Supplementary Information

Mechanochemical polymerization – controlling a polycondensation reaction between a diamine and a dialdehyde in a ball mill

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S.1 MATERIALS AND METHODES

P-benzoldicarbaldehyde and p-phenylenediamine were purchased from “abcr GmbH”. All chemicals were used without further purification.

Dynamic light scattering (DLS) was measured at an MALVERN Zetasizer Nanosizer in quartz cuvettes. The sample was dissolved in concentrated sulfuric acid and filtered through a 0.2 µm PTFE filter. Per sample 3 measurements with 11 runs each were conducted in backscattering mode. The attenuator and measurement position was determined automatically.

Dynamic scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 STAR^e System a using aluminum crucibles under argon stream with the heating rate of 10 K min^{-1}. The results were analyzed using the STAR^e SW 11.00 software. The samples were cycled from RT to 450 °C, then cooled down to RT again afterwards a second cycle was done with the same conditions. For the integrations the second heating curve was utilized.

Infrared spectroscopy (IR) was carried out on a BRUKER Vertex 70 with a Specac Golden Gate ATR unit. A resolution of 2 cm^{-1} was utilized and the resulting spectra were treated with ATR-correction by the OPUS 6.5 software.

Matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF) was carried out on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with dithranol + AgTFA as matrix.

Scattering electron microscopy (SEM) was recorded using a HITACHI SU 8020.

Solid state UV/Vis measurements were conducted on a VARIAN Cary 4000 with a HARRICK Praying Mantis unit. The step width was set to 1 nm and the sources were switched at 350 nm. The crude samples were mixed with an excess of $BaSO_4$ prior to measuring.

Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC/PG system using alumina crucibles under argon stream with the heating rate of 10 K min^{-1}.

S.2 SYNTHETIC PROCEDURES

S.2.1. Mechanosynthesis of PPI by neat grinding

For the NG experiment equimolar quantities of **p-benzoldicarbaldehyde** (4.963 g, 37 mmol) and **p-phenylenediamine** (4.001 g, 37 mmol) were placed in a 45 mL zirconium oxide grinding jar with twenty-two 10 mm-diameter zirconium oxide grinding balls. The mixture was then milled for 40 minutes in a Fritsch Pulverisett 7 premium line planetary ball mill operating at a rotation speed of 800 rpm. The samples were analyzed as made. Other milling materials were tungsten carbide and tempered steel.

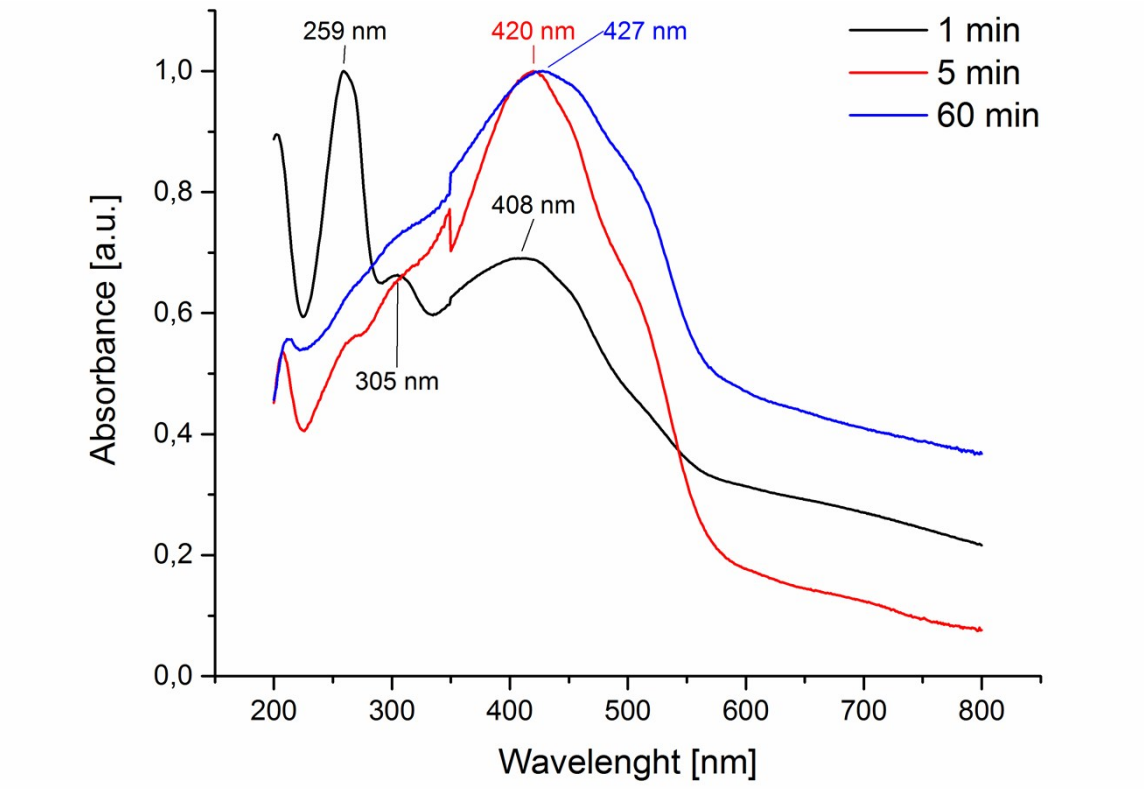
For the liquid assisted experiments 0.2 μl/gmonomer of ethanol were added to the mixture prior to grinding. If balls other than 10 mm were used, the same weight of grinding balls was utilized. (15 mm: 7 balls; 5mm: 180 balls)

S.2.1. Solution polymerization of PPI as a reference material

For the reference experiment equimolar quantities of **p-benzoldicarbaldehyde** (2.478 g, 18.5 mmol) and **p-Phenylenediamine** (2.000 g, 18.5 mmol) were placed in a 250 mL round bottom flask with 100 mL of DMF. The mixture was heated to 170 °C and was refluxed for 2 hours. Afterwards the hot mixture was filtrated and the solid was washed with EtOH and dried over night at 80 °C.

