

The kinetic story of tailor-made additives in polymorphic systems: new data and molecular insights for *p*-aminobenzoic acid.

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Supplementary information.

S1 Solubility data

S2 Crystal Aspect Ratios

S3 Preferred Orientation

S4 Induction Probability Distributions

S5 Growth Rates

S1. Effect of Additives on solubility of *α* pABA.

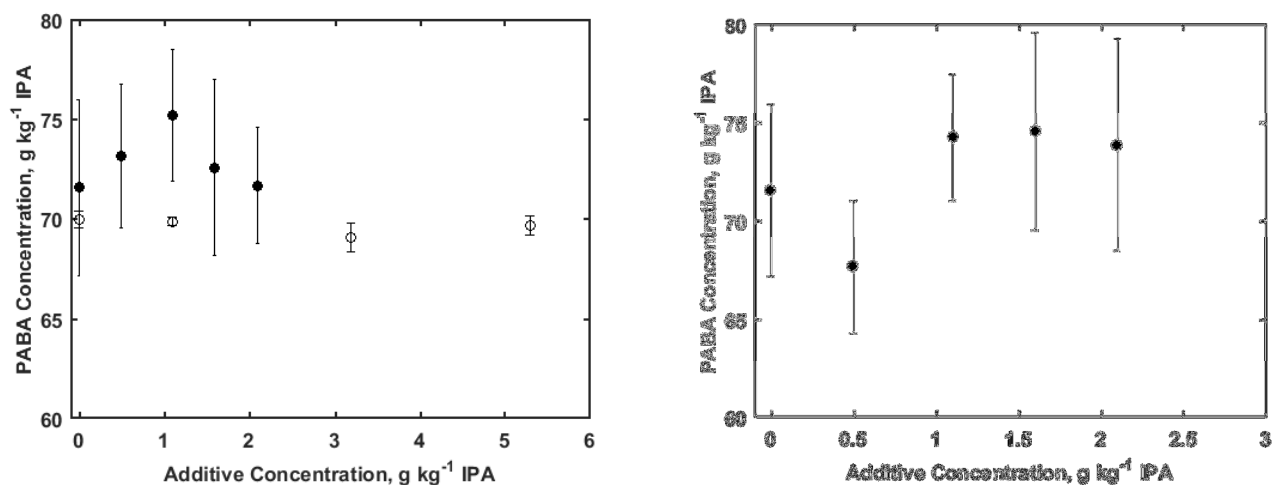


Figure S1.1. The effect of ANBA (left hand side) and AMBA (right hand side) on the solubility of *α* pABA in IPA at 20°C. Gravimetric data open circles and HPLC data filled circle.

Table S1.1 The effect of ANBA on the solubility of α pABA in IPA at 10°C - gravimetric data.

Wt % ANBA (w.r.t. pABA in slurry)	Concentration of ANBA (g kg ⁻¹ IPA)	Average Solubility of α pABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0.0	0.0	53.4	0.4
1.0	0.8	54.7	0.1
3.0	2.5	61.0	0.4
5.0	4.2	54.9	0.3

Table S1.2 The effect of ANBA on the solubility of α pABA in IPA at 20°C - gravimetric data.

Wt % ANBA (w.r.t. pABA in slurry)	Concentration of ANBA (g kg ⁻¹ IPA)	Average Solubility of α pABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0.0	0.0	70.0	0.4
1.0	1.1	69.9	0.2
3.0	3.2	69.1	0.7
5.0	5.3	69.7	0.5

Table S1.3 The effect of ANBA on the solubility of α pABA in IPA at 10°C – HPLC data.

Wt % ANBA (w.r.t. pABA in slurry)	Concentration of ANBA (g kg ⁻¹ IPA)	Average Solubility of α pABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0.0	0.0	59.6	5.1
0.5	0.4	63.2	5.3
1.0	0.8	74.5	1.6
1.5	1.3	71.9	1.3
2.0	1.7	71.5	1.7

Table S1.4 The effect of ANBA on the solubility of α pABA in IPA at 20°C – HPLC data.

Wt % ANBA (w.r.t. pABA in slurry)	Concentration of ANBA (g kg ⁻¹ IPA)	Average Solubility of α pABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0	0.0	71.6	4.4
0.5	0.5	73.2	3.6
1.0	1.1	75.2	3.3
1.5	1.6	72.6	4.4
2.0	2.1	71.7	2.9

Table S1.5 The effect of AMBA on the solubility of and α *p*ABA in IPA at 10°C – HPLC data.

