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Supporting Information to the paper

Geomimetics for Green Polymer Synthesis: Highly Ordered Polyimides *via* Hydrothermal Techniques

By

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1 Experimental details

1.1 Chemicals

p-Phenylenediamine (PDA, 97%, Sigma Aldrich) purified *via* sublimation; Pyromellitic dianhydride (PMDA, 97 % Sigma Aldrich) recrystallized from *aq. dest.*, m-cresol (99%, Merck) purified *via* vacuum distillation; isoquinoline (97 %, Sigma Aldrich) used as received; methanol (Merck, 99%) and ethanol (Sigma Aldrich, 99.5 %) used as received.

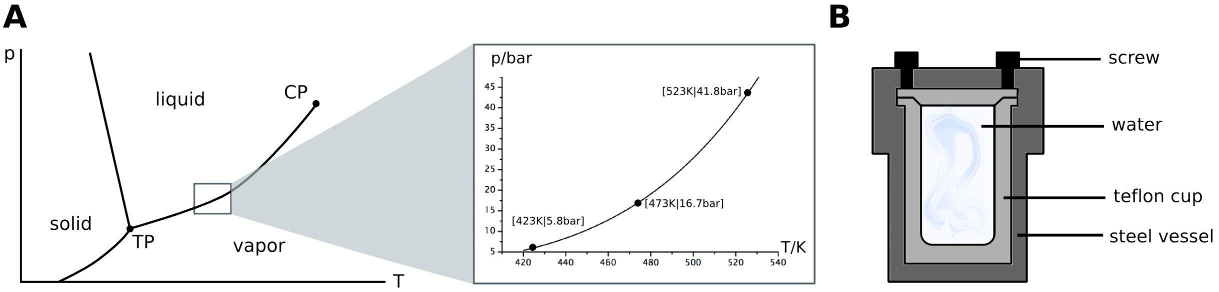
1.2 Monomer salt synthesis

0.327 g (1.5 mmol) of PDMA were placed in a 3-neck-flask under inert atmosphere, equipped with a reflux condenser and dissolved in 15mL of deionized water (previously degassed with N_2). The solution was heated to 80 °C and 0.162 g freshly resublimated PDA (1.5 mmol) were added under stirring. The white salt precipitated immediately, and the dispersion was further stirred for 2 h at 80 °C.

1.3 Polymer synthesis

***Hydrothermal pathway*:** The freshly prepared salt dispersion was transferred to a glass liner (V = 27 mL). The liner was then put into an autoclave (V = 45 mL), equipped with a Teflon liner. The autoclave was placed in an oven at different temperatures (150 °C, 200 °C or 250 °C) and kept there for various reaction times (0.25 – 60 h). At the end of the reaction, the autoclave was quickly cooled back to room temperature. The different HT-PPPI phases were isolated, washed several times with distilled water and dried *in vacuo* at 40 °C overnight.

SchemeS1 illustrates the position of the chosen reaction conditions on the phase diagram of water (***Scheme S1A***) and a schematic of a steel autoclave used to generate these conditions in the laboratory (***Scheme S1B***).



Scheme S1: *hydrothermal polymerization. A) lower HT regime on the phase diagram of water (left side); conditions used in this work, indicated by points on the liquid vapor line:150 ˚C / 5.8 bar; 200 ˚C / 16.7 bar and 250 ˚C / 41.8 bar. p-T diagram on the left side was computed using Wexler's equation as described below. B) lab-scale steel autoclave lined with a teflon vessel.*

The liquid-vaporline of water can be described by the reduced *Clausius-Clapeyron equation:*

$$\frac{1}{p}dp = \frac{\Delta H_{vap}}{RT^2}dT$$

Due the logarithmic correlation between saturation pressure and temperature resulting from 1/p dp, the saturation pressure can be computed as a Taylor series of this logarithmic correlation, which is of very high accuracy after these venth term. This is known as *Wexler's equation*:

$$ln(e_s) = \sum_{i=0}^{6} g_i T^{i-2} + g_7 lnT$$

With e_s = saturation pressure and g_i = Wexler coefficients.[1] Since the autoclaves were closed at standard conditions, 1 atm of air has to be added to each value, which leads to

$$\mathrm{e_s} = \left[\exp\left(\textstyle\sum_{\mathrm{i}=0}^{6} \mathrm{g_i T^{i-2}} + \mathrm{g_7 lnT}\right)\right] + 1\ \mathrm{atm.}$$

The used Wexler coefficients [2] are:

$g_0 = -2.8365744 \cdot 10^{3}$; $g_1 = -6.028076559 \cdot 10^{3}$; $g_2 = 1.954263612 \cdot 10^{1}$; $g_3 = -2.737830188 \cdot 10^{-2}$;

$g_4 = 1.6261698 \cdot 10^{-5}$; $g_5 = 7.0229056 \cdot 10^{-10}$; $g_6 = -1.8680009 \cdot 10^{-13}$; $g_7 = 2.7150305$.

Classical 2-step pathway: 1 g PMDA (4.6 mmol) and 0.49 g PDA (4.6 mmol) were dispersed in 40 mL of freshly distilled m-cresol under inert atmosphere. Then 2mL of dry toluene, and 0.1 mL of isoquinoline were added to the reaction mixture. The orange dispersion was stirred at 80 °C for 1 h. The resulting PAA dispersion was heated to 200 °C and kept at this temperature for 6 h. The condensate (water) was continuously removed with a Dean-Stark trap. One part of the PPPI dispersion was quenched in methanol and the other part was allowed to slowly cool down to room temperature. The products from both fractions were isolated via filtration, washed three times with ethanol and dried under high vacuum.

2 Characterization of monomer salts and PIs

2.1 Aspect of HT-PPPI

The aspect of the product dispersion after HT synthesis for different reaction times and compared to the monomer salt dispersion is depicted below (***Fig. S1***).

