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Supplementary Information

Mechanochemical Suzuki polycondensation - from linear to hyperbranched polyphenylenes

S. Grätz,[a] B. Wolfrum[a] and L. Borchardt[a]

[a]Department of Inorganic Chemistry, Technische Universität Dresden, Bergstraße 66, 01062 Dresden. Email: lars.borchardt@chemie.tu-dresden.de; Tel: +49-35146334960

S.1 MATERIALS AND METHODES

1,3,5-Tribromobenzene, Phenylboronic acid, 1,4-Dichlorobenzene, 1,4-Dibromobenzene and 1,4-Diiodobenzene were purchased from “Sigma Aldrich” . 1,4-Phenyldiboronic acid was purchased from “abcr GmbH”. Palladium(II) acetate, 4-Bromophenylboronic acid and 3,5-Dibromophenylboronic acid were purchased from “TCI-Chemicals”. Potassium carbonate was purchased from “Güssig”. All chemicals were used without further purification.

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 350 °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. Each sample was measured five times and the average of the integrals was taken in order to reduce effects caused by inhomogeneities.

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

Transmission electron microscopy (TEM) was recorded using a Carl Zeiss Libra 120.

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}.

Gel permeation chromatography (GPC) was performed with a AGILENT TECHNOLOGIES series 1200 HPLC pump, and 1 PL MIXED-C separation column 300x7,5mm and 5µm PSgel, a Fa. BURES RI and viscosity detector and a WYATT TECHNOLOGY MiniDAWN-LS detector. THF (stabilized with 0.0025% BHT) was used as an eluent with a flow rate of 1ml/min.

Nitrogen physisorption measurements were performed at 77 K on a Quantachrome Quadrasorb apparatus. High purity gases were used for physisorption measurements (N2: 99.999%). Pore size distributions were calculated using the Quenched Solid Density Functional Theory (QSDFT) method for carbon (slit/cylinder./sphere pores, adsorption kernel) on the adsorption branch. Prior to physisorption experiments, all samples were activated at 423 K for 12 h under vacuum.

S.2 SYNTHETIC PROCEDURES

S.2.1. Mechanosynthesis of 1,3,5-Triphenylbenzene; AB3 approach

For the experiment equimolar quantities of **1,4-Dibromobenzene** (0.813 g, 3.44 mmol), **1,4-Phenyldiboronic acid** (0.569 g, 3.44 mmol), **palladium acetate** (69 mg, 9.3 mol%) and **potassium carbonate** (8.549, 61.86 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 30 minutes in a Fritsch Pulverisett 7 premium line planetary ball mill operating at a rotation speed of 800 rpm. The samples were washed with water, 10wt% hydrochloric acid, ethanol and acetone and then dried over night at 80°C.

S.2.2. Mechanosynthesis of linear PPP by neat grinding; A2B2 approach

For the experiment equimolar quantities of **1,4-Dibromobenzene** (0.813 g, 3.44 mmol), **1,4-Phenyldiboronic acid** (0.569 g, 3.44 mmol), **palladium acetate** (69 mg, 9.3 mol%) and **potassium carbonate** (8.549, 61.86 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 30 minutes in a Fritsch Pulverisett 7 premium line planetary ball mill operating at a rotation speed of 800 rpm. The samples were washed with water, 10wt% hydrochloric acid, ethanol and acetone and then dried over night at 80°C.

S.2.3. Mechanosynthesis of linear PPP by neat grinding; AB approach

For the experiment **4-Bromophenylboronic acid** (1.451 g, 7.23 mmol), **palladium acetate** (139 mg, 9.3 mol%) and **potassium carbonate** (8.41, 60.85 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 30 minutes in a Fritsch Pulverisett 7 premium line planetary ball mill operating at a rotation speed of 800 rpm. The samples were washed with water, 10wt% hydrochloric acid, ethanol and acetone and then dried over night at 80°C.

S.2.4. Mechanosynthesis of hyperbrnached polyphenylene by neat grinding; A2B1 approach

For the experiment **3,5-Dibromophenylboronic acid** (1.400 g, 7.23 mmol), **palladium acetate** (101 mg, 9.3 mol%) and **potassium carbonate** (8.499, 61.50 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 30 minutes in a Fritsch Pulverisett 7 premium line planetary ball mill operating at a rotation speed of 800 rpm. The samples were washed with water, 10wt% hydrochloric acid, ethanol and acetone and then dried over night at 80°C.