Weight % AMBA (w.r.t. <i>p</i> ABA in slurry)	Concentration of AMBA (g kg ⁻¹ IPA)	Average Solubility of α <i>p</i> ABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0	0.0	59.6	5.1
0.5	0.4	62.6	8.3
1.0	0.8	67.5	2.8
1.5	1.3	68.3	4.0
2.0	1.7	67.1	5.3

Table S1.6 The effect of AMBA on the solubility of α *p*ABA in IPA at 20°C – HPLC data.

Weight % AMBA (w.r.t. <i>p</i> ABA in slurry)	Concentration of AMBA (g kg ⁻¹ IPA)	Average Solubility of α <i>p</i> ABA (g kg ⁻¹ IPA)	Standard error ($\pm$ g kg ⁻¹ IPA)
0	0.0	71.6	4.4
0.5	0.5	67.7	3.4
1.0	1.1	74.3	3.2
1.5	1.6	74.6	5.0
2.0	2.1	73.9	5.4

S2. Optical micrographs used for average aspect ratio measurement of α pABA

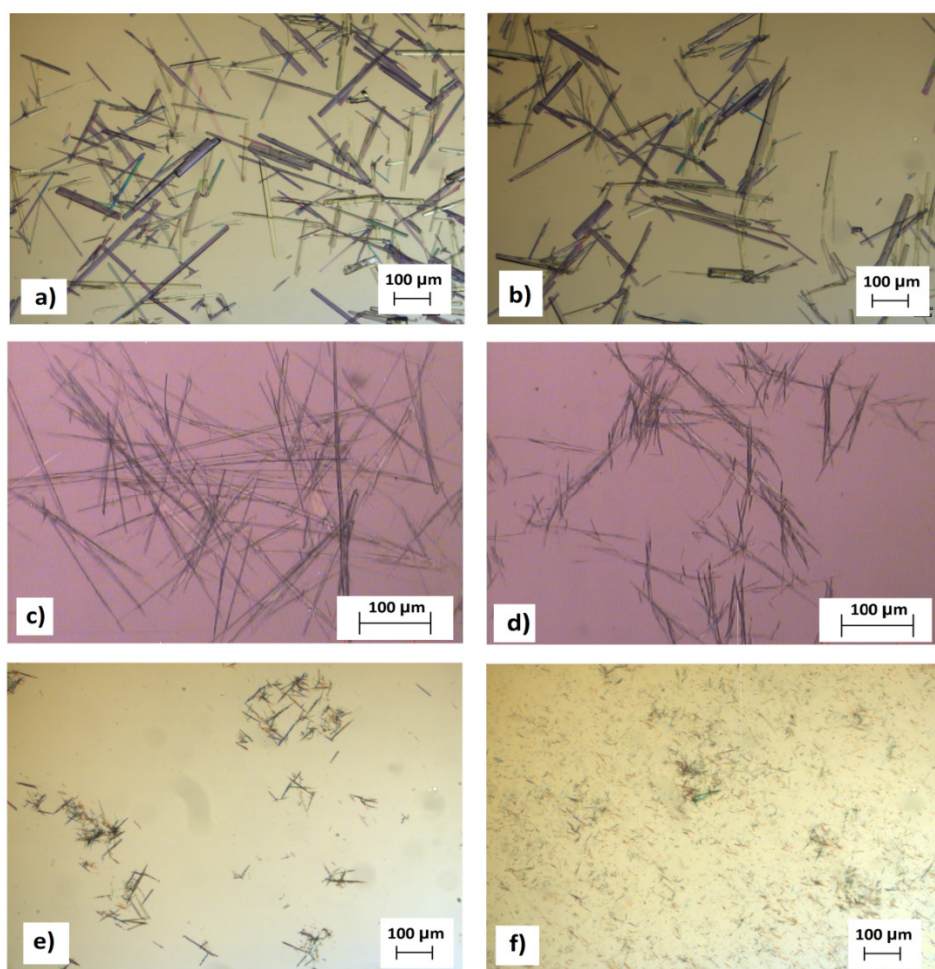


Figure S2.1 : Photomicrographs of α pABA crystallised from IPA ($S=1.6$) in the presence of ANBA at: a) 0 wt% 10°C, b) 0 wt% 20°C c) 1 wt% 10°C d) 1 wt% 20°C e) 2 wt% 10°C f) 3 wt% 10°C