S.3 SUPPORTING FIGURES

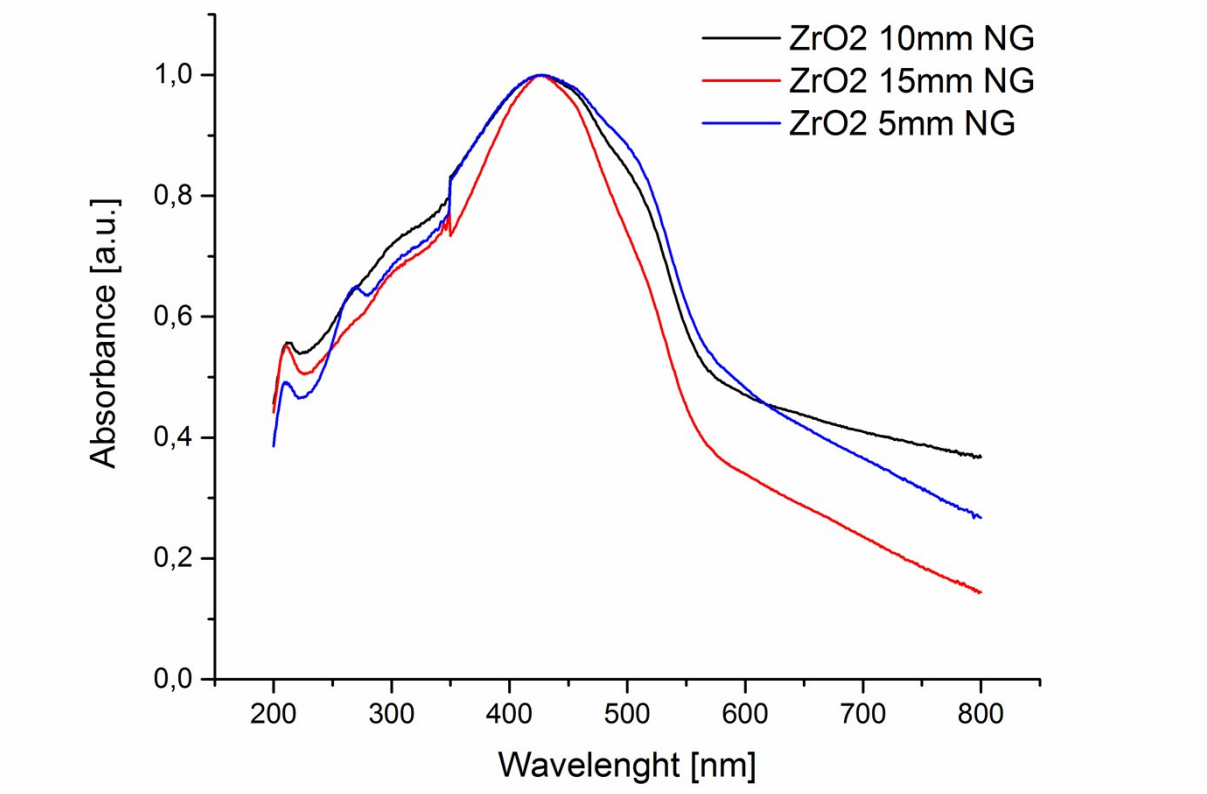
S.3.1 Characterization of the polymer



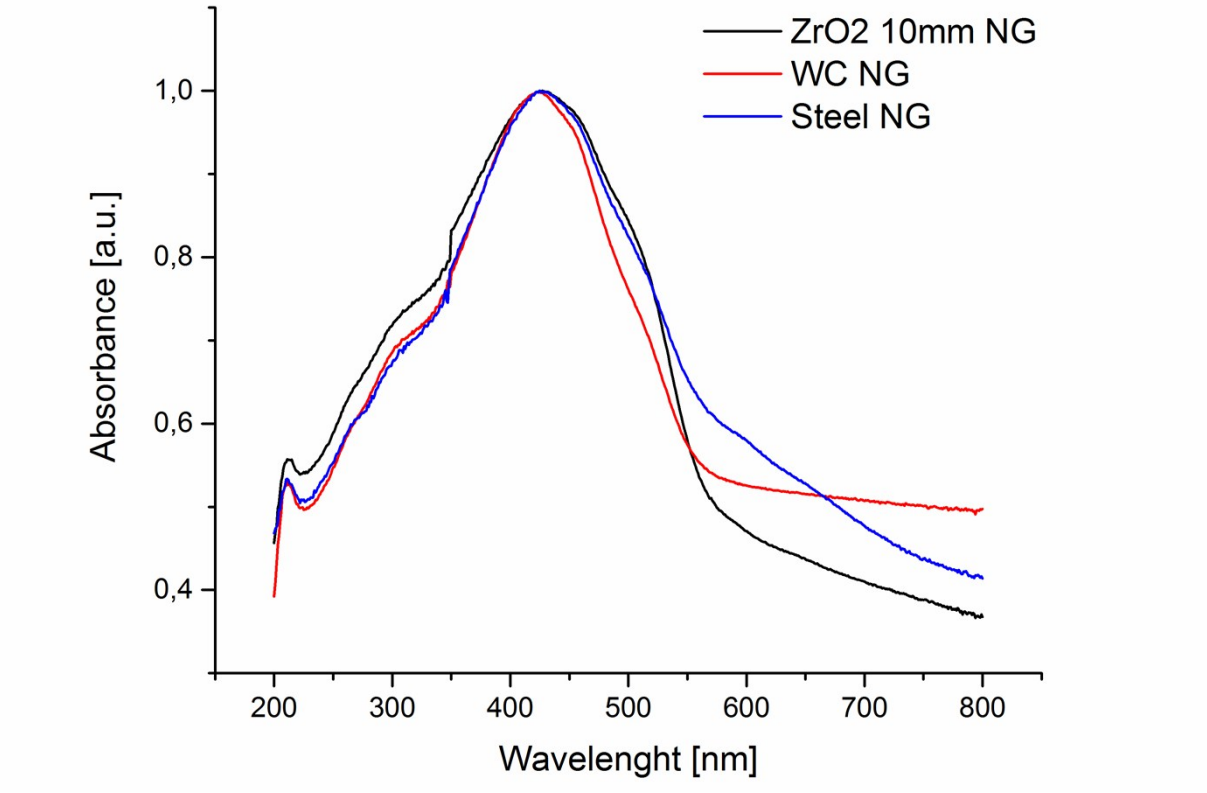
SFig. 1: Changes in the UV/Vis spectrum during the milling with 10 mm ZrO_2 balls in an NG experiment

STable 1: Overview of the samples investigated by solid state UV/Vis spectrometry. Sample: Material, Ball size, neat grinding or LAG with EtOH

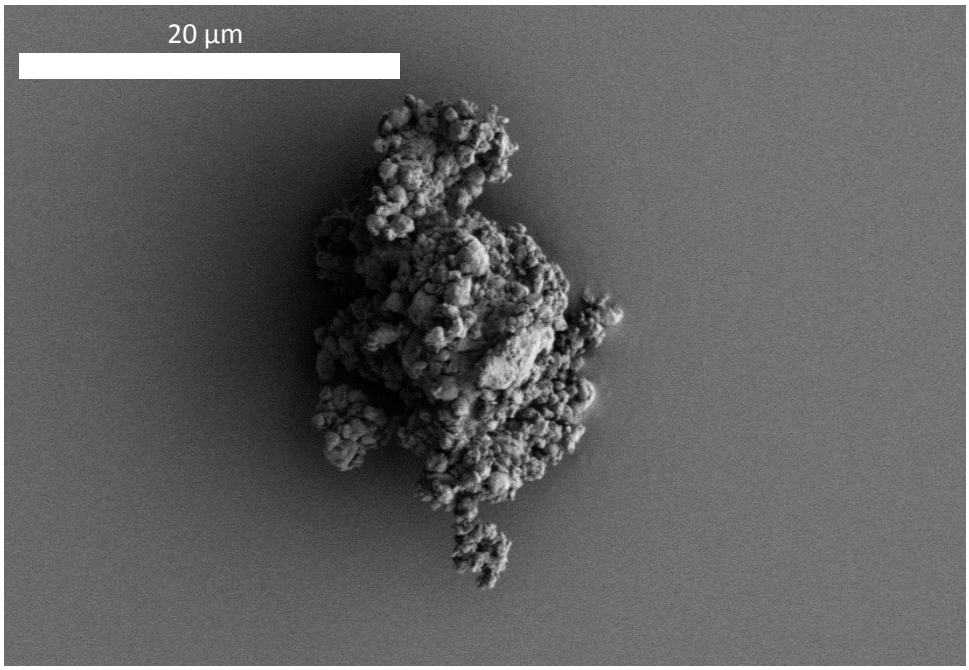
sample	λ_{MAX} [nm]	optical band gap [eV]
Steel 10mm NG	428	2,21
Zirconium dioxide 10mm NG	427	2,19
Tungsten carbide 10mm NG	427	2,21
Zirconium dioxide 5mm NG	428	2,19
Zirconium dioxide 10mm NG	427	2,18
Zirconium dioxide 15mm NG	428	2,21
Tungsten carbide 10mm NG	427	2,23
Tungsten carbide 10mm LAG	456	2,30
Steel 10mm NG	428	2,21
Steel 10mm LAG	454	2,28



