Electronic Supporting Information

for

Immobilization of MacMillan Catalyst *via* Controlled Radical Polymerization: Catalytic Activity and Reuse

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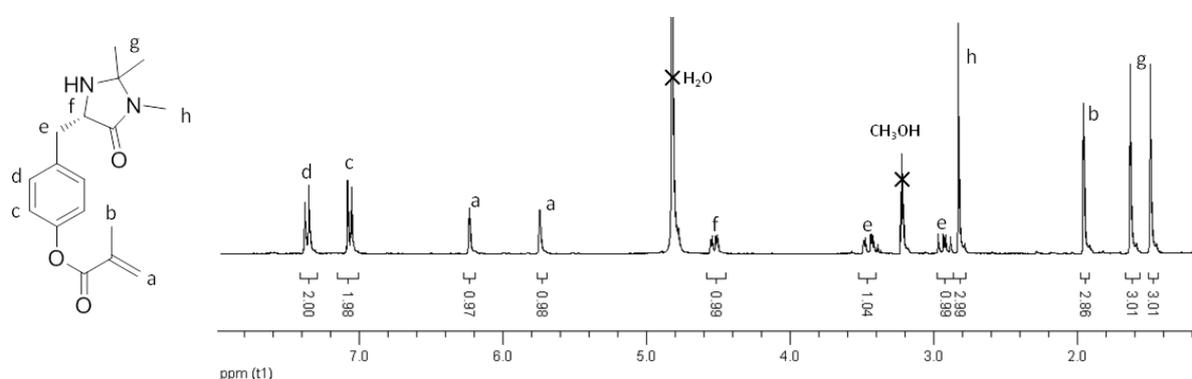
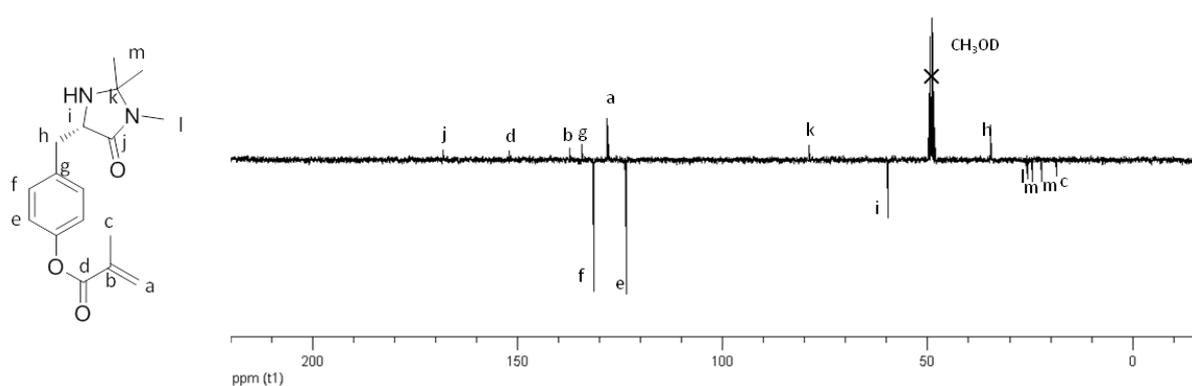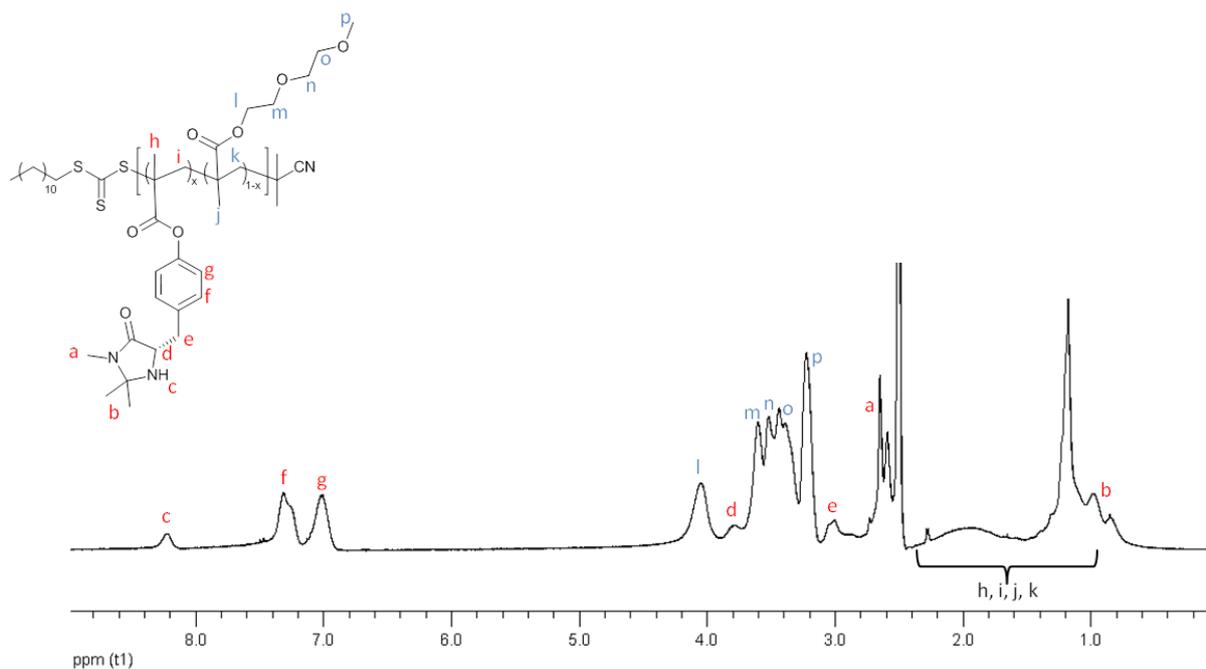**Figure S1.** ^{1}H NMR (300 MHz) spectrum of **M1** in CD$_3$OD.

