Electronic Supplementary Information

On the importance of simultaneous infrared/fiber-optic temperature monitoring in the microwave-assisted synthesis of ionic liquids

David Obermayer and C. Oliver Kappe*

Christian Doppler Laboratory for Microwave Chemistry (CDLMC) and Institute of Chemistry, Karl-Franzens-University Graz, Heinrichstrasse 28, A-8010 Graz, Austria.
E-mail: oliver.kappe@uni-graz.at; Fax: +43 316 3809840; Tel: +43 316 3805352

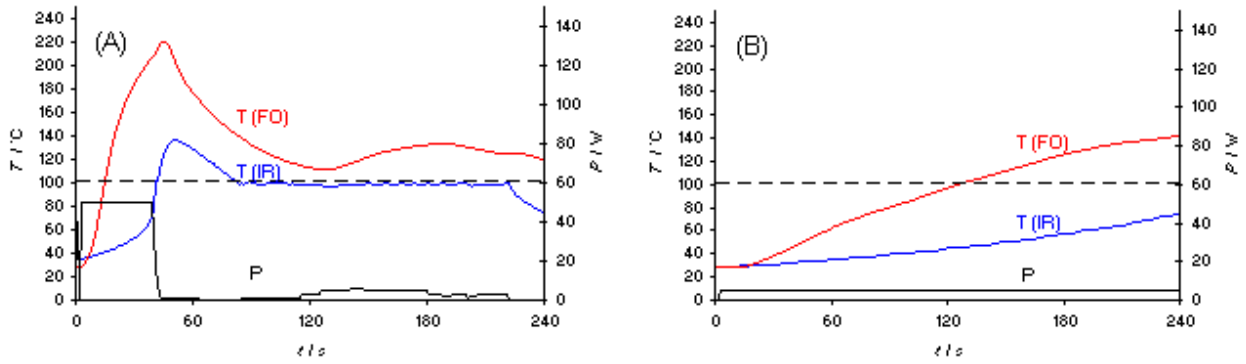

Figure S1. FO/IR temperature (T) and power (P) profiles for a 3 mL sample of ionic liquid bmimBr heated in a CEM Discover LabMate single-mode reactor using external IR temperature control. The internal reaction temperature was additionally monitored (slave) by a FO probe (OpSens fiber). Set temperature 100 °C, magnetic stirring ("high"), 10 mL Pyrex vial, flow valve "on" (3.5 bar). (**A**): 50 W maximum initial magnetron output power; (**B**) 5 W maximum initial magnetron output power.

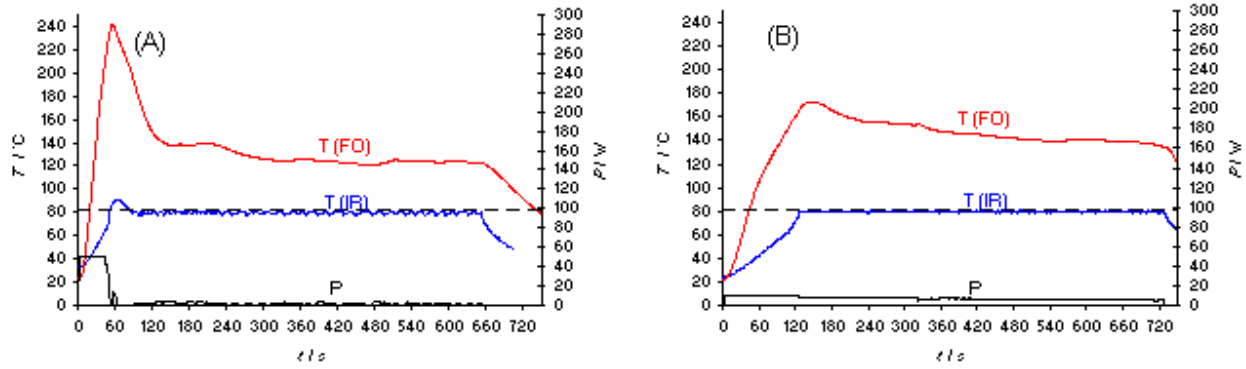

Figure S2. FO/IR temperature (T) and power (P) profiles for a 2.8 mL sample of ionic liquid Ammoeng 100 heated in a CEM Discover LabMate single-mode reactor using external IR temperature control. The internal reaction temperature was additionally monitored (slave) by a FO probe (OpSens fiber). Set temperature 100 °C, magnetic stirring ("high"), 10 mL Pyrex vial, flow valve "on" (3.5 bar). **(A)**: 50 W maximum initial magnetron output power; **(B)** 10 W maximum initial magnetron output power.

