Supporting Information

The Design of Hypercrosslinked Polymers from Benzyl Ether Self-Condensing Compounds and External Crosslinkers

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Experimental

Materials

Benzyl methyl ether, 1,4-bis(methoxymethyl)benzene and 4,4'-bis(methoxymethyl)biphenyl were purchased from Tokyo Chemical Industry. p-Terphenyl, 1,2-dichloroethane and iron(III) chloride were purchased from Sigma Aldrich and methanol was purchased from VWR. All materials were used as received.

Polymerisation of hypercrosslinked networks

In a typical self-condensation reaction to produce BMMBP, anhydrous 1,2-dichloroethane (20 mL) was added to 4,4'-bis(methoxymethyl)biphenyl (1.454 g, 6 mmol) and purged with N_2 for at least 30 minutes. After purging, iron(III) chloride (2.925 g, 18 mmol) was quickly added to the solution and the mixture was heated to 80 °C for a further 24 h, during which the reaction was kept under a constant flow of N_2. The resulting mixture was then allowed to cool before the solid polymer was isolated *via* filtration using a Buchner funnel and washed with methanol until the filtrate was almost colourless. The polymer was then transferred to a soxhlet thimble for further purification by Soxhlet extraction in methanol for at least 24 h. Finally, the polymer was dried in a vacuum over at 70 °C for a further 24 h. Yields for HCPs from benzyl methyl ether, 1,4-bis(methoxymethane)benzene and 4,4-bis(methoxymethane)biphenyl were 122 %, 118 % and 109%, respectively, based on hypothetical 100% polycondensation.

Characterisation

Fourier-transform infrared spectroscopy was performed on finely ground samples in the range of 500 – 4000 cm^{-1} using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer equipped with an MXR3 Al Kα monochromated X-ray source (hv = 1486.6 eV). X-ray gun power was set to 72 W (6 mA and 12 kV). Samples were ground and attached to the sample holder using conductive carbon tape. Thermo Avantage software (ThermoFisher Scientific) was used to analyse the data. XPS spectra were shifted to align the peak for adventitious carbon (C− C) at 285.0 eV. All gas sorption isotherms were measured using a porosity analyser (Micromeritics 3Flex). Prior to measurement, samples were degassed overnight at 120 °C and ~0.2 mbar pressure, before degassing in situ for 4 h at 120 °C and 0.003 mbar. Nitrogen sorption isotherms were ran at both 77 K (to derive textural properties) and 298 K, while all CO_2 isotherms were ran at 298 K. Sample surface areas were calculated using the Brunauer−Emmett−Teller (BET) method.[1] The total volume of pores, V_{TOT}, was calculated from the volume of N_2 adsorbed at $P/P_0 = 0.97$, while the micropore volume, V_{MICRO}, was determined using the Dubinin−Radushkevich method.[2] Pore size distributions was derived from the isotherms by using an built-in software from Micromeritics and selecting the DFT model for carbon slit shape pores (N_2@77 on Carbon Slit Pores by NLDFT). Gas sorption selectivity was calculated using an ideal selectivity approach from low pressure isotherms (up to 1 bar) collected on a Micromeritics 3Flex sorption analyser at 298 K. Ideal selectivity, IS, was calculated using the following equation:

$$IS = (\frac{n_1}{y_1})/(\frac{n_2}{y_2})$$

Where n_1 is the number of mols of adsorbed CO_2 at a pressure y_1, and n_2 is the number of mols of adsorbed N_2 at a pressure y_2. The temperature of adsorption was controlled using a water bath. High-resolution scanning electron microscope (SEM) images were obtained using a high-resolution field emission gun SEM (FEGSEM (5 kV, InLens detector)) (Leo Gemini 1525 coupled with SmartSEM software interface, Carl Zeiss NTS Ltd., UK). HCP samples were fixed on Al stubs (Agar Scientific Ltd., UK) using conductive carbon tape and coated with chromium (15 nm) prior to imaging. Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 ADVANCE diffractometer at 40 kV and 20 mA with a Cu target tube and a graphite monochromator. Thermal analyses were performed using a Netzsch TG209 F1 Libra thermogravimetric analyser. Approximately 15 mg of sample was heated from room temperature to 900 °C at a rate of 10 °C min^{-1} under either air or N_2 gas flow (100 mL min^{-1}). An isothermal step of 1 h was included at 120 °C to ensure removal of residual water before heating continued. The purity of the gases used was 99.999% for nitrogen and 99.99% for carbon dioxide.

Supporting data

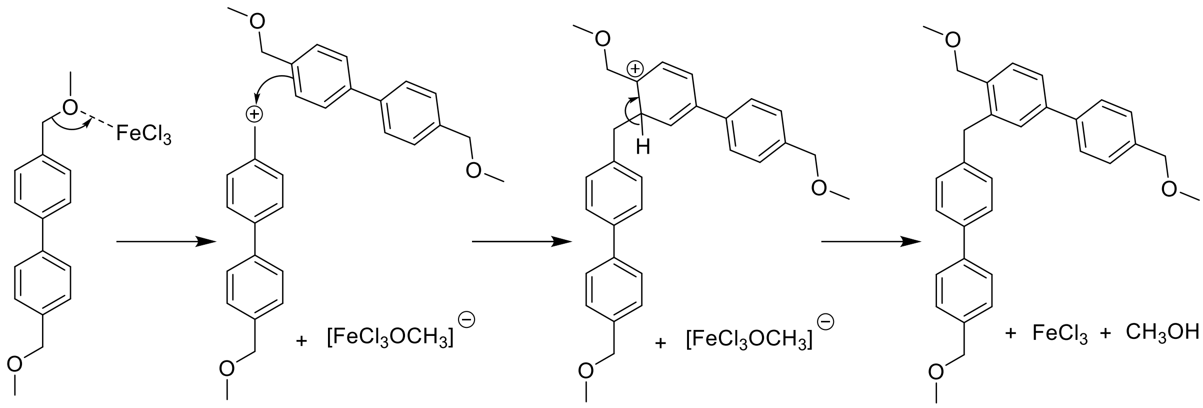

Figure S1. A suggested mechanism for the formation of a crosslink in a BMMBP hypercrosslinked polymer. An SN1 reaction involving a Lewis-acid FeCl$_3$ catalyst, enabling electrophilic aromatic substitution.

