SUPPORTING INFORMATION to the paper

Mechanistic Study of Hydrothermal Synthesis of Aromatic Polyimides

by

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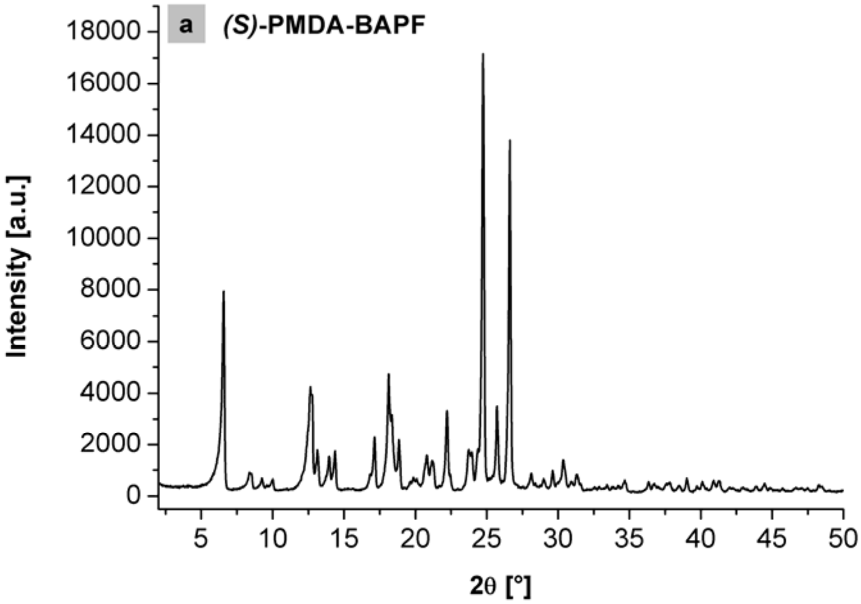
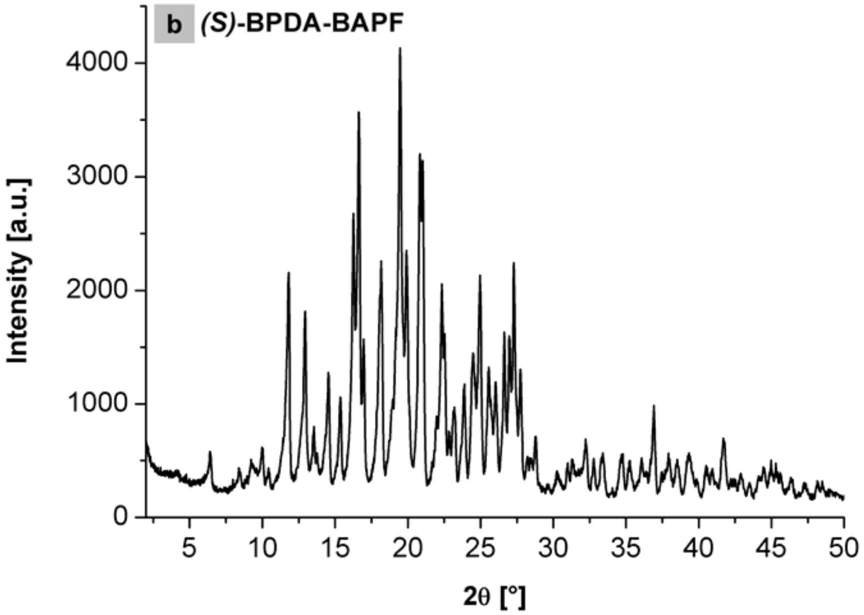
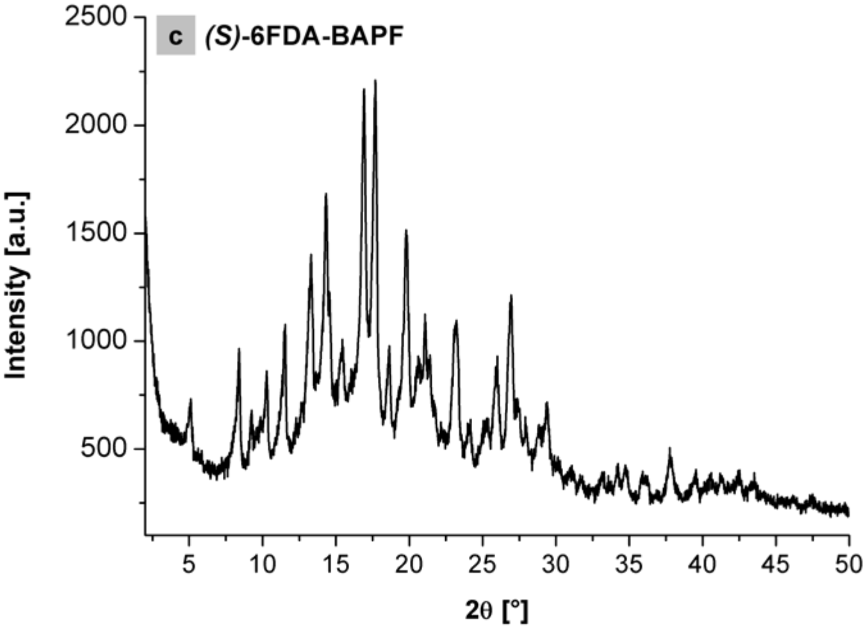
The WAXS patterns (**Fig.S1**) of the monomer salts (a) ***(S)*-PMDA-BAPF**, (b) ***(S)*-BPDA-BAPF**, (c) ***(S)*-6FDA-BAPF** and (d) ***(S)*-ODPA-BAPF** from **Fig.2** are shown below isolatedly, as the superimposition with corresponding monomer spectra may have hindered a clear vision of the spectra.




b
(S)-BPDA-BAPF
Intensity [a.u.]
0
1000
2000
3000
4000
5
10
15
20
25
30
35
40
45
50
2θ [°]


c
(S)-6FDA-BAPF
Intensity [a.u.]
500
1000
1500
2000
2500
5
10
15
20
25
30
35
40
45
50
2θ [°]

