Electronic Supplementary Material (ESI) for Polymer Chemistry.

Understanding Structure-property relationships of main chain cyclopropanes in linear polyesters

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Synthetic scheme for cyclopropane diacrylate preparation

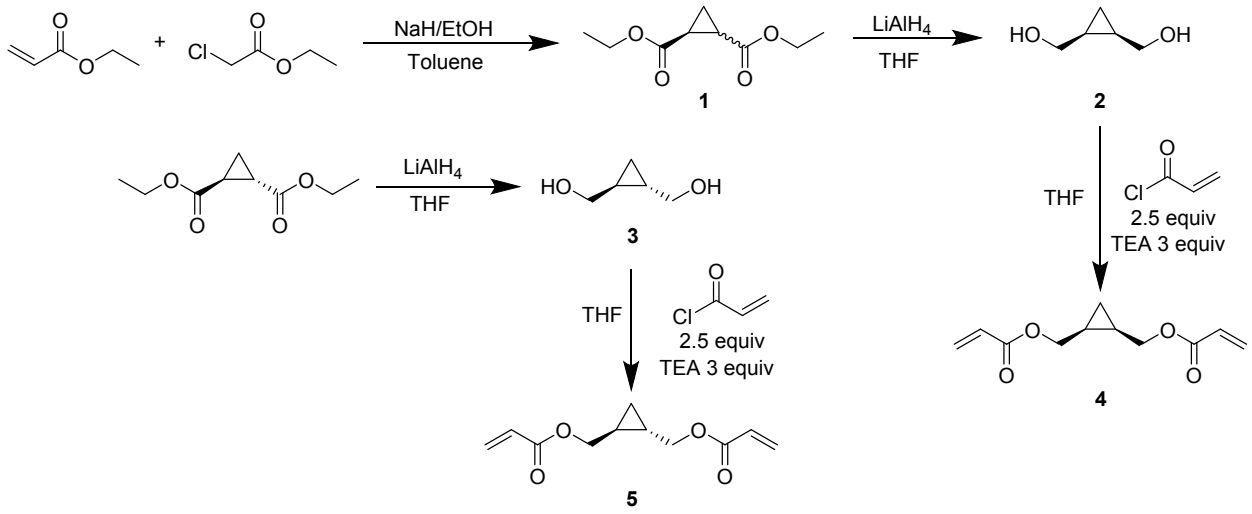

Figure S1 Synthetic scheme for the preparation of cyclopropane diacrylate monomers

