

Supporting Information

Exploration of polymorph landscape for 1,1,4,4-tetraphenyl-1,3-butadiene

A. Bacchi*,^a A. Brillante^b, D. Crocco,^a M.R. Chierotti,^c R. G. Della Valle,^b A. Girlando,^a M. Masino,^a P. Pelagatti,^a and E. Venuti^b

^a Department of Chemistry, University of Parma, Parco Area Scienze 17/A, 43124 Parma, Italy

^b Dipartimento di Chimica Industriale 'Toso Montanari' and INSTM-UdR
Bologna, Bologna University, I-40136, Bologna, Italy

^c Department of Chemistry and NIS, University of Torino, Via P. Giuria 7, 10125 Torino, Italy.

We present a rationalization of the solid state behaviour of 1,1,4,4-tetraphenyl-1,3-butadiene (TPB), a well-known blue luminescent molecule, which retains its emissive properties in the solid state. The crystal structures of four polymorphs and one solvate form are discussed and their relative thermal stability is assessed. The experimental occurrence of the four polymorphs is rationalized on the basis of thermodynamic and kinetic considerations

Solvent	
Toluene	TOL
Nitromethane	NME
Water	H2O
Heptane	HEP
Acetonitrile	ACN
2-Propanol	ISP
1,2-Dichloroethane	DCE
Benzene	BZN
Butanone	BNA
Ethanol	EOH
Ethyl Acetate	ETA
n-Hexane	HEX
Ciclohexane	CHEX
Methanol	MET
Tetrahydrofuran	THF
Chloroform	CLF
Acetone	ACE
Dichloromethane	DCM
n-Pentane	PEN

Legend for solvent labels

Table S1. Crystallization form PEO gel

- doped PEO gel

A supersaturated solution of TPB in 1ml solvent was microfiltered and 50 mg of PEO were added under stirring. The solution was allowed to stand in a closed vial. G indicates the formation of the gel, F indicates the formation of the floccules and I that the PEO is insoluble; whereas r.t indicates that the experiments were conducted at room temperature.

SOLVENTS	T	OUTCOME	NOTES
DCM	r.t.	Around 3 days Morfology: needles α phase	G
ACN	r.t.	Around 45 days Morfology: prismatic α phase	G
NME	r.t.	Around 3 days Morfology: needles α phase	G
CLF	r.t.	Around 20 days Morfology: needles α phase	G
DCM/EOH (1:1)	r.t.		F
DCM/EOH (4:1)	r.t.		F
DCM/EOH (1:4)	r.t.	Around 3 days Morfology: needles α phase.	F
DCM/THF (1:1)	r.t.	-	G
DCM/THF (4:1)	r.t.	-	G
DCM/THF (1:4)	r.t.	-	F
DCM/BNA (1:1)	313 K	Around 4 hours Morfology: needles α phase.	G

DCM/ETA (1:1)	r.t.	-	F
DCM/MET (1:1)	r.t.	-	F
DCM/ISP (1:1)	r.t.	-	G
DCM/TOL (1:1)	r.t.	-	G

- **counterdiffusion**

Crystallizations were carried out in a glass U-tube. A gel was prepared in DCM and inserted in the middle section of the tube, a saturated solution of TPB was added in the chosen solvent on the one hand and on the other the anti-solvent

SOLVENT/ANTISOLVENT	T	OUTCOME	NOTES
DCM/hexane	r.t.	Around 20 gg Morfology: needles α phase.	G
DCM/ISP	r.t.	Around 20 gg Morfology: needles α phase.	G

Figure S1. SEM image of gamma crystals grown by sublimation on a gamma seed

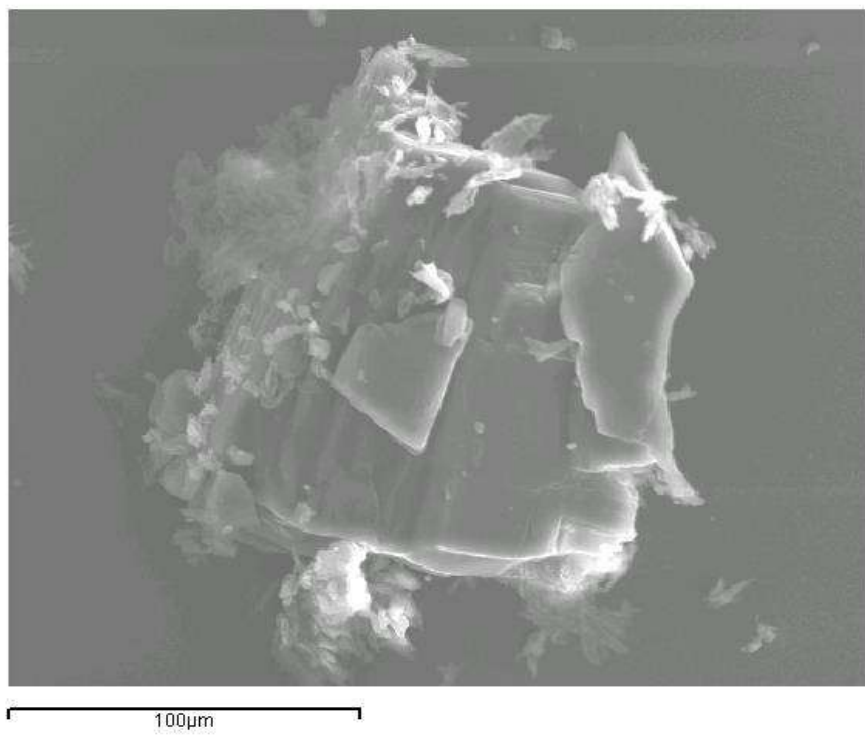


Figure S2. Unpolarized Raman spectra of the four polymorphs of TPB in the high-frequency diagnostic spectral region