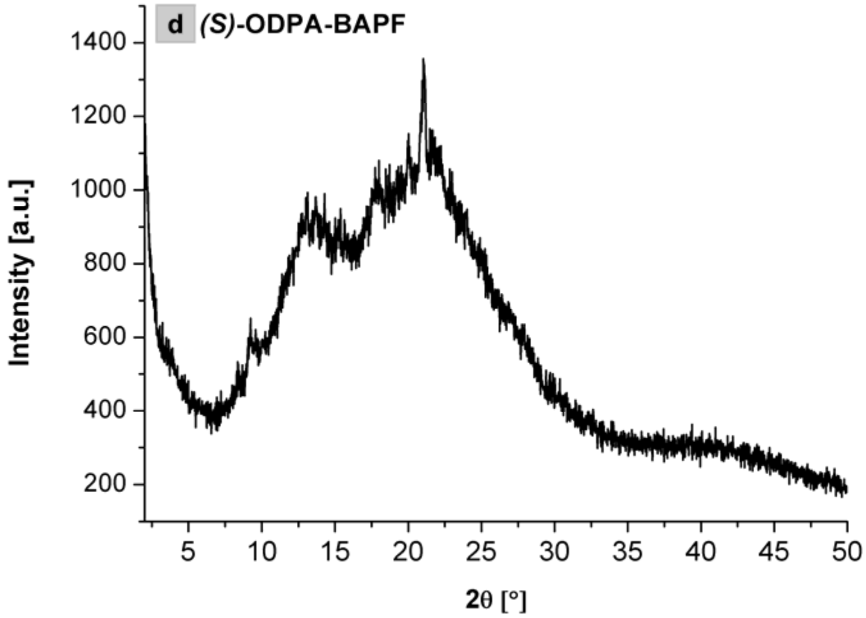
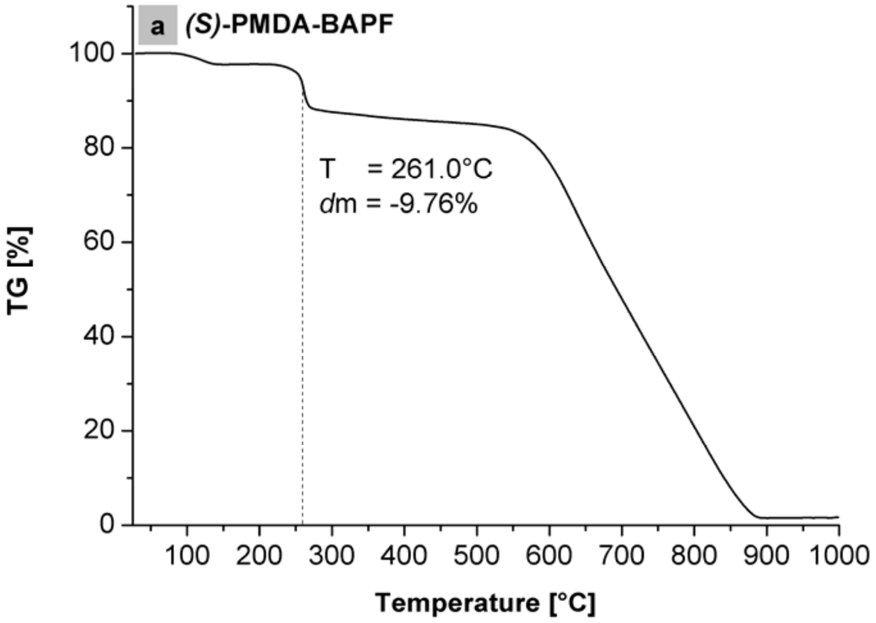
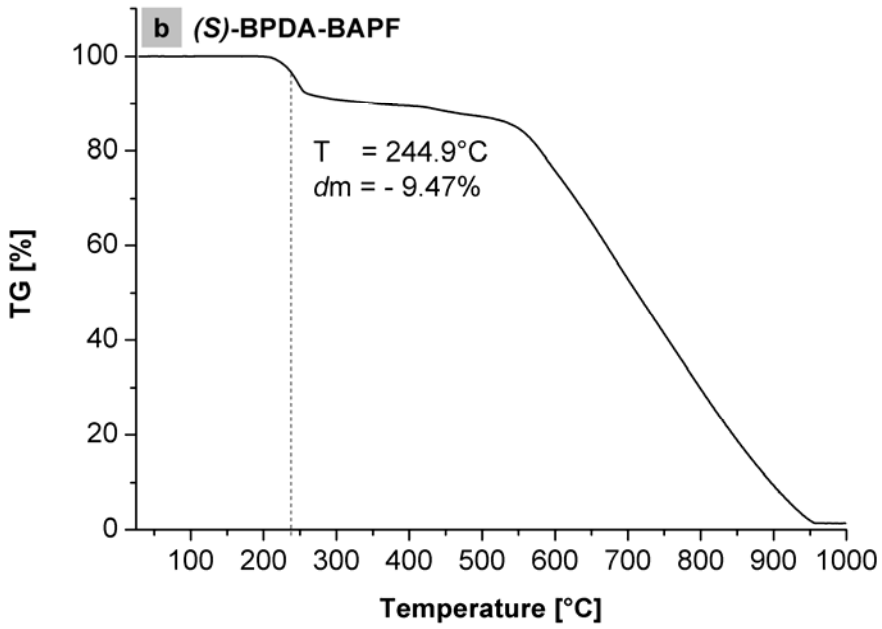
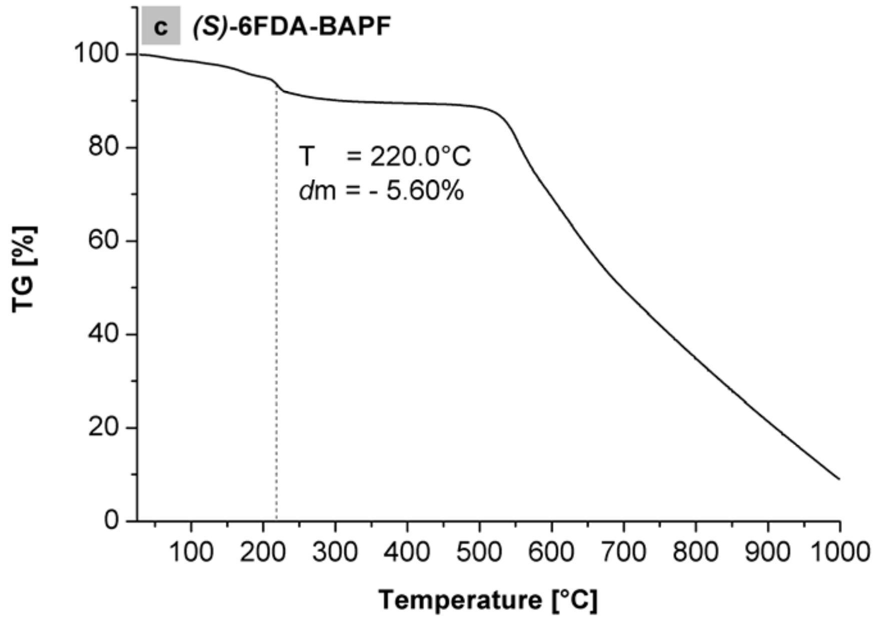


Fig.S1: WAXS patterns of the monomer salts (a) **_(S)_-PMDA-BAPF**, (b) **_(S)_-BPDA-BAPF**, (c) **_(S)_-6FDA-BAPF** and (d) **_(S)_-ODPA-BAPF**. Intensity in arbitrary units [a.u.] plotted *versus* the scattering angle 2θ.

TGA data of the four monomer salts (a) **_(S)_-PMDA-BAPF**, (b) **_(S)_-BPDA-BAPF**, (c) **_(S)_-6FDA-BAPF** and (d) **_(S)_-ODPA-BAPF** is displayed below:




b
(S)-BPDA-BAPF
T = 244.9°C
dm = - 9.47%
TG [%]
0
20
40
60
80
100
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]


c
(S)-6FDA-BAPF
T = 220.0°C
dm = - 5.60%
TG [%]
0
20
40
60
80
100
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]