NMR spectra of monomers and precursors

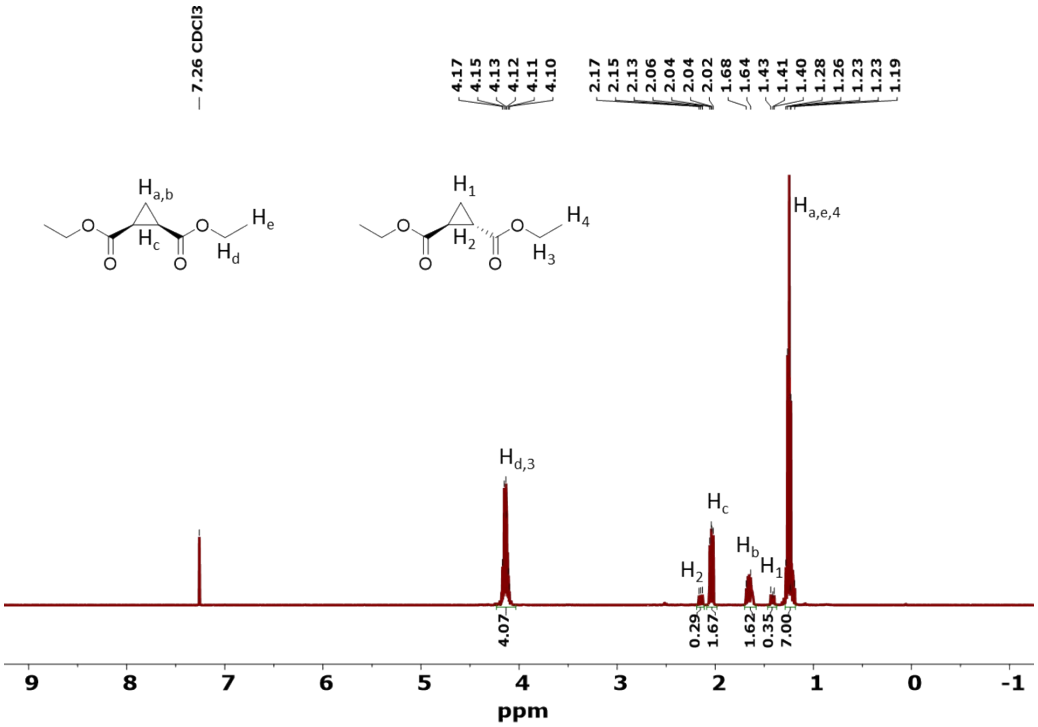

Figure S2 ^{1}H NMR spectrum of racemic diethyl-1,2-cyclopropane dicarboxylate in $CDCl_3$ (400 MHz, 298 K) **(1)**

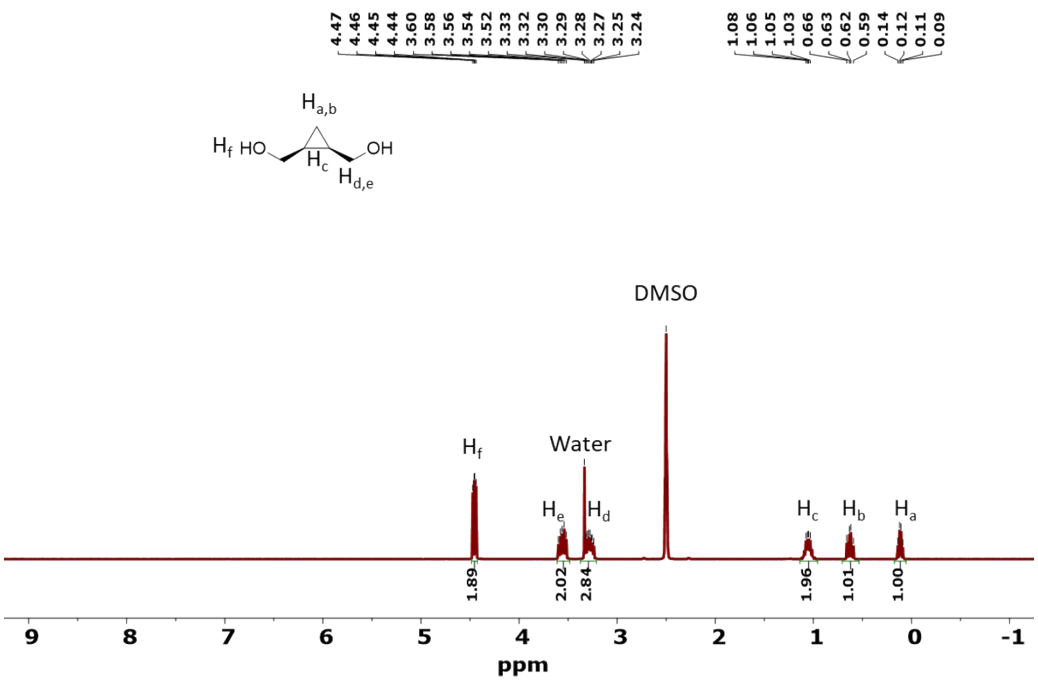

Figure S3 [1]H NMR spectrum of *cis*-1,2-cyclopropanedimethanol **(2)** in DMSO-d6 (400 MHz, 298 K)

