Supplementary Information (SI) for Polymer Chemistry.

Investigating the synthesis, properties and Diels-Alder reactivity of diene-functional branched polyesters using copolymerisation of furfuryl methacrylate under transfer-dominated branching radical telomerisation (TBRT) conditions

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Supplementary Information:

Materials

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1. Materials

Ethylene glycol dimethacrylate (EGDMA, 98 %, 100 ppm MEHQ as inhibitor) was purchased from Alfa Aesar. 2,2'-azobis(2-methylpropionitrile) (AIBN, 98 %), chloroform-d ($CDCl_3$, 99.8 atom% D), 1-dodecanethiol (DDT, ≥ 98 %), furfuryl methacrylate (FMA, 97 %, stabilised with MeHQ) and 1,1'-(Methylenedi-1,4-phenylene) bismaleimide (BMI, 95 %) were purchased from Merck (Sigma Aldrich). Dichloromethane (DCM, analytical grade), dimethylformamide (DMF, 99 %), methanol (MeOH, ≥ 99.9 %, analytical reagent grade), tetrahydrofuran (THF, 99.5 %, laboratory reagent grade) and toluene (99.8 %, analytical reagent grade) were purchased from Fisher Scientific. All materials were used as received unless otherwise stated.

2. Methods of characterisation

2.1. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer (Materials Innovation Factory, Liverpool, UK) operating at a frequency of 400 MHz. Samples were analysed using deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm). All spectra were processed using MestReNova 14.0 software.

2.2. Triple detection size exclusion chromatography (TD-SEC)

Triple-detection size exclusion chromatography (TD-SEC) of hyperbranched polymers was performed using an Agilent 1260 Infinity II system equipped with an Agilent Vialsampler, two PLgel mixed columns (and a guard column), and a triple detector array containing a refractive index (RI) detector, dual angle light scattering detector (90 ° and 15 °) and viscometer. A mobile phase of THF containing 0.5 % v/v triethylamine was used at 40 °C and at a flow rate of 1 mL min^{-1}. The sample was dissolved at 5 mg mL^{-1} in the eluent, rolled overnight at ambient temperature, and filtered through a 0.20 µm PTFE syringe filter prior to injection (100 µL).

2.3. Differential scanning calorimetry (DSC)

Thermal analyses were conducted using a TA Instruments Discovery DSC 25 instrument equipped with an RSC90 cooling environment. Heat flow and temperature calibration was achieved using indium ($\Delta_{fus}H$ = 28.45 J g^{-1} and T_m = 156.6 °C). The sample was analysed using an aluminium pan with crimped hermetic aluminium lid, referenced against an empty pan.

The sample was subject to a heat-cool-heat cycle, with analysis of the glass transition performed for the second heat ramp. (heat 1: 10 °C min^{-1} to 120 °C; Isotherm = 3 min; cool: 10 °C min^{-1} to – 90 °C; isotherm = 3 min; heat 2: 10 °C min^{-1} to 100 °C). Data processing was performed using TA Instruments TRIOS software.

2.4. Fourier transform-infrared (FT-IR) spectroscopy

FT-IR spectra were acquired using a Vertex 70v FT-IR spectrometer equipped with an A225/Q Platinum ATR unit and a single reflection diamond crystal. Transmittance spectra were obtained at 16 scans in the region from 4000 cm^{-1} to 600 cm^{-1} using deuterated triglycine sulphate and mercury cadmium telluride detectors. Before measurement, the diamond tip and sample plate were cleaned with isopropyl alcohol and dried. The background signal was obtained directly before the measurement.