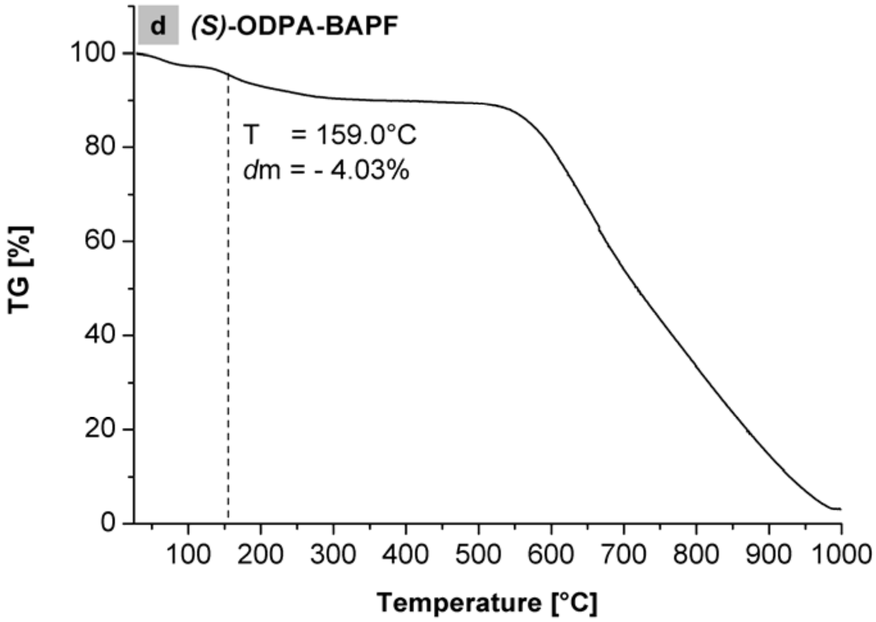
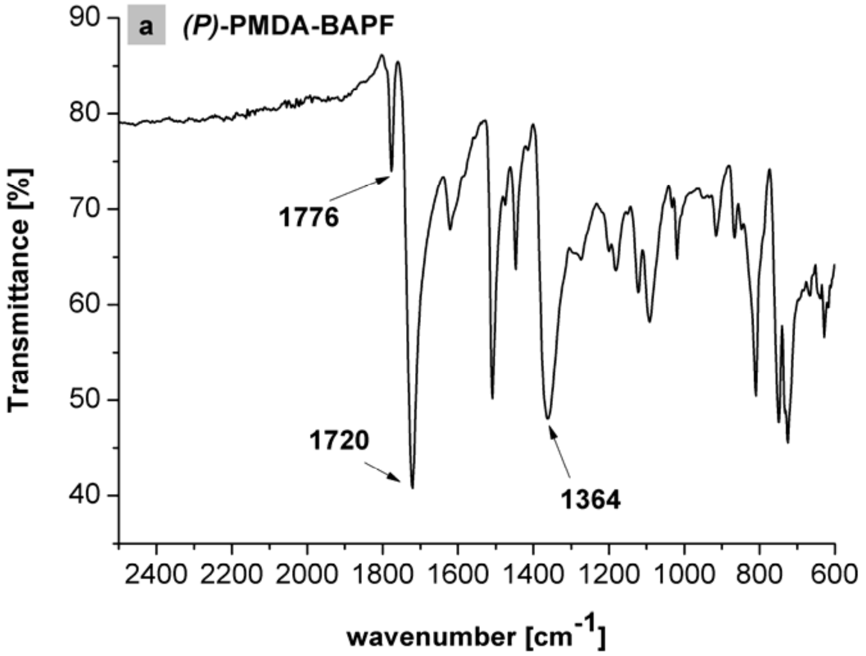
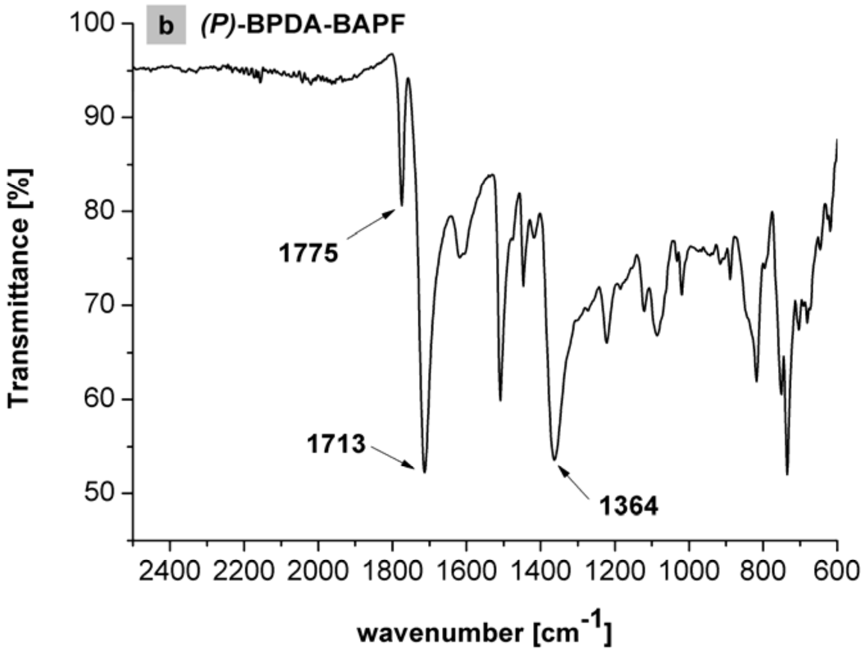
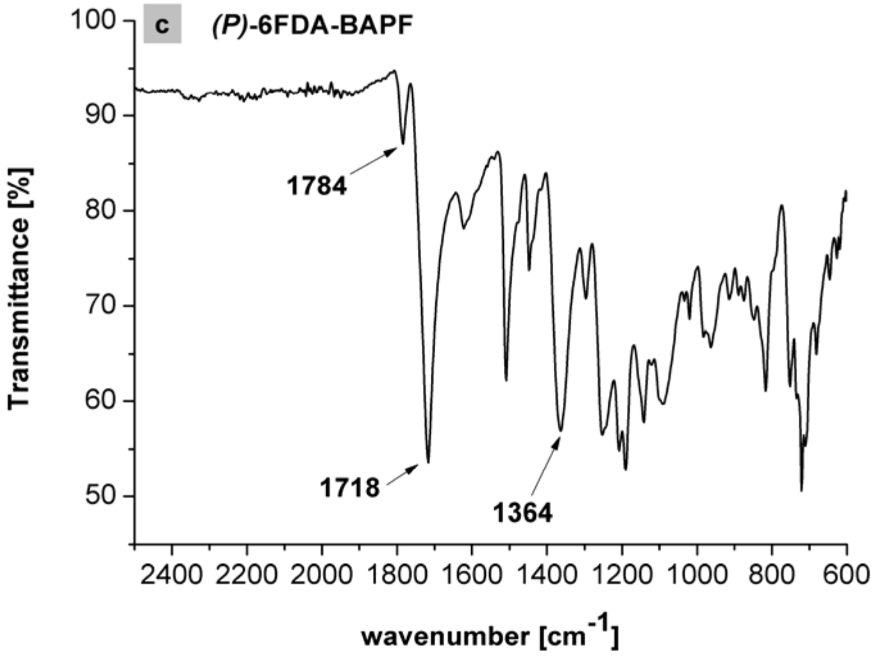


Fig.S2: Mass loss *versus* temperature of (a) ***(S)*-PMDA-BAPF**, (b) ***(S)*-BPDA-BAPF**, (c) ***(S)*-6FDA-BAPF** and (d) ***(S)*-ODPA-BAPF**.