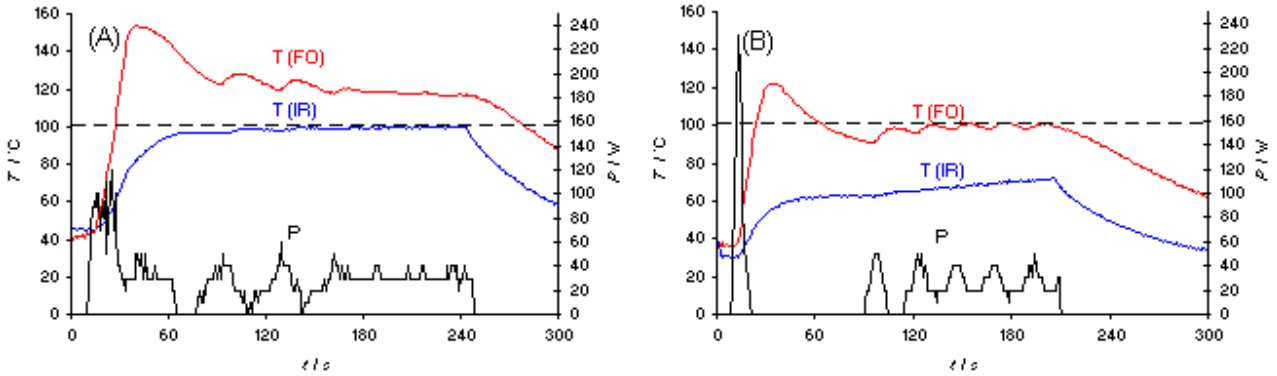

Figure S3.. FO/IR temperature (T) and power (P) profiles for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1). Experiments were performed on a 15.9 mmol scale (1.02 equiv of BuBr)in an Anton Paar Monowave 300 single-mode reactor using using either external IR (**A**) or internal FO temperature control (**B**). Set temperature 100 °C, set ramp time 2 min, magnetic stirring on (600 rpm), 10 mL Pyrex vial.