Figure S2. ^{13}C NMR (75 MHz) spectrum of **M1** in CD$_3$OD.

Figure S3. A representative ^{1}H NMR spectrum (300 MHz) in CD$_3$OD of the synthesized functional copolymers; polymer presented is **P4**. The relative incorporation of the two monomers was determined from the signals of g and l.
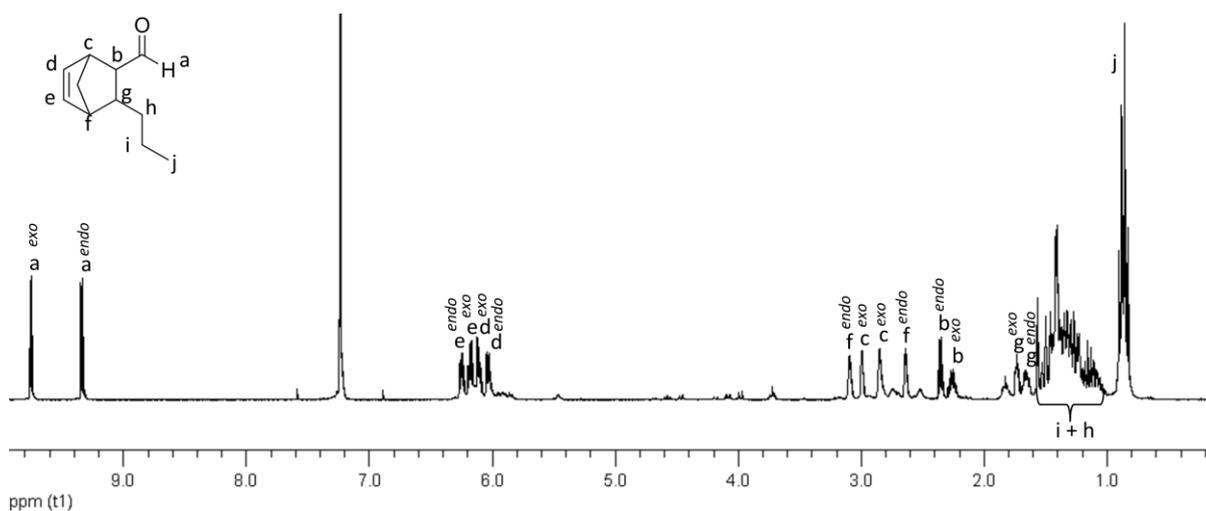
Figure S4. A representative ^{1}H NMR (300 MHz) spectrum in CDCl$_3$ of the Diels-Alder products.
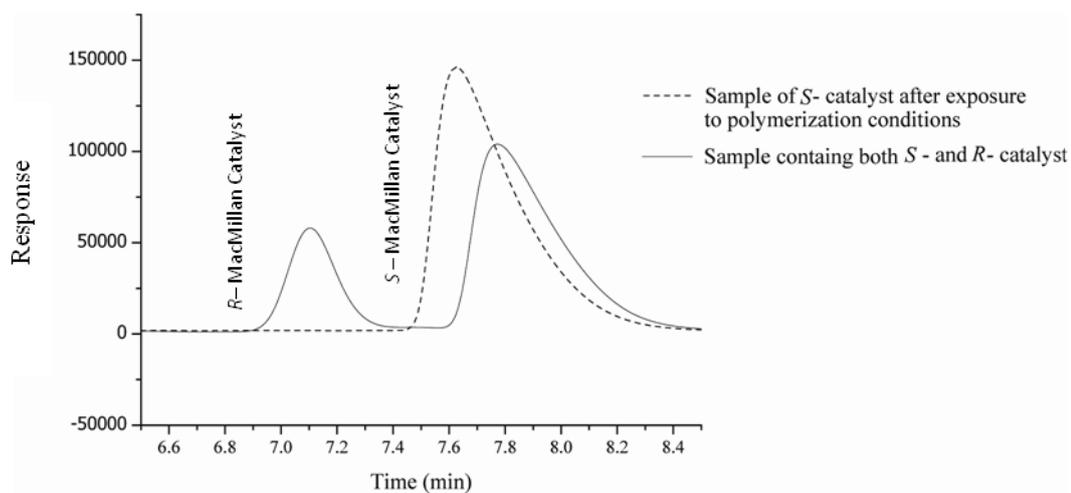