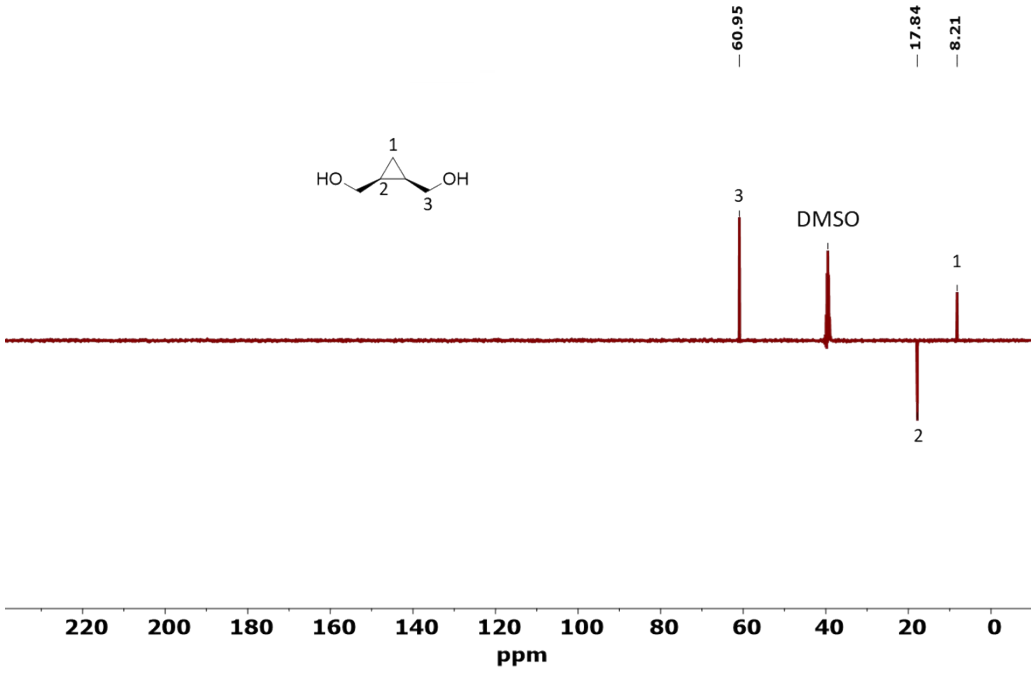

Figure S4 [13]C NMR spectrum of *cis*-1,2-cyclopropanedimethanol **(2)** in DMSO-d6 (400 MHz, 298 K)

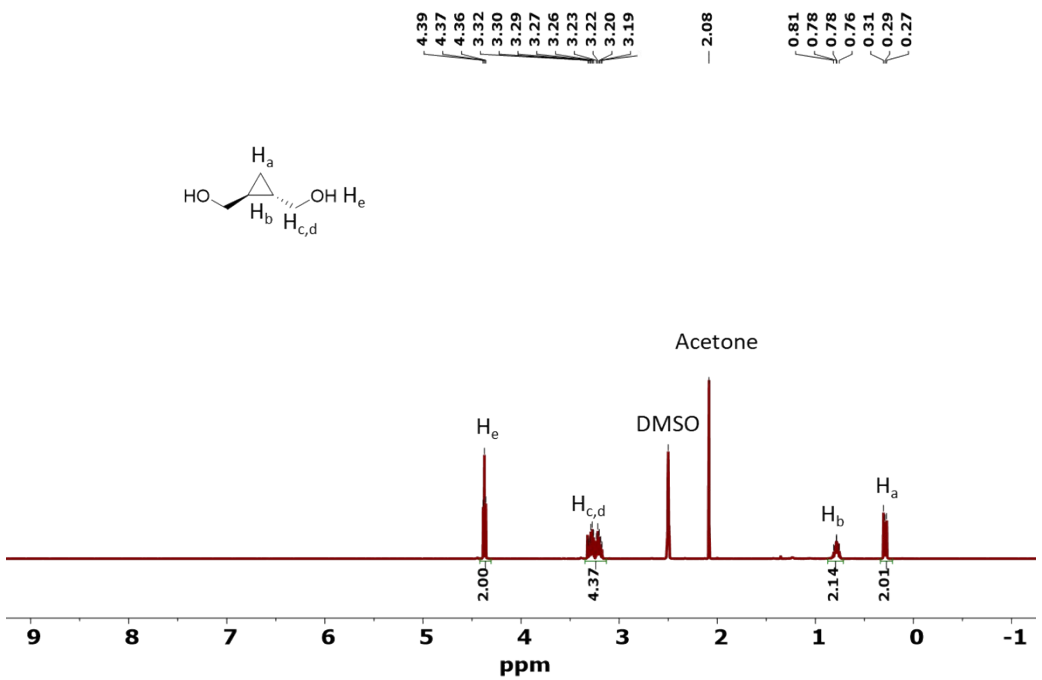

Figure S5 [1]H NMR spectrum of *trans*-1,2-cyclopropanedimethanol **(3)** in DMSO-d6 (400 MHz, 298 K)