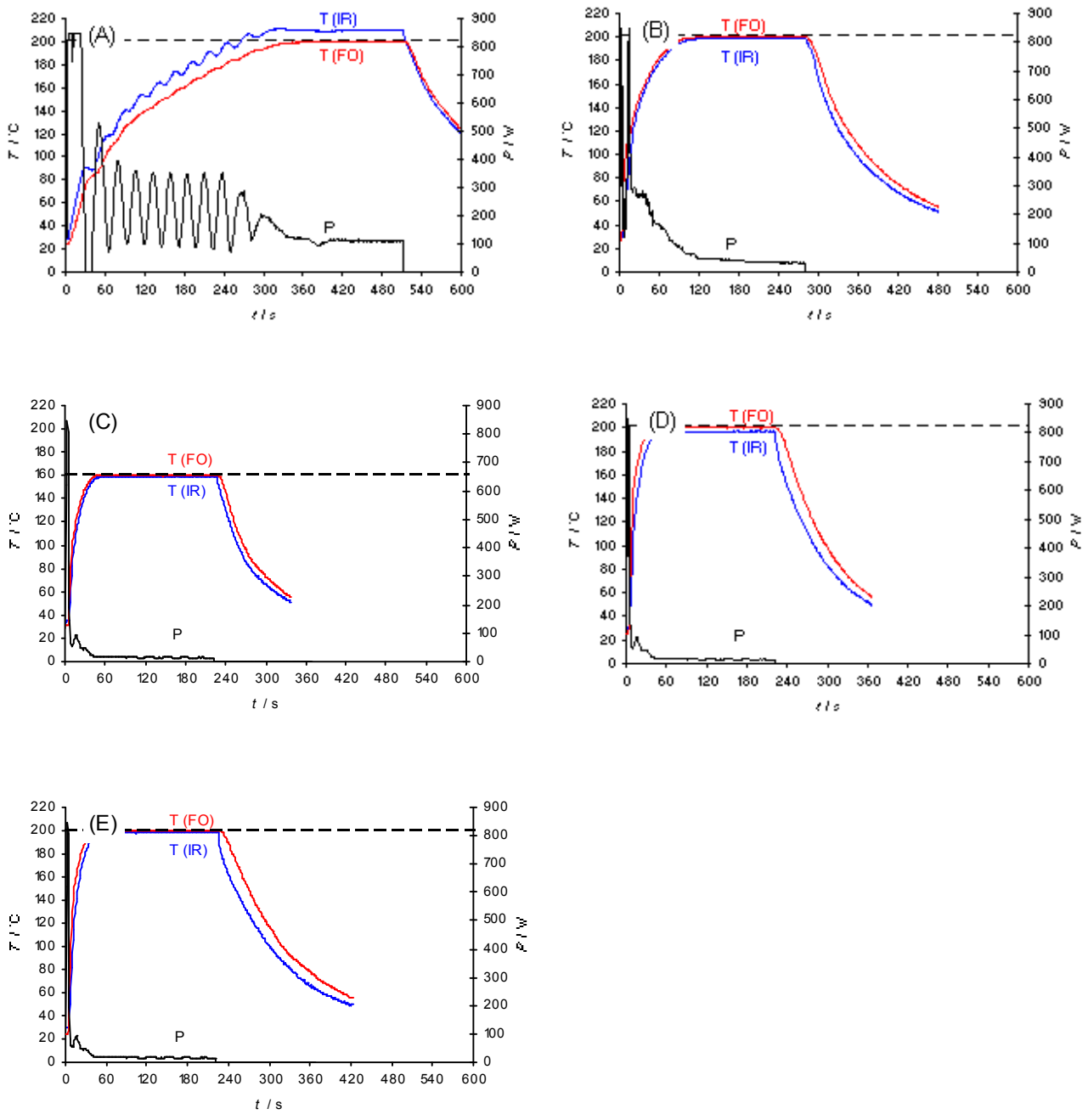

Figure S4. FO/IR Temperature profiles for 3 mL samples of (**A**) toluene (tan δ = 0.04), (**B**) water (tan δ = 0.123), (**C**) 1-methyl-2-pyrrolidone (tan δ = 0.275), (**D**) methanol (tan δ = 0.659), and (**E**) ethylene glycol (tan δ = 1.350) heated in an Anton Paar Monowave 300 single-mode reactor using internal FO temperature control. Set temperature 200 °C and 160°C for methanol, respectively; "as-fast-as-possible" heating mode, magnetic stirring on (600 rpm), 10 mL Pyrex vial. The IR sensor was adjusted using an accurate multi-point calibration method from (50-300 °C in 20 °C steps). It should be noted that using the full power of the 850 W magnetron, even toluene can be heated to 200 °C taking advantage of the wall-heating effect of the slightly microwave absorbing Pyrex reaction vessel. The reversed temperature gradient in this wall-heating effect can be recognized by the higher IR temperatures compared to the internally measured FO temperatures in Figure S4A.

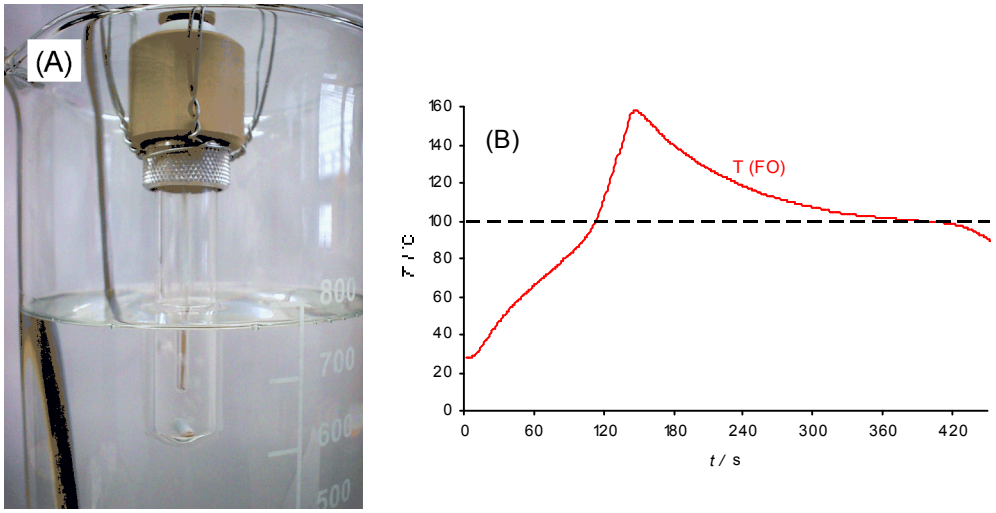

Figure S5. (**A**): Oil-bath set-up for detecting the exotherm in the solvent-free synthesis of bmimBr on a 15.9 mmol scale (1.02 equiv of BuBr) (Scheme 1). Bath temperature 100 °C, magnetic stirring (600 rpm), 10 mL Pyrex vial, internal FO probe (OpSens). (**B**) Internal FO temperature (T) profile for the solvent-free synthesis of ionic liquid bmimBr using an oil bath.