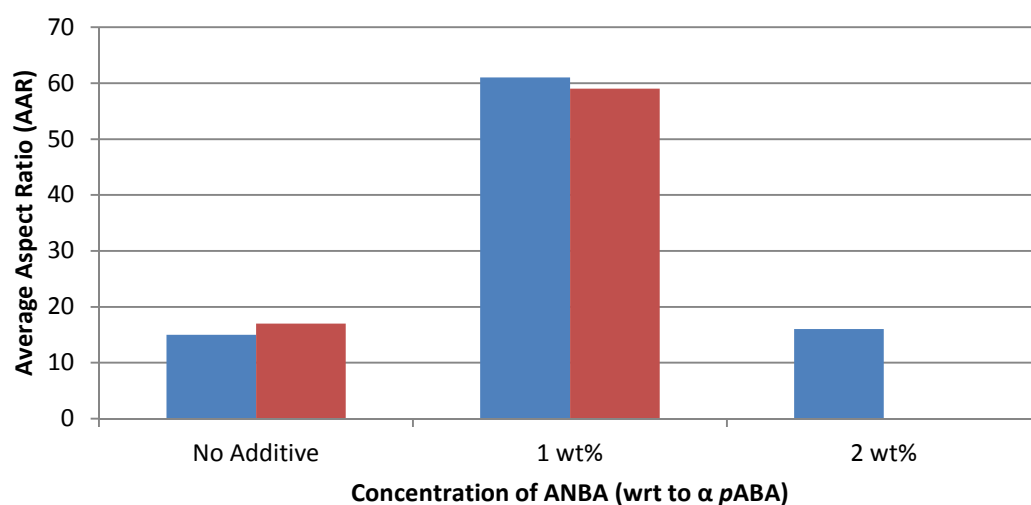


Figure S2.2: Effects of ANBA on the average aspect ratio of α pABA crystallised from IPA ($S=1.6$) at 10°C (blue) and 20°C (red)