S.3 SUPPORTING FIGURES

S.3.1 A2B2/AB – Polymers

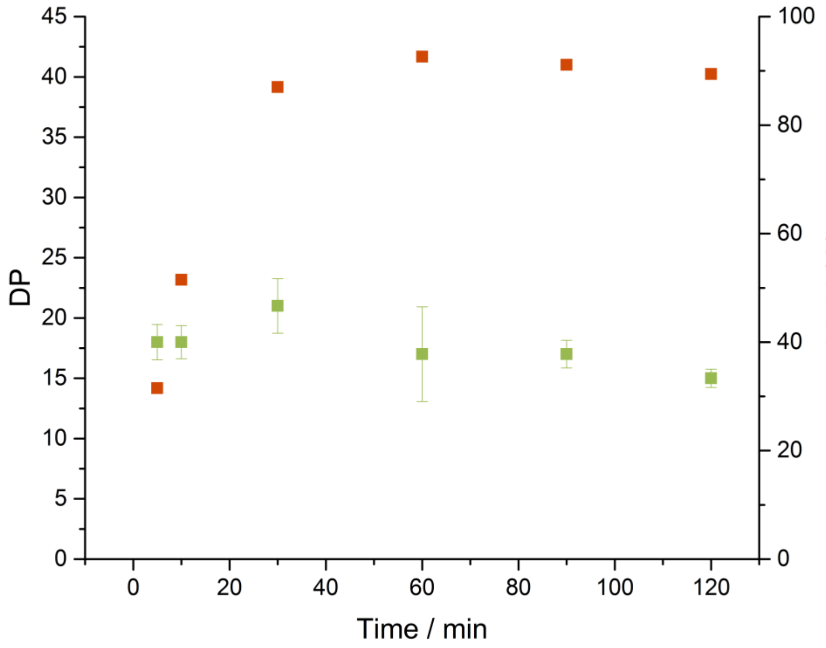

Fig.S1 DP and yield of the A2B2 polymers synthesized after different milling times

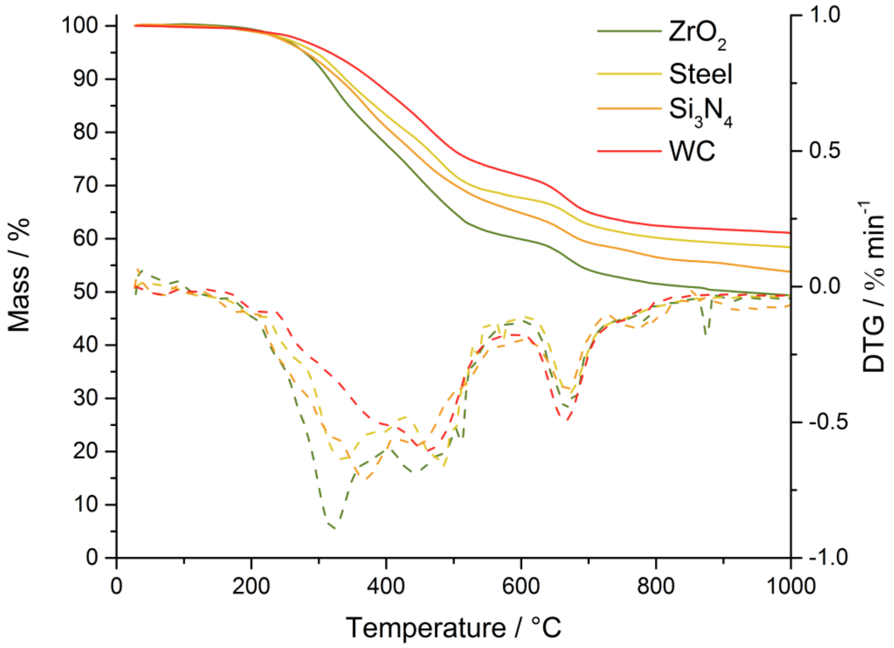

Fig.S2 Comparison of the TGA curves of A2B2 polymers synthesized with different milling materials