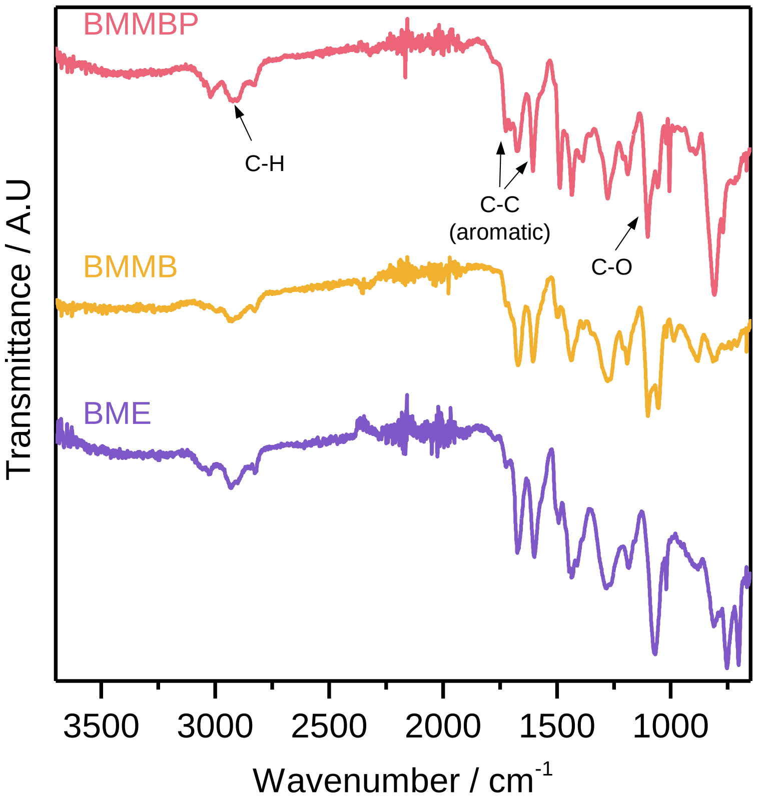

Figure S2. FTIR spectra of BMMBP (pink), BMMB (yellow), and BME (purple).

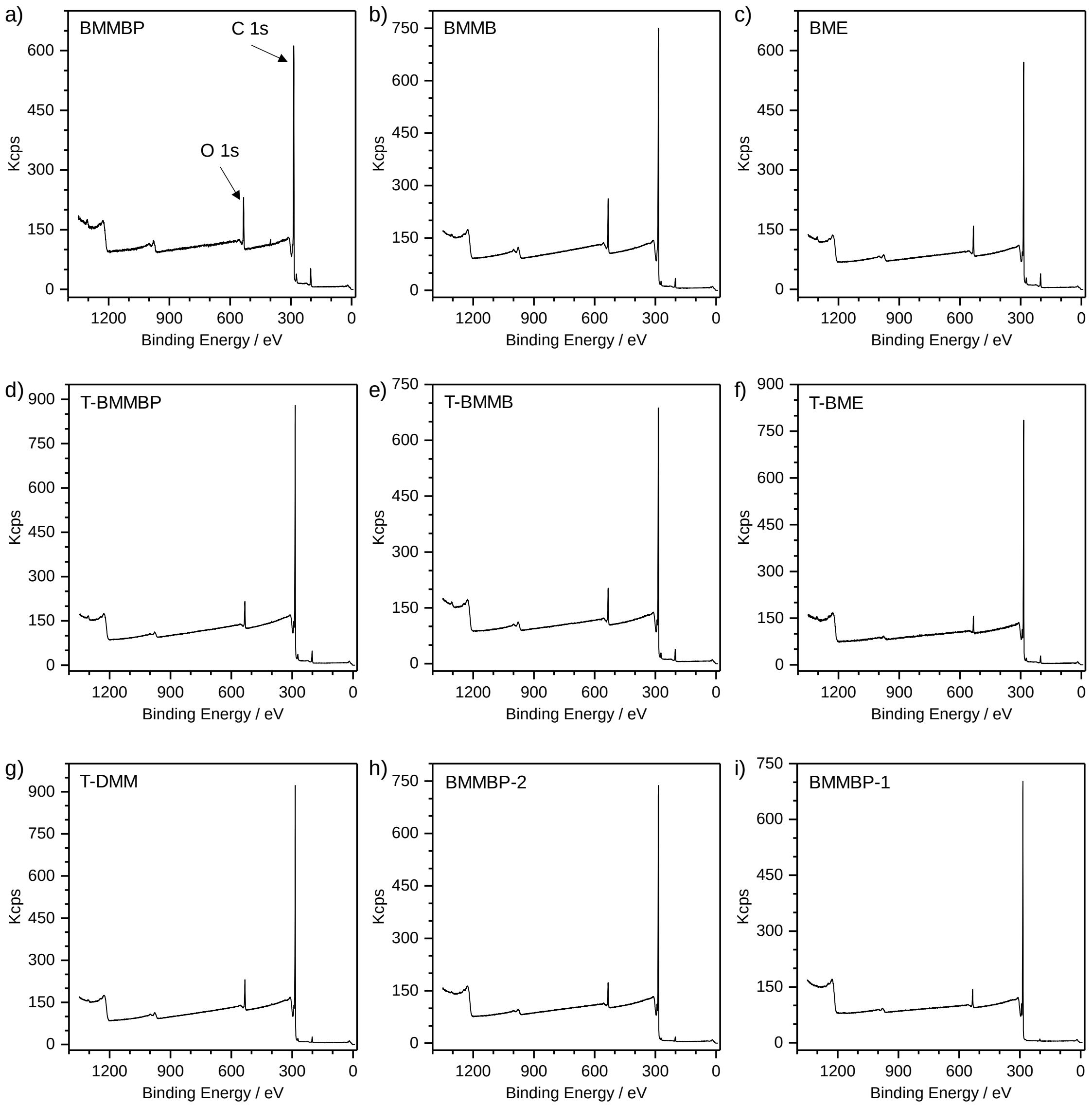

Figure S3. X-ray photoelectron spectroscopy survey spectra for all polymers. Peaks for C 1s and O 1s are highlighted in a). a) BMMBP, b) BMMB, c) BME, d) T-BMMBP, e) T-BMMB, f) T-BME, g) T-DMM, h) BMMBP-2, and i) BMMBP-1.