3. Experimental methods

3.1. Synthesis of p([DDT-EGDMA]-*stat*-FMA) *using TBRT*

For a TBRT conducted using EGDMA, FMA and DDT as the multi-vinyl taxogen, mono-vinyl co-taxogen and telogen, respectively, and targeting feedstock ratios of $[\text{EGDMA}]_0/[\text{DDT}]_0 = 0.83$, and $[\text{FMA}]_0/[\text{EGDMA}]_0 = 1.00$, EGDMA (5.00 g, 25.22 mmol, 0.83 equiv.), FMA (4.19 g, 25.22 mmol, 0.83 equiv.), DDT (6.15 g, 30.39 mmol, 1 equiv.), AIBN (0.19 g, 1.14 mmol, 1.5 mol% *versus* vinyl bonds) and EtOAc (15.34 g, 0.17 mol, 50 wt% *versus* EGDMA + FMA + DDT) were loaded into a 50 mL round-bottomed flask equipped with a magnetic stirrer bar and homogenised by agitation. A sample of the solution was extracted for ^{1}H NMR analysis of the $[\text{EGDMA}]_0:[\text{FMA}]_0:[\text{DDT}]_0$ feedstock ratio prior to initiation. The solution was deoxygenated for 20 minutes using a nitrogen sparge, with stirring. The solution was then heated with stirring to 70 °C and allowed to react for 24 hours. The reaction was ceased *via* exposure to air and cooling to ambient temperature, and the crude reaction mixture sampled for determination of the vinyl conversion by ^{1}H NMR analysis. The crude reaction mixture was diluted using THF and precipitated twice into rapidly stirring MeOH (10× vol/vol) at ambient temperature. The supernatant was decanted, and the polymer product washed with MeOH (3 x 100 mL). The polymer was finally dried *in vacuo* at 40 °C for 24 hours, and a sample of the purified polymer was taken for ^{1}H NMR and TD-SEC analysis.

3.2. Model reaction studies of 2-methyl furan and DDT under TBRT conditions

To study the potential for furan ring reaction within TBRT copolymerisations, a model reaction between 2-methyl furan and DDT was undertaken following the conditions described above for TBRT, but in the absence of EGDMA. 2-Methyl furan was utilised at the same mole equivalent as FMA to replace this mono-vinyl taxogen. The reaction was conducted at a 50wt% solvent content in EtOAc and allowed to react initially in the absence of 2-methyl furan for 1 hour at 70 °C and then a further 24 hours at 50 °C after addition of 2-methyl furan. For clarity, the feedstock ratio was $[\text{2-MF}]_{0.83}$:$[\text{DDT}]_{1.00}$ and consistent with polymerisation feedstock performed at $[\text{EGDMA}]_{0.83}$:$[\text{FMA}]_{0.83}$:$[\text{DDT}]_{1.00}$.

Calculations from the T=0 and T=24 hr reaction, normalised against the methyl resonances from DDT, suggest as little as 0.25 mol% of any adduct is formed.

3.3. Monitoring of Diels-Alder equilibrium for model small molecules in solution

^{1}H NMR experiments were performed on the Diels-Alder equilibrium of maleimide (MI) and 2-methylfuran (MF) in DMSO-d_6. Maleimide and 2-methylfuran were homogenised in DMSO-d_6 at [MI]:[MF] ratios of 1:1, 1:2 and 1:3 in sample vials. The solutions were stirred for 24 hours at ambient temperature, aliquots taken and the association of maleimide estimated by ^{1}H NMR spectroscopy. The solutions were then heated to 30 °C for 24 hours before further sampling for ^{1}H NMR analysis. Each spectroscopy analysis was conducted within 5 minutes of sample removal from heating. The equilibrium association of maleimide was estimated at temperatures varying by 10 °C intervals between 30 – 90 °C after 24 hours equilibrating at each temperature. The relative proportion of *endo* and *exo* diastereomeric Diels-Alder adducts was also determined at each temperature interval. Subsequently, the reactions initially conducted at 50 °C were monitored by ^{1}H NMR spectroscopy every 24 hours over 10 days of equilibration at ambient temperature.

3.4. Demonstrating reversible gelation in solution

To investigate the reversible gelation of the Diels-Alder networks in solution, a solution of *p*([DDT-EGDMA]-*stat*-FMA) (10 wt%) in DMF was prepared, and 1,1’-(Methylenedi-1,4-phenylene) bismaleimide (BMI) was added at 0.9 mole equivalents of maleimide *versus* furan. The mixture was homogenised *via* agitation and stirring and photographed in solution. The solution was subsequently heated to 60 °C and left stirring until macroscopic gelation was observed. Once gelled, the sample was heated to 120 °C and monitored until it returned to a flowing solution phase. A second cycle of gelation and de-gelation was then conducted.