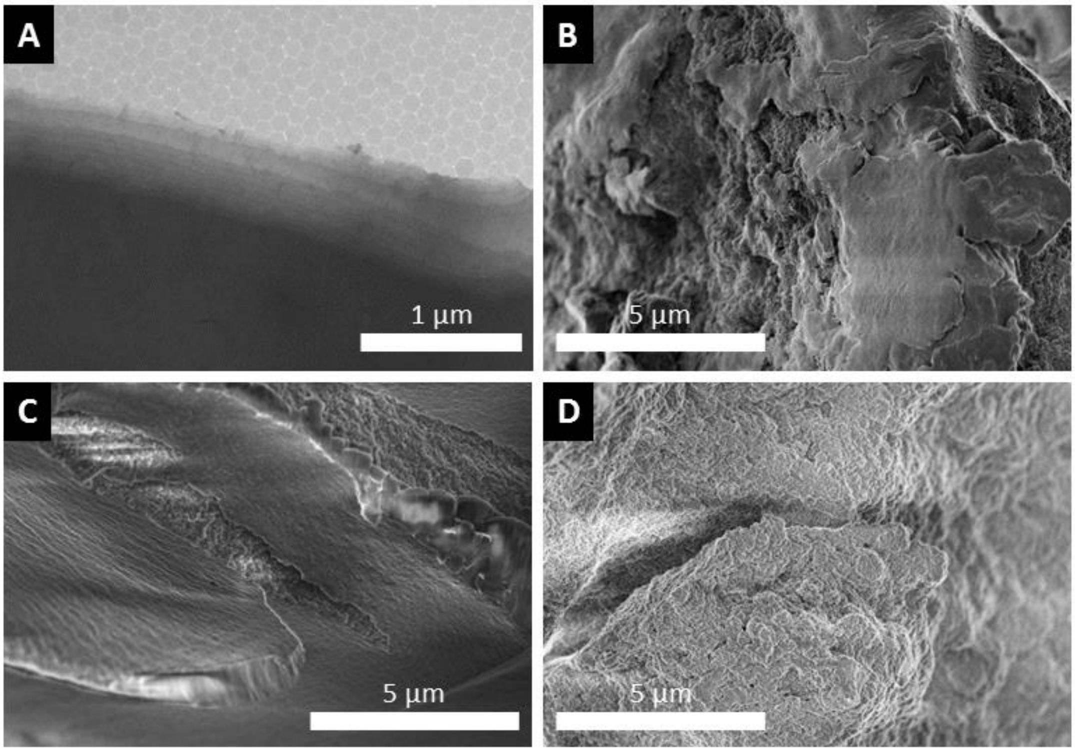

Fig.S3 A: TEM micrograph of A2B2-1 (ZrO$_2$); B: SEM micrograph of A2B2-1(ZrO$_2$); C: SEM micrograph of AB-1(ZrO$_2$); C: SEM micrograph of AB-3(Si$_3$N$_4$); Scale is given for each picture

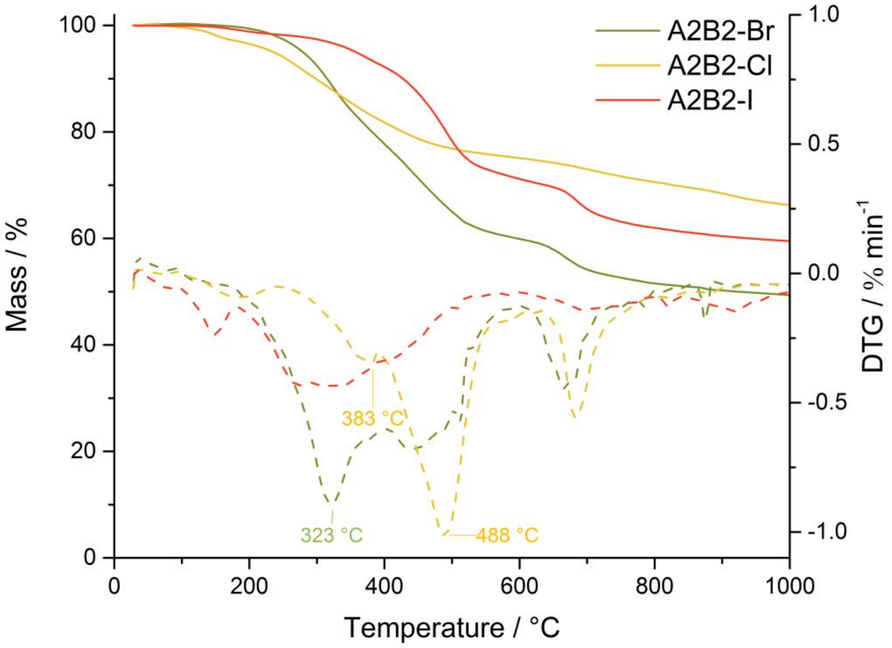

Fig.S4 Comparison of the TGA curves of A2B2 polymers synthesized out of A2 monomers with different halogen functions