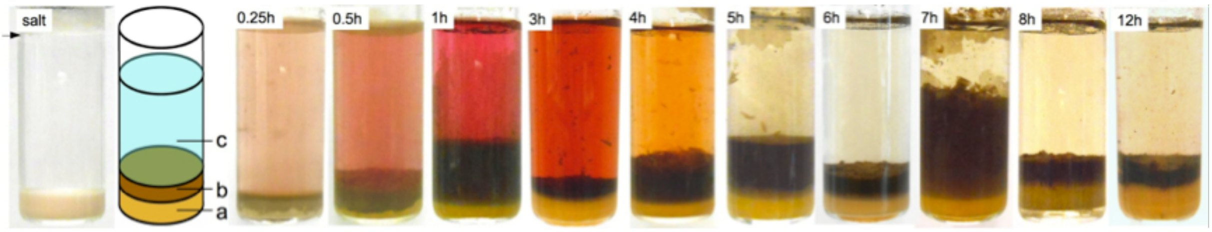


Fig. S1: Aspect of monomer salt and HT-PPPI dispersions*. From left to right:* ***3*** *dispersed in distilled water (arrow indicates air-water interface) prior to HT polymerization; schematic of a glassliner after polymerization at* 200 °C *with nomenclature of the product phases: a=orange product phase, b=brownish product phase, c=supernatant; photographs of liners after 0.25, 0.5, 1, 2, 3, 4, 5, 7, 8 and 12 h of reaction.*

2.2 Solubility of PPPI

The solubility of HT-PPPI a-phase, HT-PPPI b-phase, classical PPPI quenched and classical PPPI slowly cooled was tested in various solvents according to the following procedure: 2mL of the respective solvent was added to 25mg of the respective PPPI. The resulting dispersion was heated up to the boiling temperature of the respective solvent. The dispersion was kept a reflux for several hours. ***Table S1*** shows the used solvents and the outcome of the solubility tests for the four different PPPIs.

Table S1. Solubility experiments for PPPI (synthesized classically and via HT-synthesis)*. Used solvents and boiling points: acetone (bp = 56 °C), MeOH = methanol (bp = 65 °C), EtOH = ethanol (bp = 78 °C), ^{n}-BuOH = n-buthanol (bp = 117 °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_2SO_4conc. = concentrated sulfuric acid (heated to 200 °C as it decomposes at bp), benzene (bp = 80 °C).*

	HT-PPPI $_{a}$	**HT-PPPI $_{b}$**	**PPPI $_{quenched}$**	**PPPI $_{slow\ cooling}$**
acetone	no	no	no	no
MeOH	no	no	no	no
EtOH	no	no	no	no
^{n}-BuOH	no	no	no	no
^{i}-PrOH	no	no	no	no
NMP	no	no	no	no
DMSO	no	no	no	no
DMF	no	no	no	no
H_2SO_4, *conc.*	no	no	no	no
benzene	no	no	no	no

2.3 FT-IR-ATR analysis monomer salt and PPPIs

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}.

Fig. S2 shows a superimposition of normalized FT-IR-ATR spectra of dried monomer salt **3**(green), with the HT-PPPI a- and b- phase (orange and dark red, respectively) after t_R = 1 h at 200 °C. The monomer salt spectrum depicts the aryl-ammonium modes at 2830 cm^{-1} (asymmetric vibration) and 2580 cm^{-1} (symmetric vibration). The monomer salt's anion contains two carboxylate and two carboxylic acid functions: both the aryl-carboxylic acid C=O mode at 1680 cm^{-1}, and the aryl-carboxylate C=O modes at 1605 cm^{-1} and 1570 cm^{-1} are present. The broad mode at 3150 cm^{-1} is neither present in the spectra of PDA nor of PMA; we attribute it to intermolecular H-bonding between Ar-CO_2^- and Ar-CO_2H of two neighboring PMA^{2-} anions within the solid monomer salt. Both a- and b-phase of HT-PPPI can be qualified as fully imidized from FT-IR-ATR: they lack monomer salt modes, but instead show the classical cyclic imide vibrations: $C{=}O_{,imide}$ (asymmetric) at 1775 cm^{-1}, $C{=}O_{,imide}$ (symmetric) at 1720 cm^{-1}, and $C\text{-}N_{,imide}$ (symmetric) at 1365 cm^{-1}.

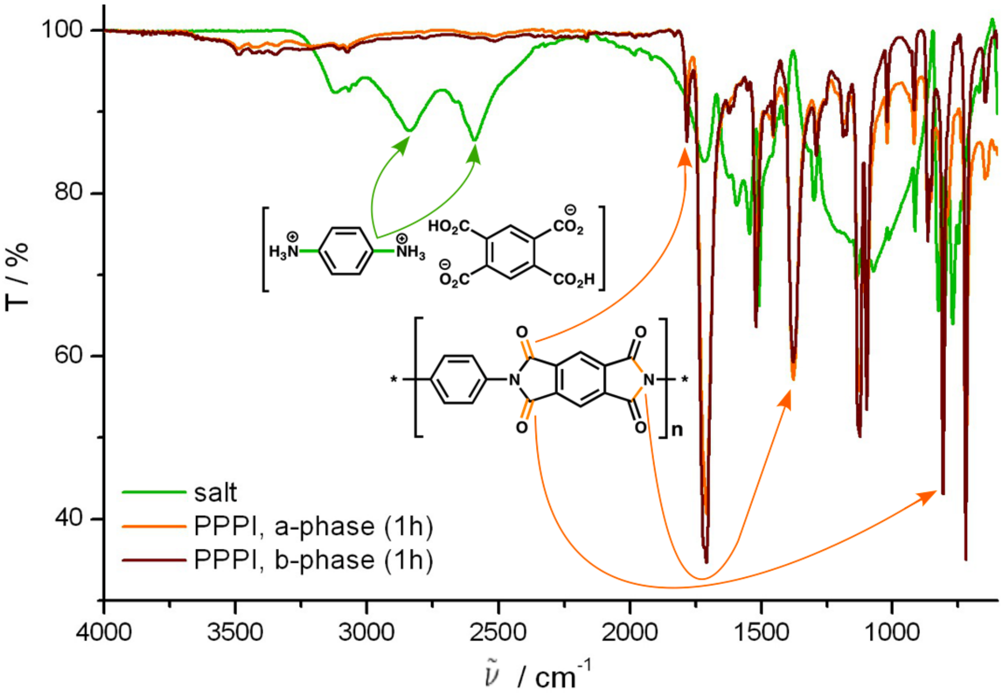


Fig. S2: *FT-IR-ATR spectra of monomer salt* ***3*** *(green), HT-PPPI a-phase (orange) and HT-PPPI b-phase (dark red).*

Fig. S3 shows a superimposition of normalized FT-IR-ATR spectra of dried monomer salt **3**(grey), with the HT-PPPI a- low reaction times (t_R = 0.25 h, 0.5 h and 1 h) obtained at 200 °C. The spectra of products obtained after 0.25 h and 0.5 h are still strongly depict monomer salt modes, aside weak imide modes. The spectra from HT-PPPI obtained after 1 h does not show monomer salt modes at all, but appears to be fully imidized: the classical cyclic imide modesare present.

