer salts are depicted in Fig.S13. The monomer salts depict a polymerization point \(T_p\) at 149 °C for \([\text{H}_2\text{PDA}^{2+}\text{BTA}^2\text{]}\) and 172 °C for \([\text{H}_2\text{Bz}^{2+}\text{BTA}^2\text{]}\). The initial mass loss around 100°C is due to physisorbed water.

The mass losses \(d_m\) determined via TGA are 14% for \([\text{H}_2\text{PDA}^{2+}\text{BTA}^2\text{]}\) and 13% for \([\text{H}_2\text{Bz}^{2+}\text{BTA}^2\text{]}\). This corresponds well to two equivalents of water per imide ring, which are eliminated upon polymerization. The theoretical mass losses are 15.4 % for \([\text{H}_2\text{PDA}^{2+}\text{BTA}^2\text{]}\), 13.3 % for \([\text{H}_2\text{Bz}^{2+}\text{BTA}^2\text{]}\).

\[
d_m = \frac{(M_{ms} - M_{RU})}{M_{ms}} \times 100
\]

With \(M_{ms}\) = molecular weight of the monomer salt, and \(M_{RU}\) = molecular weight of the corresponding polyimide’s repeating unit.

\[
M_{ms}([\text{H}_2\text{PDA}^{2+}\text{BTA}^2\text{}]) = 466.4 \text{ g/mol} \quad M_{RU}(p(\text{PDA-BTA})) = 394.4 \text{ g/mol}
\]

\[
M_{ms}([\text{H}_2\text{Bz}^{2+}\text{BTA}^2\text{}]) = 542.5 \text{ g/mol} \quad M_{RU}(p(\text{Bz-BTA})) = 470.5 \text{ g/mol}
\]
Fig. S13: Thermogravimetric analysis of the two monomer salts. A: [H₂PDA²⁺BTA⁻²⁻], with \( d_m = 14\% \), \( T_p = 149\, ^\circ\text{C} \) and \( T_d = 517\, ^\circ\text{C} \). B: [H₂Bz²⁺BTA⁻²⁻], with \( d_m = 13\% \), \( T_p = 172\, ^\circ\text{C} \) and \( T_d = 544\, ^\circ\text{C} \). \( T_p \) = solid-state polymerization temperature; \( T_d \) = temperature of decomposition (onset). (*) indicates mass loss due to physisorbed water.

### 2.6 Scanning electron microscopy

Scanning electron microscopy was carried out with a Quanta 200F FEI microscope. Typically the samples were measured at 5 kV or 10 kV, with a working distance of 9-10 mm and spot size 2.0 or 2.5. Prior to imaging, samples were loaded on carbon-coated stubs and coated by sputtering with a 17 nm thick layer of Au/Pd 60/40 alloy with a Quarum Q105T S sample preparation system.
Fig.S14: SEM overview image of p(PDA-BTA) a-phase ($t_R = 1\ h$, $T_R = 200\ ^\circ C$).

Fig.S15: SEM overview image of p(PDA-BTA) b-phase ($t_R = 1\ h$, $T_R = 200\ ^\circ C$).
Fig.S16: SEM overview image of p(PDA-BTA) α-phase ($t_R = 2$ h, $T_R = 200^\circ$C).

Fig.S17: SEM overview image of p(PDA-BTA) β-phase ($t_R = 2$ h, $T_R = 200^\circ$C).
Fig.S18: SEM overview image of p(PDA-BTA) a-phase (t_R = 4 h, T_R = 200°C).

Fig.S19: SEM overview image of p(PDA-BTA) b-phase (t_R = 4 h, T_R = 200°C).
**Fig. S20:** SEM overview image of p(PDA-BTA) a-phase ($t_R = 12\ h, T_R = 200^\circ\text{C}$).

**Fig. S21:** SEM overview image of p(PDA-BTA) b-phase ($t_R = 12\ h, T_R = 200^\circ\text{C}$).
Fig.S22: SEM overview image of p(Bz-BTA) a-phase ($t_R = 1\ h$, $T_R = 200^\circ C$).