Figure S5. HPLC chromatogram of a sample containing both *S*- and *R*-MacMillan catalyst and recovered *S*-MacMillan catalyst after exposure to polymerization conditions. Only the *S*-catalyst is detected after exposure to the polymerization conditions.
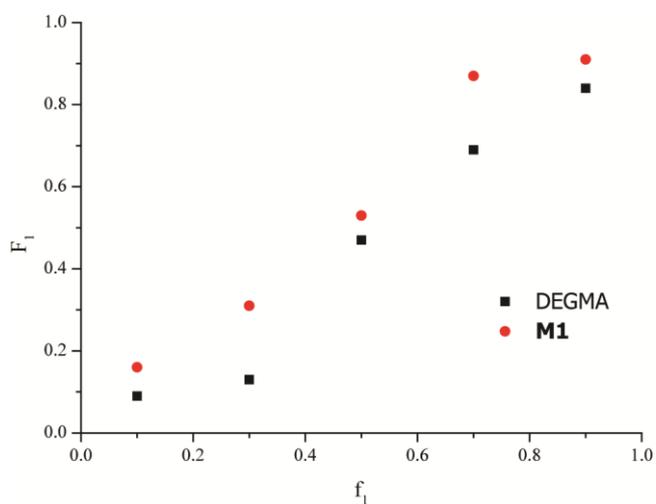
Figure S6. Plot of monomer incorporations for the copolymerization of **M1** (red) and DEGMA (black) monomers in order to determine reactivity ratios.
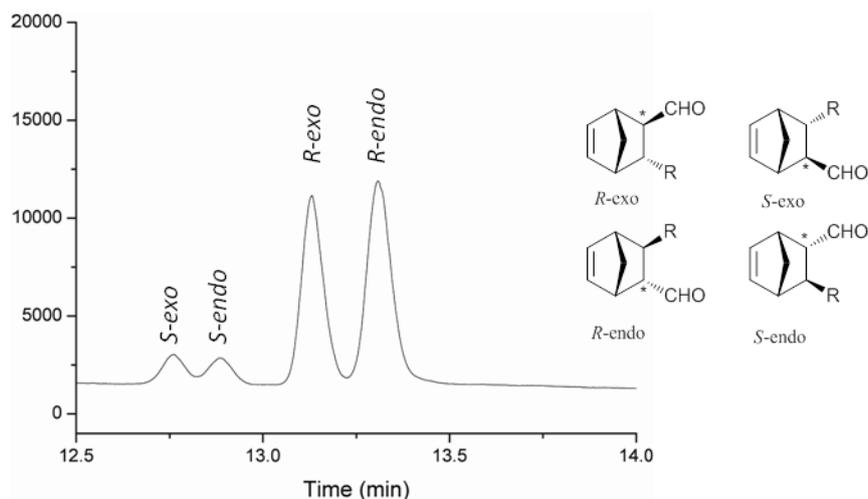
Figure S7. A representative GC chromatogram of the Diels-Alder products.