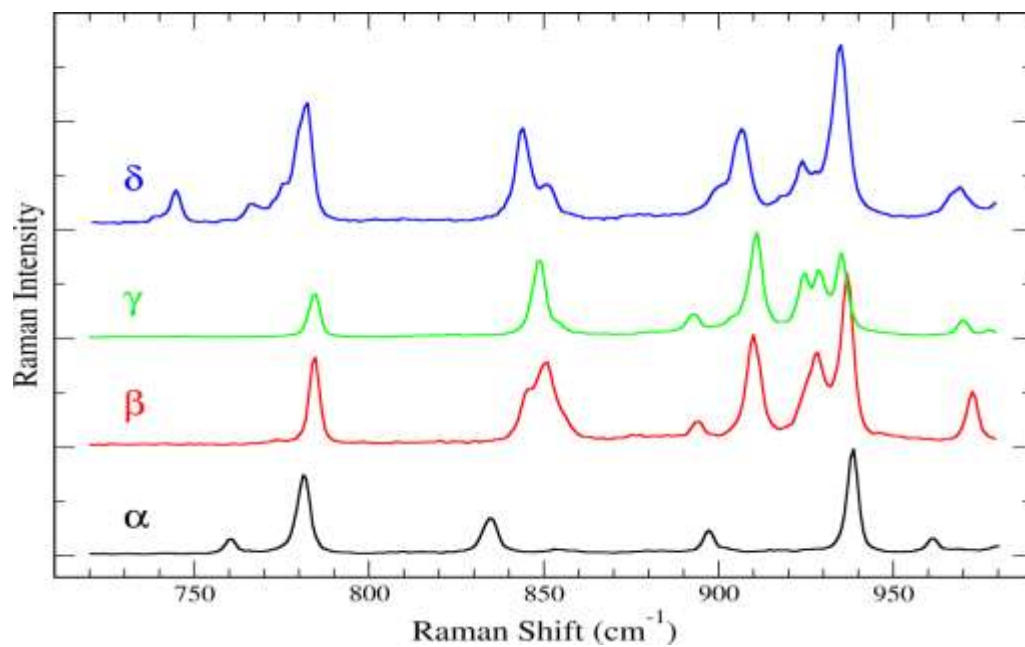
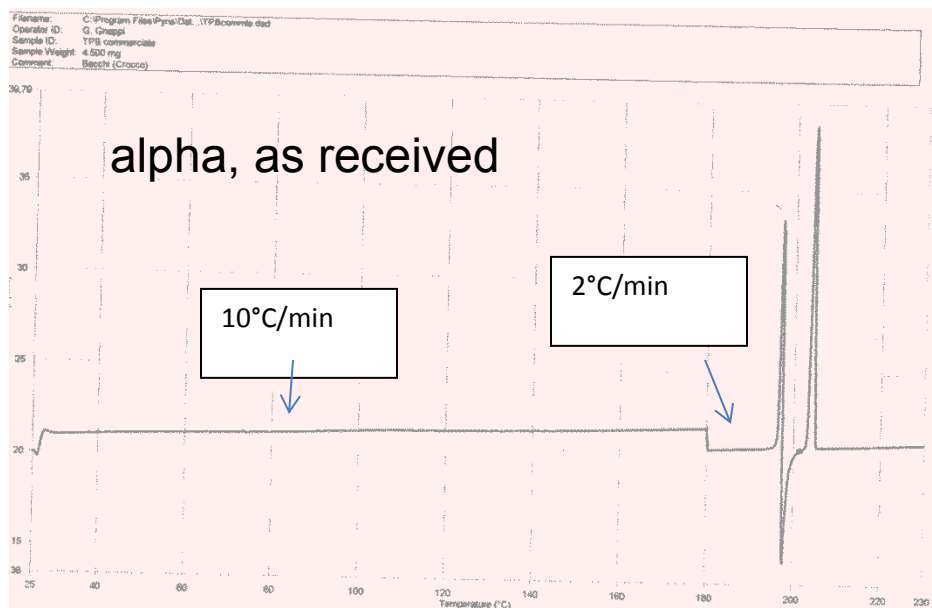
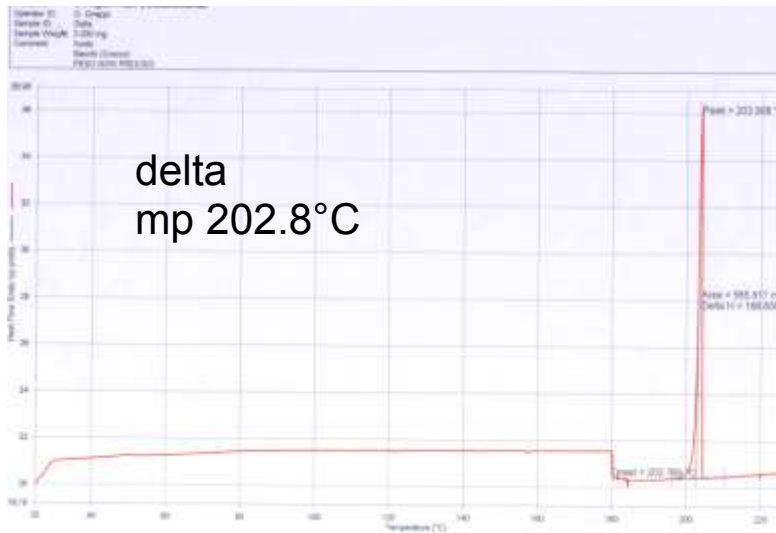
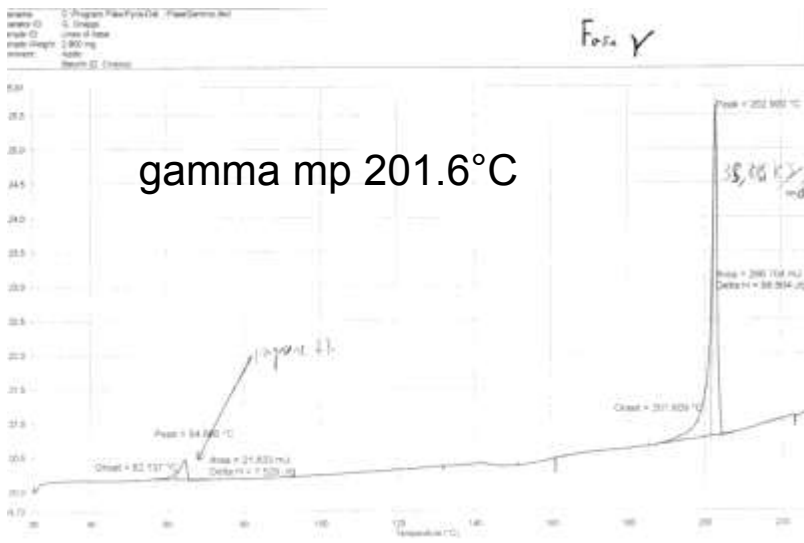