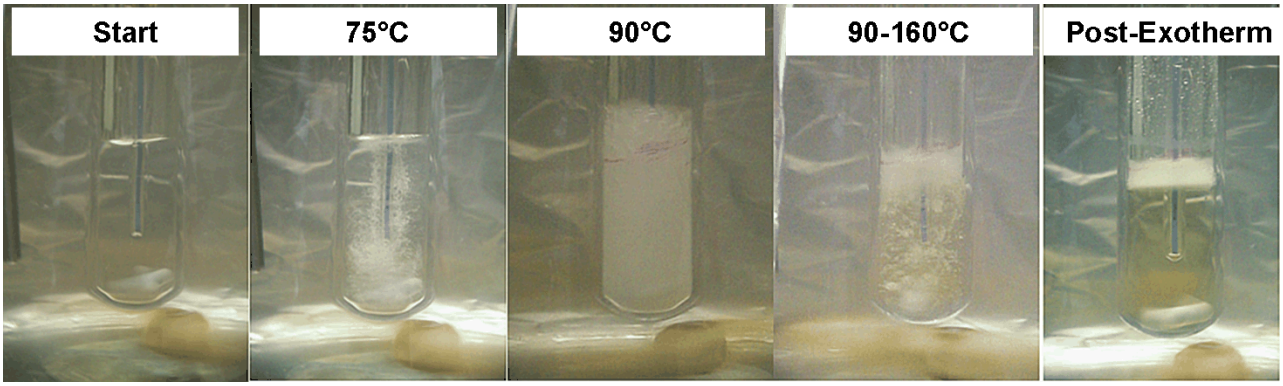

Figure S6. Solvent-free synthesis of ionic liquid bmimBr on a 15.9 mmol scale (1.02 equiv of BuBr). Bath temperature 100 °C (silicone oil), magnetic stirring (600 rpm), 10 mL Pyrex vial, internal FO probe (OpSens). Pictures show the different stages of reaction and corresponding internal temperatures during the heating up phase, beginning at the moment of immersion of the reaction vessel into the preheated oil bath up to the top of the exotherm at more than 160 °C.

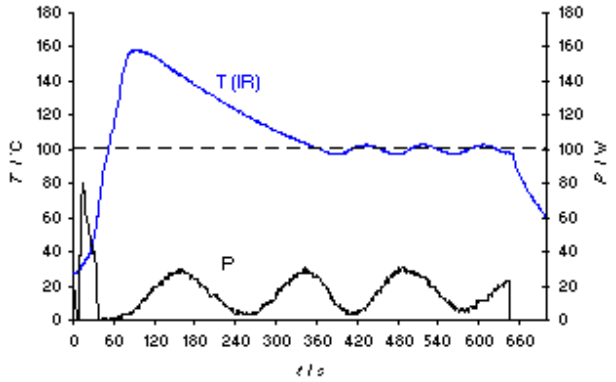

Figure S7. Temperature (T) and power (P) profiles for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1). Experiments were performed on a 15.9 mmol scale (1.02 equiv of BuBr) in a Biotage Initiator EXP 2.5 single-mode reactor using external IR temperature control. Set temperature 100 °C, magnetic stirring (720 rpm), 10 mL Pyrex vial, absorption level "very high".