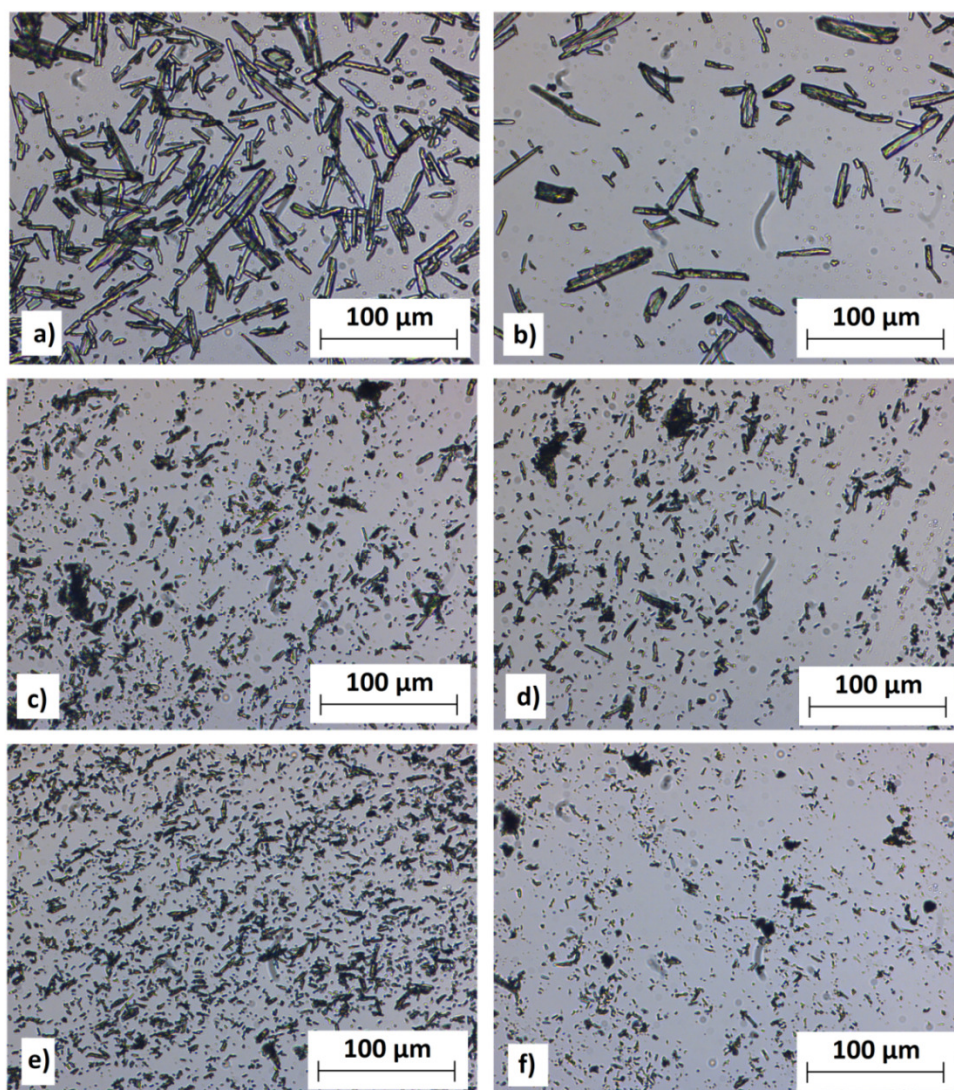


Figure S2.3 Photomicrographs of α *p*ABA crystallised from IPA ($S=1.6$) in presence of AMBA at: a) 1 wt%, 10°C, b) 1 wt%, 20°C c) 2 wt%, 10°C d) 2 wt%, 20°C e) 5 wt%, 10°C f) 5 wt%, 20°C

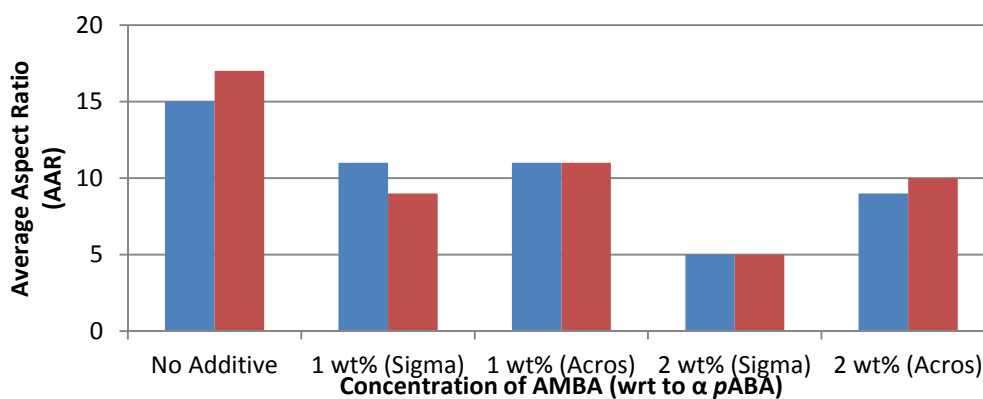


Figure S2.4: Effects of AMBA on the average aspect ratio of α *p*ABA crystallised from IPA ($S=1.6$) at 10°C (blue) and 20°C (red). Results for AMBA sourced from both SigmaAldrich and Acros are shown.