Figure S3. DSC experiments for alpha (as received), alpha (recrystallized), gamma, delta polymorphs. The heat of fusion for the delta polymorph has been measured from the transition observed in the first diagram (see Figure 2 in the manuscript), since the sample weight in the measure on pure delta was unreliable. The vertical steps in the baselines are the predicted consequence of a change of heating rate from 10°C/min to 2°C/min; the scan has been slowed down to better detect the melting temperature. The endothermic phenomenon marked by an arrow on the DSC trace of the gamma phase is attributed to impurities, that are reported to possibly contaminate commercial TPB.





The DSC of the commercial alpha phase was recorded also at 1°C/min and 20°C/min to detect any possible phase transition prior to melting, with no evidence of such a phenomenon.

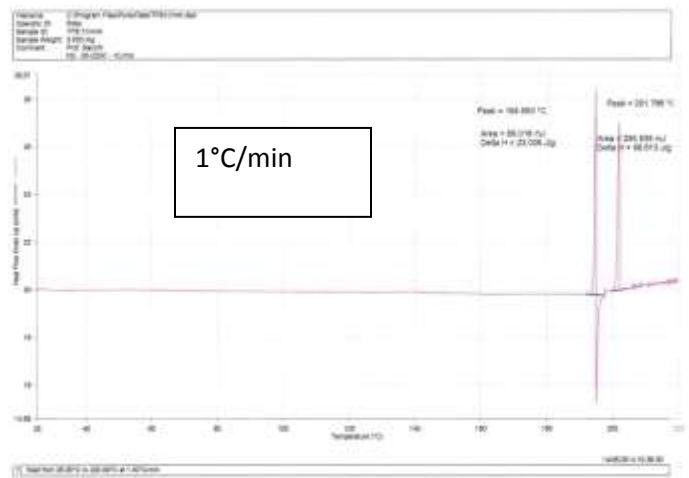
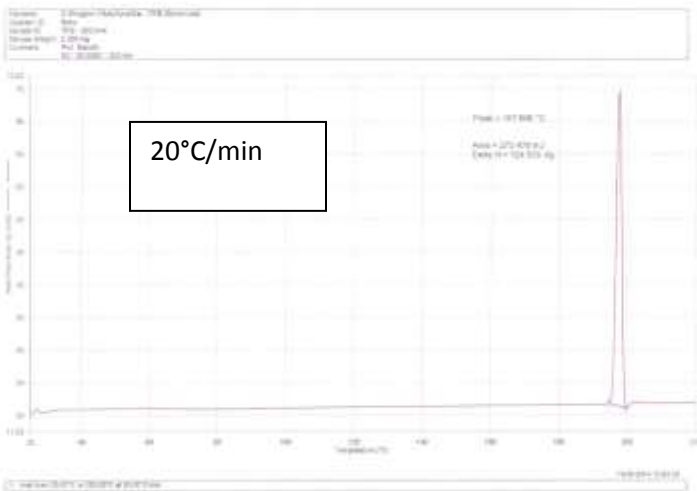


Figure S4. Variable Temperature Raman spectra for thermal treatment of gamma polymorph heated to 170°C and cooled down to RT, showing the transformation $\gamma \rightarrow \alpha$ on cooling.