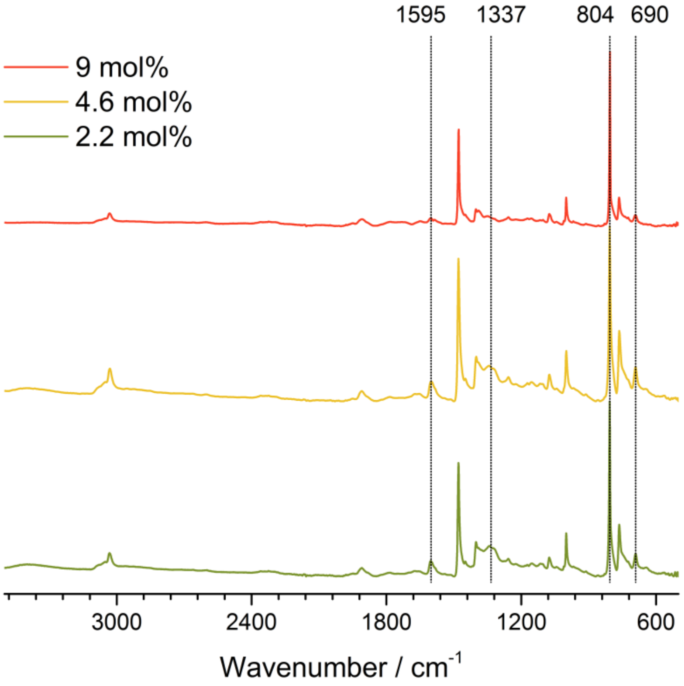

Fig.S5 Comparison of the IR spectra of A2B2 polymers synthesized with different catalyst concentrations

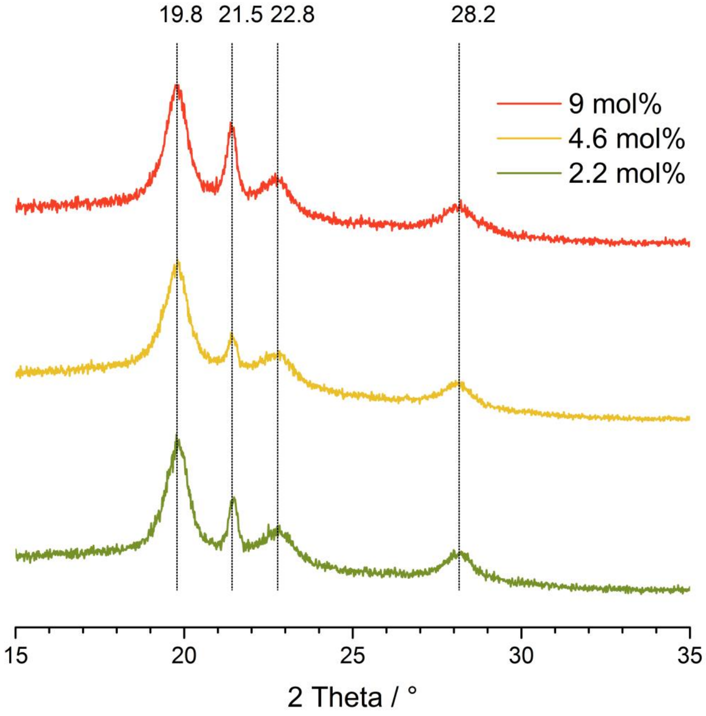

Fig.S6 Comparison of the XRD diffractograms of A2B2 polymers synthesized with different catalyst concentrations

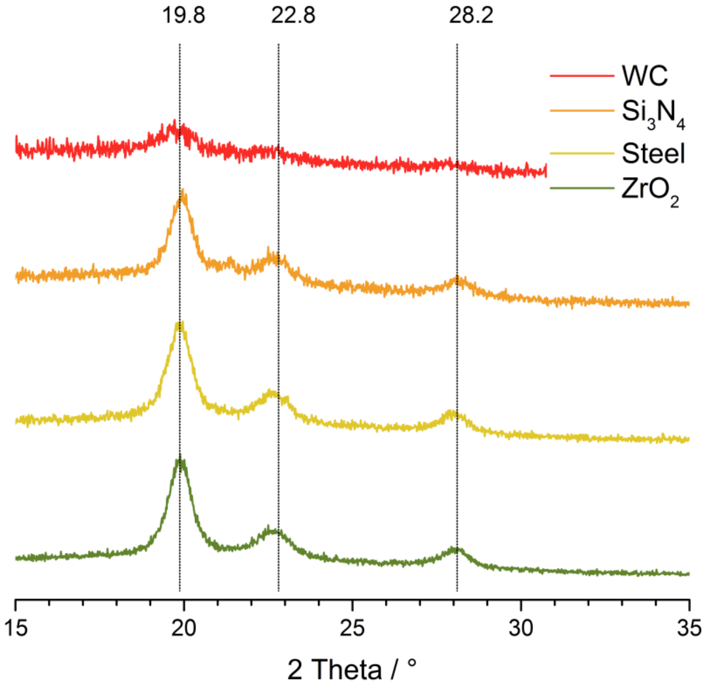

Fig.S7 Comparison of the XRD diffractograms of AB polymers synthesized with different milling materials