4. Supplementary figures and tables

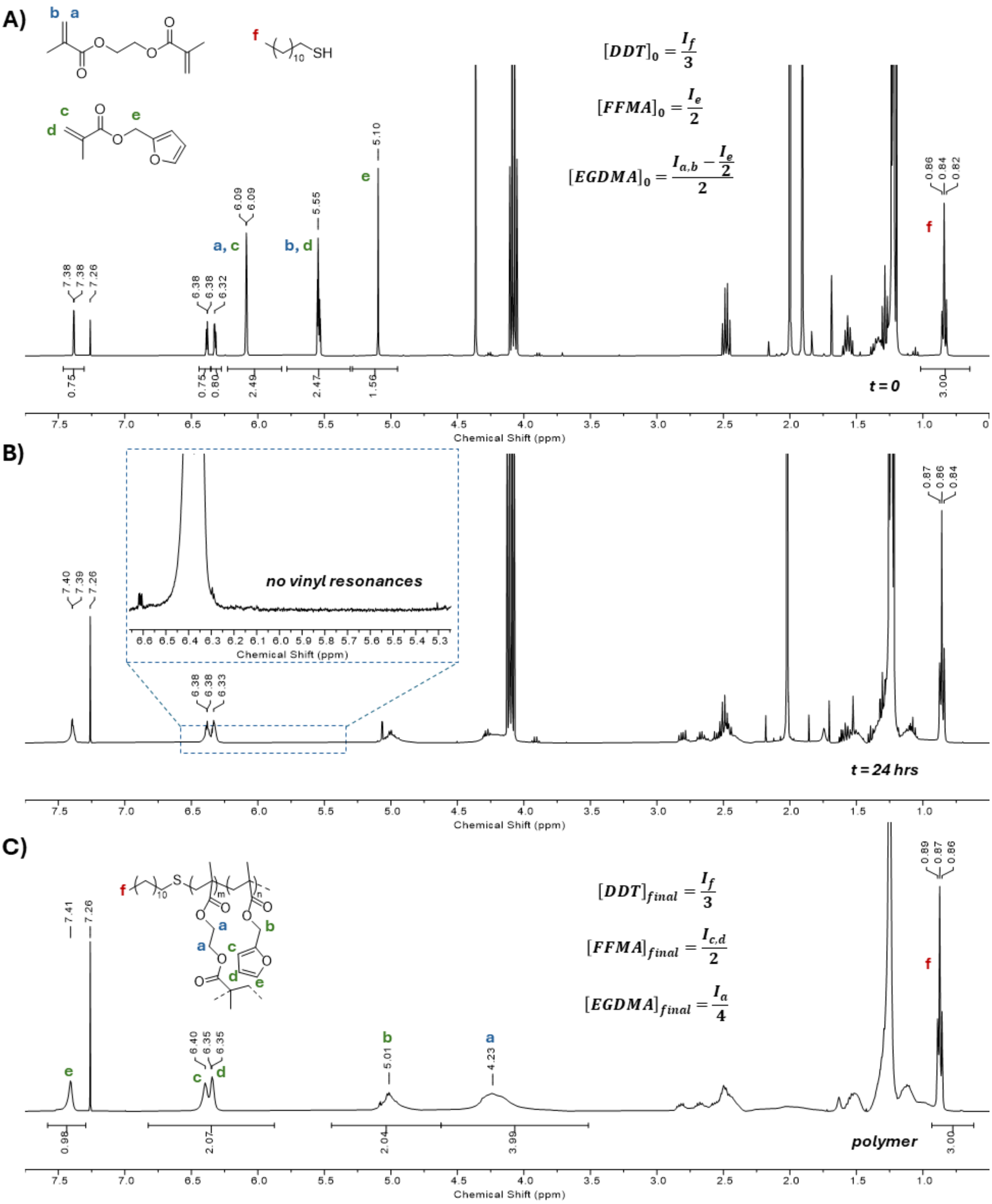

Figure S1 ^{1}H NMR analysis for the TBRT of EGDMA and FMA with DDT. A) Analysis performed at t = 0, for the calculation of the feedstock ratio $[\mathrm{EGDMA}]_0$:$[\mathrm{FMA}]_0$:$[\mathrm{DDT}]_0$, provided the calibration of I_f = 3. B) Analysis performed after 24 hours of reaction, indicating the disappearance of vinylic hydrogen