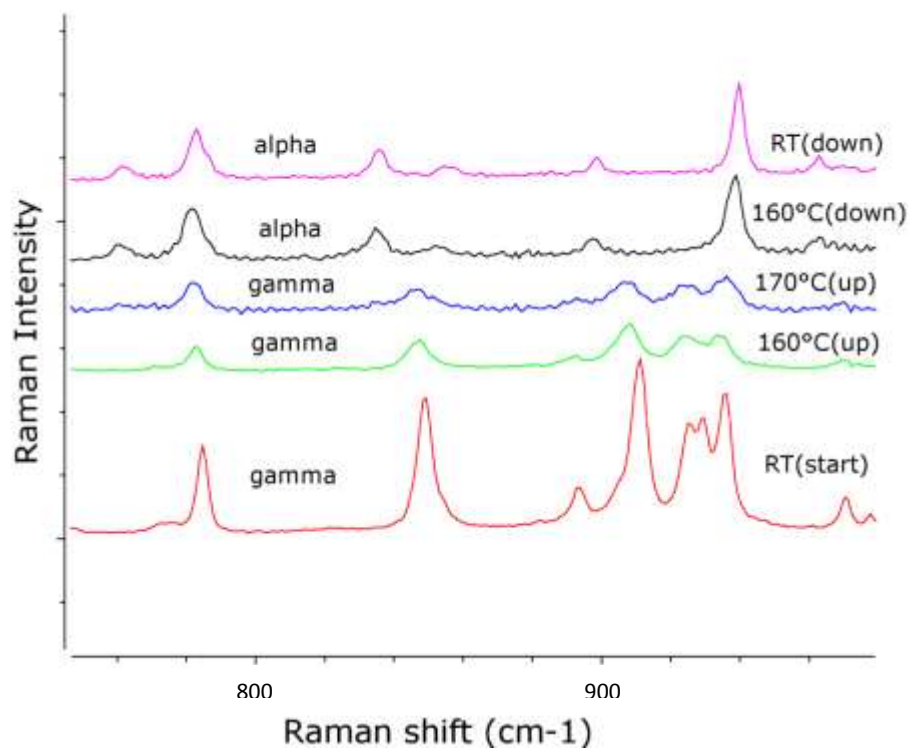


Figure S5. Plot of ΔG for the three possible phase transitions $\alpha \rightarrow \delta$, $\alpha \rightarrow \gamma$ and $\delta \rightarrow \gamma$ as a function of temperature

$$\Delta G_{A \rightarrow B} = (\Delta H_{Am} - \Delta H_{Bm}) - T (\Delta S_{Am} - \Delta S_{Bm})$$

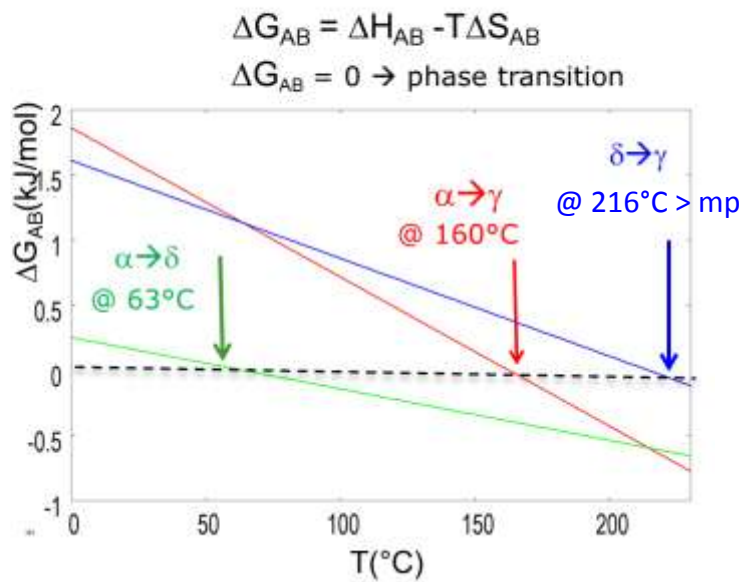


Figure S6. Face indexing of a crystal of alpha-TPB. In pink the shortest intermolecular contact is evidenced.