FT-IR spectra of the resulting polymers (a) ***(P)*-PMDA-BAPF**, (b) ***(P)*-BPDA-BAPF**, (c) ***(P)*-6FDA-BAPF** and (d) ***(P)*-ODPA-BAPF**, in the relevant region (2500-600 cm^{-1}):




b
(P)-BPDA-BAPF
Transmittance [%]
100
90
80
70
60
50
1775
1713
1364
2400 2200 2000 1800 1600 1400 1200 1000 800 600
wavenumber [cm-1]


c
(P)-6FDA-BAPF
Transmittance [%]
100
90
80
70
60
50
1784
1718
1364
2400 2200 2000 1800 1600 1400 1200 1000 800 600
wavenumber [cm-1]

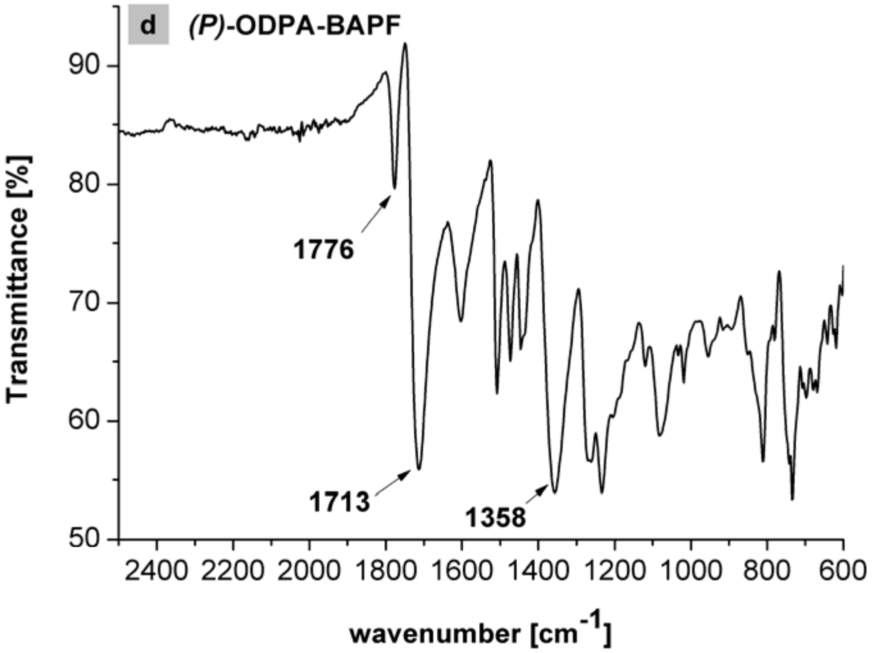
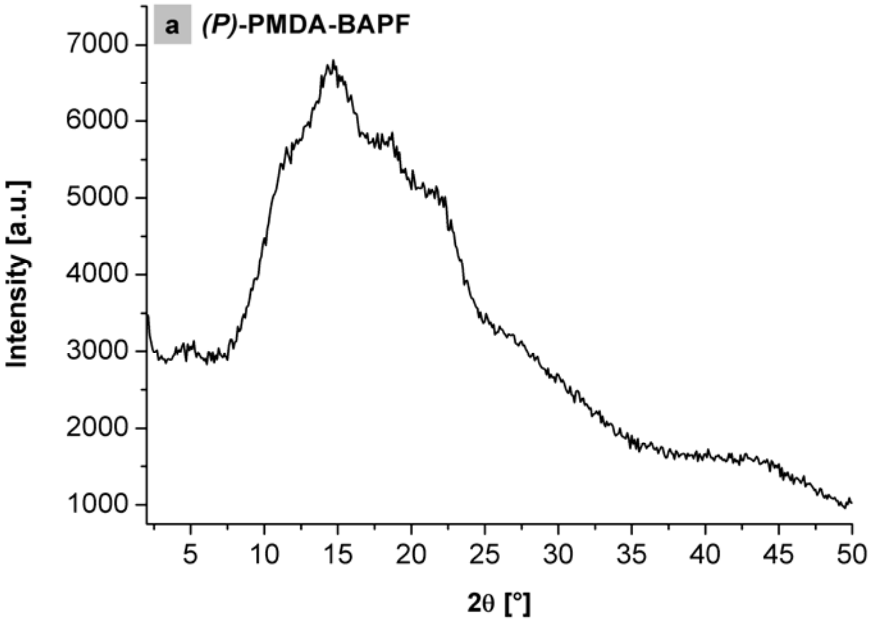
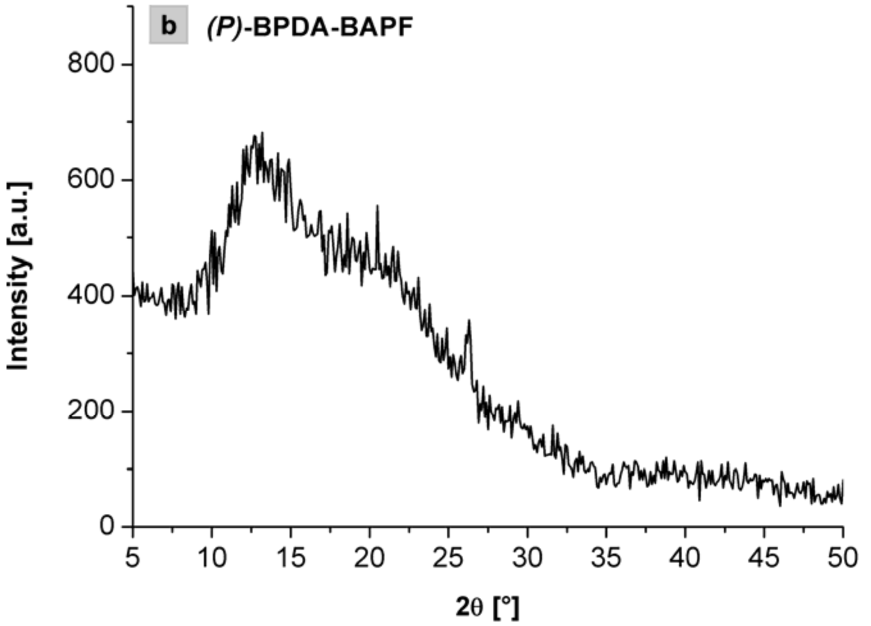
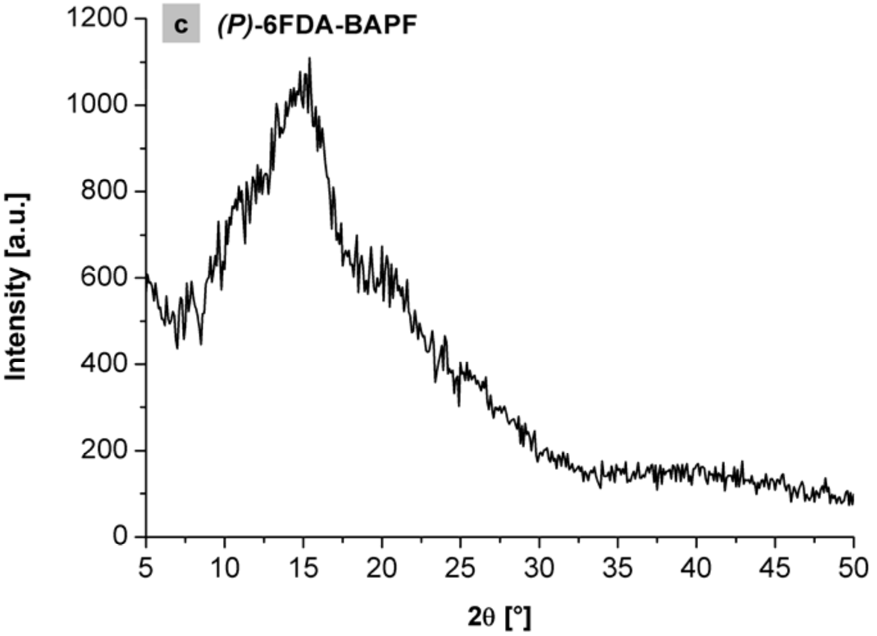


Fig.S3: FT-IR spectra of (a) ***(P)*-PMDA-BAPF**, (b) ***(P)*-BPDA-BAPF**, (c) ***(P)*-6FDA-BAPF** and (d) ***(P)*-ODPA-BAPF**.