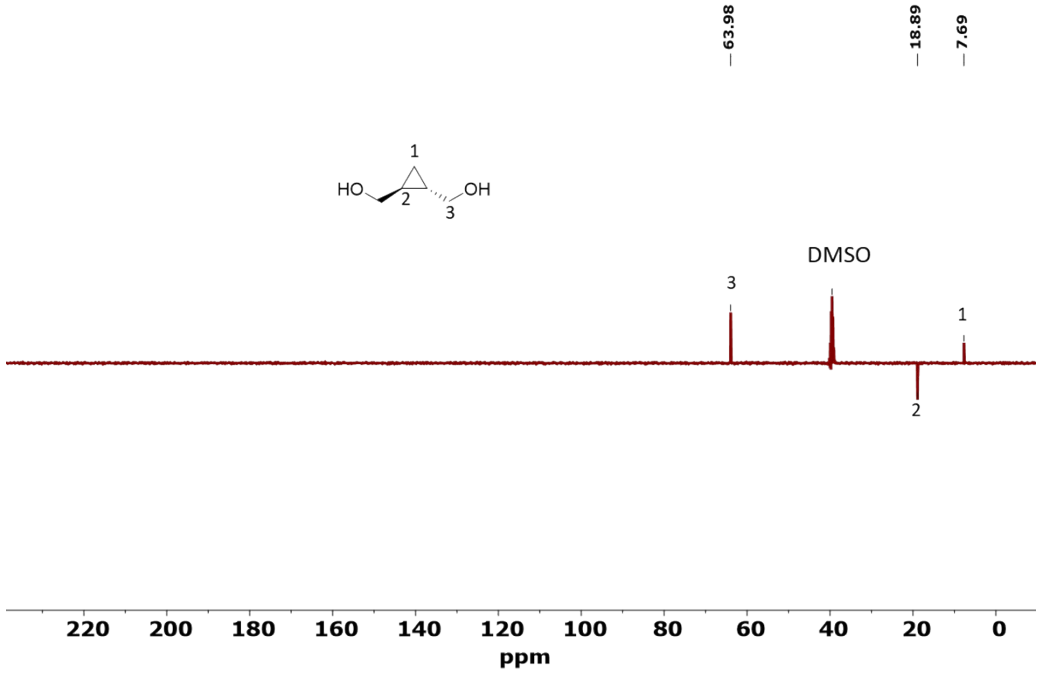

Figure S6 [13]C NMR spectrum of *trans*-1,2-cyclopropanedimethanol **(3)** in DMSO-d6 (400 MHz, 298 K)