resonances (denoted > 99 % consumption). C) Analysis of the purified polymer, for the calculation of the polymer composition $[\mathrm{EGDMA}]_{\mathrm{final}}$:$[\mathrm{FMA}]_{\mathrm{final}}$:$[\mathrm{DDT}]_{\mathrm{final}}$, provided the calibration of I_f = 3.

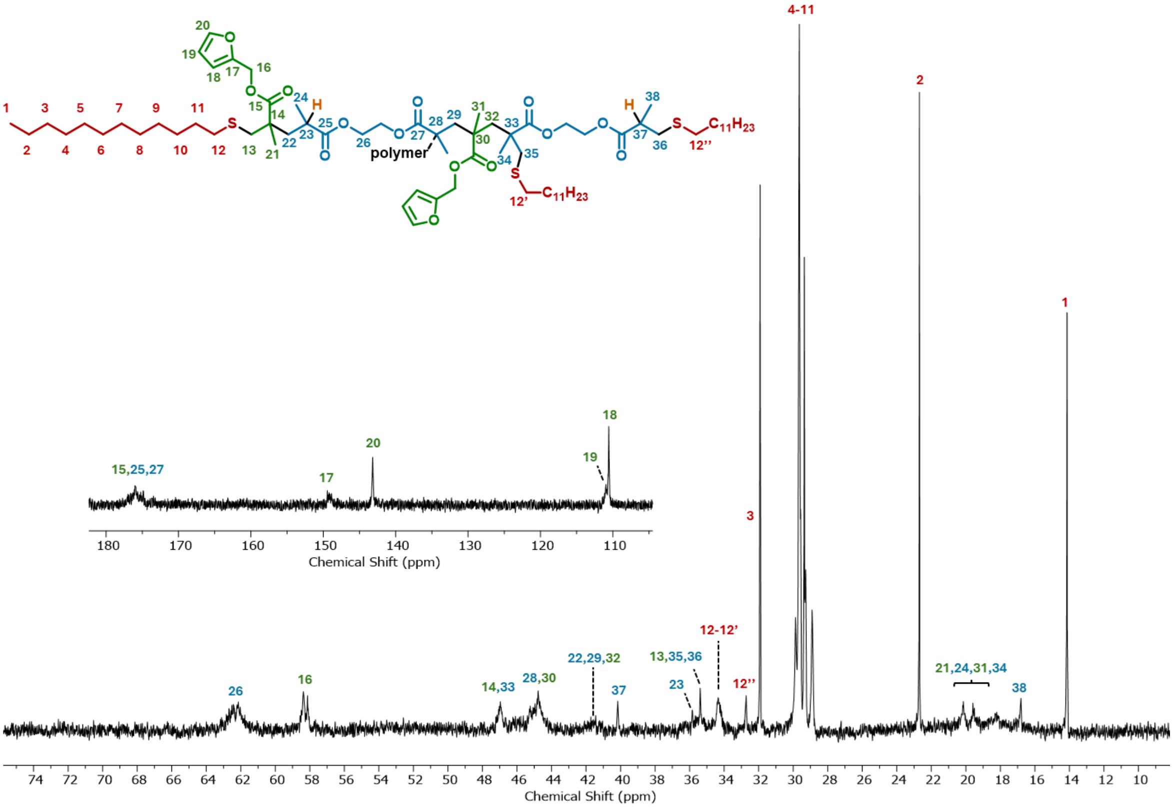

Figure S2 ^{13}C NMR spectroscopic analysis of p([DDT-EGDMA]-*stat*-FMA) including assignment of ^{13}C environments.