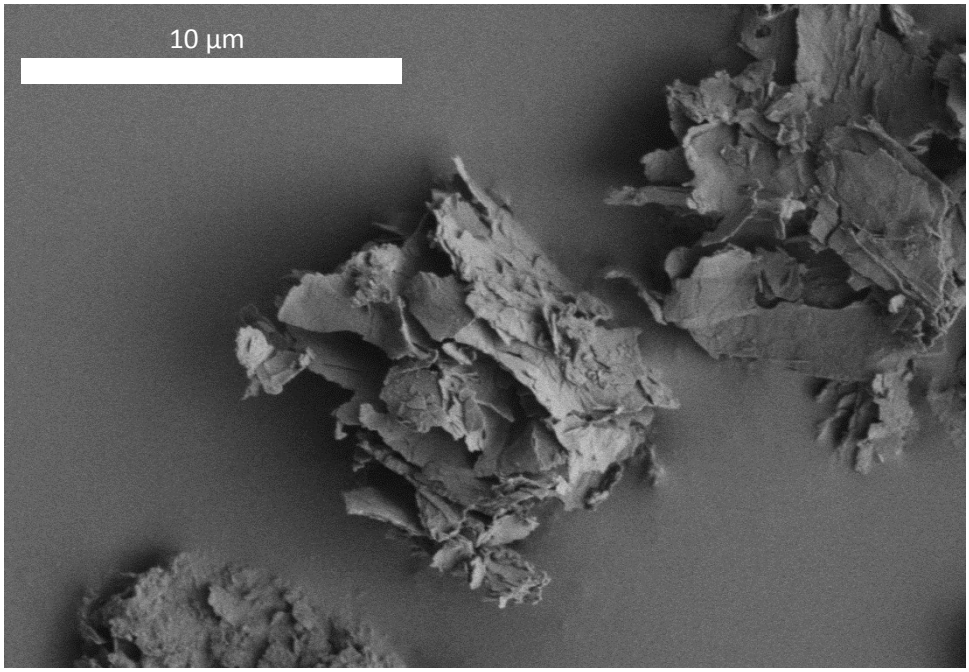
SFig. 2: Influence of the ball size on the UV/Vis spectrum of the product



SFig. 3: Influence of the milling material on the UV/Vis spectrum of the product



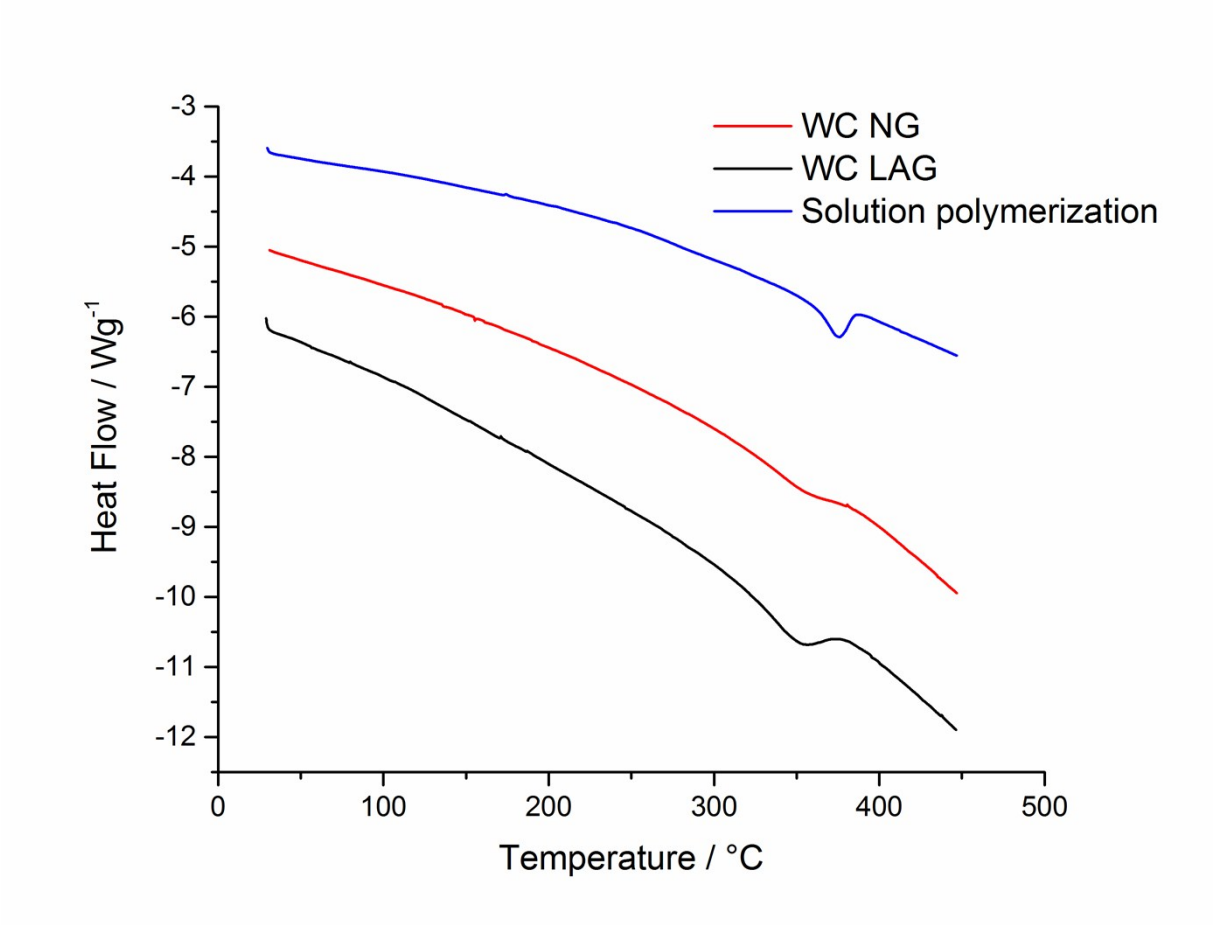
SFig. 4: SEM picture of the polymer prepared by ball milling



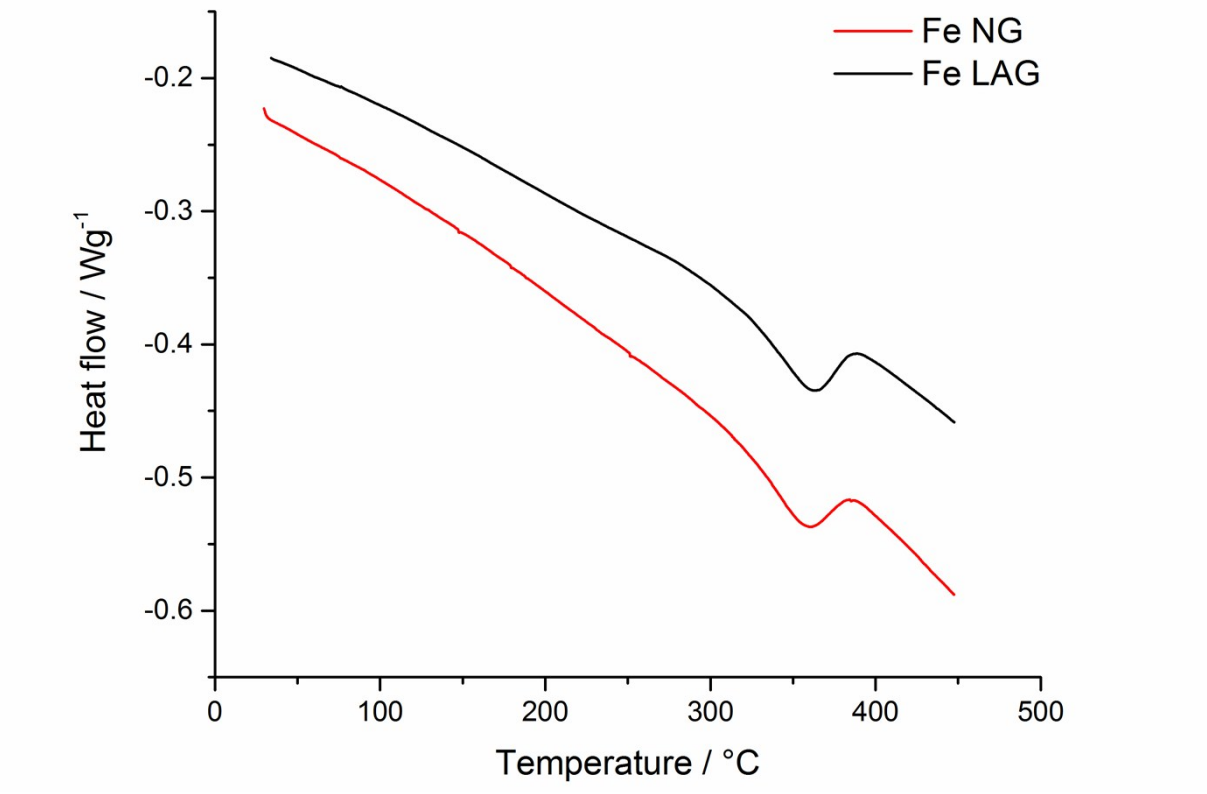
SFig. 5: SEM picture of the polymer prepared by solution polymerization