S3 Measurement of preferred orientation of β plates using pXRD

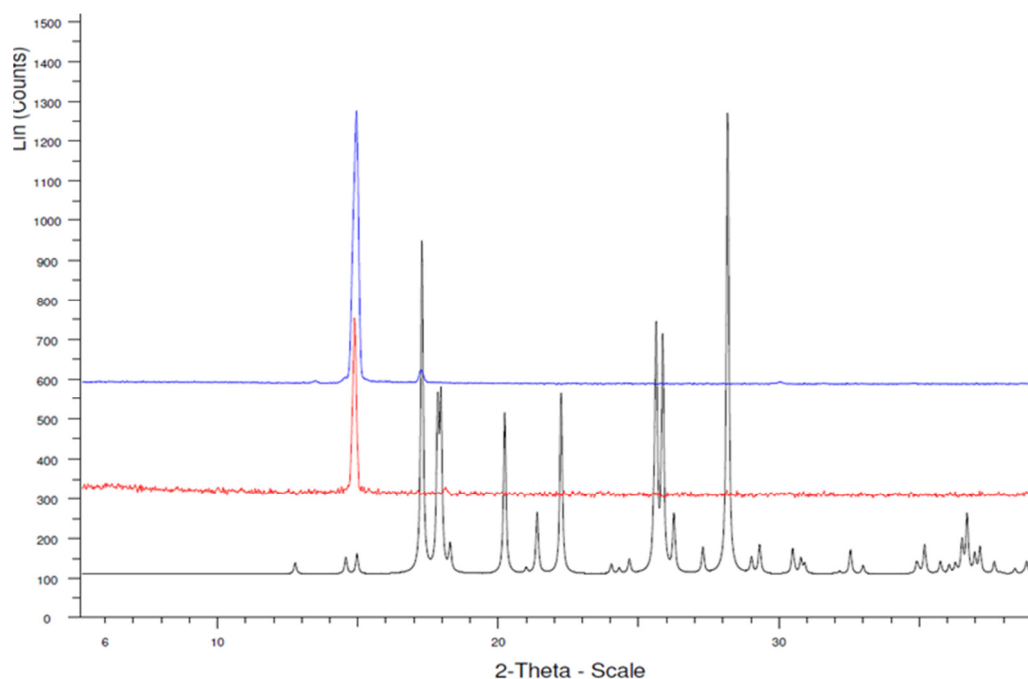


Figure S3.1: pXRD diffractograms for β *p*ABA: Calculated from Mercury (black), 2.5 wt% ANBA (red) and no additive (blue)

In Figure S3.1 it can be seen that the diffractogram for the pure β *p*ABA seeds and the impure β seeds grown in the presence of ANBA exhibit significant and identical preferred orientation with a major peak at 15°. This confirms the major face to be $(\bar{1}01)$ for β *p*ABA grown from both pure and impure solutions.

S4 Nucleation Rate Data.

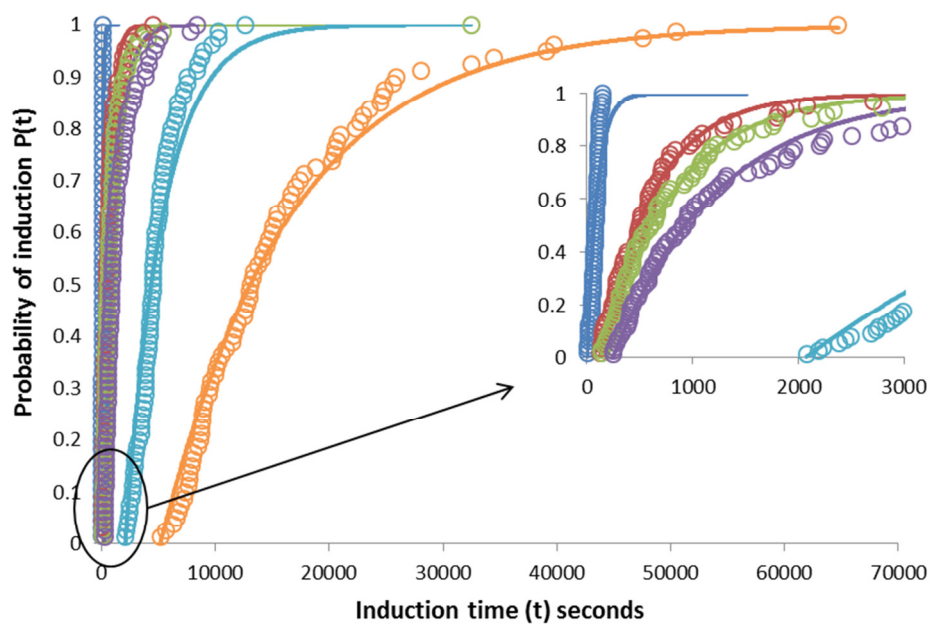


Figure S4.1 ANBA at 20°C. Probability function fitted to induction time data: No additive (dark blue), 0.5% (red), 1.0% (green), 1.5% (purple), 2.0% (light blue), 2.5% (orange).