Table S1. Conversion of ether (C-O-C) groups into crosslinks, determined by oxygen loss relative to C using XPS

	C/O ratio in precursors[a]	C/O ratio in HCPs[b]	C-O-C group conversion during hypercrosslinking (%)
BMMBP	8	9.2	13
BMMB	5	9.0	45
BME	8	14.0	43
BMMBP-2	8	18.2	56
BMMBP-1	8	26.0	69
T-BMMBP	11	17.7	38
T-BMMB	8	13.1	39
T-BME	14	27.5	49
T-DMM	4.5	15.8	72

[a] Determined from atomic % of O and C in precursors and considering monomer feed ratio. [b] Determined using atomic % of C and O from XPS survey spectra.

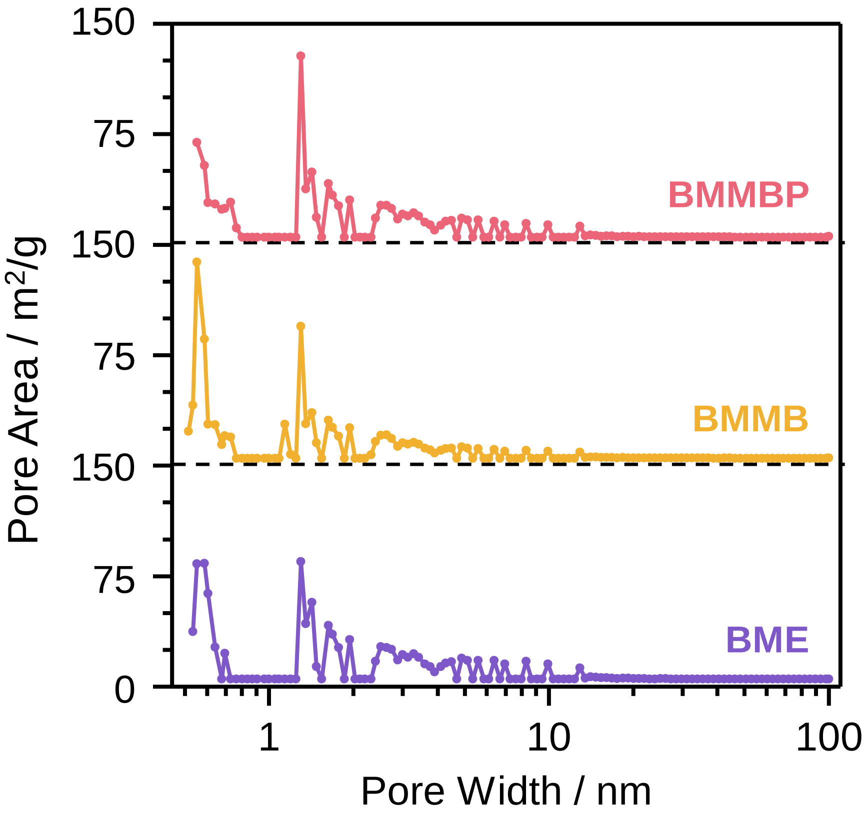

Figure S4. Pore size distributions for BMMBP (pink), BMMB (yellow) and BME (purple).