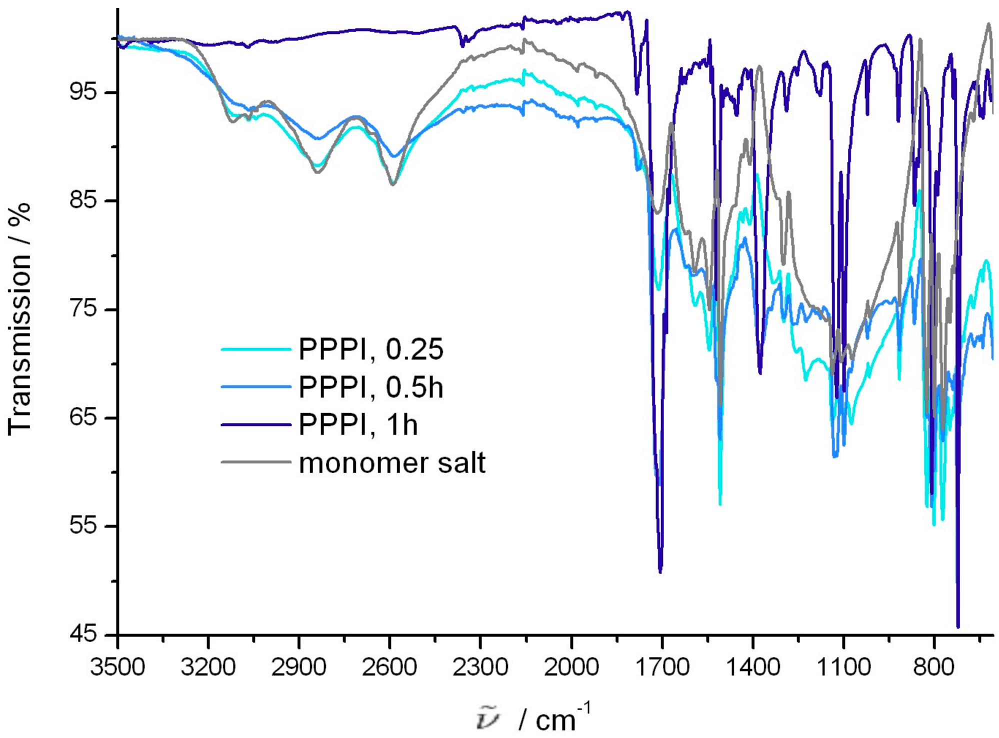


Fig. S3: *Superimposition of FT-IR-ATR spectra of monomer salt* ***3*** *(grey), with HT-PPPI a-phases obtained after different reaction times at 200 °C: 0.25 h, 0.5 h and 1 h.*

Fig. S4 shows a superimposition of classically synthesized PPPI, which was allowed to slowly cool down (light blue) and quenched by precipitation in methanol (dark blue). Both spectra show a fully imidized product lacking remainings of monomer modes, polyamic acid modes or endgroups (potentially amino-, carboxylic acid- or anhydride modes). Moreover, it can be concluded that the mode of cooling does not affect the chemical nature of the product.

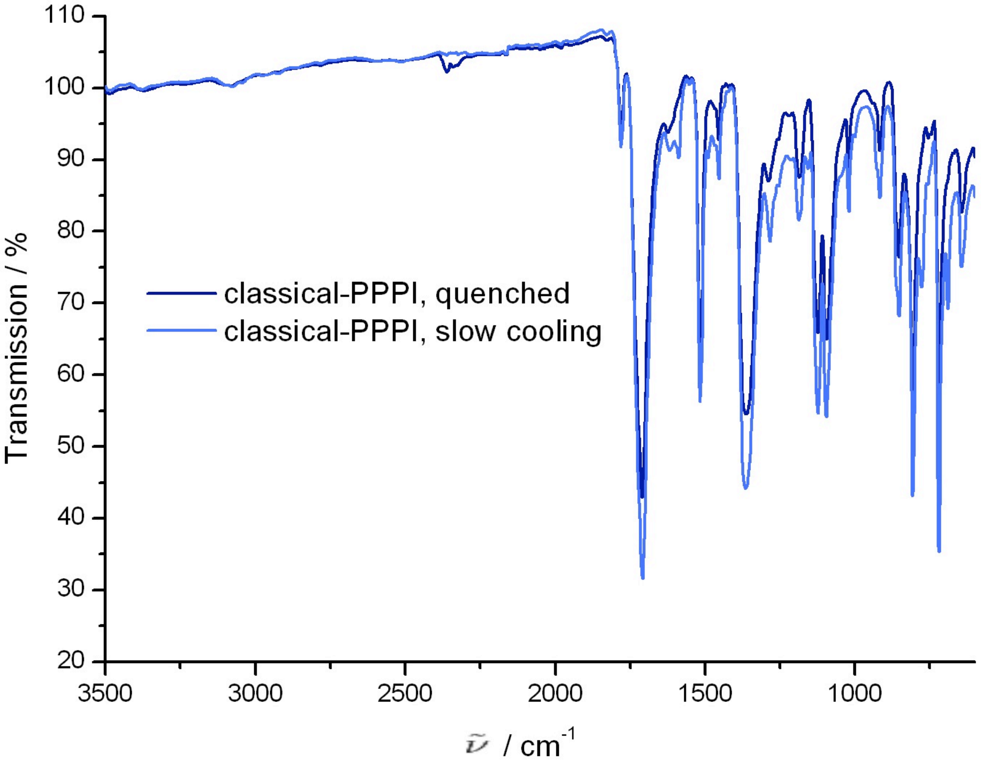


Fig. S4: FT-IR-ATR spectra of classically synthesized PPPI. *Classical-PPPI allowed to cool slowly (light blue); classical-PPPI quenched (dark blue).*

2.4 Characterization of c-phase

The c-phase was carefully removed from the product mixture with a pipette. Its pH was measured using a conventional pH electrode: the pH was reproducibly of 1-2, no matter the HT polymerization time and temperature. The solvent water of all c-phases was then removed with a rotary evaporator. The remaining violet-brownish solid was redissolved in deuterated DMSO and 1H solution NMR analysis was performed.