STable 2: Overview of the samples investigated by DSC. Sample: Material, Ball size, neat grinding or LAG with EtOH

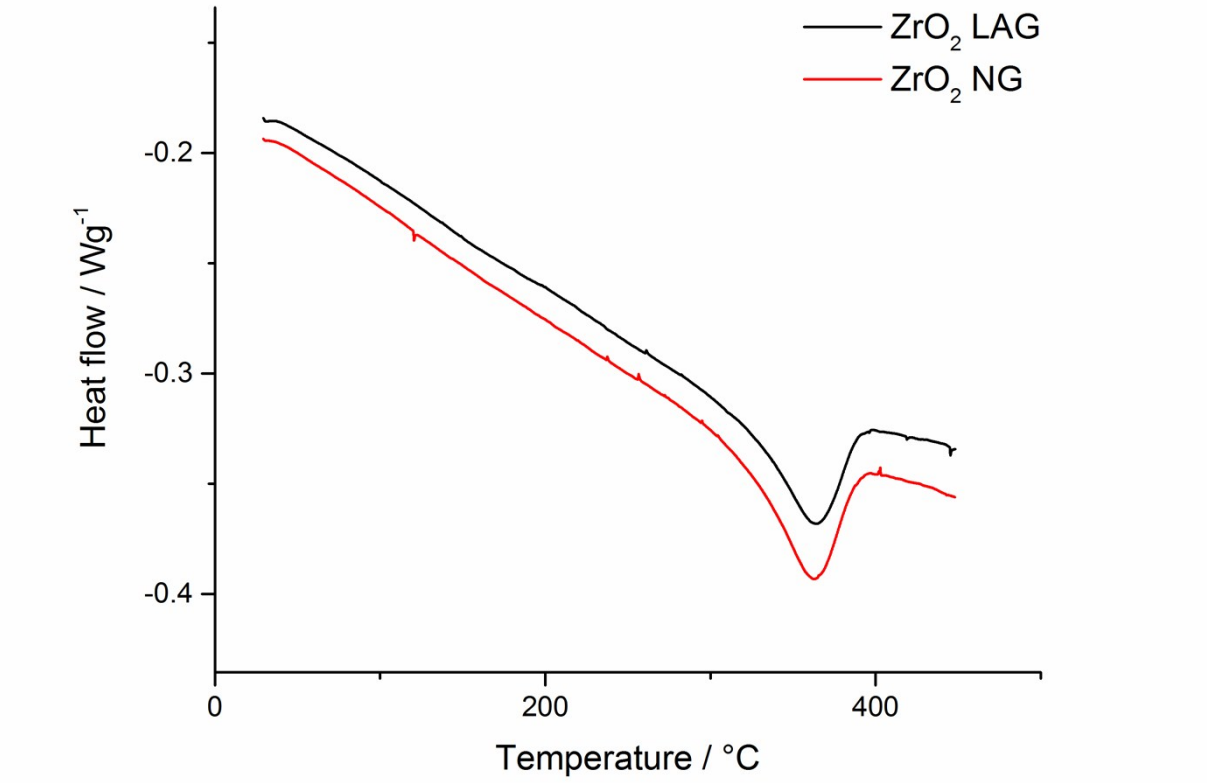
sample	enthalpy of fusion [J/g]	peak temperature [°C]
Steel 10mm NG	-9.76	358.46
Zirconium dioxide 10mm NG	-15.73	362.67
Tungsten carbide 10mm NG	-3.7	354.27
Steel 10mm LAG	-9.92	360.55
Tungsten carbide 10mm LAG	-7.99	351.46
Solution polymerization	-15.27	375.41



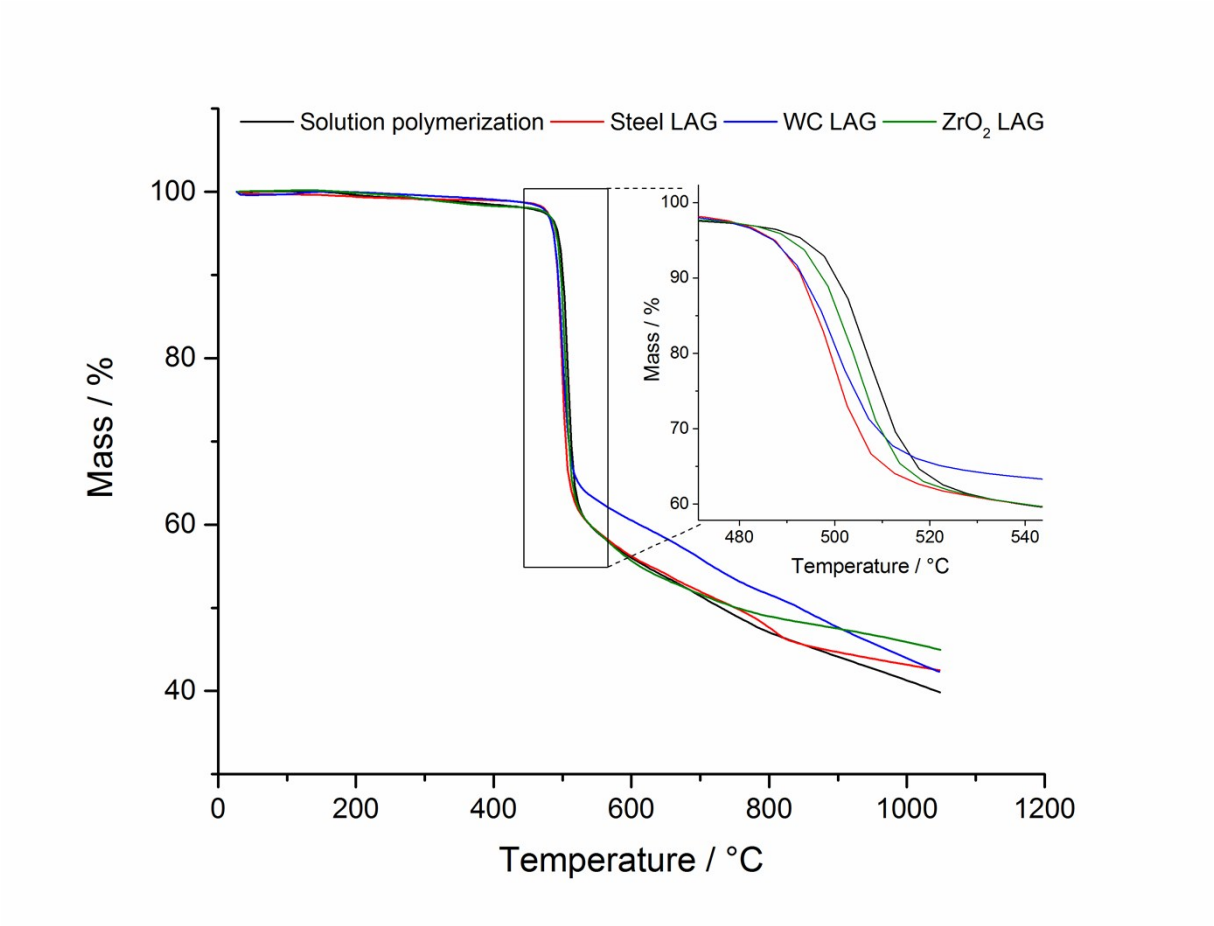
SFig. 6: DSC curves of the tungsten carbide and reference samples