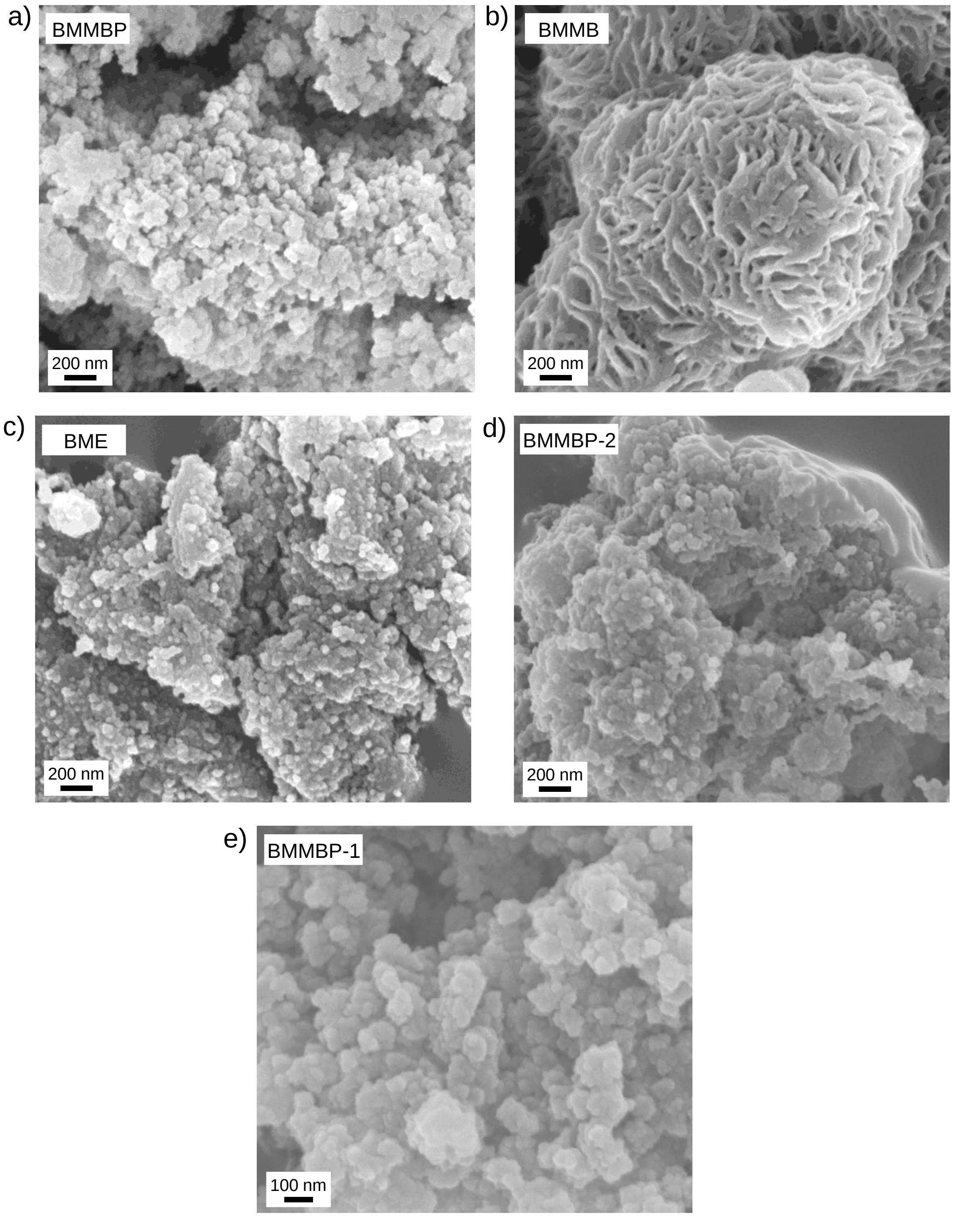

Figure S5. Scanning electron micrographs for all self-condensed polymers. a) BMMBP, b) BMMB, c) BME, d) BMMBP-2 and e) BMMBP-1.

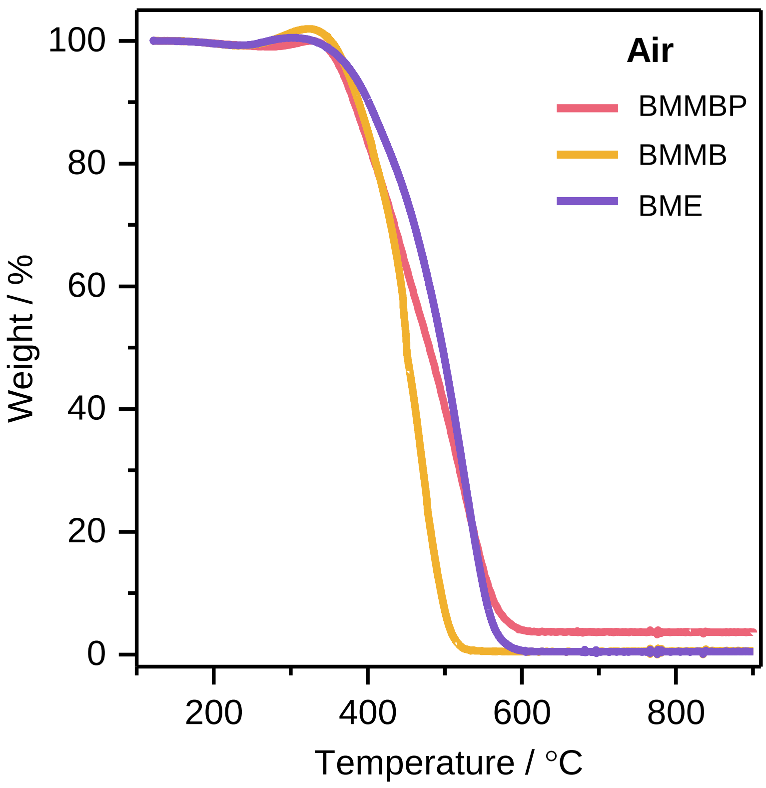

Figure S6. Thermogravimetric analysis in air of BMMBP (pink), BMMB (yellow), and BME (purple), heating from 120 to 900 °C at a heating rate of 10 °C/min. Air was flowed over samples at 100 mL/min.

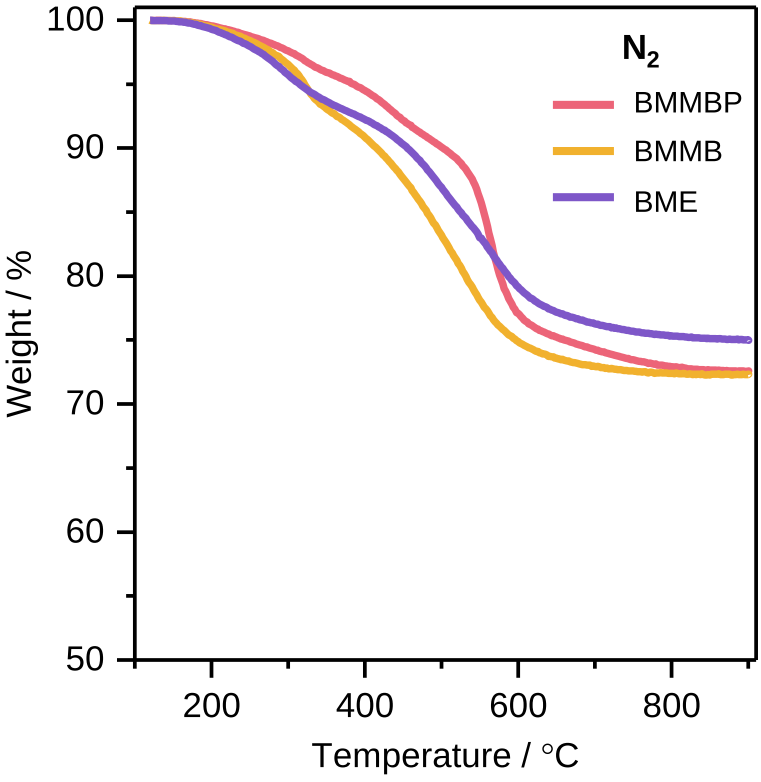

Figure S7. Thermogravimetric analysis in N_2 of BMMBP (pink), BMMB (yellow), and BME (purple), heating from 120 to 900 °C at a heating rate of 10 °C/min. N_2 was flowed over samples at 100 mL/min.