1H 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 NMR spectra of dried c-phases after t_R=1h and t_R=12h are shown in ***Fig.S5*** and ***Fig.S5***, respectively. Both spectra show a singlet at 8.18 ppm, which corresponds to the aromatic protons of pyromelltic dianhydride. Although the acidity of the c-phases is due to pyromelltic acid, the removal of water under reduced pressure causes its dehydration the anhydride, which we find *via* 1H NMR. The triplets in ***Fig.S5*** (7.31 ppm, 7.10 ppm, 6.90 ppm) and ***Fig.S6*** (7.48 ppm, 7.27 ppm, 7.07 ppm) both exhibit a roof effect. These triplets are attributed to aromatic protons of oxidation oligomers of PDA (see ***Fig.S6***). In the case of t_R = 12 h (***Fig.S5***), we find an additional peak at 6.75 ppm, which we attribute to imino protons. Note the decrease of integrals of the triplets at t_R = 12 h compared to t_R = 1 h, which is due to PDA-derived oligomers growing longer after higher reaction times and joining the b-phase.

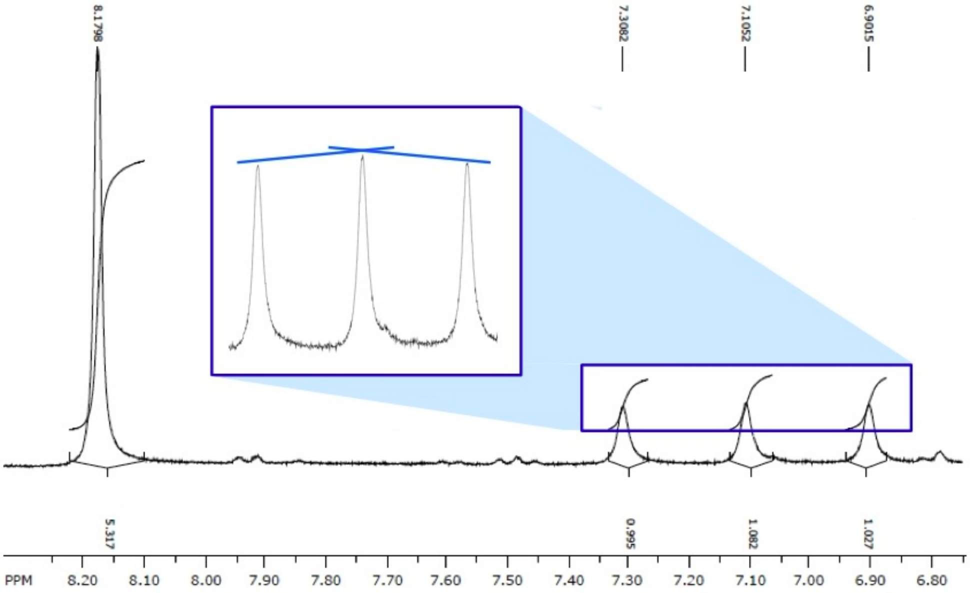


Fig. S5: NMR-spectra of c-phase (t_R = 1 h)

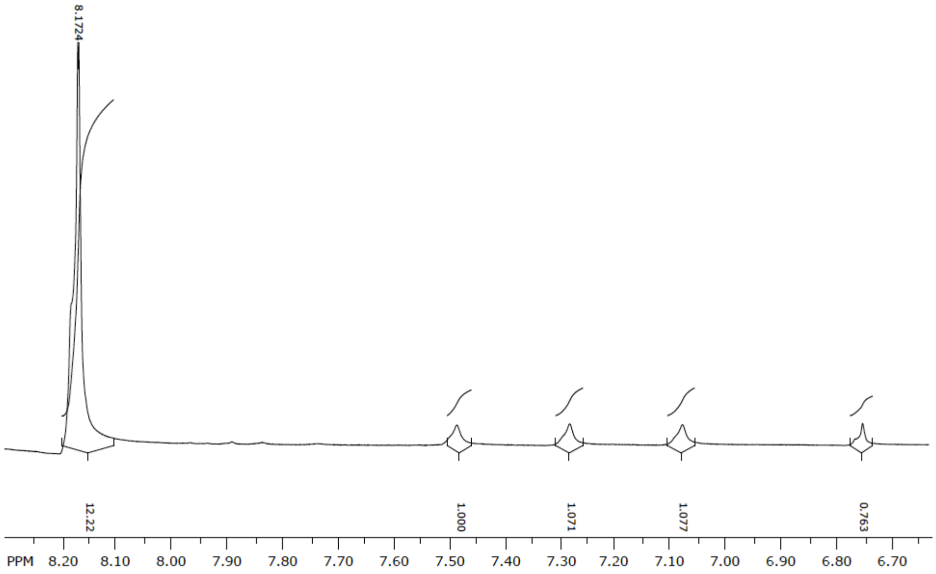


Fig. S6: NMR-spectra of c-phase (t_R = 12 h)

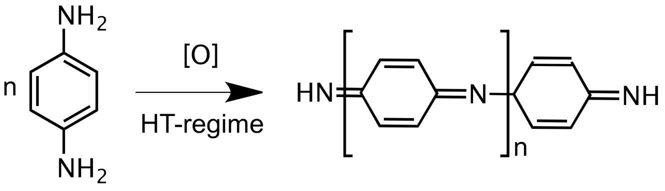


Fig. S7: Oxidation of p-phenylendiamine. (*adapted from* [3])*:*PDA forms strongly colored para-imino oligomers in the presence of oxygen.

2.5 Thermogravimetric analysis of monomer salt and PPPI

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.

Fig. S8 shows the thermogravimetric analysis of HT-PPPI a-phase, obtained after t_R = 12h. The product is stable up to 600°C. This decomposition onset is indicated with an arrow.

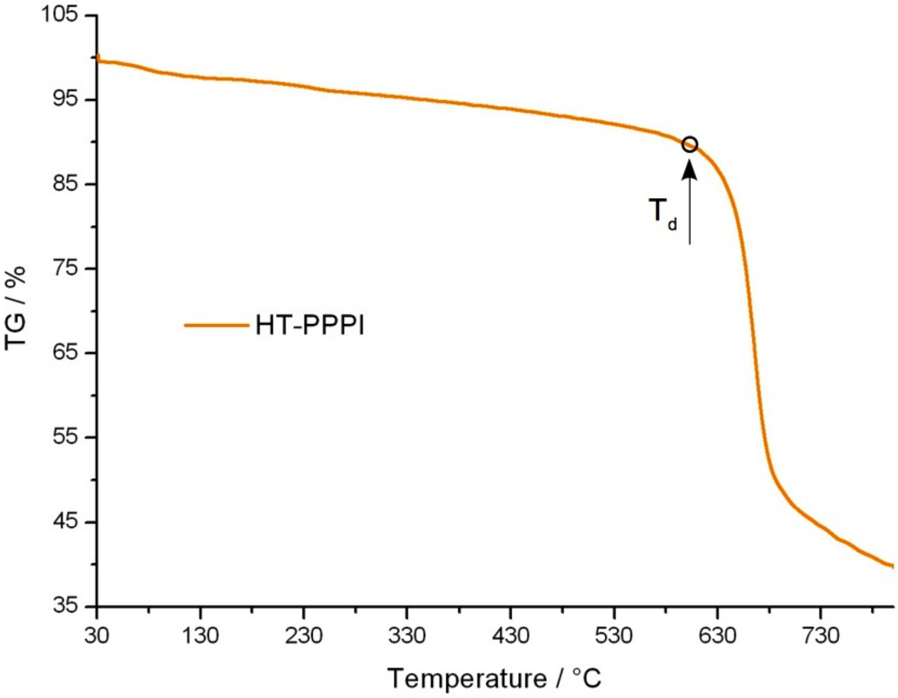


Fig. S8:Thermogravimetric analysis of HT-PPPI (a-phase, t_R = 12 h).*The degradation point is indicated by an arrow.*