| Polymer	Concentration (mg mL^{-1})	LCST Cloud Point (°C)
Homopolymer PDEGMA (MWt = 16.7 kDa)	0.5	27.4
	1.0	28.2
	2.0	26.2
	5.0	24.4
P1 (6 % loading)	0.5	37.7
	1.0	27.0
	2.0	25.5
	5.0	26.5
P2 (26 % loading)	0.5	58.8
	1.0	52.0
	2.0	50.9
	5.0	42.4

Table S1. LCST cloud point data for homopolymer PDEGMA, **P1** and **P2** across a range of concentrations. The data was recorded at 500 nm with a heating/cooling rate of 1 °C min^{-1}. The cloud point was taken at the temperature when the absorbance equalled 0.5 after the data had been normalized between 0 and 1 absorbance units.

Material	Time (min)	Conversion (%)	*exo:endo*	*exo* ee %	*endo* ee %
P2	25	53	1.00:1.15	70	78
	70	71	1.00:1.09	69	77
	100	76	1.00:1.12	70	75
	133	88	1.00:1.11	68	74
	175	86	1.00:1.08	68	76
	215	92	1.00:1.06	68	77
	240	93	1.00:1.11	69	80
P6	25	66	1.00:1.19	70	79
	70	83	1.00:1.14	69	75
	100	89	1.00:1.12	70	75
	133	93	1.00:1.10	98	73
	175	92	1.00:1.15	68	74
	215	96	1.00:1.11	68	74
	240	96	1.00:1.11	67	76

Table S2. Kinetic data for the Diels-Alder reaction of *trans*-hexen-1-al and cyclopentadiene catalyzed by **P2** and **P6** The reactions were carried out in H_2O, conversions measured by ^1H NMR spectroscopy and enantioselectivity by GC analysis. As before, these reactions were carried out (akin to previous reactions) with the same reagent concentration changing only the concentration of the polymer to maintain 5 mol % catalyst loading (same number of catalyst species).