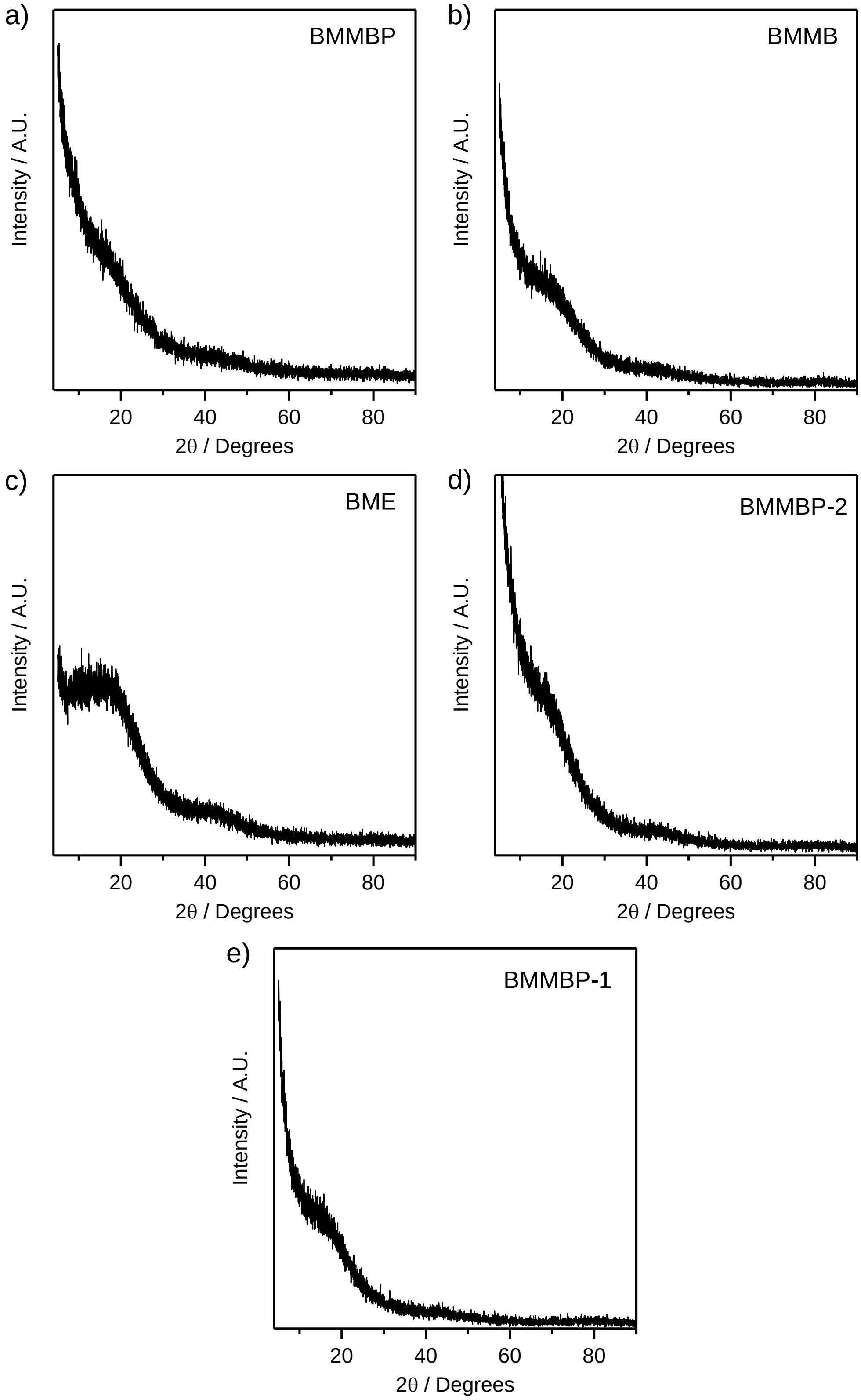

Figure S8. X-ray powder diffractions of all self-condensed polymers. a) BMMBP, b) BMMB, c) BME, d) BMMBP-2, and e) BMMBP-1.

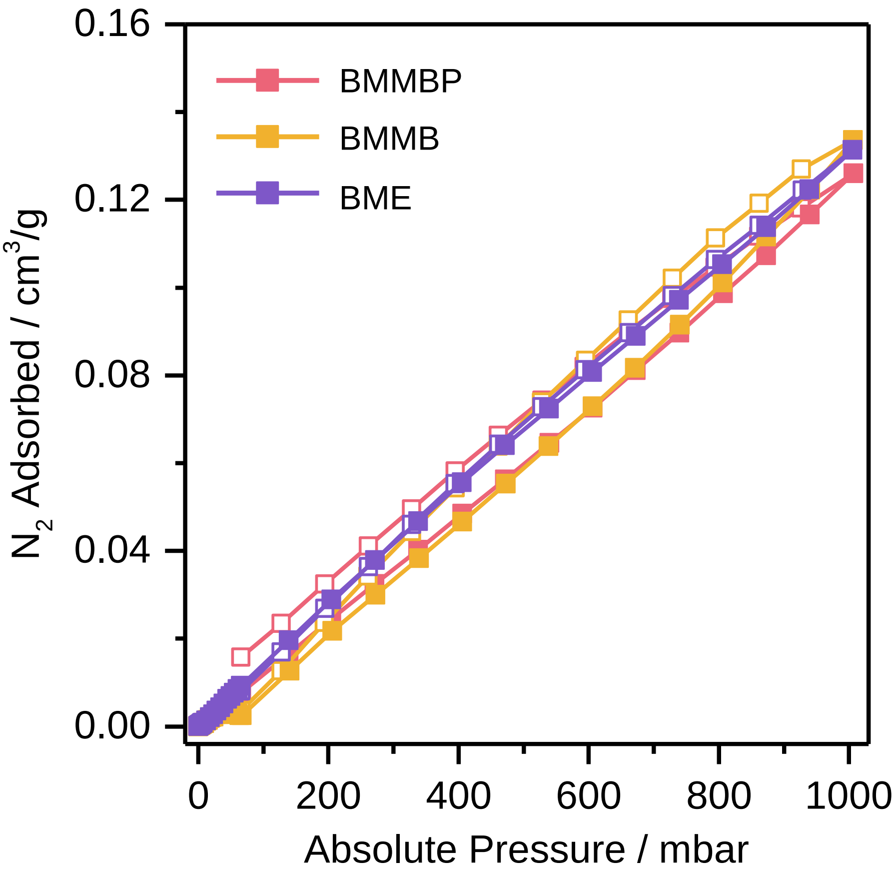

Figure S9. N_2 adsorption isotherms at 298 K of BMMBP (pink), BMMB (yellow), and BME (purple). Filled shapes represent uptake and empty shapes represent desorption.