SFig. 7: DSC curves of the steel samples

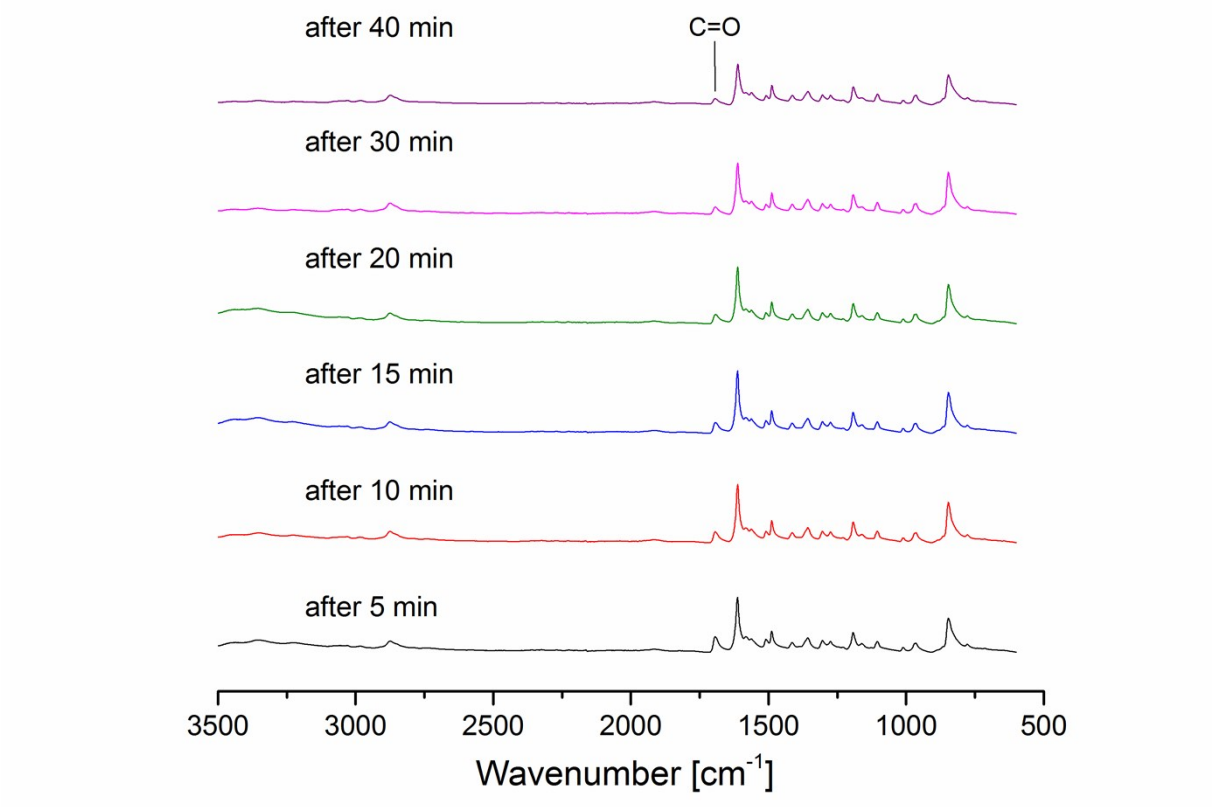


SFig. 8: DSC curves of the zirconium dioxide samples

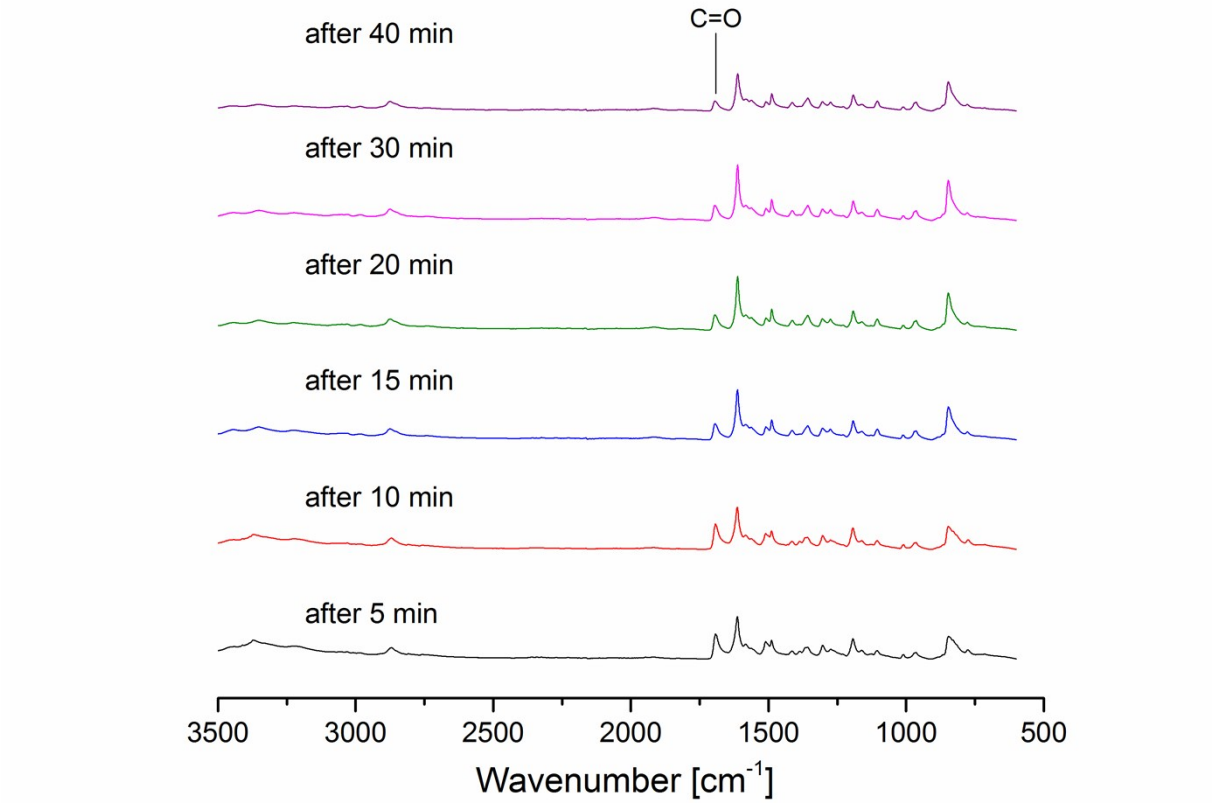


SFig. 9: TGA curve of the samples prepared by LAG and the reference. Inlet shows the enlarged main decomposition around 500 °C