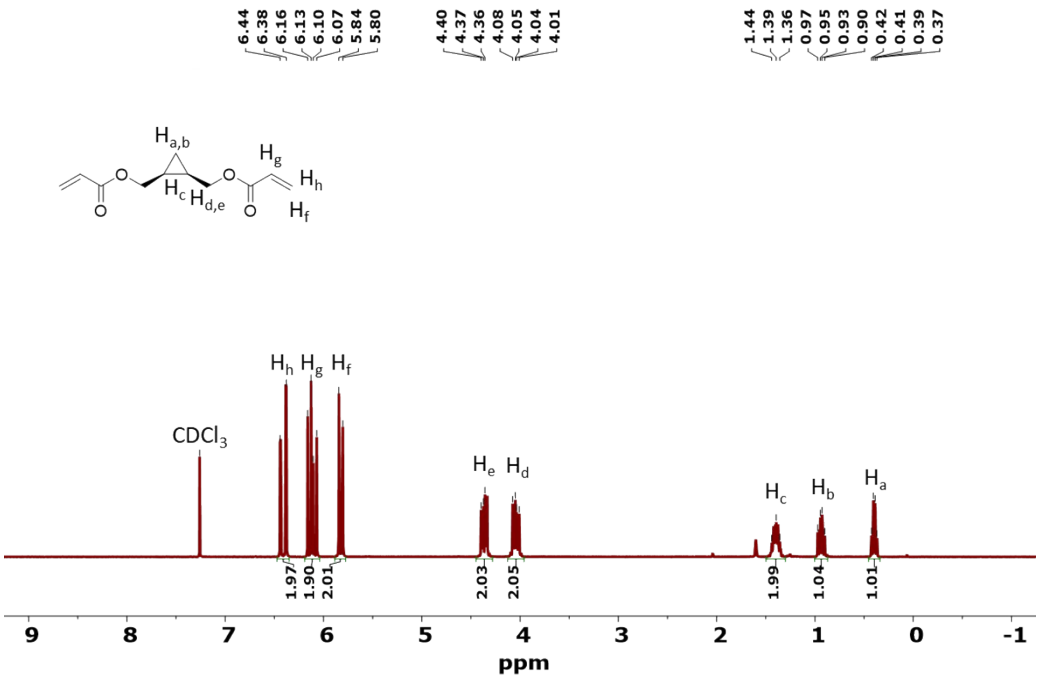

Figure S7 ^{1}H NMR spectrum of *cis* Cy-diacrylate monomer **(4)** in $CDCl_3$ (400 MHz, 298 K)

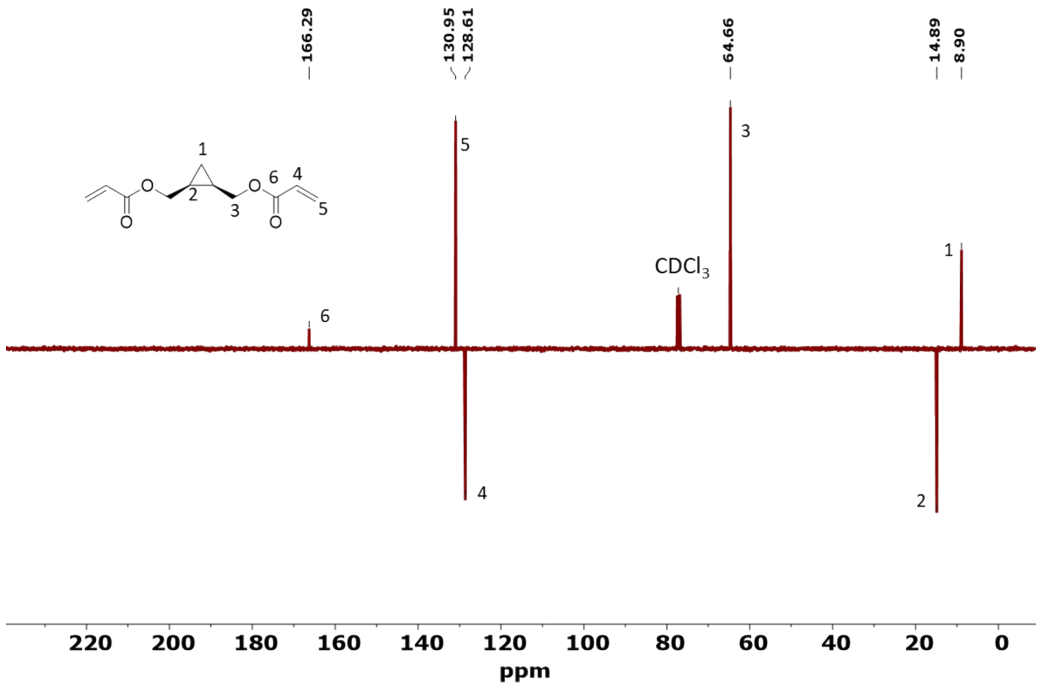

Figure S8 ^{13}C NMR spectrum of *cis* Cy-diacrylate monomer **(4)** in $CDCl_3$ (400 MHz, 298 K)