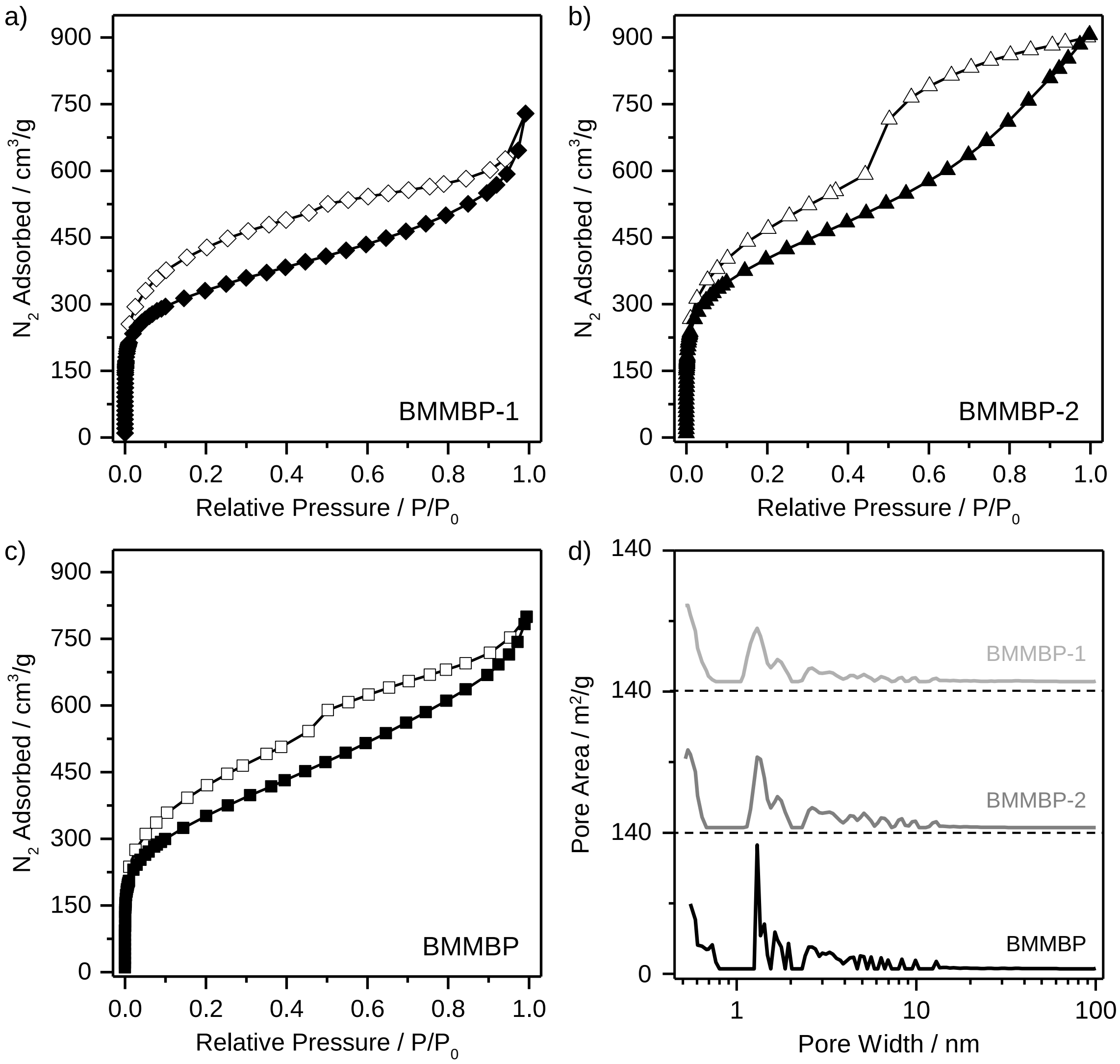

Figure S10. Porous properties of BMMBP networks produced using various concentrations of $FeCl_3$ catalyst. a) N_2 adsorption isotherm of BMMBP-1 at 77 K, b) N_2 adsorption isotherm of BMMBP-2 at 77 K, c) N_2 adsorption isotherm of BMMBP-3 at 77 K, and d) Pore size distributions of BMMBP-1 (light grey), BMMBP-2 (dark grey), and BMMBP (black).

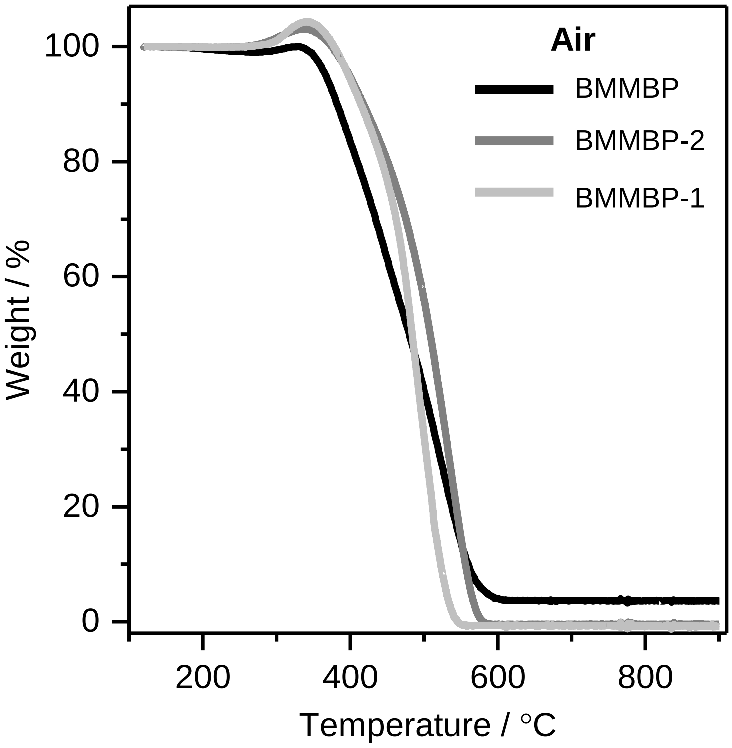

Figure S11. Thermogravimetric analysis in air of BMMBP (black), BMMBP-2 (grey), and BMMBP-1 (light grey) heating from 120 to 900 °C at a heating rate of 10 °C/min. Air was flowed over samples at 100 mL/min.