WAXS patterns of the four products ((a) ***(P)*-PMDA-BAPF**, (b) ***(P)*-BPDA-BAPF**, (c) ***(P)*-6FDA-BAPF** and (d) ***(P)*-ODPA-BAPF)**:




b
(P)-BPDA-BAPF
Intensity [a.u.]
0
200
400
600
800
5
10
15
20
25
30
35
40
45
50
2θ [°]


c
(P)-6FDA-BAPF
Intensity [a.u.]
0
200
400
600
800
1000
1200
5
10
15
20
25
30
35
40
45
50
2θ [°]

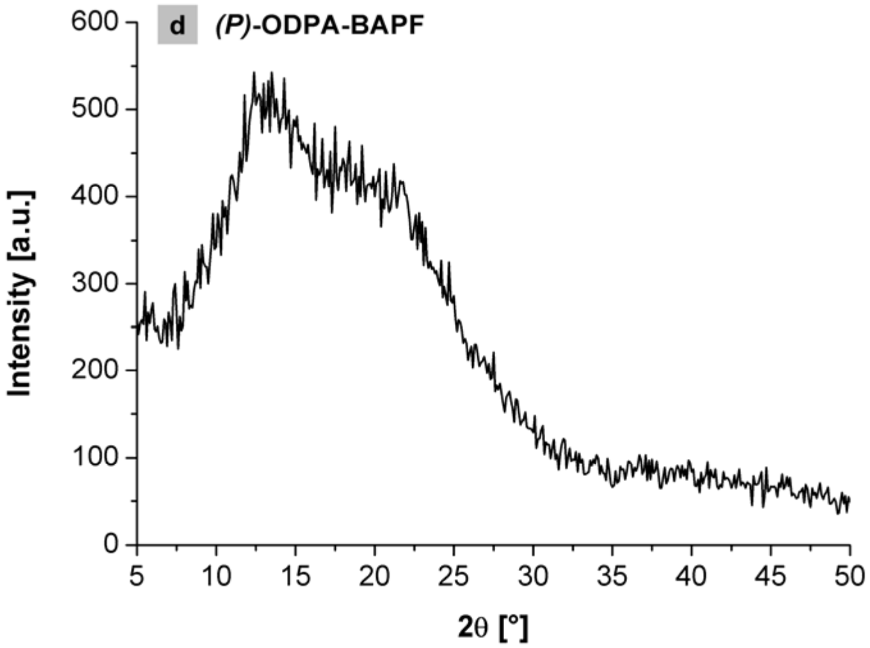


Fig.S4: WAXS patterns of (a) **_(P)_-PMDA-BAPF**, (b) **_(P)_-BPDA-BAPF**, (c) **_(P)_-6FDA-BAPF** and (d) **_(P)_-ODPA-BAPF**. Intensity in arbitrary units [a.u.] plotted *versus* the scattering angle 2θ.

Tab.S1: Table of all fractions obtained via fractionate precipitation, their corresponding polydispersity indices, average molecular weights and yields in respect to the starting monomers.

Compound	$\overline{M}_w(RI)_{F-1}$ [g/mol]	$D(RI)_{F-1}$	Yield [%]
_(P)_-PMDA-BAPF-f1	24,100	4.69	22
_(P)_-PMDA-BAPF-f2	8,400	2.17	14
_(P)_-PMDA-BAPF-f3	5,000	1.74	21
_(P)_-PMDA-BAPF-f4	4,500	1.70	30
_(P)_-BPDA-BAPF-f1	22,000	1.40	17
_(P)_-BPDA-BAPF-f2	16,600	2.41	13
_(P)_-BPDA-BAPF-f3	13,800	1.78	28
_(P)_-BPDA-BAPF-f4	10,500	1.61	5
_(P)_-6FDA-BAPF-f1	48,000	1.66	2
_(P)_-6FDA-BAPF-f2	34,200	1.78	3
_(P)_-6FDA-BAPF-f3	25,000	1.46	28
_(P)_-6FDA-BAPF-f4	17,800	1.36	24
_(P)_-6FDA-BAPF-f5	10,100	1.32	17
_(P)_-6FDA-BAPF-f6	6,100	1.36	2
_(P)_-ODPA-BAPF-f1	33,700	1.60	16
_(P)_-ODPA-BAPF-f2	21,400	1.38	24
_(P)_-ODPA-BAPF-f3	18,100	1.43	27
_(P)_-ODPA-BAPF-f4	10,200	1.41	15
_(P)_-ODPA-BAPF-f5	6,900	1.77	3

Fractionations were carried out quantitatively from a solution of the polymer in *N*-Methyl-2-pyrrolidone. A typical fractionation procedure is given in the following:

0.4287 g of ***(P)*-BPDA-BAPF** were dissolved in 20mL of *N*-Methyl-2-pyrrolidone by moderate stirring under ambient conditions for 2 hours. A translucent yellowish solution resulted. Methanol was added milliliter-wise under continuous stirring. After the addition of 9 mL the first enduring precipitation occurred. The dispersion was then centrifuged at 6000 rpm for 15 minutes. Liquid and solid phase were separated by decantation. This step was repeated until no further precipitation occurred. Fractions precipitated at the following added volumes of methanol:

fraction	Overall added volume of MeOH $\sum V$ in [mL]
CP-f1	9
CP-f2	10
CP-f3	11
CP-f4	12
CP-f5	13
CP-f6	14
CP-f7	15
CP-f8	16
CP-f9	17
CP-f10	18
CP-f11	20
CP-f12	21
CP-f13	22
CP-f14	23
CP-f15	24
CP-f16	25
CP-f17	27
CP-f18	29
CP-f19	31
CP-f20	32

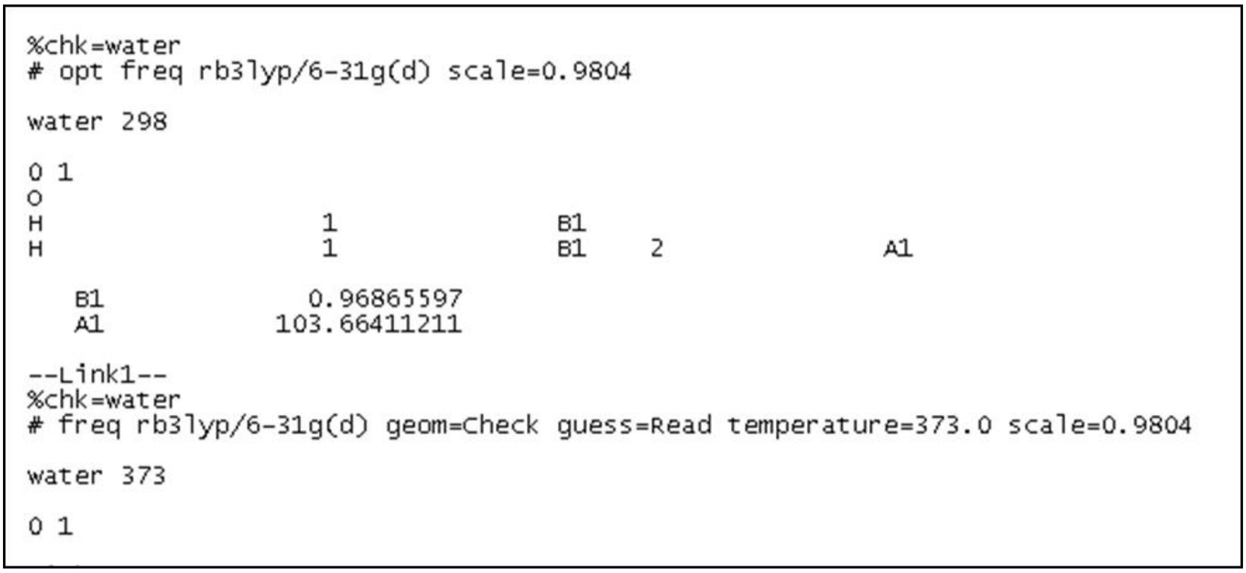
The precipitates were then dried overnight at 40°C under vacuum. The obtained fractions CP-f1 to CP-f20 were analyzed via SEC. Several fractions lead to the same average molecular weight within the error of the method and were thus united. The resulting fractions of identical $\overline{M}_w(RI)$ were:

Fractions of the same $\overline{M}_w(RI)$	Containing fractions
f-1	CP-f1, CP-f2
f-2	CP-f3 to CP-f7
f-3	CP-f8 to CP-f15

f-4	CP-f16 to CP-f18
f-5	CP-f19, CP-f20

The last fraction f-5 corresponds to residual diamine monomer (BAPF).