TGA of the dried monomer salt is depicted in ***Fig.9*** the monomer salt depicts no melting, but a polymerization point at 210°C.

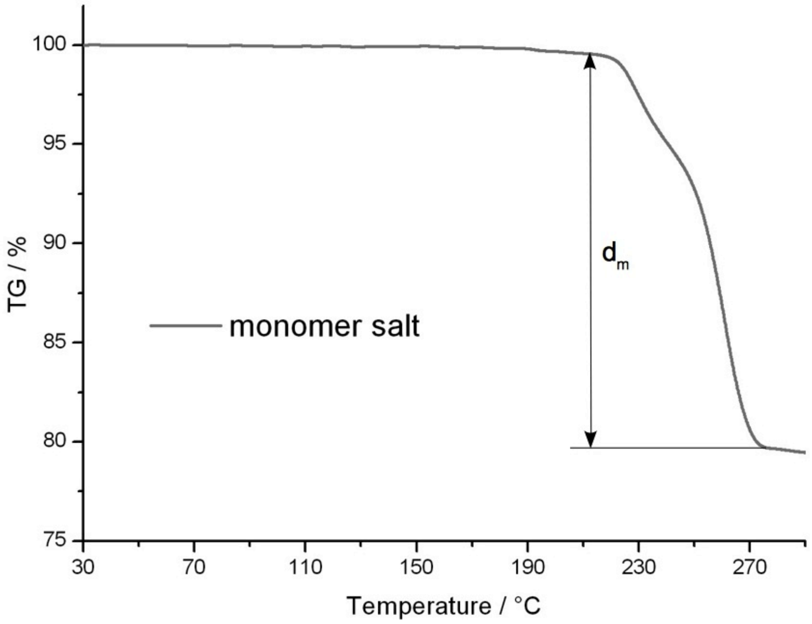


Fig. S9: TGA of monomer salt: *polymerization starts at 210°C and a mass loss of 20% equals to the amount of condensated water.*

The mass loss determined *via* TGA is of *dm* = 20%. This corresponds nicely to two equivalents of water per imide ring, which are eliminated upon polymerization.

The theoretical mass loss is of 19.89%, calculated according to the following equation:

$$mass\ loss\ d_m = \frac{(M_{salt} - M_{PPPI\ monomeric\ unit})}{M_{salt}} \cdot 100 = 19.89\ \%$$

with: M_{salt} = 362,29 g/mol and $M_{PPPI\ monomeric\ unit}$ = 290,23 g/mol.

2.6 Scanning electron microscopy

Scannning electron microscopy was carried out with a *Quanta 200F FEI*microscope. Typically the samples were measured at 5 kV, with a working distance of 9 mm and spot size 2.0. Prior to imaging, samples were loaded on carbon coated stubs and coated by sputtering with an 8nm thick layer of Au/Pd 60/40 alloy with a *Quarum Q105T S* sample preparation system.

Fig. S10 shows overview images of the samples depicted in this paper.