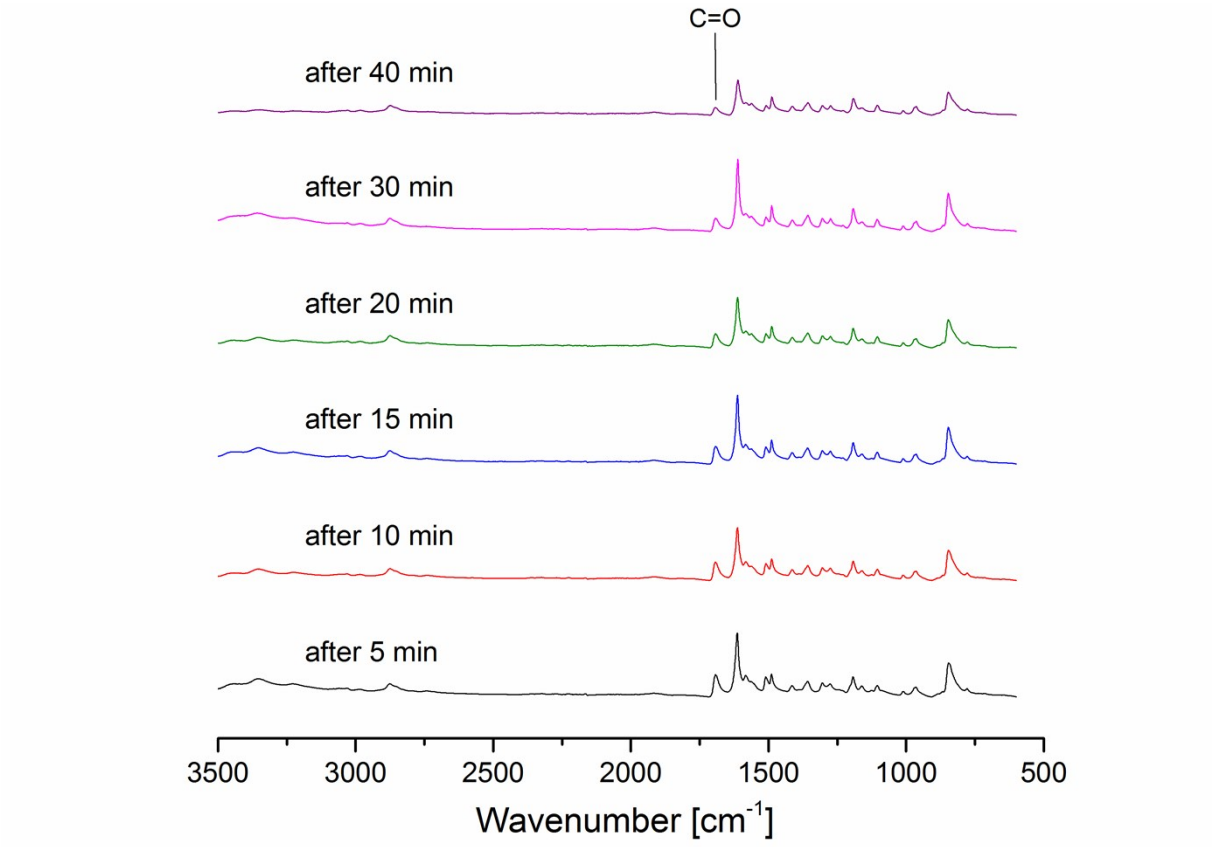
S.3.2. Kinetics of the reaction



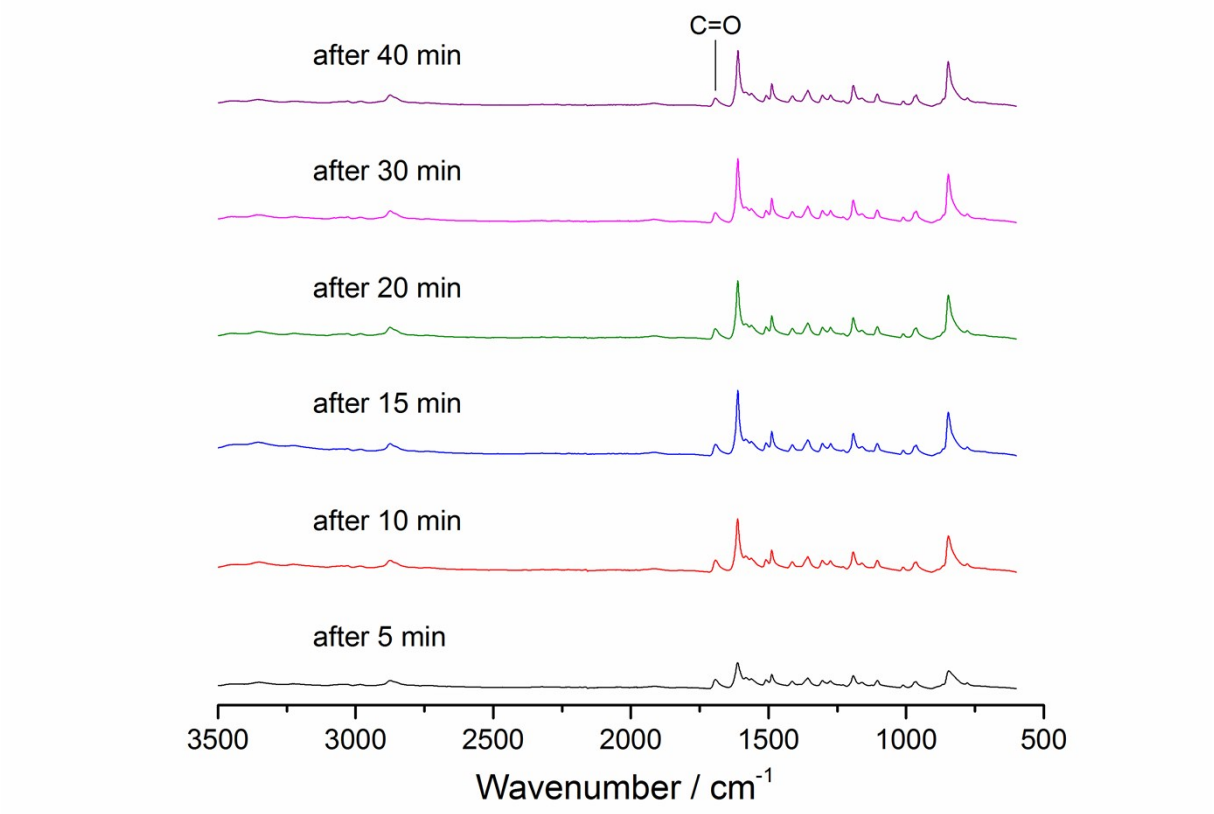
SFig. 10: Development of the IR-spectrum during grinding with 15 mm zirconium oxide balls



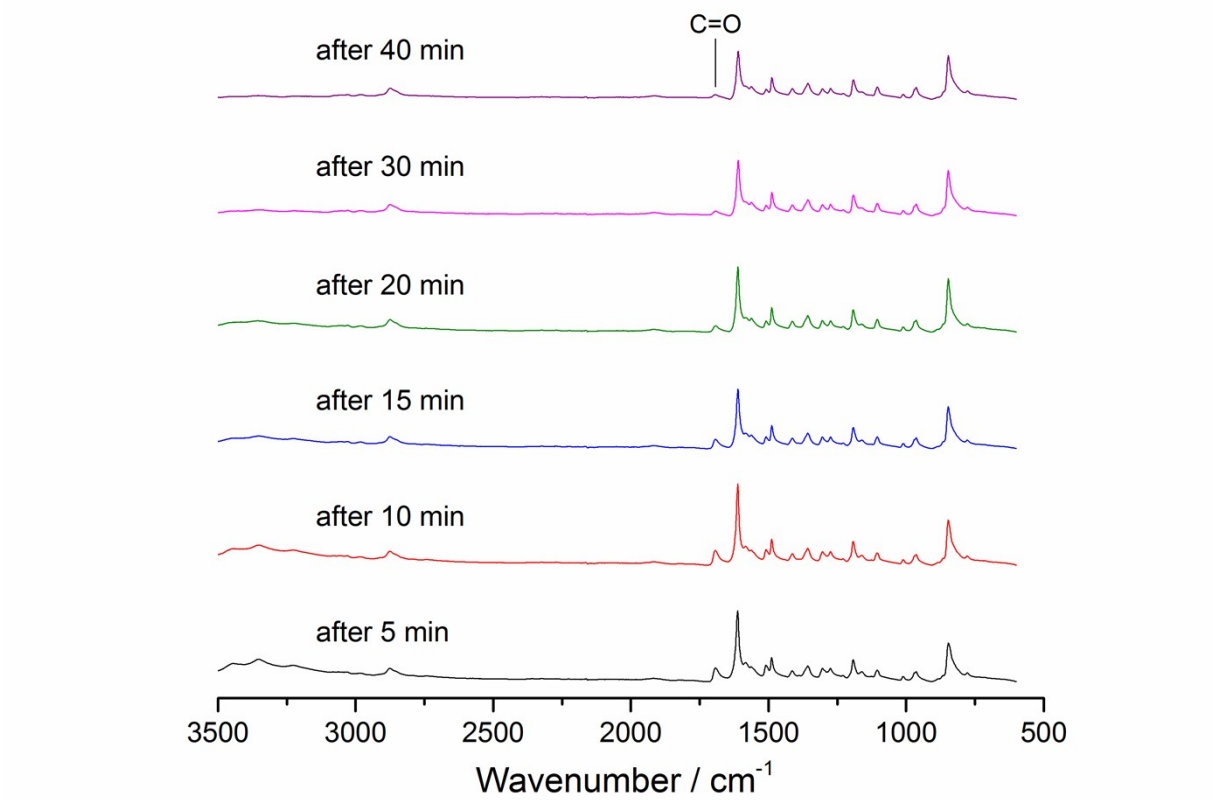
SFig. 11: Development of the IR-spectrum during grinding with 5 mm zirconium oxide balls