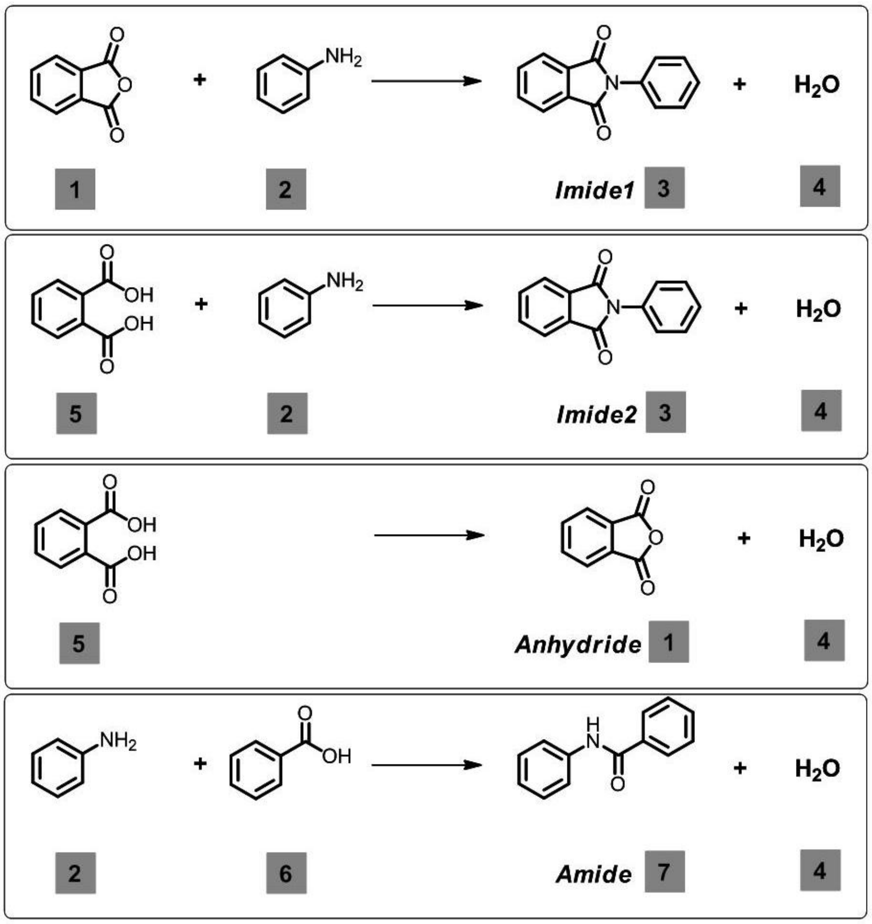
Depicted below, a typical Gaussian input file, exemplarily for water at 298K and 373K. Note the scaling factor for computation of thermal contributions and zero point energies.



```
%chk=water
# opt freq rb3lyp/6-31g(d) scale=0.9804

water 298

0 1
O
H                    1               B1
H                    1               B1     2               A1

   B1               0.96865597
   A1             103.66411211

--Link1--
%chk=water
# freq rb3lyp/6-31g(d) geom=Check guess=Read temperature=373.0 scale=0.9804

water 373

0 1
```

Fig.S5: Exemplary Gaussian input file for water at 298 and 373K.

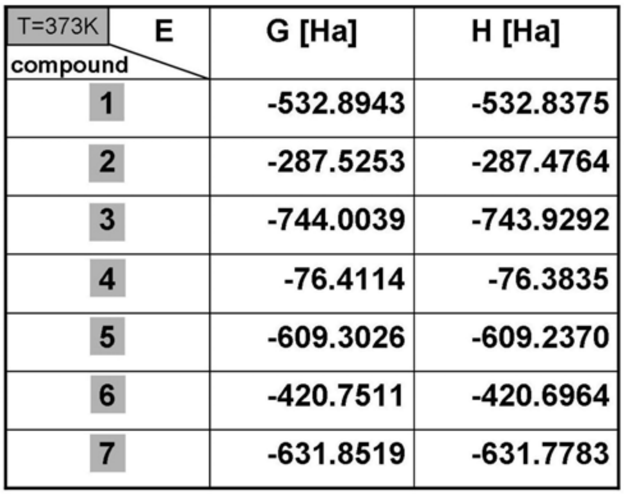
Tables **Tab.S2a-Tab.S2e** show Gibb's Free Energy G and Enthalpy H values obtained via Gaussian calculations, for the computed compounds (numbering according to **Scheme S.1**, below) at corresponding temperatures.



Scheme S1: possible reactions leading to imides, amides or anhydrides.

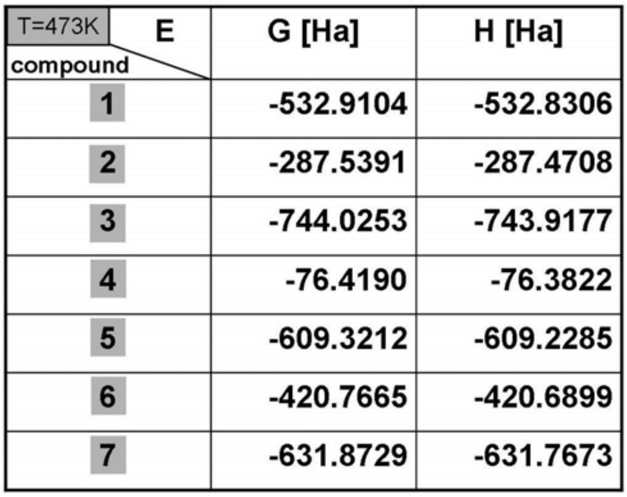
T=298K E compound	G [Ha]	H [Ha]
1	-532.8834	-532.8418
2	-287.5159	-287.4798
3	-743.9897	-743.9363
4	-76.4059	-76.3844
5	-609.2900	-609.2422
6	-420.7406	-420.7003
7	-631.8379	-631.7851

Table S2a: G and H of compounds 1-7 at 298K. Energies given in Hartree [Ha].