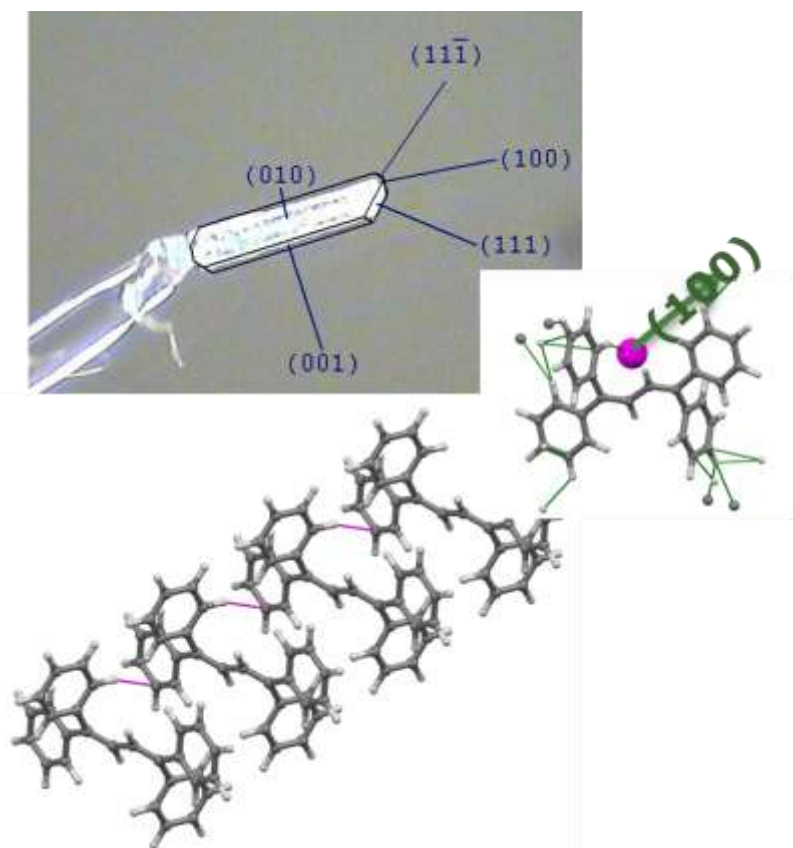


Figure S7 IR spectra of TPB.c-hex freshly prepared (**a**), and after 15 min of exposition of the powder to vapour of cyclohexanone (**b**); the ketone peak is present at 1709 cm^{-1} .

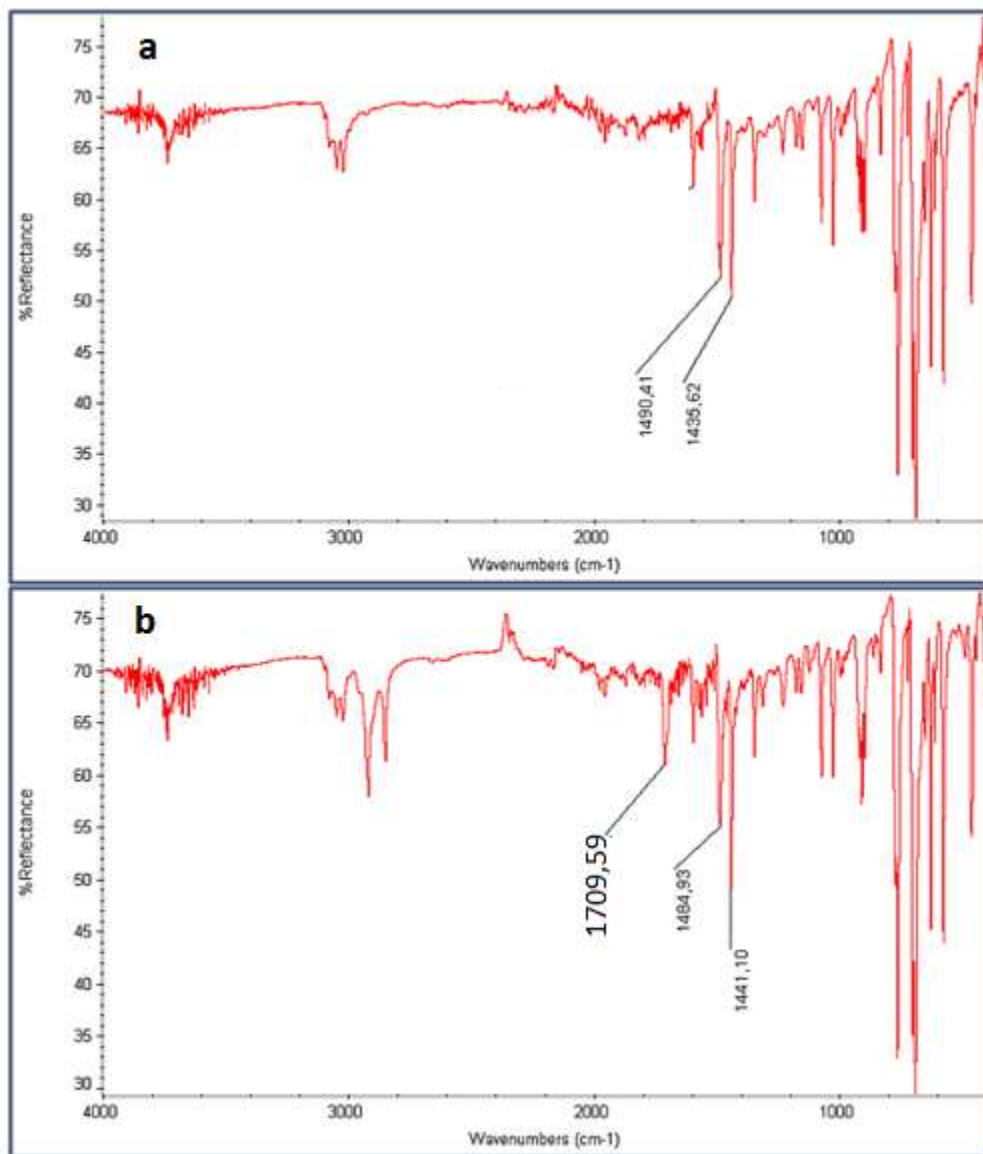


Figure S8. Example of a bent crystal of alpha-TPB, constituting roughly 30% of the commercial product and of recrystallized batches.



Figure S9. X-ray Powder Diffraction traces of commercial alpha-TPB, with superimposed the calculated trace of the alpha and the delta forms. No detectable traces of impurities are visible.