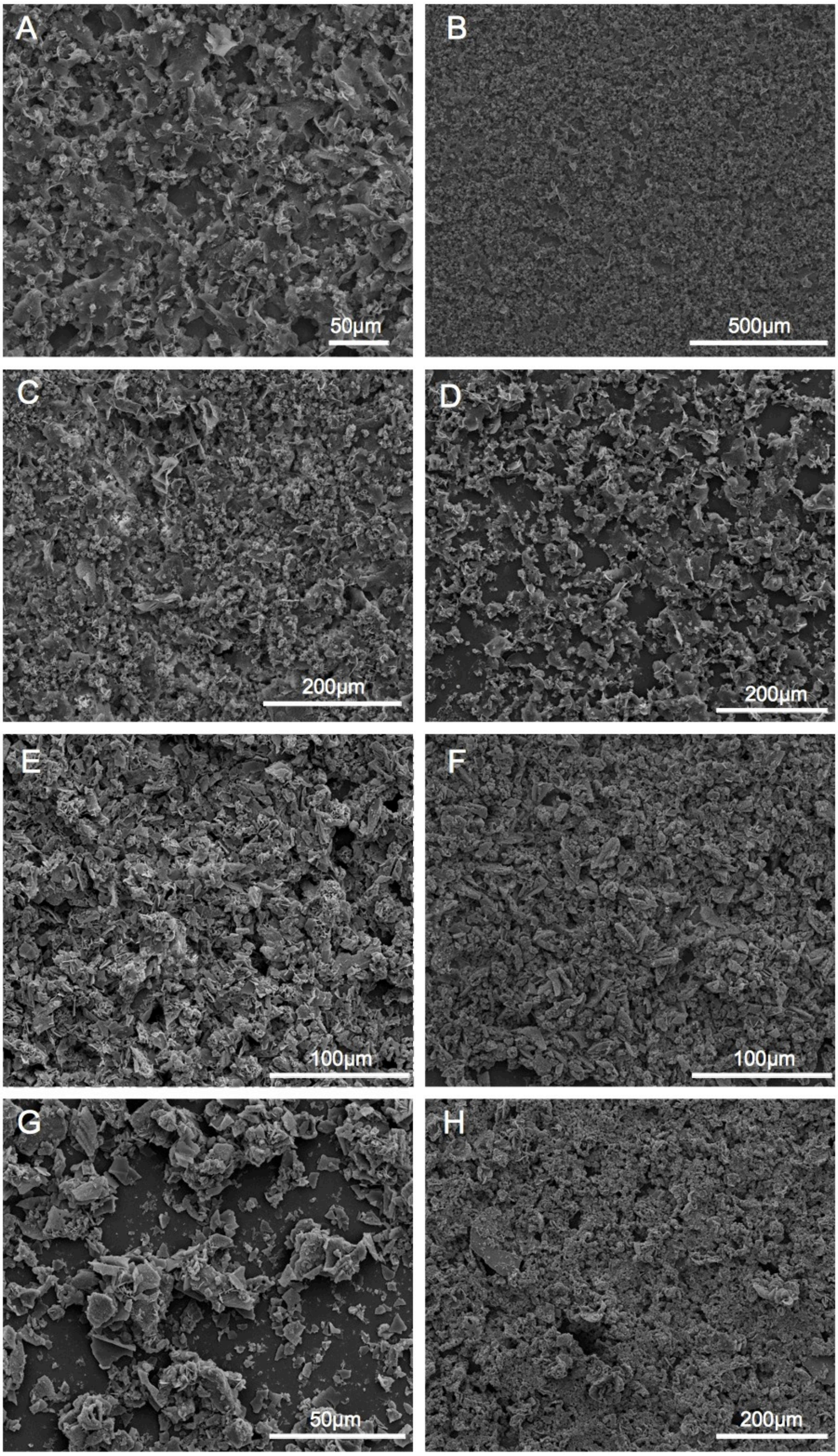


Fig. S10: SEM micrograph overviews of monomer salt and PPPI. A-D) *PPPI b-phases of* t_R*=1h (****A****), 3h (****B****), 8h (****C****),12h (****D****);* ***E-G)*** *PPPI a-phases of* t_R*=1h (****E****), 3h (****F****), 8h (****G****),12h (****H****).*

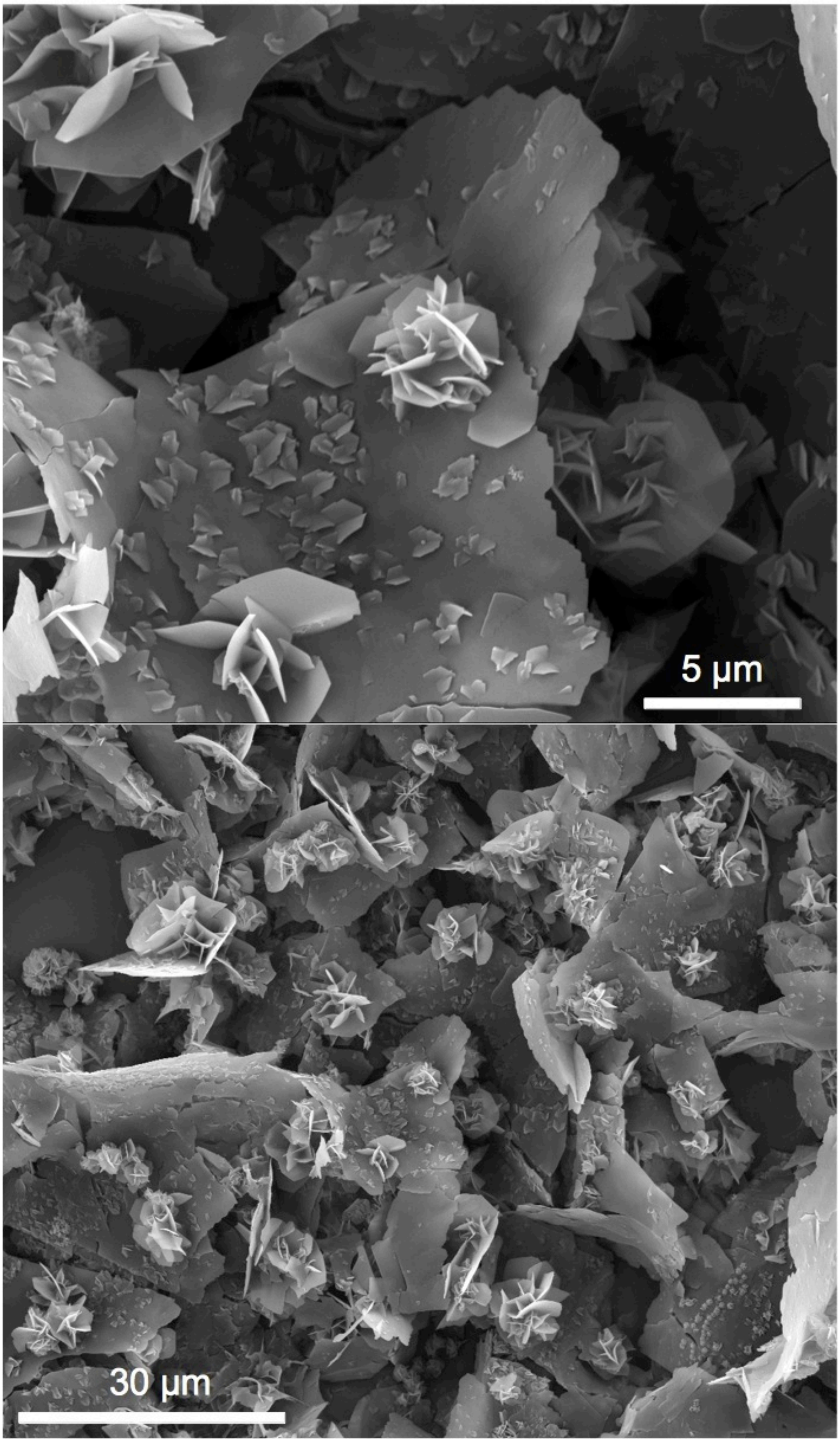


Fig. S11: SEM micrographs of PPPI b-phase *illustrating the formation of poly crystalline aggregates*