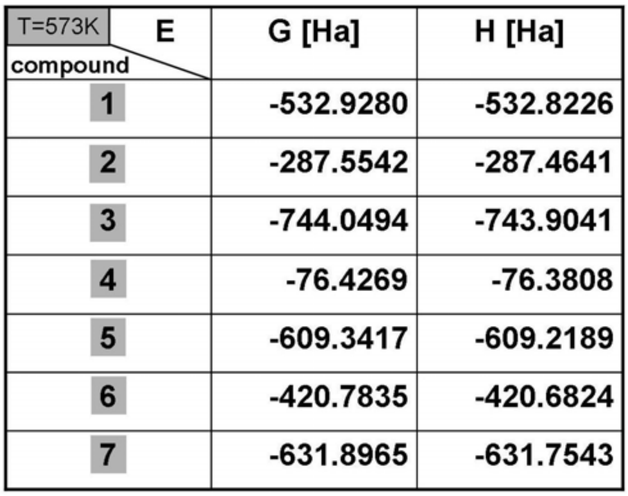
T=373K E compound	G [Ha]	H [Ha]
1	-532.8943	-532.8375
2	-287.5253	-287.4764
3	-744.0039	-743.9292
4	-76.4114	-76.3835
5	-609.3026	-609.2370
6	-420.7511	-420.6964
7	-631.8519	-631.7783

Table S2b: G and H of compounds 1-7 at 373K. Energies given in Hartree [Ha].



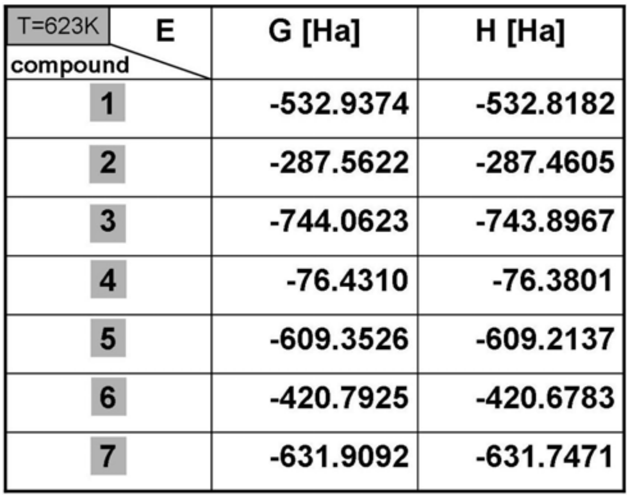
T=473K E compound	G [Ha]	H [Ha]
1	-532.9104	-532.8306
2	-287.5391	-287.4708
3	-744.0253	-743.9177
4	-76.4190	-76.3822
5	-609.3212	-609.2285
6	-420.7665	-420.6899
7	-631.8729	-631.7673

Table S2c: G and H of compounds 1-7 at 473K. Energies given in Hartree [Ha].



T=573K E compound	G [Ha]	H [Ha]
1	-532.9280	-532.8226
2	-287.5542	-287.4641
3	-744.0494	-743.9041
4	-76.4269	-76.3808
5	-609.3417	-609.2189
6	-420.7835	-420.6824
7	-631.8965	-631.7543

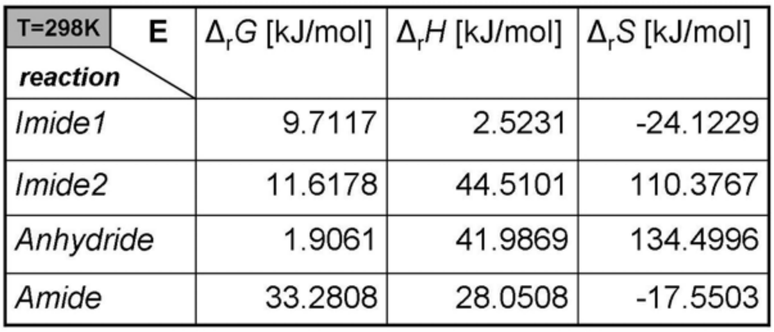
Table S2d: G and H of compounds 1-7 at 573K. Energies given in Hartree [Ha].



T=623K E compound	G [Ha]	H [Ha]
1	-532.9374	-532.8182
2	-287.5622	-287.4605
3	-744.0623	-743.8967
4	-76.4310	-76.3801
5	-609.3526	-609.2137
6	-420.7925	-420.6783
7	-631.9092	-631.7471

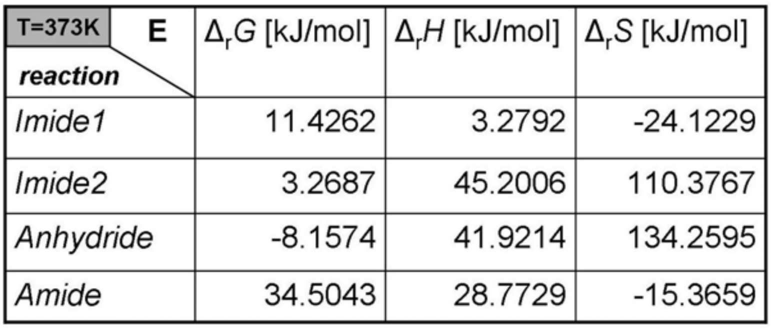
Table S2e: G and H of compounds 1-7 at 573K. Energies given in Hartree [Ha].

The reaction energies ΔG, ΔH and ΔS for the four model reactions were calculated based on the energies for each participating compound, as depicted in tables **Tab.S2a – Tab.S2e**, are depicted below (**Tab.S3a-Tab.S3e**).



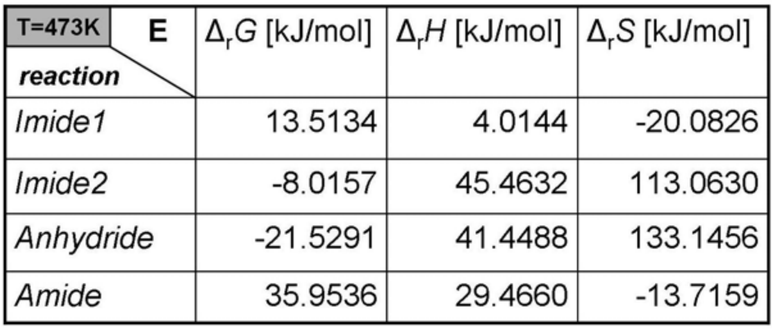
T=298K E *reaction*	$\Delta_r G$ [kJ/mol]	$\Delta_r H$ [kJ/mol]	$\Delta_r S$ [kJ/mol]
Imide1	9.7117	2.5231	-24.1229
Imide2	11.6178	44.5101	110.3767
Anhydride	1.9061	41.9869	134.4996
Amide	33.2808	28.0508	-17.5503

Table S3a: $\Delta_r G$ $\Delta_r H$ and $\Delta_r S$ of model reactions at 298K. Energies given in kJ/mol.



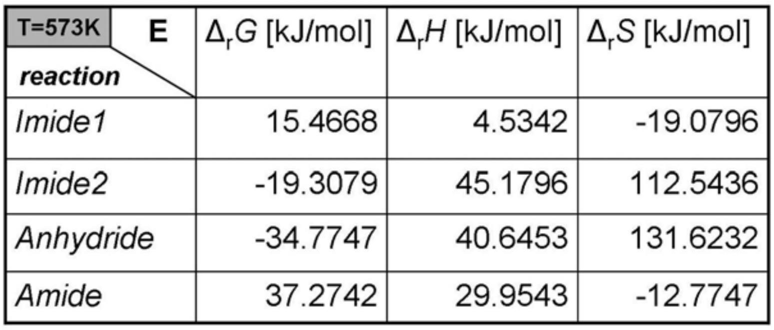
T=373K E *reaction*	$\Delta_r G$ [kJ/mol]	$\Delta_r H$ [kJ/mol]	$\Delta_r S$ [kJ/mol]
Imide1	11.4262	3.2792	-24.1229
Imide2	3.2687	45.2006	110.3767
Anhydride	-8.1574	41.9214	134.2595
Amide	34.5043	28.7729	-15.3659

Table S3b: $\Delta_r G$ $\Delta_r H$ and $\Delta_r S$ of model reactions at 373K. Energies given in kJ/mol.