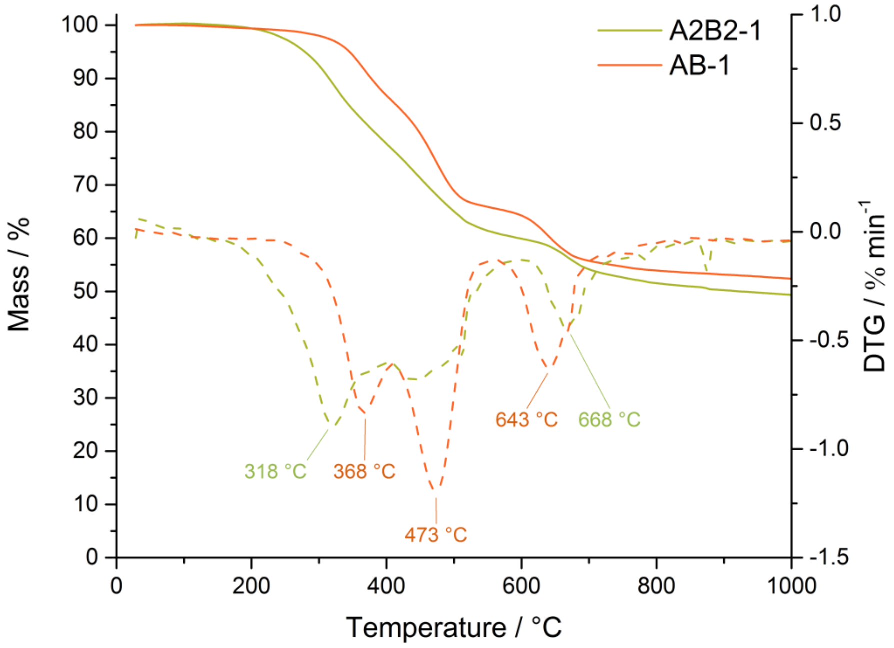

Fig.S8 Comparison of the TGA curves of A2B2 and AB type polymers synthesized with ZrO_2 balls

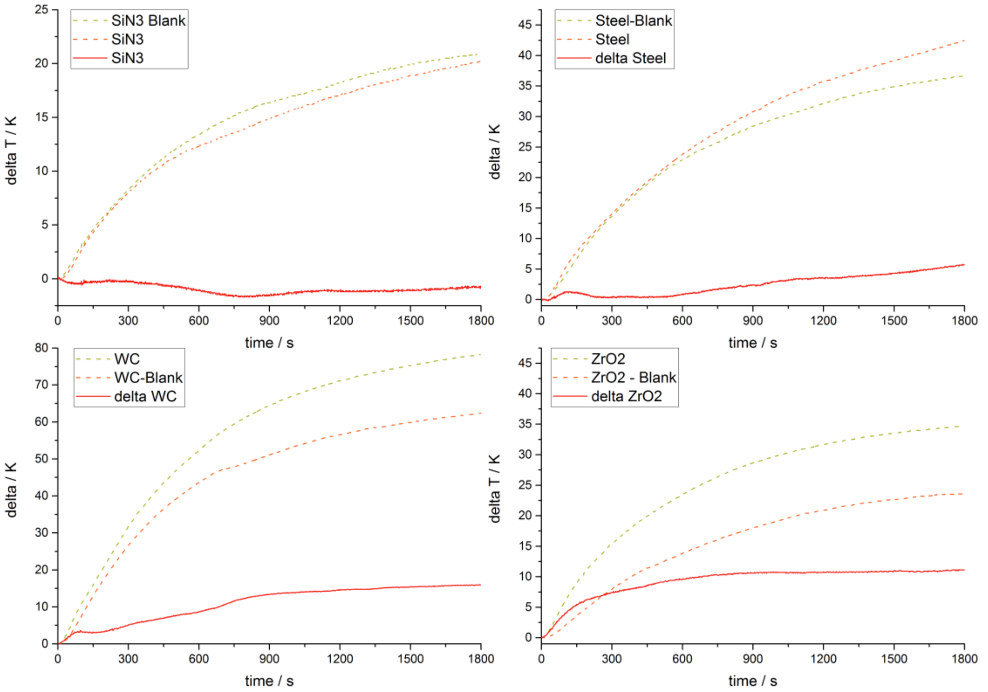

Fig.S9 Comparison of the temperature increase during milling for different milling materials. Blank corresponds to a milling vessel filled only with the base. The solid line is the difference between blank and polymerization experiment