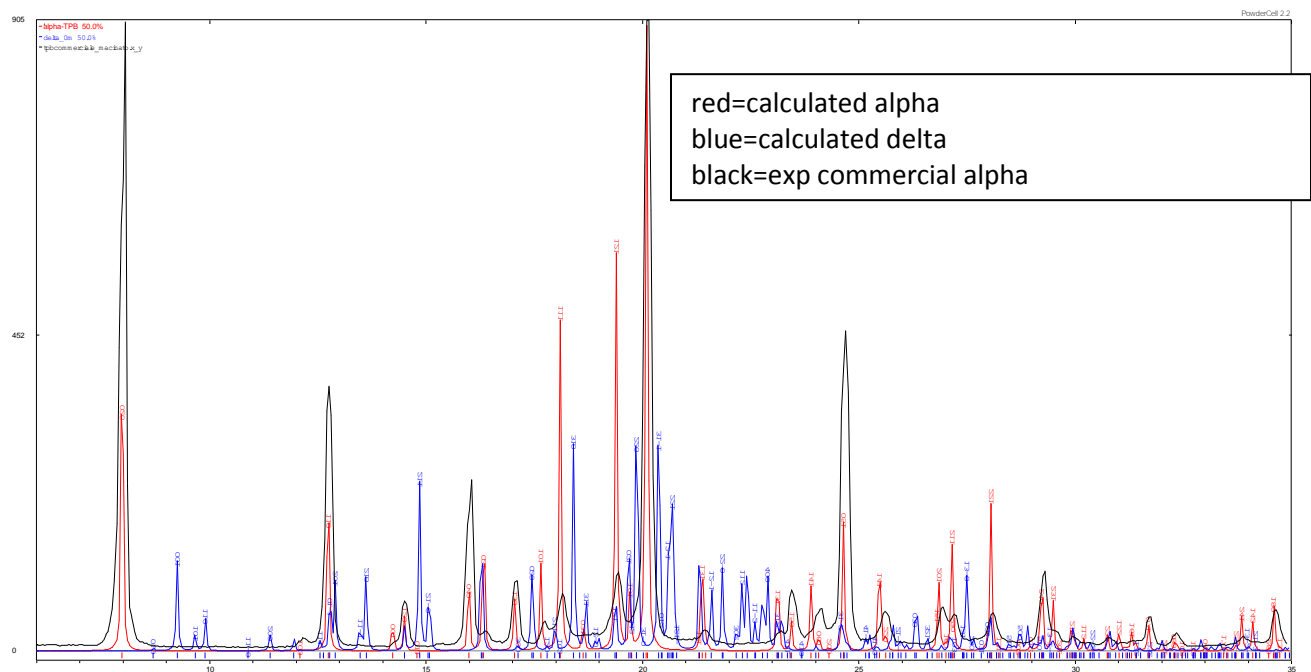


Figure S10. XRPD of the commercial alpha TPB at room temperature, and after 3 hours at 140°C. No phase transition is detected. Peak shift is due to thermal expansion.