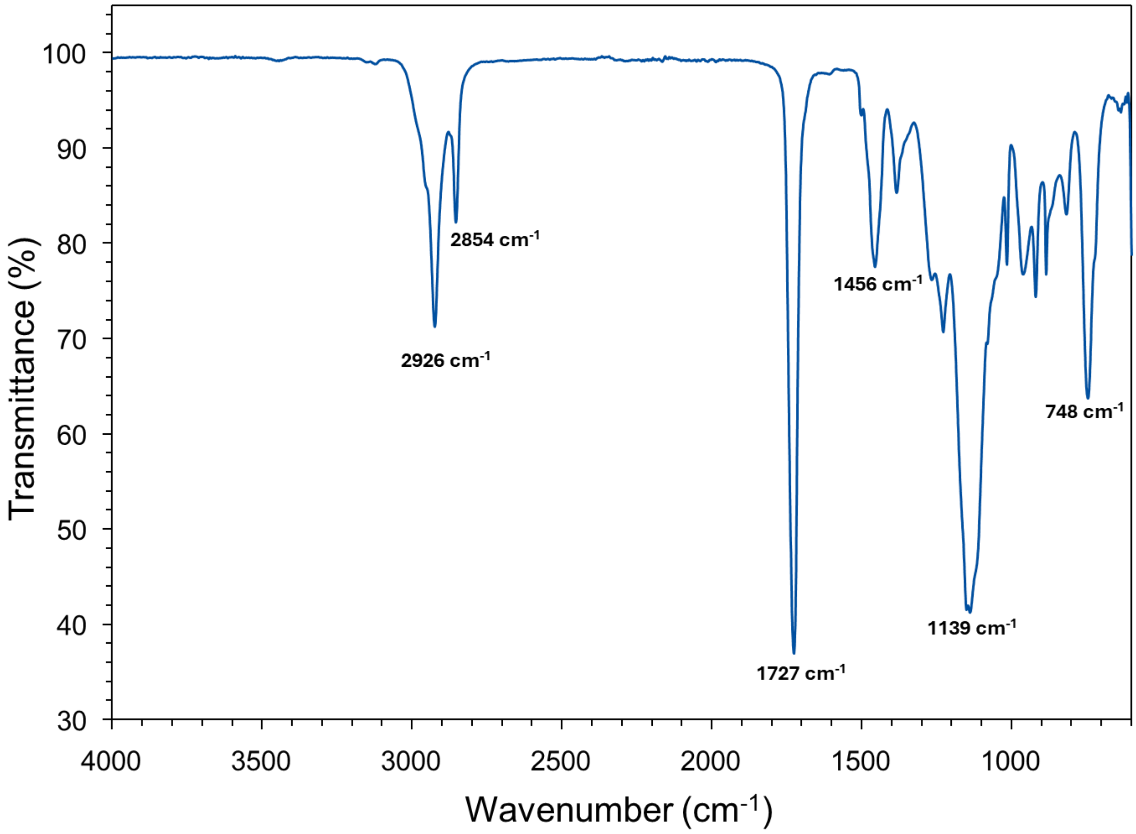

Figure S3 FT-IR spectroscopic analysis of p([DDT-EGDMA]-*stat*-FMA).