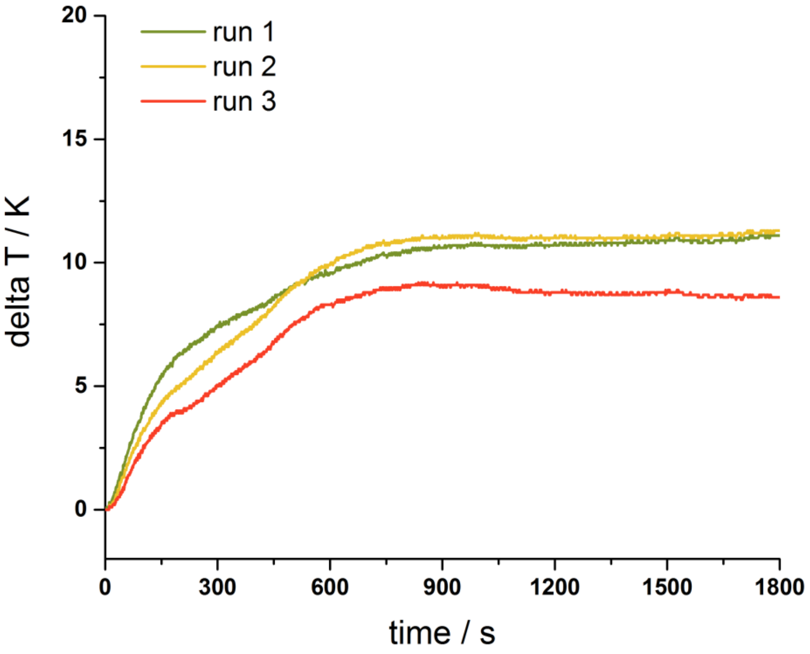

Fig.S10 Study of the reproducibility of the GTM experiment in the zirconia beaker. Blank reference has been subtracted. The plateau is reached around the same time while the plateau temperature is subject to multiple variables and should be viewed as general indications.

S.3.2 A2B1 – Polymers

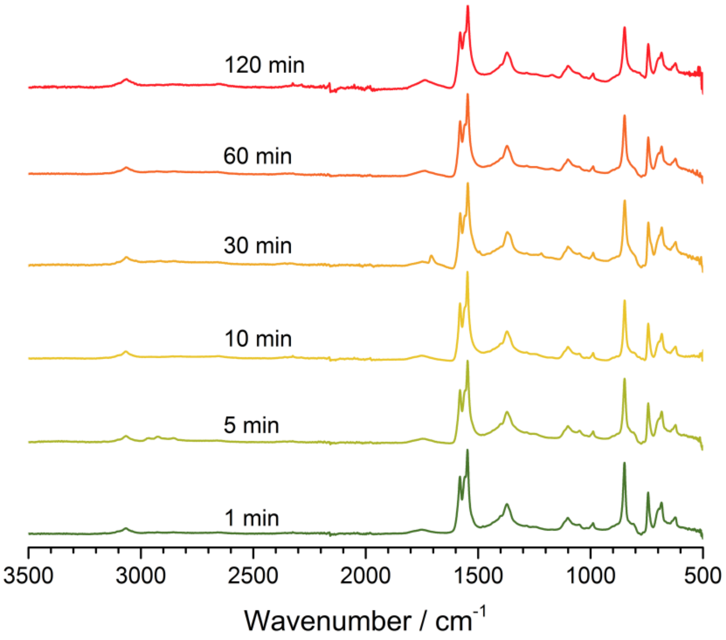

Fig.S11 Comparison of the IR spectra of the hyperbranched polyphenylene formed by the reaction after 1 minutes up to 120 minutes