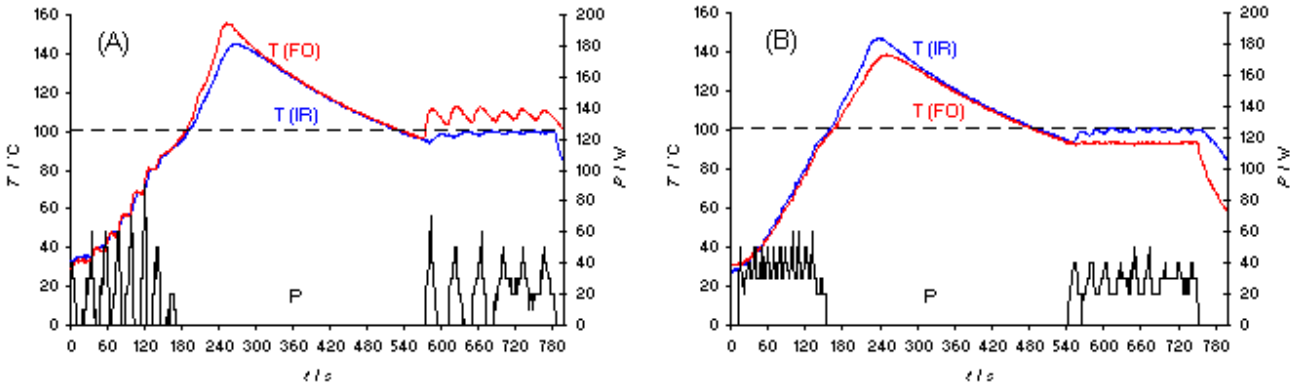

Figure S8. FO temperature (T) and power (P) profiles for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1). Experiments were performed in an Anton Paar Monowave 300 single mode reactor on a 15.9 mmol scale (1.02 equiv of BuBr) using either external IR temperature control **(A)** or internal FO temperature control **(B)**. Set temperature 100 °C, ramp time 2 min, magnetic stirring on (600 rpm), 10 mL Pyrex vial.

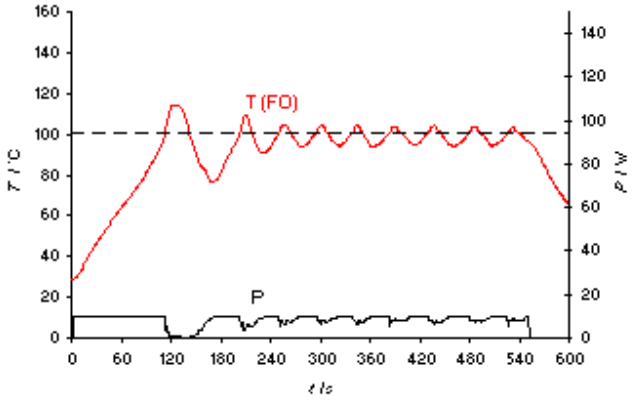

Figure S9. FO temperature (T) and power (P) profiles for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1), using a reaction vial made of SiC. Experiments were performed on a 15.9 mmol scale (1.02 equiv of BuBr) in a CEM Discover LabMate single-mode reactor using internal FO control (10 W initial magnetron power). Set temperature 100 °C, magnetic stirring ("high"), 10 mL SiC vial, flow valve "on" (3.5 bar). Note that the IR temperature can not be recorded using this protocol.

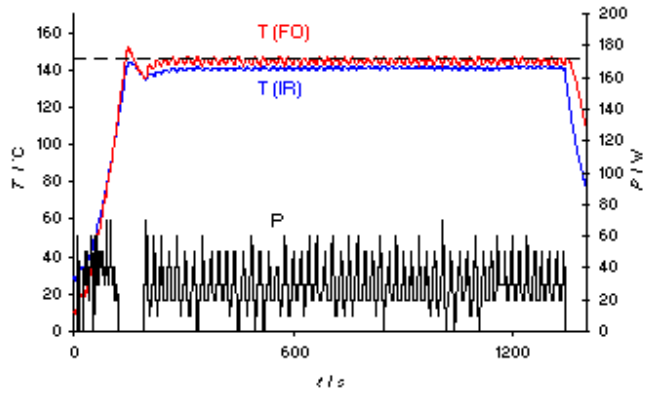

Figure S10. FO/IR temperature (T) and power (P) profiles for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1). Experiments were performed on a 15.9 mmol scale (1.02 equiv of BuBr) in an Anton Paar Monowave 300 single-mode reactor using FO temperature control. Set temperature 145 °C, ramp time 2 min, magnetic stirring on (600 rpm), 10 mL Pyrex vial.

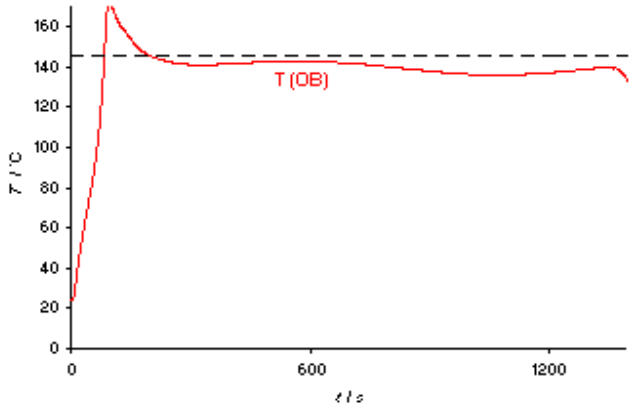

Figure S11. Internal FO temperature (T) profile for the solvent-free synthesis of ionic liquid bmimBr (Scheme 1) using oil bath heating (Figure S5A). Bath temperature 145 °C, 15.9 mmol scale (1.02 equiv of BuBr), magnetic stirring (600 rpm), 10 mL Pyrex vial, internal FO probe (OpSens).