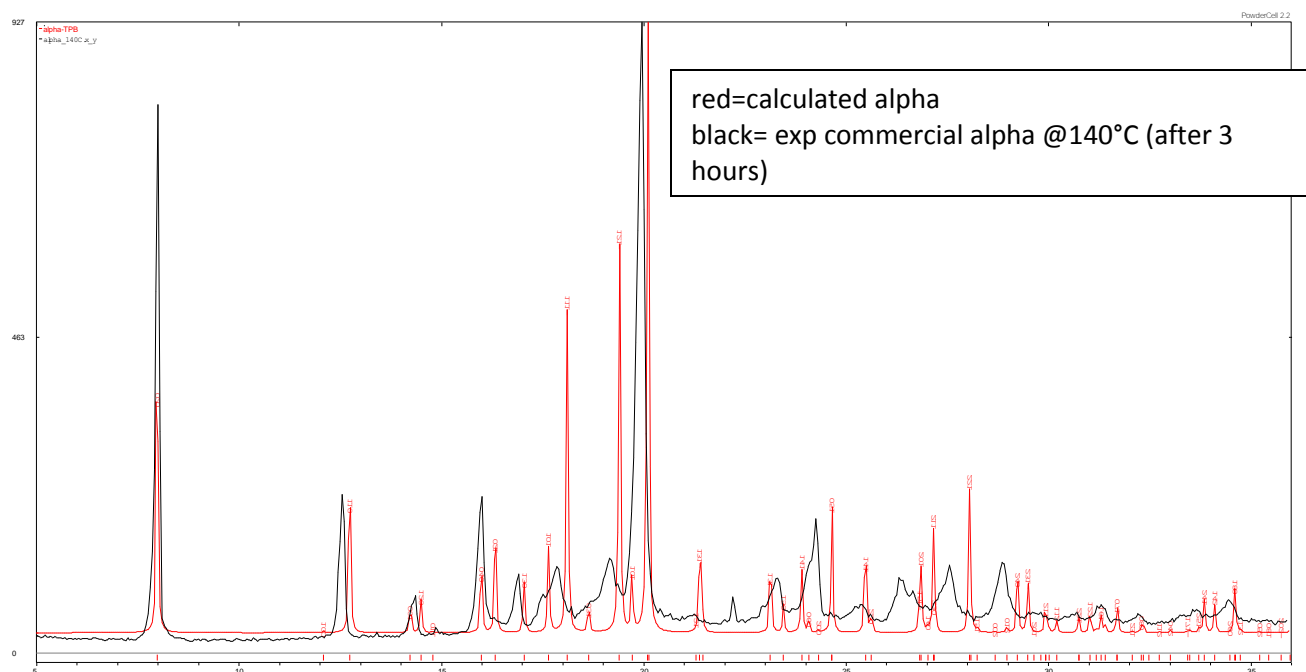
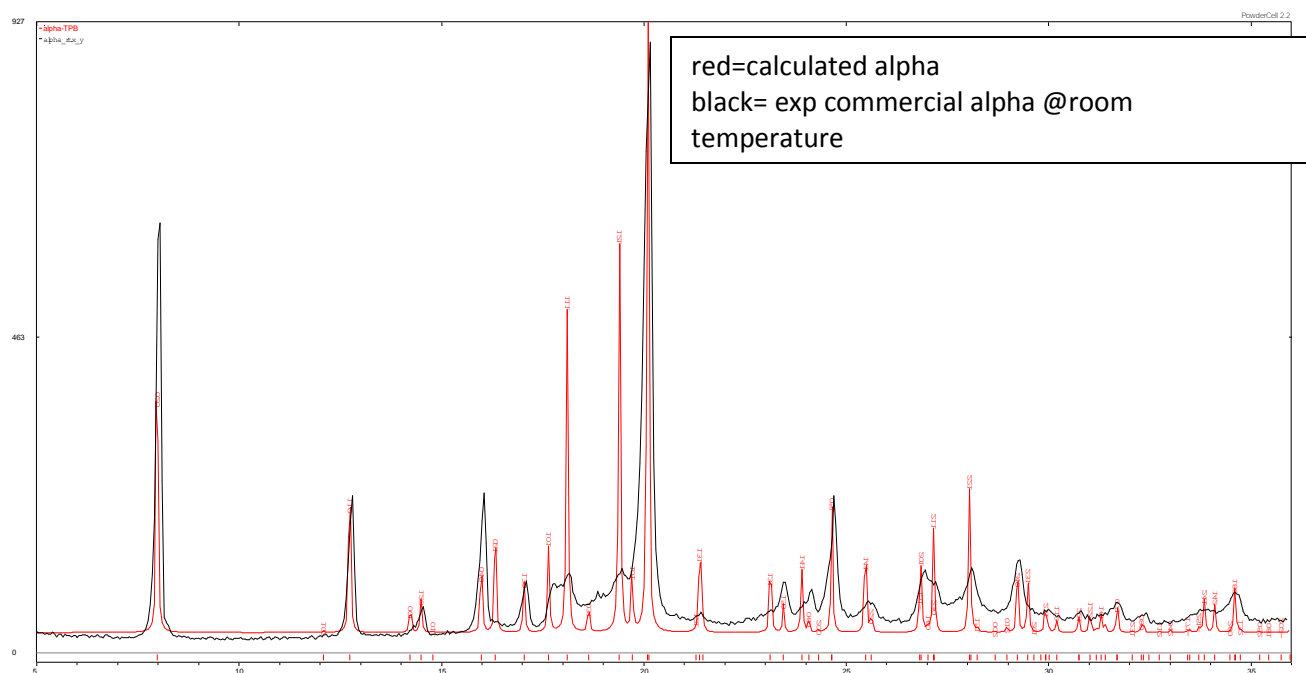
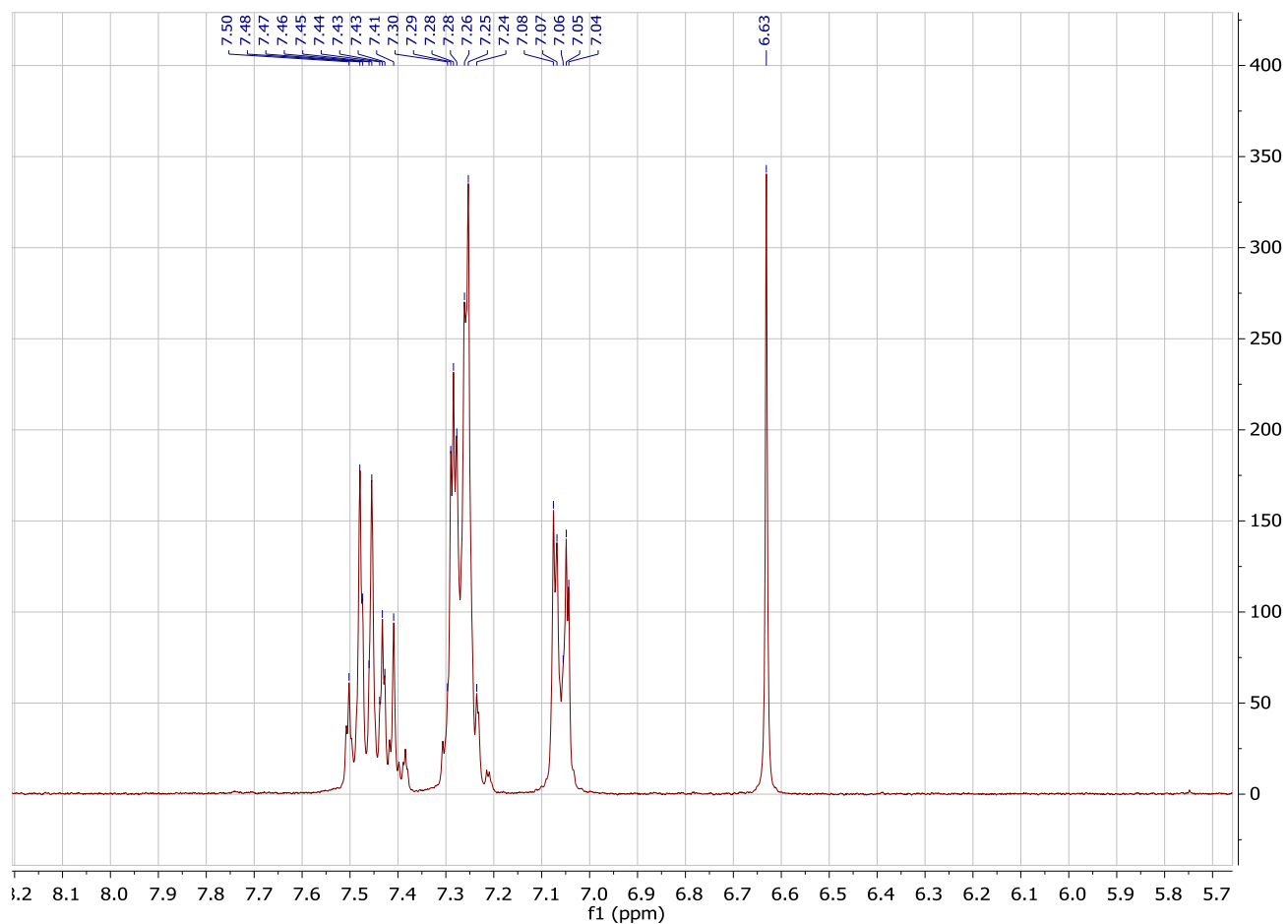
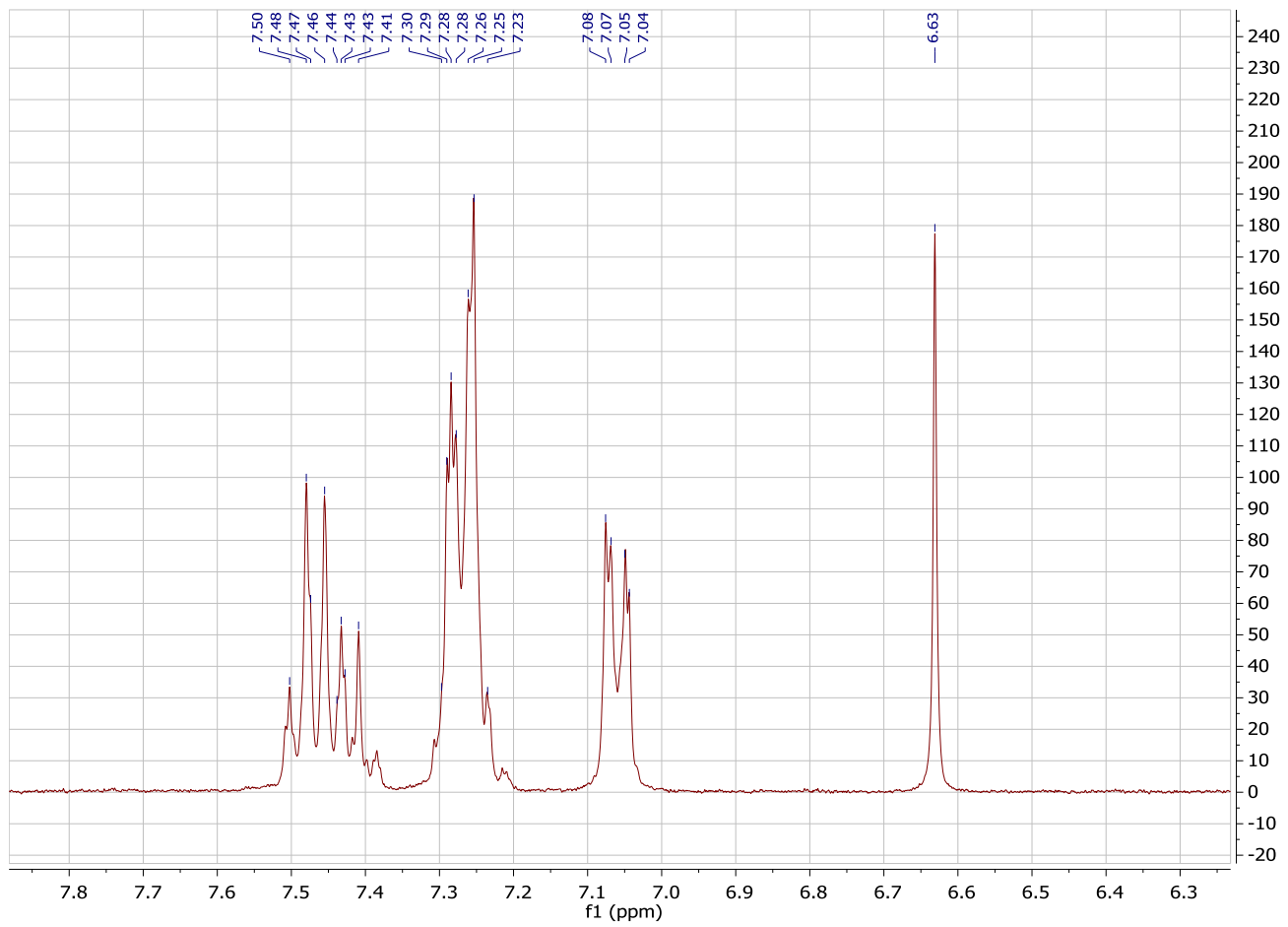


Figure S11. ^1H NMR spectra of TPB at different dilution and conditions to investigate molecular aggregation.



Aromatic region of the ^1H NMR spectrum of TPB in dms0-d_6 (50 mM)



Aromatic region of the ^1H NMR spectrum of TPB in dms0-d_6 (5 mM)