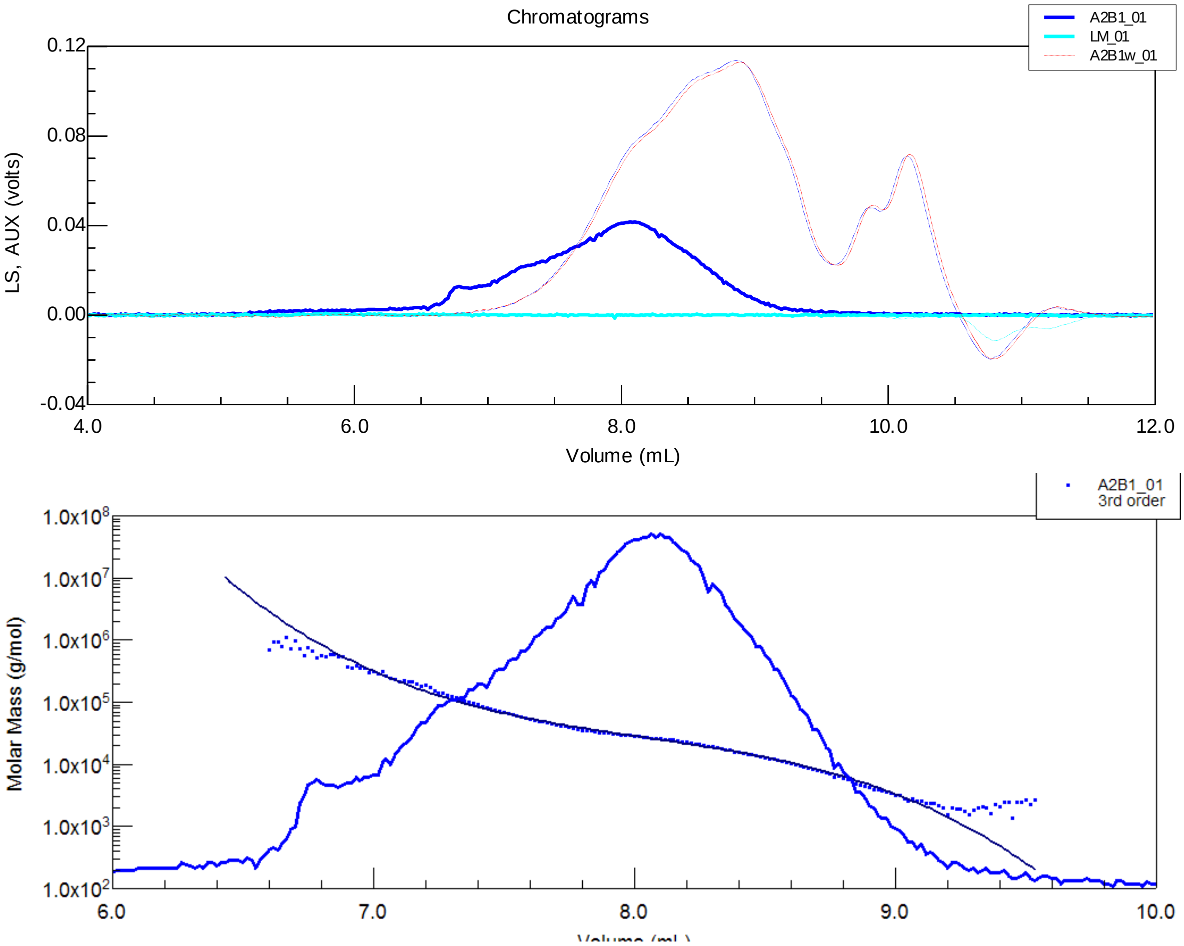

Fig.S12 (top): LS and RI chromatogram of A2B1-300; Molar mass calibration curve with 3rd order fit.

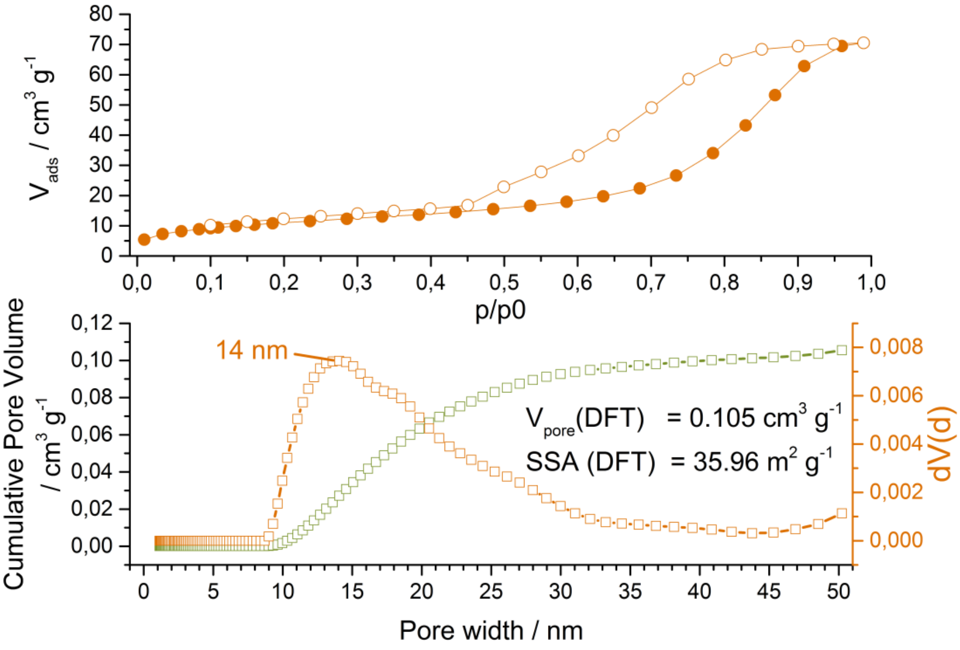

Fig.S13 Top: N_2-Physisorption of the hyperbranched polyphenylene after 30 minutes of milling. Bottom: QSDFT calculations illustrating the pore size distribution.