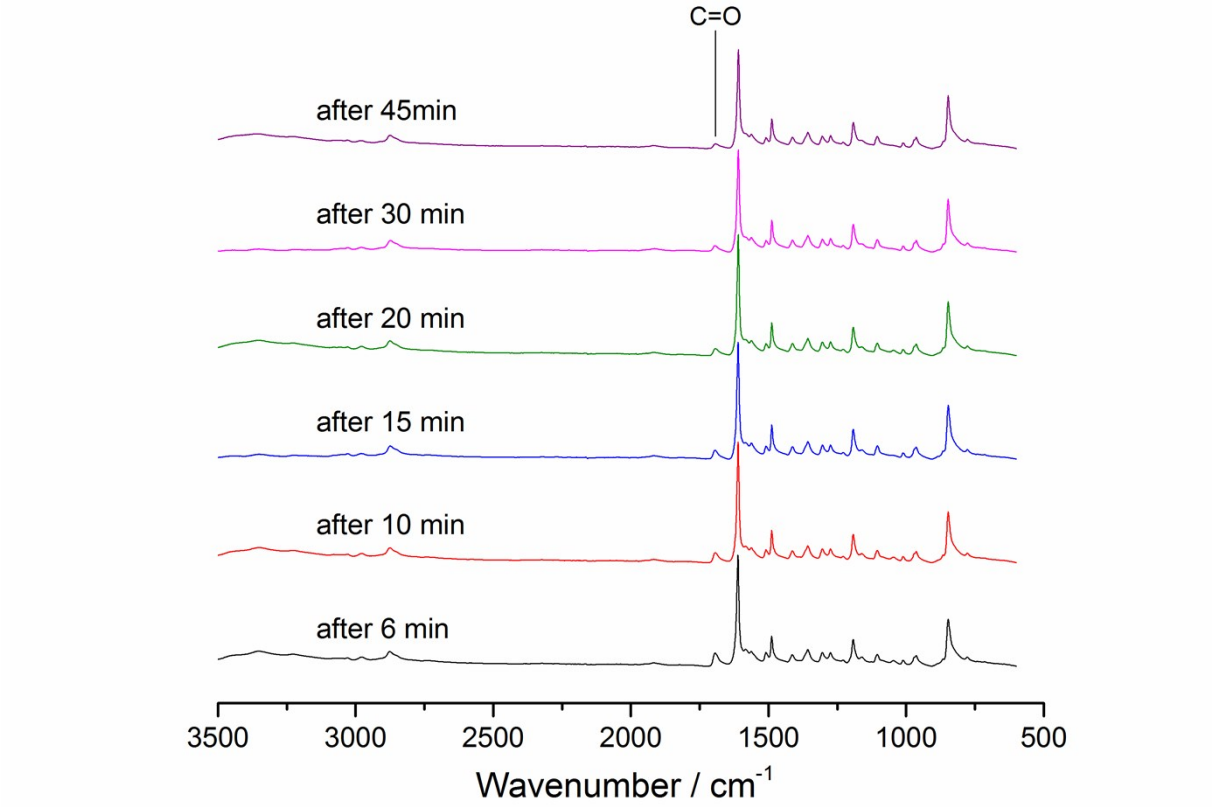
SFig. 12: Development of the IR-spectrum during grinding with 10 mm zirconium oxide balls



SFig. 13: Development of the IR-spectrum during grinding with 10 mm tempered steel balls

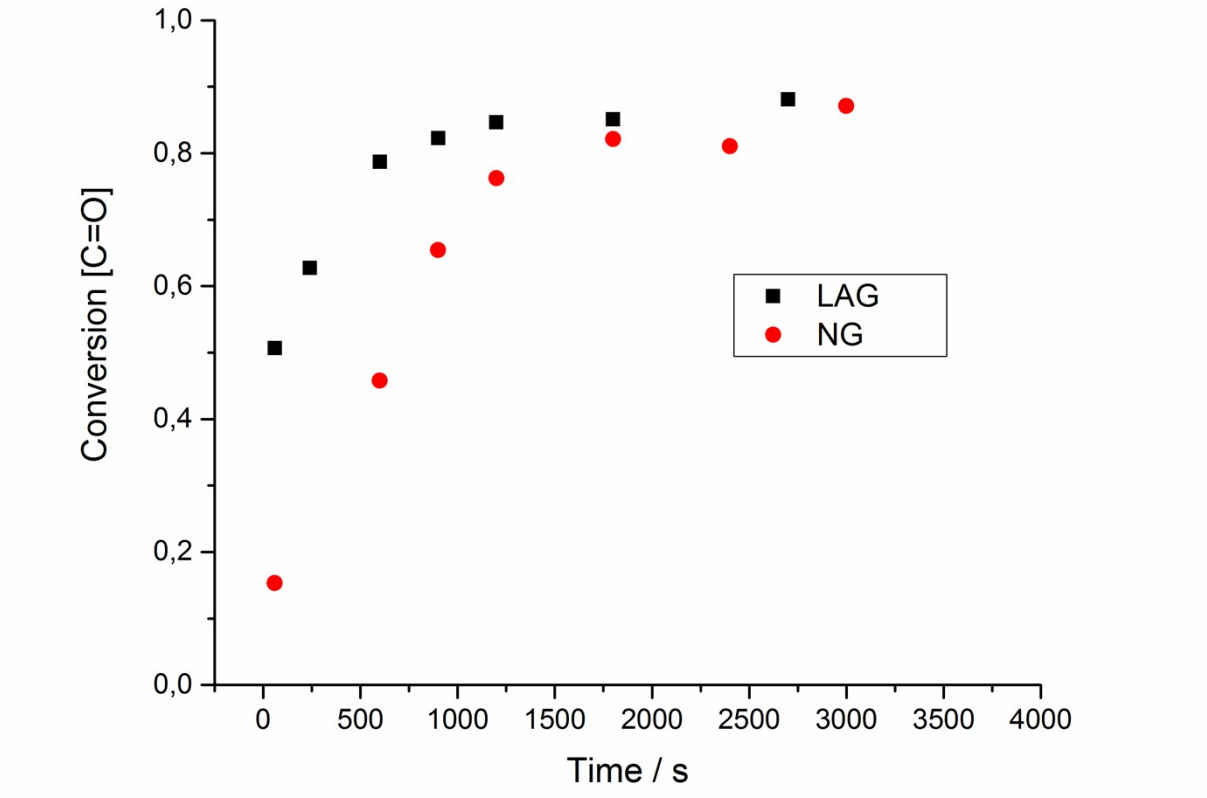


SFig. 14: Development of the IR-spectrum during grinding with 10 mm tungsten carbide balls