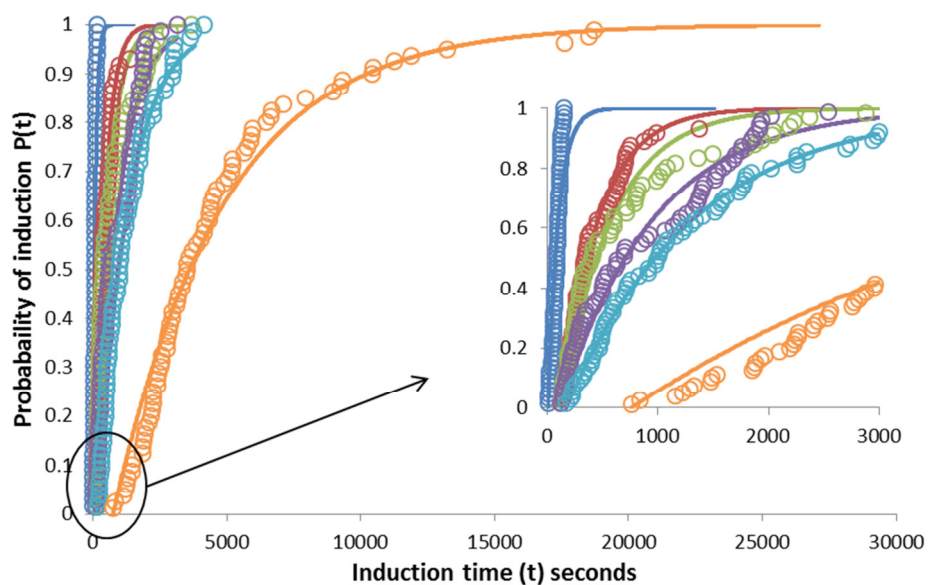


Figure S4.2 AMBA at 20°C. Probability function fitted to induction time data: No additive (dark blue), 0.5% (red), 1.0% (green), 1.5% (purple), 2.0% (light blue), 3.0% (orange).

Table S4.1. The impact of additive loading and temperature on the nucleation rates and growth times for α pABA at S = 1.6.

Additive	ANBA											
Temp.	10°C						20°C					
Additive Conc.wt%	0.0	0.5	1.0	1.5	2.0	2.5	0.0	0.5	1.0	1.5	2.0	2.5
Nucleation rate, J ($\text{m}^{-3}\text{s}^{-1}$)	1435	727	530	242	37	22	6999	1301	970	577	101	58
Growth time, t_g (seconds)	121	139	123	508	5193	18768	3	126	137	249	2080	5159

Additive	AMBA											
Temp.	10°C						20°C					
Additive Conc.	0.0	0.5	1.0	1.5	2.0	3.0	0.0	0.5	1.0	1.5	2.0	2.5
Nucleation rate, J ($\text{m}^{-3}\text{s}^{-1}$)	1435	817	617	505	311	96	6999	1943	1445	794	574	162
Growth time, t_g (seconds)	121	143	131	214	672	3608	3	120	121	120	167	759

S5 Crystal Growth Rates

S5.1 Time-distance data

Figures below provide typical examples of distance time plots from which growth rates were calculated. Note the good linearity of the plots.