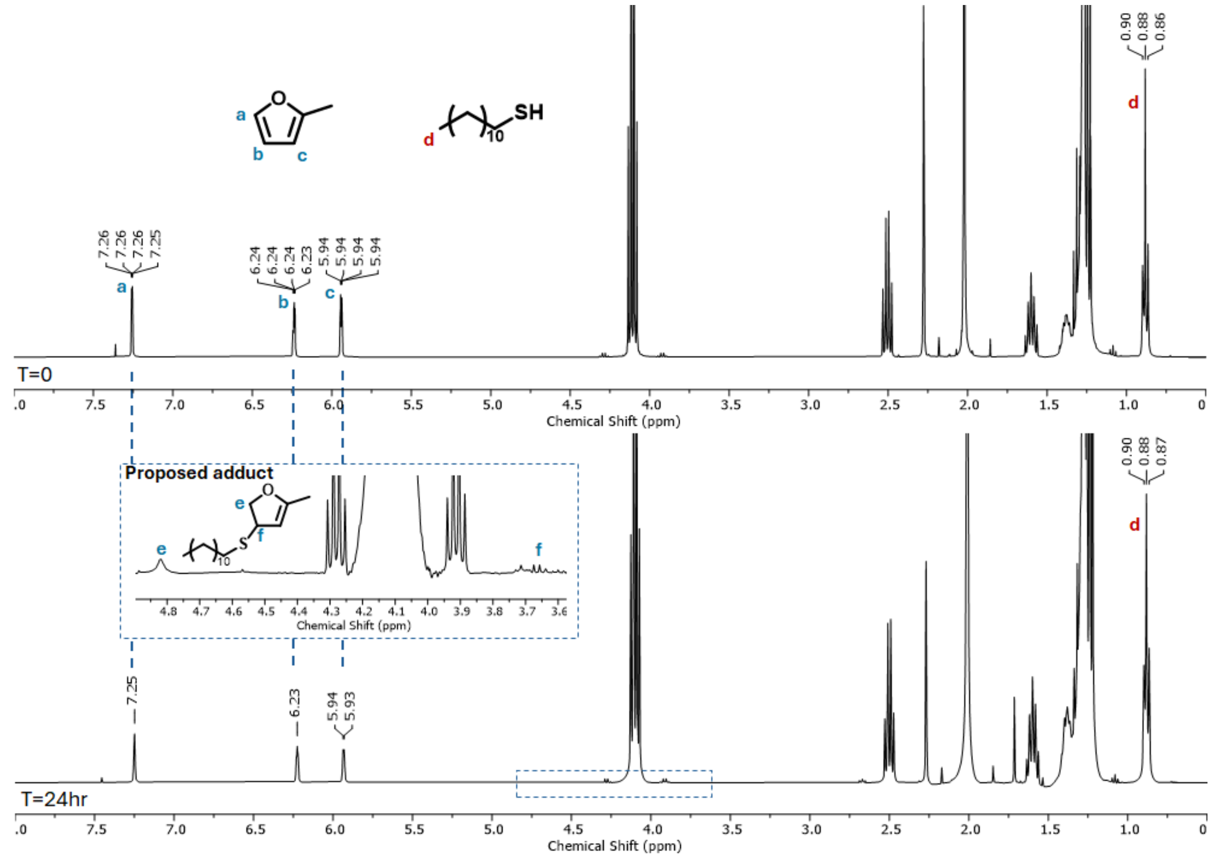

Figure S4 ^{1}H NMR analysis for the attempted model reaction of 2-methyl furan with DDT under TBRT polymerisation conditions. Expansion of 24 hr spectrum shows minor new resonances that may indicate adduct formation. Assuming no change in the DDT resonance H_d, the adduct appears to represent 0.25 mol % reaction of furan and DDT under these conditions.

$$\textbf{Maleimide assocation}\ (\%) = \frac{\int(\mathbf{e}+\mathbf{f})}{\int(\mathbf{e}+\mathbf{f}) + \frac{1}{2}\int \mathbf{a}} \times 100 \qquad \textbf{Eqn. S1}$$

$$\textbf{Exo product}\ (\%) = \frac{\int \mathbf{f}}{\int \mathbf{e} + \int \mathbf{f}} \times 100 \qquad \textbf{Eqn. S2}$$