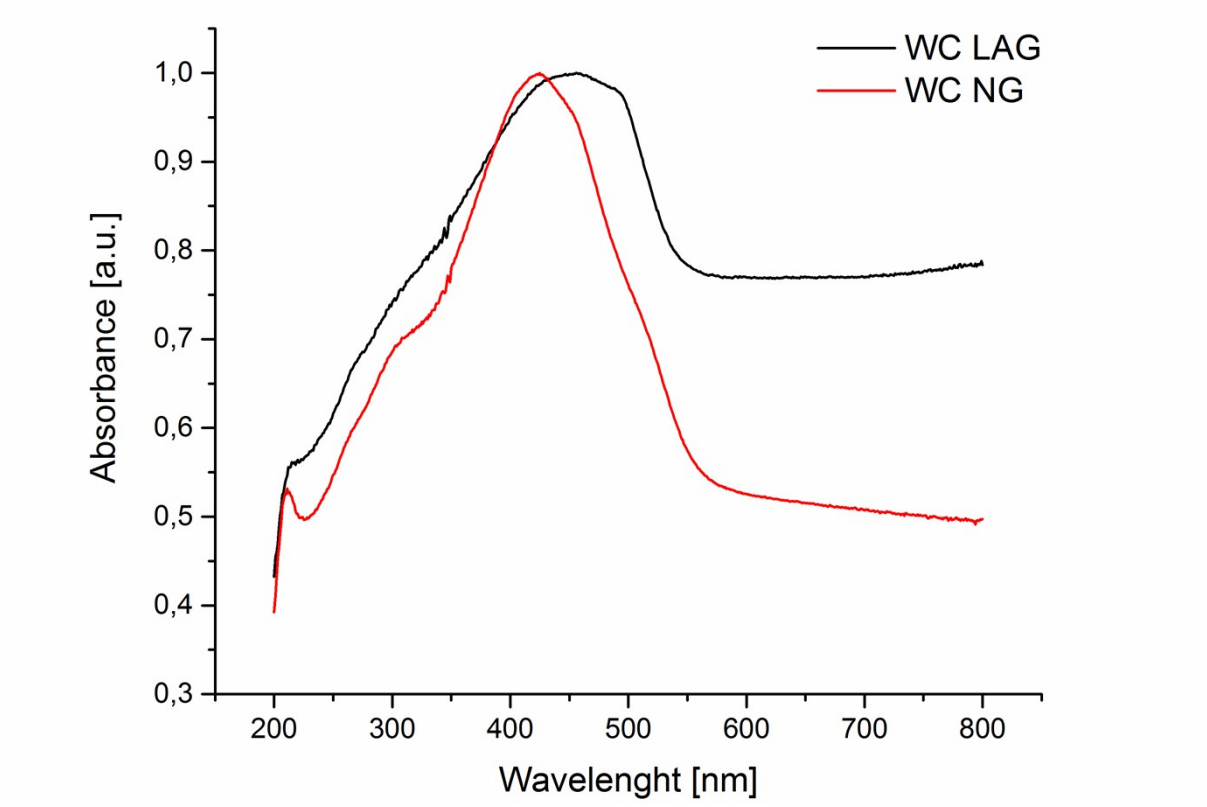


SFig. 15: Development of the IR-spectrum during grinding with 10 mm tungsten carbide balls and 0.2 µl/g of ethanol

S.3.3. Liquid assisted grinding

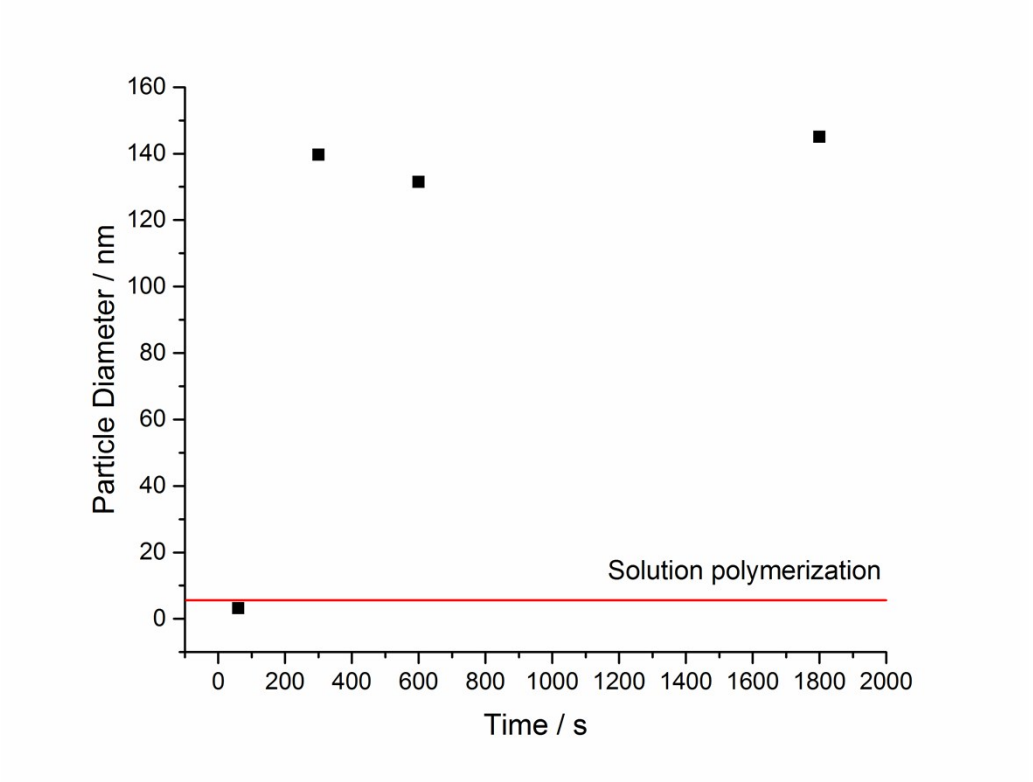


SFig. 16: Conversion of C=O during grinding with 10 mm tungsten carbide balls without (NG) and with (LAG) 0.2 µl/g of ethanol



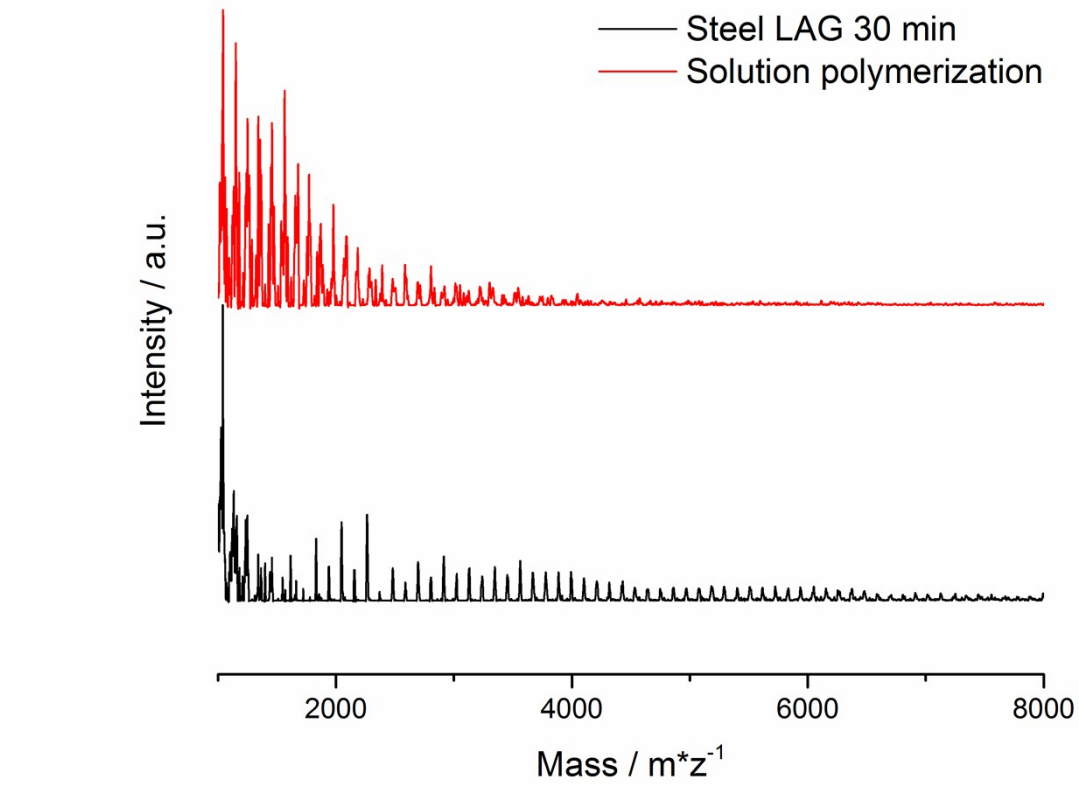
SFig. 17: Influence of the addition of ethanol on the UV/Vis spectrum of the product grinding with 10 mm tungsten carbide balls without (NG) and with (LAG) 0.2 µl/g of ethanol

S.3.4 Particle size by DLS



SFig. 18: Particle diameter (volume mean) determined by DLS of the tungsten carbide LAG sample (▪) vs the solution polymerized reference (red line)

S.3.5 MALDI-TOF



SFig. 19: MALDI-TOF curves of the reference sample (red) and the Steel LAG sample (black)