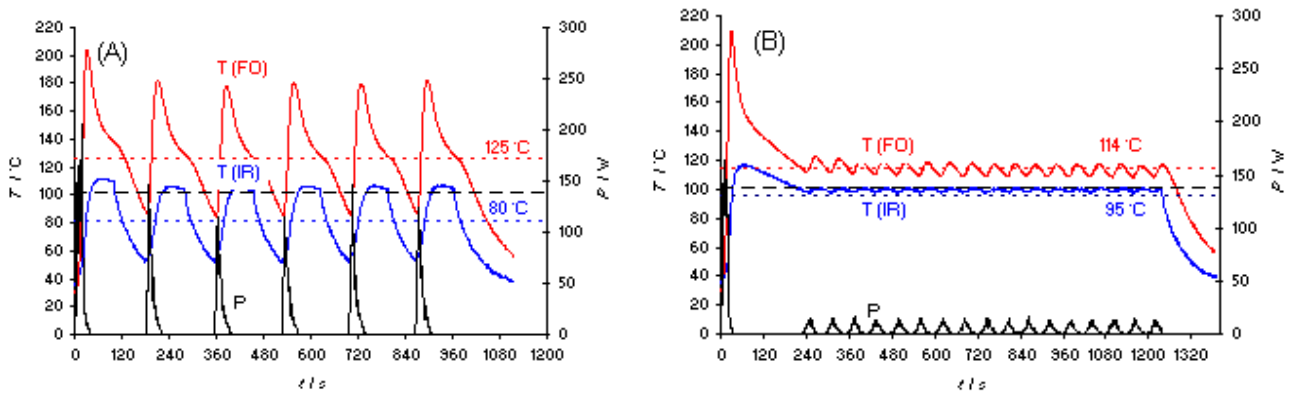

Figure S12. FO/IR temperature (T) and power (P) profiles for 3 mL samples of bmimBr heated in an Anton Paar Monowave 300 single-mode reactor using IR temperature control. Six cycles of heating to 100 °C, 1 min holdtime, and cooling to 50 °C using the "as-fast-as-possible mode" were programmed (total of ~ 20 min)(**A**). Additionally, a FO/IR temperature (T) and power (P) profile for the same total irradiation time of ~ 20 min without pulsing was recorded (**B**).

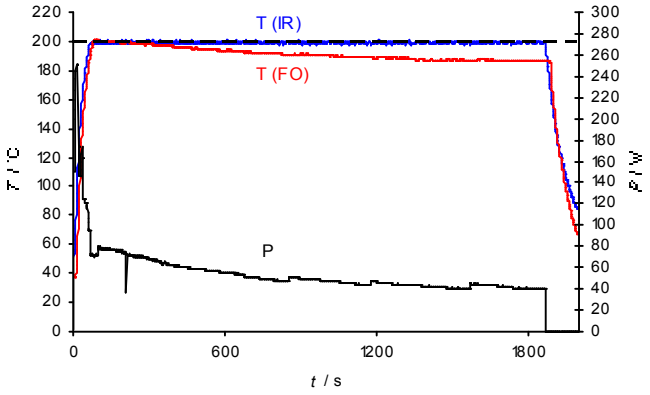

Figure. S13. FO/IR temperature (T) and power (P) profiles for a 3 mL sample of *N*-methylpyrrolidone (NMP) heated in a CEM Discover LabMate single-mode reactor using external IR temperature control and 300 W initial magnetron power. The internal reaction temperature was additionally monitored (slave) by a FO probe (OpSens fiber). Set temperature 200 °C, magnetic stirring ("high"), 10 mL Pyrex vial, flow valve "on" (1.5 bar). The IR sensor was accurately calibrated at 200 °C using NMP and an OpSens FO probe before the experiment was performed. After 20 min, the internal temperature has dropped ~10 °C, after 30 min ~ 15°C below the displayed IR-temperature. Simultaneously, also the applied magnetron power is progressively reduced by the controlling software. This clearly indicated a drift of the IR sensor leading to an erroneous temperature measurment, as the factual reaction temperature inside the vessel is significantly lower.