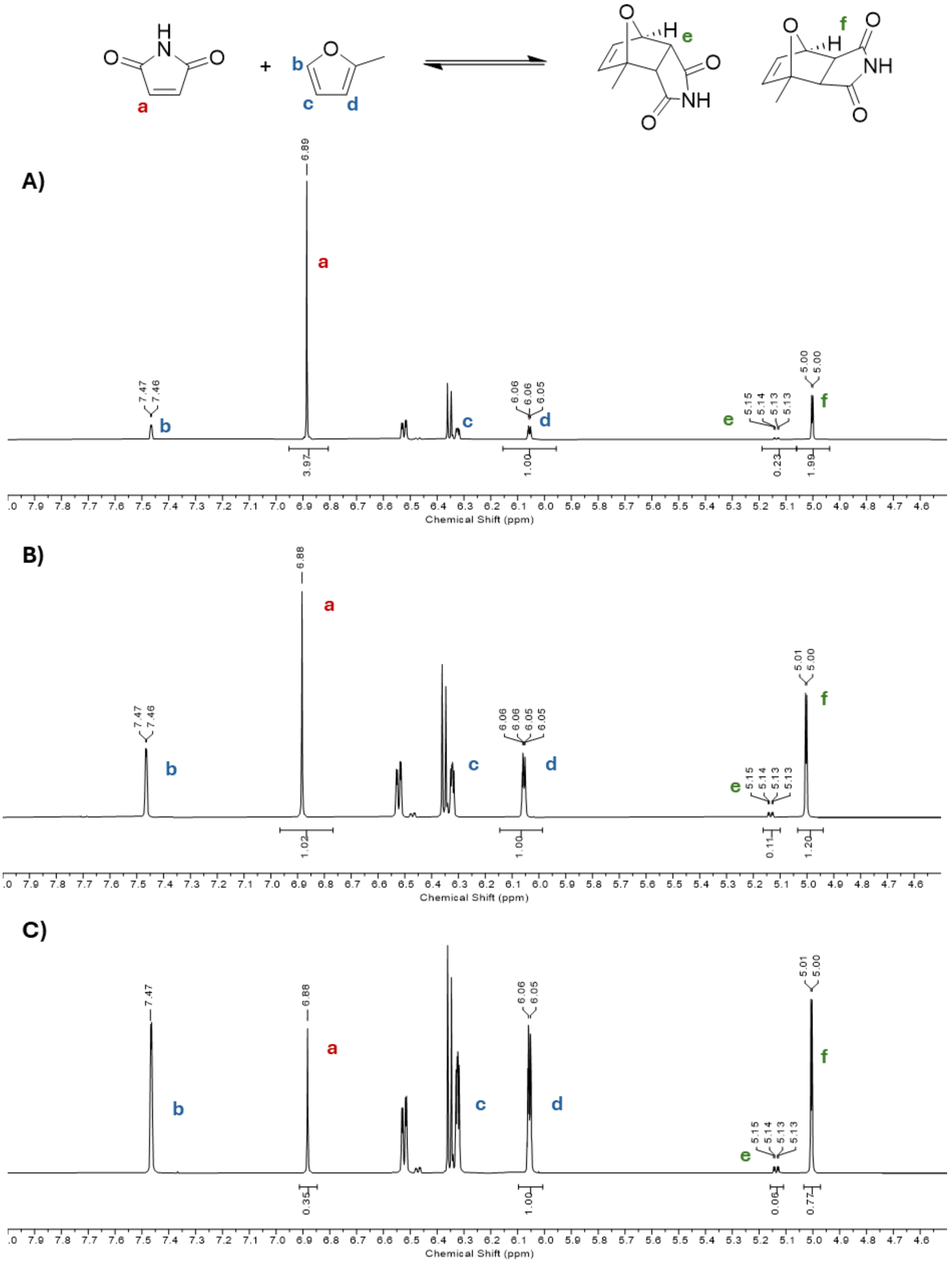

Figure S5 ^{1}H NMR spectra (DMSO-d$_6$) of the Diels-Alder equilibrium between maleimide (MI) and 2-methylfuran (MF) for samples prepared at [MI]:[MF] ratios of a) 1:1, b) 1:2 and c) 1:3, after 24 hours at 60 °C. Peaks integrals included were used to calculate the overall association of maleimide and the relative proportions of diastereomeric products.