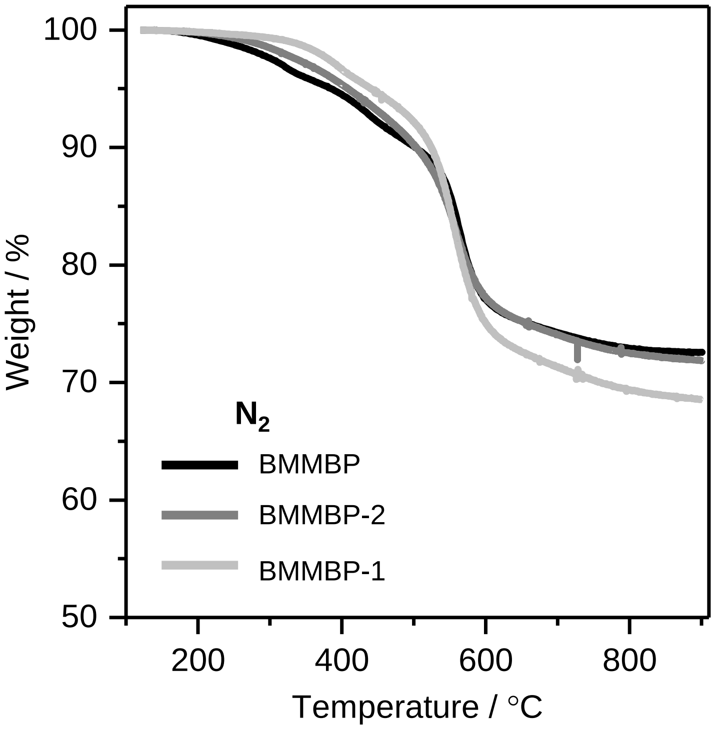

Figure S12. Thermogravimetric analysis in N_2 of BMMBP (black), BMMBP-2 (grey), and BMMBP-1 (light grey) heating from 120 to 900 °C at a heating rate of 10 °C/min. N_2 was flowed over samples at 100 mL/min.

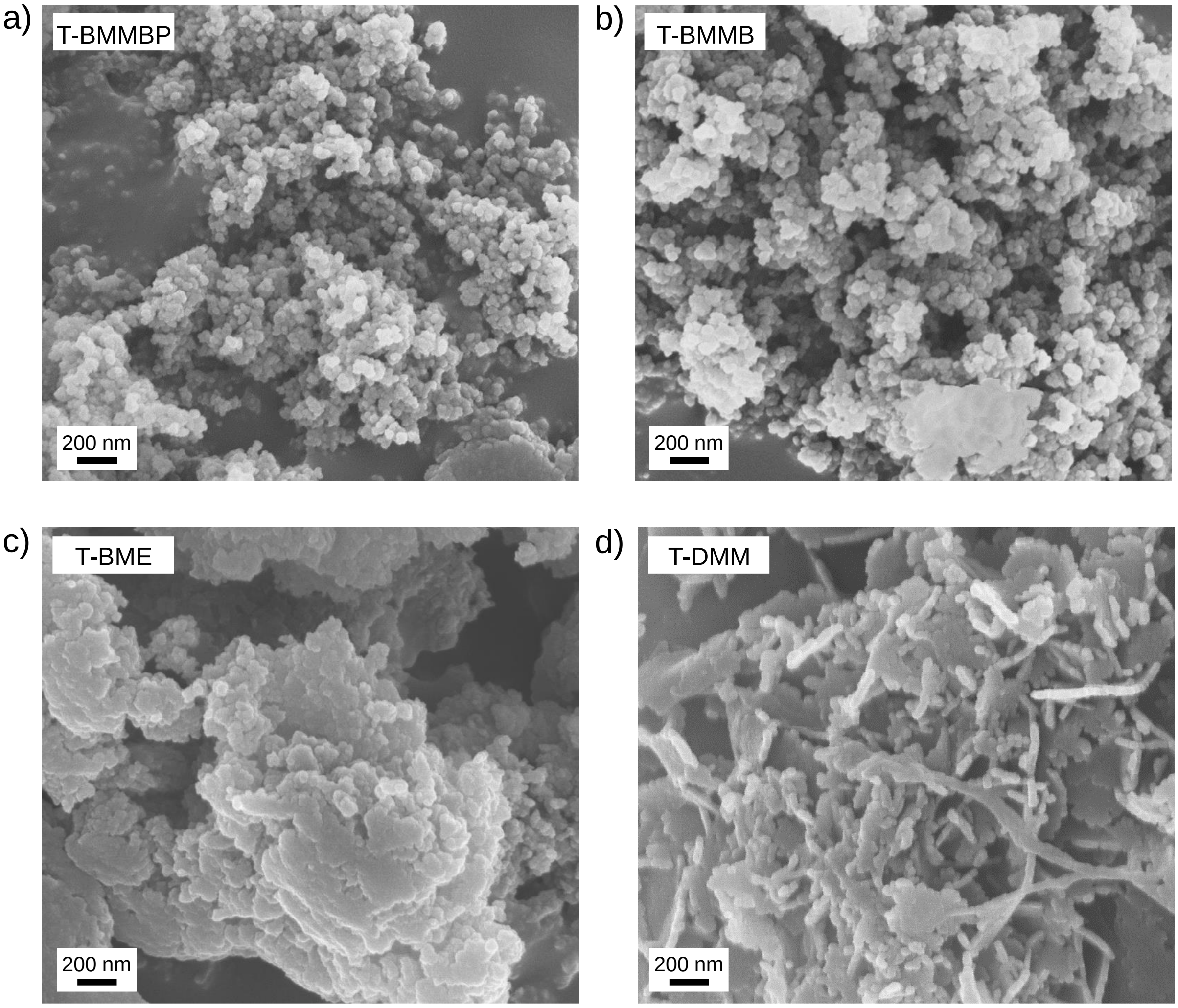

Figure S13. Scanning electron micrographs for all terphenyl polymers. a) T-BMMBP, b) T-BMMB, c) T-BME and d) T-DMM.