Fig.S23: SEM overview image of p(Bz-BTA) b-phase ($t_R = 1\ h$, $T_R = 200^\circ C$).
**Fig.S24:** SEM overview image of p(Bz-BTA) a-phase ($t_R = 2$ h, $T_R = 200^\circ$C).

**Fig.S25:** SEM overview image of p(Bz-BTA) b-phase ($t_R = 2$ h, $T_R = 200^\circ$C).
Fig. S26: SEM overview image of p(Bz-BTA) a-phase ($t_R = 4$ h, $T_R = 200$˚C).

Fig. S27: SEM overview image of p(Bz-BTA) b-phase ($t_R = 4$ h, $T_R = 200$˚C).
**Fig. S28:** SEM overview image of p(Bz-BTA) $a$-phase ($t_R = 12 \text{ h}$, $T_R = 200^\circ \text{C}$).

**Fig. S29:** SEM overview image of p(Bz-BTA) $b$-phase ($t_R = 12\text{h}$, $T_R = 200^\circ \text{C}$).
Fig. S30: SEM overview image of p(PDA-BTA) a-phase $T_R < T_p$ (with $t_R = 12$ h, $T_R = 140^\circ$C).

Fig. S31: SEM overview image of p(PDA-BTA) b-phase $T_R < T_p$ (with $t_R = 12$ h, $T_R = 140^\circ$C).
**Fig. S32:** SEM overview image of p(Bz-BTA) a-phase \( T_R < T_p \) (with \( t_R = 1 \text{ 2h}, \ T_R = 160^\circ C \)).

**Fig. S33:** SEM overview image of p(Bz-BTA) b-phase \( T_R < T_p \) (with \( t_R = 12 \text{ h}, \ T_R = 160^\circ C \)).
Fig S34: SEM overview image of p(PDA-BTA) a-phase synthesized at half of the typical concentration (with $t_R = 12$ h, $T_R = 160 ^\circ$C, c = 0.015 mol/L).

Fig S35: SEM overview image of p(PDA-BTA) b-phase synthesized at half of the typical concentration (with $t_R = 12$ h, $T_R = 160 ^\circ$C, c = 0.015 mol/L).
Fig.S36: SEM overview image of p(PDA-BTA) α-phase synthesized at higher concentration (with $t_R = 12$ h, $T_R = 160^\circ$C, $c = 0.5$ mol/L).

Fig.S37: SEM overview image of p(PDA-BTA) β-phase synthesized at higher concentration (with $t_R = 12$ h, $T_R = 160^\circ$C, $c = 0.05$ mol/L).
Fig.S38: SEM overview image of p(Bz-BTA) a-phase synthesized at half of the typical concentration (with $t_R = 12$ h, $T_R = 160^\circ$C, $c = 0.01$ mol/L).

Fig.S39: SEM overview image of p(Bz-BTA) b-phase synthesized at half of the typical concentration (with $t_R = 12$ h, $T_R = 160^\circ$C, $c = 0.01$ mol/L).
Fig S40: SEM overview image of p(Bz-BTA) a-phase synthesized at higher concentration (with $t_R = 12$ h, $T_R = 160^\circ C$, $c = 0.05 \text{ mol/L}$).

Fig S41: SEM overview image of p(Bz-BTA) b-phase synthesized at higher concentration (with $t_R = 12$ h, $T_R = 160^\circ C$, $c = 0.05 \text{ mol/L}$).
**Fig.S42:** SEM overview image of $[\text{H}_2\text{PDA}^{2+}\text{BTA}^{2-}]$ refluxed for 12 h in water. White frames highlight areas where isolated roundish particles are visible.

**Fig.S43:** SEM overview image of $[\text{H}_2\text{Bz}^{2+}\text{BTA}^{2-}]$ refluxed for 12 h in water. White frames highlight areas where isolated roundish particles are visible.
3 References to the supporting information