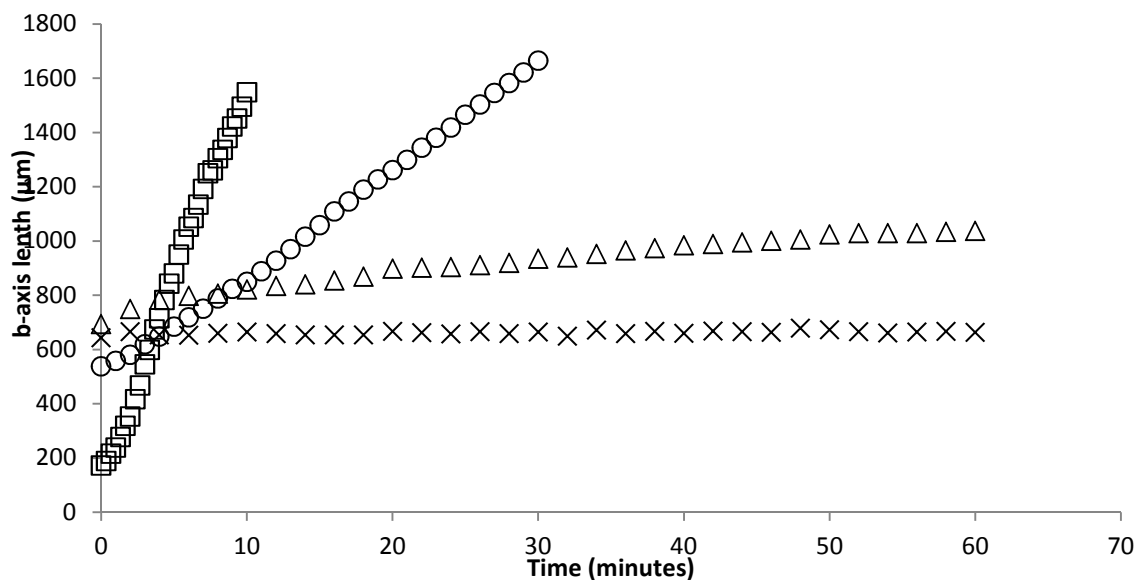


Figure S5.1. α -pABA b-axis growth: no additive (circle), 0.25% ANBA (square), 0.50% ANBA (triangle), 0.75% ANBA (cross) @ 10⁰C.

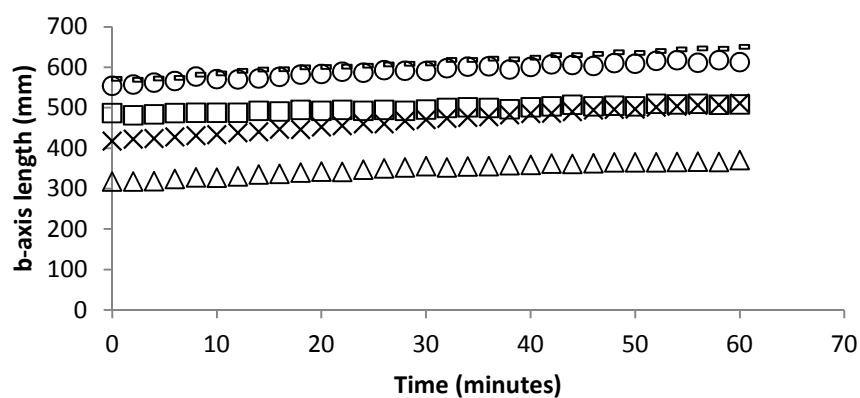


Figure S5.2 β -pABA b-axis growth: no additive (circle), 0.25% ANBA (square), 0.50% ANBA (triangle), 0.75% ANBA (cross), 1.00% ANBA (dash) @ 10⁰C.

Table S5.1 Growth Rates in the Presence of Additives.

a) 4-amino-3-nitro benzoic acid

ANBA effect on α pABA			
ANBA Loading Wt%	a-axis Growth rate μmin^{-1}	b-axis Growth rate μmin^{-1}	T °C
0	2.1	38.6	10
0.25	0.1	89.5	
0.5	0	5.1	
0.75	0	0.2	
0	7.3	45.8	20
0.25	0.8	147.7	
0.5	0	10.2	
0.75	0	7.6	

ANBA effect on β pABA			
ANBA Loading wt%	c- axis Growth Rate μmin^{-1}	b-axis Growth Rate μmin^{-1}	T °C
0	2.8	0.99	10
0.25	2.4	0.44	
0.5	1.1	0.89	
0.75	1.7	1.58	
1.0	2.4	1.34	
0	3.8	2.1	20
0.25	2.7	2.42	
0.5	2.4	2.7	
0.75	3.7	1.9	
1.0	2.9	2.12	

b) 4-amino-3-methoxybenzoic acid

AMBA effect on α pABA			
AMBA Loading wt%	a- axis Growth Rate μmin^{-1}	b-axis Growth Rate μmin^{-1}	T °C
0	2.1	38.6	10
0.5	0.2	8.9	
0.75	0.2	6.6	
1.0	0	0	
0	7.3	45.8	20
0.5	1.9	35.2	
0.75	0.1	14.2	
1.0	0.2	6.9	

AMBA effect on β pABA			
AMBA Loading wt%	c- axis Growth Rate μmin^{-1}	b-axis Growth Rate μmin^{-1}	T °C
0	2.8	1.0	10
0.5	1.4	1.1	
0.75	0.7	1.1	
1.0	0.5	1.0	
0	3.8	2.1	20
0.5	1.9	1.9	
0.75	1.7	1.9	
1.0	1.5	2.0	