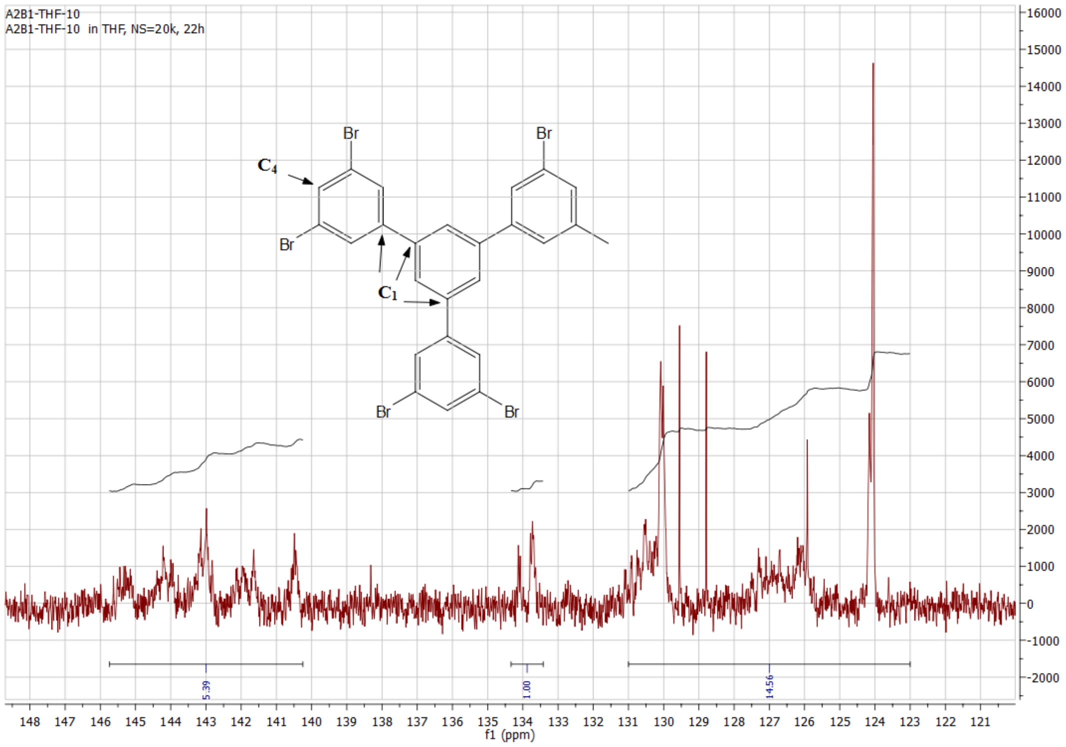

Fig.S14 ^{13}C NMR of the THF-soluble fraction fo the A2B1 polymer after 10 minutes of milling in ZrO_2

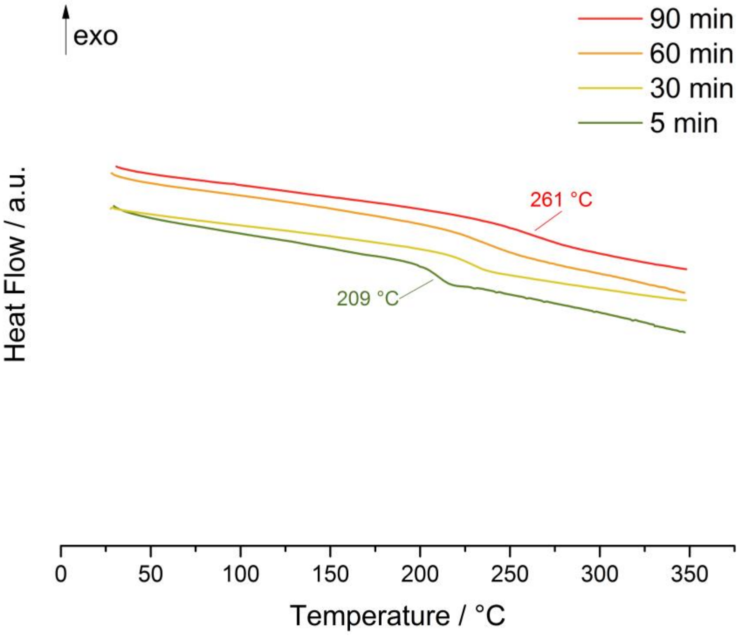

Fig.S15 Comparison of the DSC curves of the hyperbranched polyphenylene formed by the reaction after different times