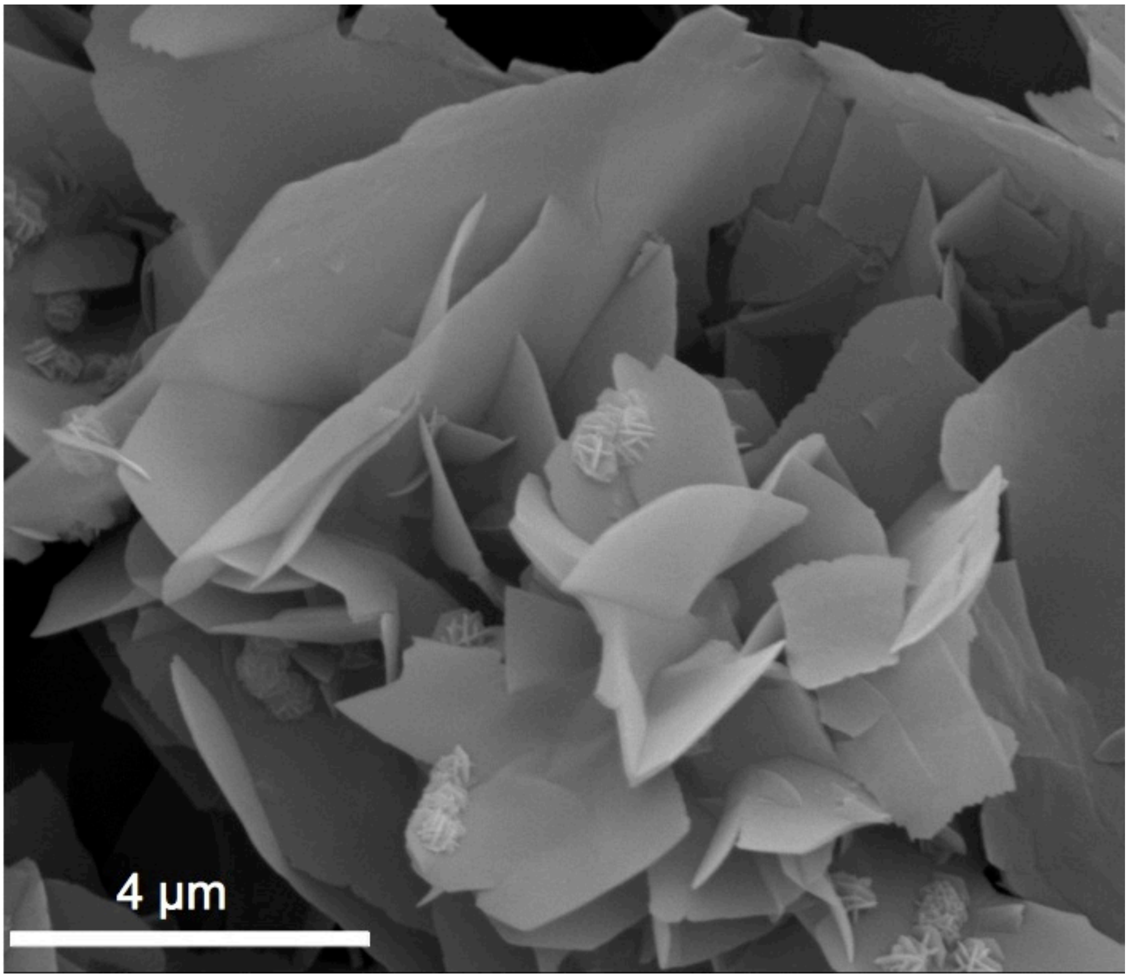


Fig. S12: SEM micrograph of PPPI b-phase *illustrating the formation of poly crystalline aggregates.*

2.7 Powder X-ray diffraction

Powder X-ray diffraction data was collected in two different set-ups for reproducibility, and diffraction pattern were selected by optimal resolution and signal -to-noise ratio. In one case, a PANalyticalX'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 70° (2θ) with 69.215 s/step and a step size of 0.0050134°, sample holders where rotated during the measurement with 4s/turn. High resolution PXRD data were collectedon a PANalytical Empyrean equipped with a hybrid monochromator (2x Ge (220) for Cu) at 45 kV, 40 mA and a PIXcel 3D detector. LaB_6 was used as a standard for determination of the resolution of the diffractometer. Structural refinement and Le Bail fitting was carried out using the *TOPAS-Academic* software.[4]

Fig. S13 shows a the PXRD patterns of HT-PPPI a-phase obtained after t_R = 12 h at different reaction temperatures (150 °C, 200 °C, 250 °C). Peaks attributed to unreacted monomer salt are present in the pattern of the sample obtained at 150 °C only and are denoted by an asterisk (*). The PXRD pattern of products obtained at 200 and 250 °C correspond to the typical HT-PPPI pattern.

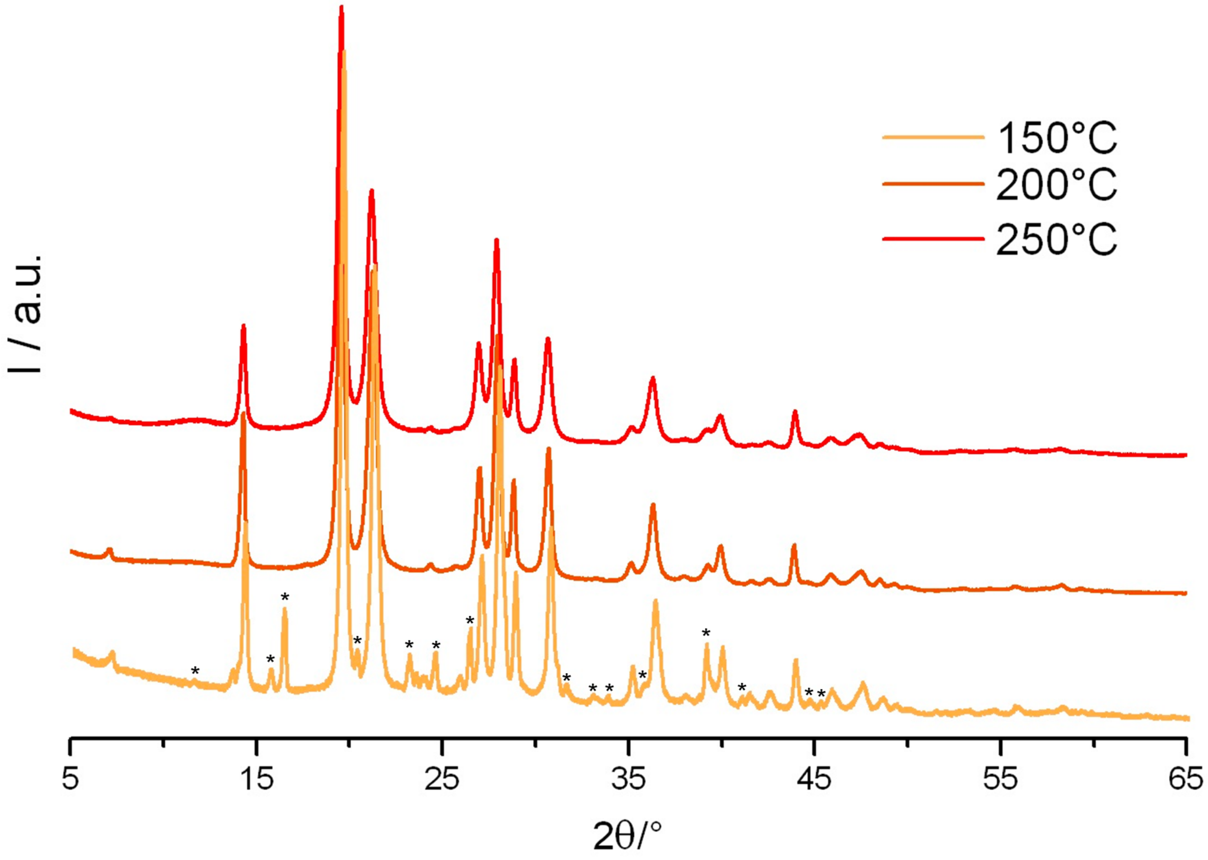


Fig. S13:pXRD patterns of HT-PPPI obtained at different reaction temperatures, at t_R = 12 h. *T = 150 °C (yellow), T=200 °C (orange) and T=250 °C (red).Peaks attributed to unreacted monomer-salt are denoted by asterisks (*).*