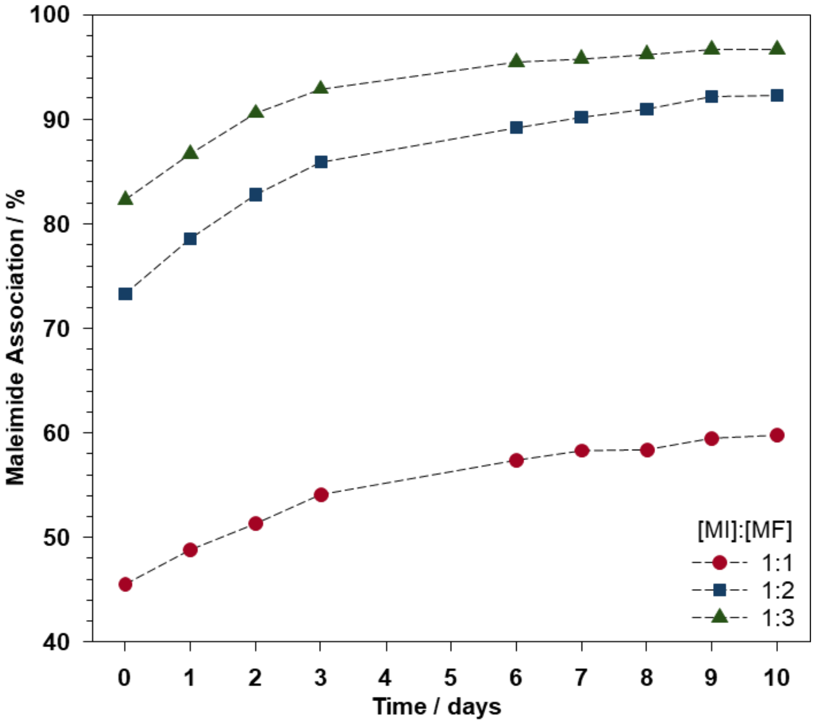

Figure S6 Equilibrium position of the reaction between maleimide and 2-methylfuran (with respect to maleimide double bond consumption), monitored by ^{1}H NMR spectroscopy over 10 days after reaction at 50 °C for 24 hours.

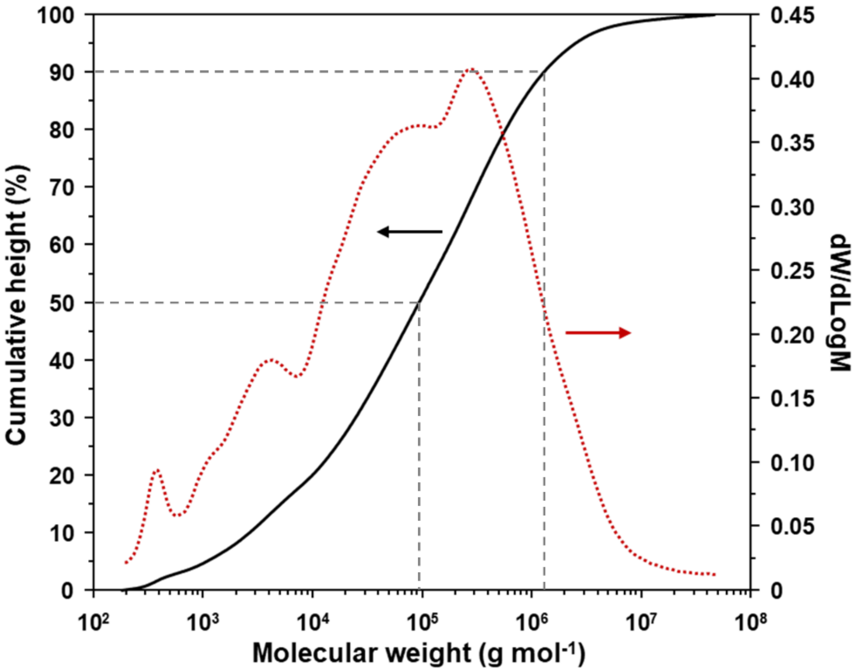

Figure S7 Cumulative (black line) and differential weight fraction (red dashed line) of *p*([DDT-EGDMA]-*stat*-FMA) polymers as a function of their calculated molecular weight, as obtained by TD-SEC analysis.