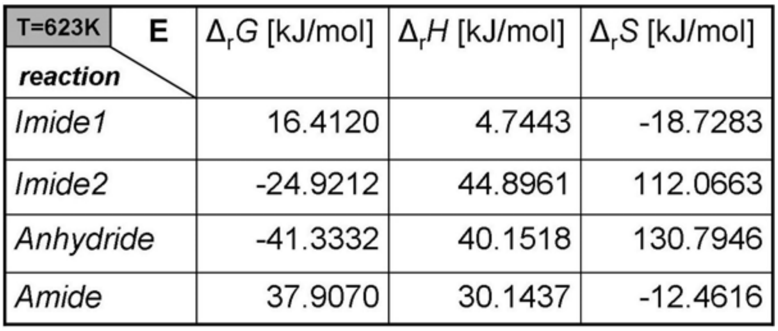
T=473K E reaction	$\Delta_r G$ [kJ/mol]	$\Delta_r H$ [kJ/mol]	$\Delta_r S$ [kJ/mol]
Imide1	13.5134	4.0144	-20.0826
Imide2	-8.0157	45.4632	113.0630
Anhydride	-21.5291	41.4488	133.1456
Amide	35.9536	29.4660	-13.7159

Table S3c: $\Delta_r G$ $\Delta_r H$ and $\Delta_r S$ of model reactions at 473K. Energies given in kJ/mol.



T=573K E reaction	$\Delta_r G$ [kJ/mol]	$\Delta_r H$ [kJ/mol]	$\Delta_r S$ [kJ/mol]
Imide1	15.4668	4.5342	-19.0796
Imide2	-19.3079	45.1796	112.5436
Anhydride	-34.7747	40.6453	131.6232
Amide	37.2742	29.9543	-12.7747

Table S3d: $\Delta_r G$ $\Delta_r H$ and $\Delta_r S$ of model reactions at 573K. Energies given in kJ/mol.



T=623K E reaction	$\Delta_r G$ [kJ/mol]	$\Delta_r H$ [kJ/mol]	$\Delta_r S$ [kJ/mol]
Imide1	16.4120	4.7443	-18.7283
Imide2	-24.9212	44.8961	112.0663
Anhydride	-41.3332	40.1518	130.7946
Amide	37.9070	30.1437	-12.4616

Table S3e: $\Delta_r G$ $\Delta_r H$ and $\Delta_r S$ of model reactions at 623K. Energies given in kJ/mol.

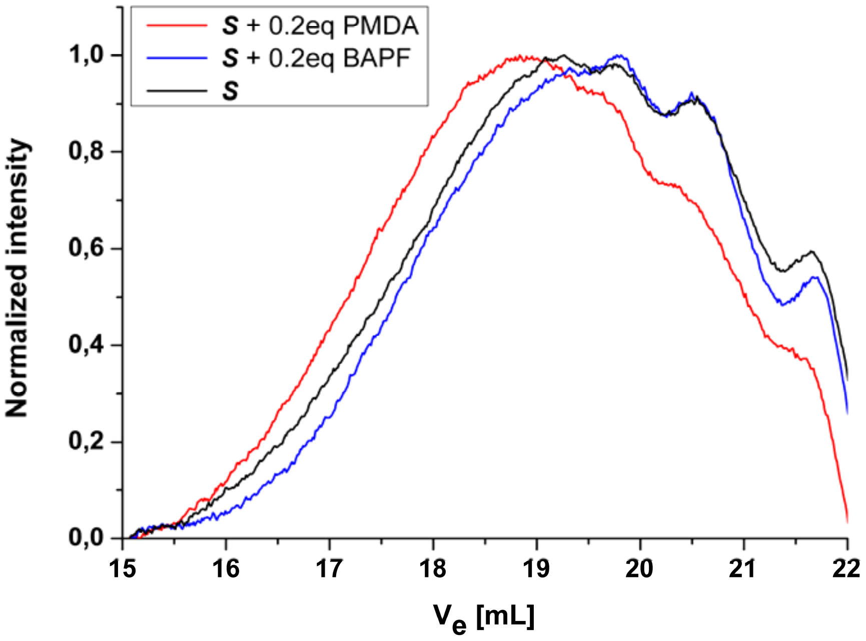


Fig.S6: Superposition of the elugrams of the crude products obtained from cases (a)-(c) (see fulltext). Elugrams of polymers obtained from the pure salt ***S*** (in black), S with an excess of pyromellitic acid (red curve, ***S*** + 0.2eq PMDA) and from S with an excess of bisamine added to the salt dispersion (blue, ***S*** + 0.2eq BAPF).

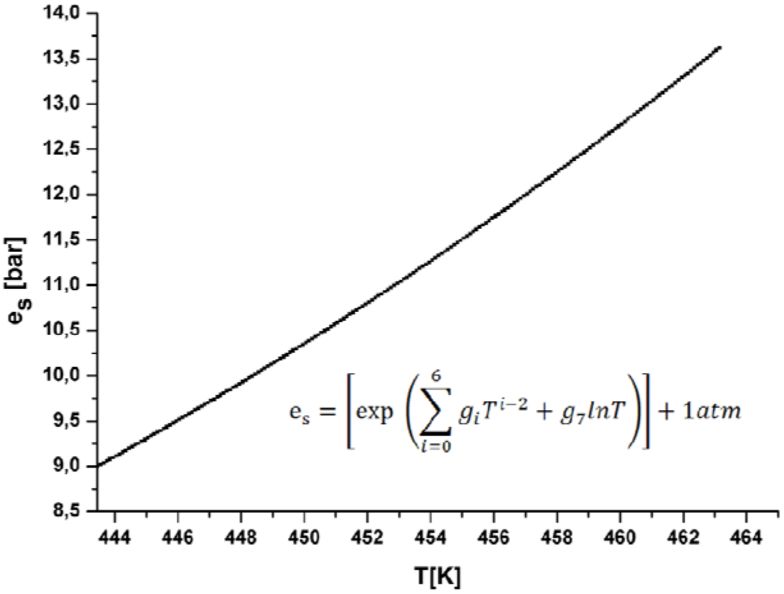


Fig.S7: *Claculated saturation pressure of water in steps of 0.1K*. Saturation pressure e_s in [bar] plotted *vs*. temperature in [K]. the calculated values were obtained via WEXLER's equation[25] and subsequent addition of 1atm to each value (as the autoclaves are closed at standard state, 1 atm of air is present in the closed system and has to be added). The used WEXLER coefficients[25] are:

$g_0=$	$-2.8365744\cdot 10^{3}$
$g_1=$	$-6.028076559\cdot 10^{3}$
$g_2=$	$1.954263612\cdot 10^{1}$
$g_3=$	$-2.737830188\cdot 10^{-2}$
$g_4=$	$1.6261698\cdot 10^{-4}$
$g_5=$	$7.0229056\cdot 10^{-10}$
$g_6=$	$-1.8680009\cdot 10^{-13}$
$g_7=$	2.7150305

References

25 (a) A. Wexler, *J. Res. Natl. Bur. Stand., Sect. A*, 1976, 80, 775; (b) B. Hardy, ITS-90 Formulations for Vapor Pressure, Frostpoint Temperature, Dewpoint Temperature, and Enhancement Factors in the Range _100 to +100 _C, in *Proceedings of Third International Symposium on Humidity & Moisture*, Teddington, London, England, 1998.