A superimposition of pXRD patterns of a- and b-phase is depicted below. Both phases show the same peak positions, thus the same unit cell.

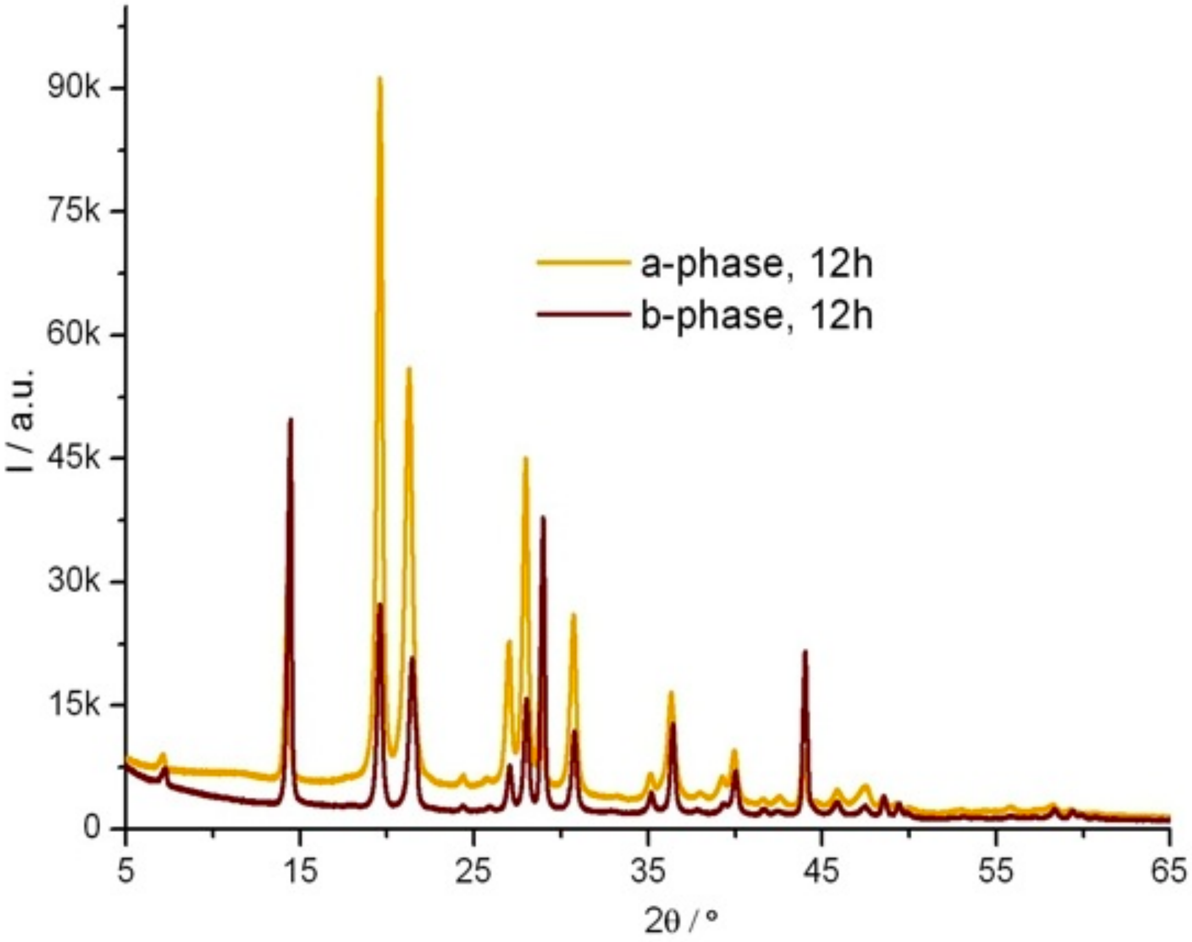


Fig. S14: pXRD patterns of HT-PPPI a- and b-phase obtained at t_R = 12 h. *a-phase (yellow); b-phase (brown).*

The unit cell parameters in cif format obtained *via* refinement of a HT-PPPI pattern measured with monochromatic radiation are shown in ***Fig. S15***.

```
_pd_phase_name                    'HT-PPPI'
_cell_length_a                  5.38960
_cell_length_b                  8.34130
_cell_length_c                  12.36460
_cell_angle_alpha                 90
_cell_angle_beta                 90
_cell_angle_gamma                  90
_symmetry_space_group_name_H-M        'P b a m'
_symmetry_Int_Tables_number          55

loop_
_symmetry_equiv_pos_as_xyz
   'x, y, z'
   '-x, -y, -z'
   '-x, -y, z'
   'x, y, -z'
   '-x+1/2, y+1/2, -z'
   'x+1/2, -y+1/2, z'
   'x+1/2, -y+1/2, -z'
   '-x+1/2, y+1/2, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
   C2       1.0    0.322640     0.411420     0.444130    Uiso  0.045010 C
   C9       1.0    0.111210    0.038160     0.095190    Uiso  0.083080 C
   C11       1.0    0.181220     0.076110     0.222290    Uiso  0.122790 C
   O19       1.0    0.370120     0.142430     0.234540    Uiso  0.121090 O
   H23       1.0    0.183790     0.341660     0.400420    Uiso  0.310930 H
   C1       1.0    0.000000     0.000000     0.386740    Uiso  0.014540 C
   N7       1.0    0.000000     0.000000     0.275800    Uiso  0.018660 N
   C15       1.0    0.229180     0.093610     0.000000    Uiso  0.052550 C
   H28       1.0    0.403080     0.161280     0.000000    Uiso  0.000140 H
```

Fig. S15: *Unit-cell parameters and atomic coordinates for HT-PPPI in CIF format.*

References:

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