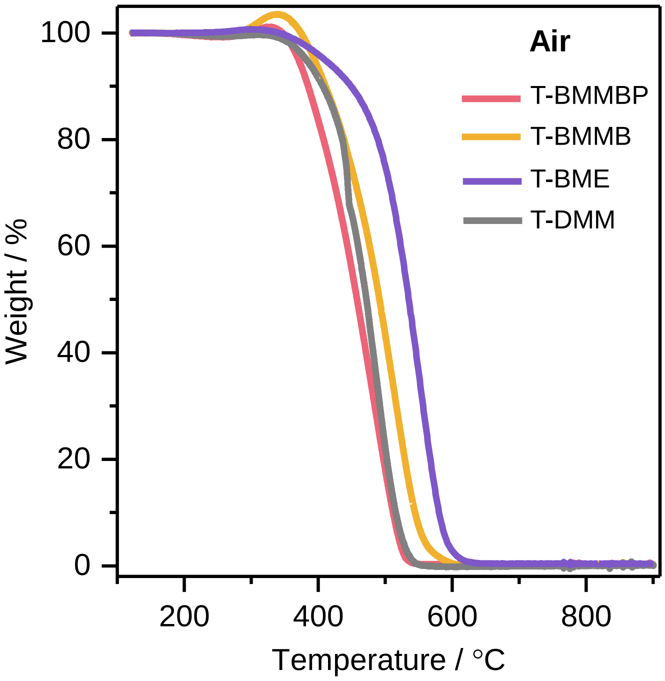

Figure S14. Thermogravimetric analysis in air of T-BMMBP (pink), T-BMMB (yellow), T-BME (purple), and T-DMM (grey) heating from 120 to 900 °C at a heating rate of 10 °C/min. Air was flowed over samples at 100 mL/min.

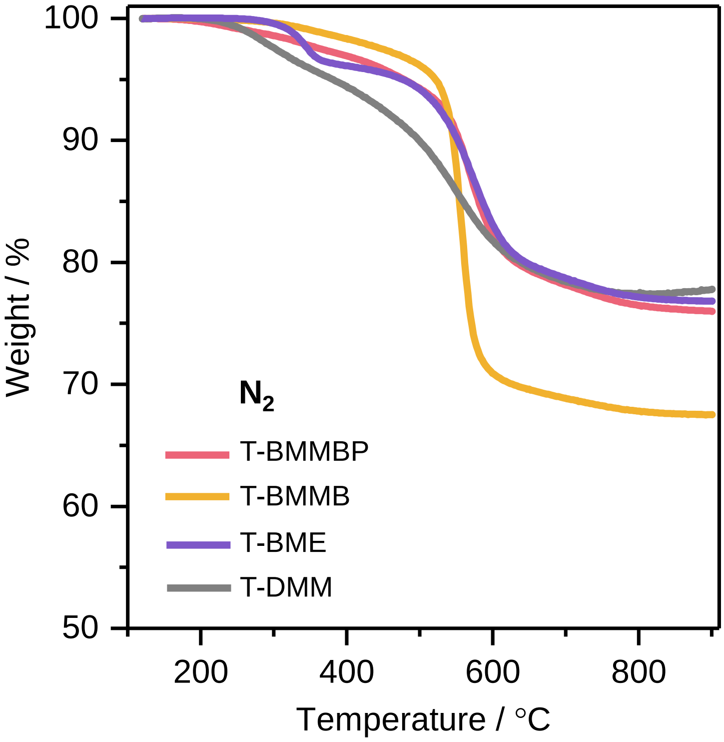

Figure S15. Thermogravimetric analysis in N_2 of T-BMMBP (pink), T-BMMB (yellow), T-BME (purple), and T-DMM (grey) heating from 120 to 900 °C at a heating rate of 10 °C/min. N_2 was flowed over samples at 100 mL/min.

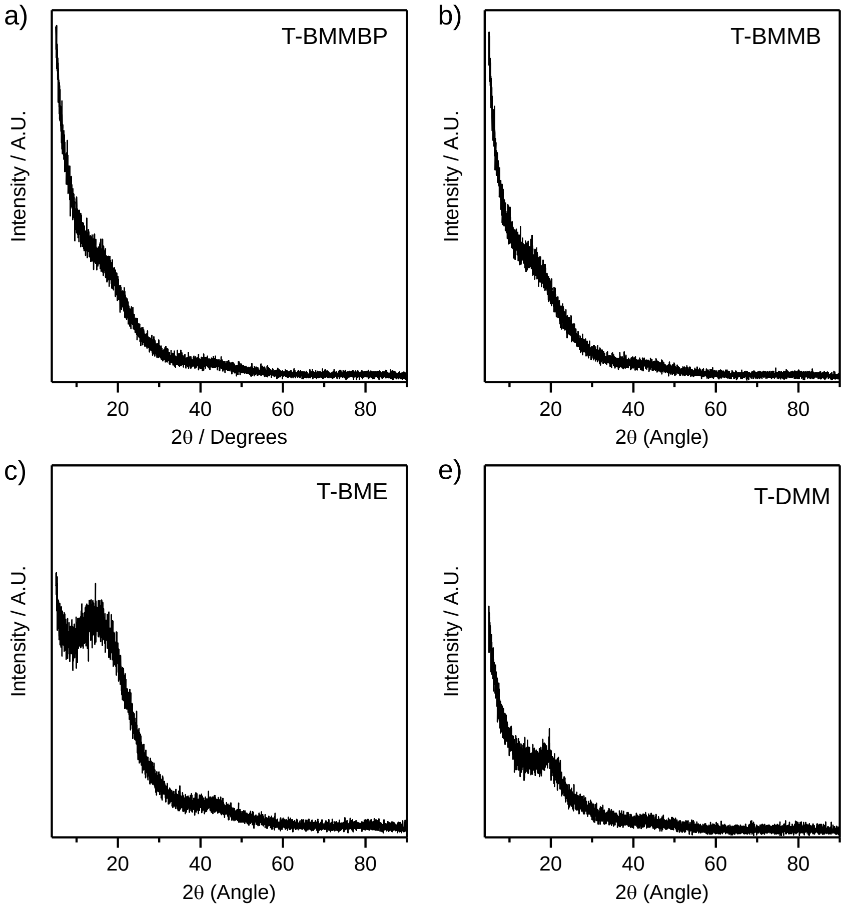

Figure S16. X-ray powder diffractions of all terphenyl-based polymers. a) T-BMMBP, b) T-BMMB, c) T-BME, and d) T-DMM.

1. S. Brunauer, P. H. Emmett and E. Teller, *Journal of the American chemical society*, 1938, **60**, 309-319.
2. S. Chen and R. Yang, *Langmuir*, 1994, **10**, 4244-4249.