Catalyst	Temperature (˚C)	Conversion (%)	*exo:endo*	*exo* ee %	*endo* ee %
M1	4	89	1.00;1.13	78	88
	20	94	1.00:1.05	73	88
	40	100	1.00:1.02	66	88
	60	100	1.00:0.84	65	78
P2	4	83	1.00:1.21	73	79
	20	70	1.00:1.08	73	81
	40	88	1.00:1.04	62	72
	60	100	1.00:0.74	54	64
P7	4	78	1.00:1.20	78	84
	20	86	1.00:1.13	76	85
	40	100	1.00:1.09	69	76
	60	100	1.00:0.93	62	74

Table S3. Diels-Alder reaction of *trans*-hexen-1-al and cyclopentadiene catalyzed by **M1**, **P2** (T_g = 36.1 ˚C) and **P7** (T_g = 140.0 °C) carried out at different temperatures. The reaction was carried out in H_2O, conversions measured by ^{1}H NMR spectroscopy and enantioselectivity by GC analysis. The different temperatures were achieved by performing the reactions in pre-heated oil-baths or in the fridge.

P6 – end group   **P6** – no end group
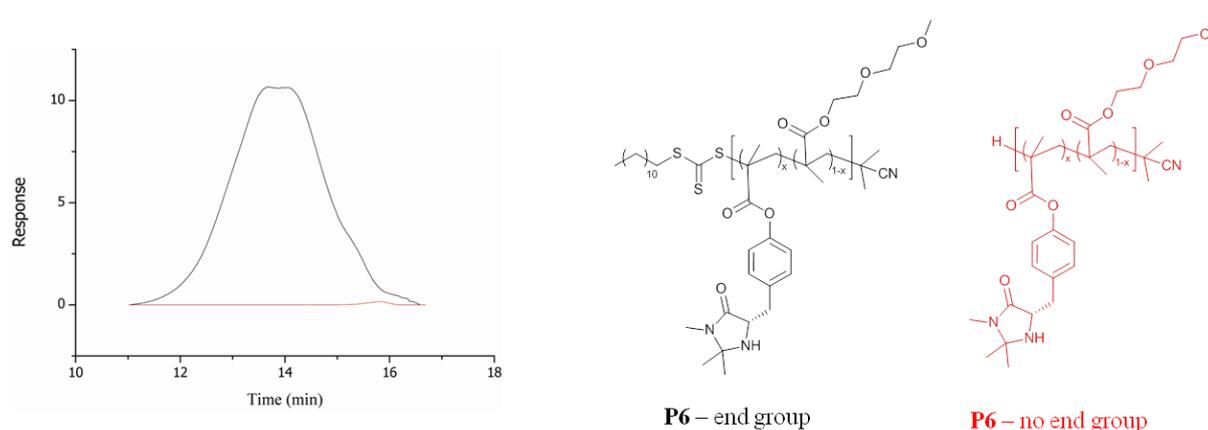
Figure S8. THF SEC UV 309 nm trace of **P6** before end group removal (black line) and after end group removal (red line), along with the structures of the two polymers.

Catalyst	Conversion (%)	*exo:endo*	*exo* ee %	*endo* ee %
P6 - end group	91	1.00:1.07	74	82
P6 – no end group	91	1.00:1.05	70	75

Table S4. Diels-Alder reaction of *trans*-hexen-1-al and cyclopentadiene catalyzed by **P6** with and without RAFT end group. The data for the reaction without end group is the average of 2 repeats. The structures of the polymers can be seen in Fig S8.

Cycle	Conversion (%)	*exo*:*endo*	*exo* ee%	*endo* ee%	Recovery (%)
1	86	1.00:1.33	67	61	60
2	85	1.00:1.17	65	65	49
3	46	1.00:1.40	59	52	13
4	70	1.00:1.40	56	50	10

Table S5. Recycling data for the Diels-Alder reaction catalyzed by **P6** where the polymer was recovered through dialysis followed by freeze-drying.

Cycle	Conversion (%)	*exo*:*endo*	*exo* ee%	*endo* ee%
1	72	1.00:0.96	64	75
2	95	1.00:1.12	58	72
3	94	1.00:1.35	35	57

Table S6. *Pseudo* continuous data for P6 where additional TFA is added along with the solvents for each cycle.