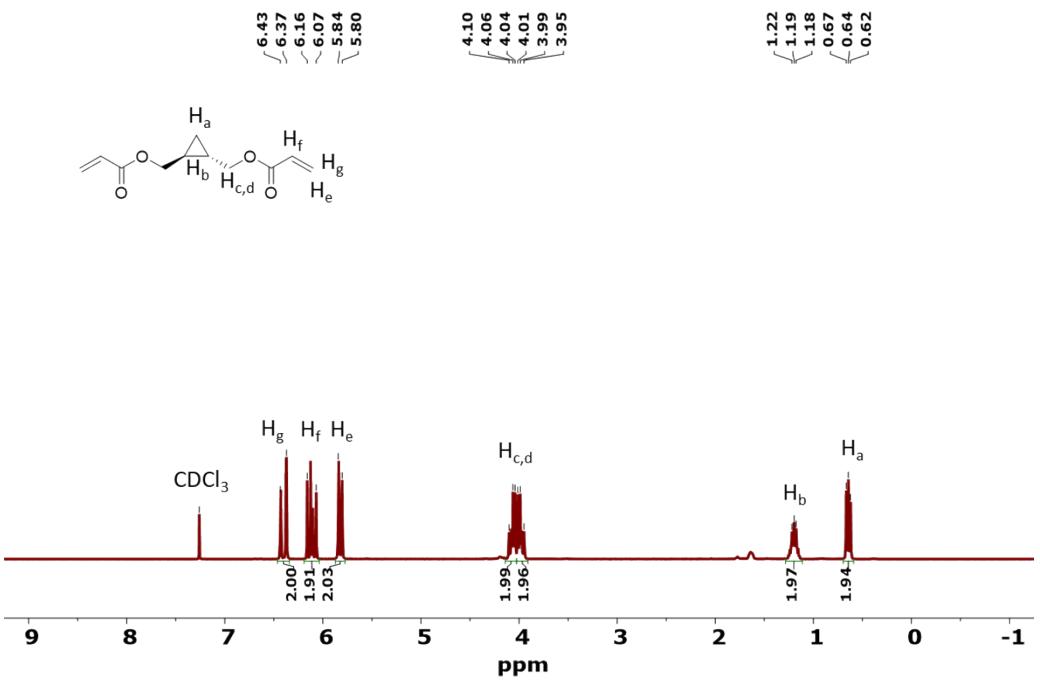

Figure S9 ^{1}H NMR spectrum of *trans* Cy-diacrylate monomer **(5)** in $CDCl_3$ (400 MHz, 298 K)

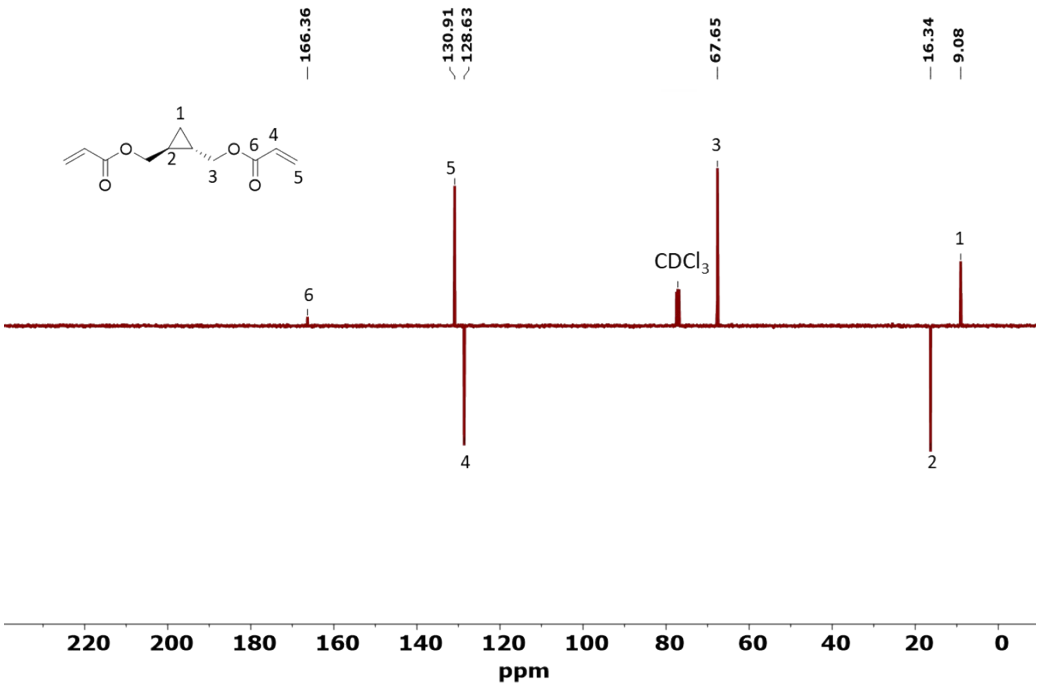

Figure S10 ^{13}C NMR spectrum of *trans* Cy-diacrylate monomer **(5)** in $CDCl_3$ (400 MHz, 298 K)

NMR spectra of Homopolymers

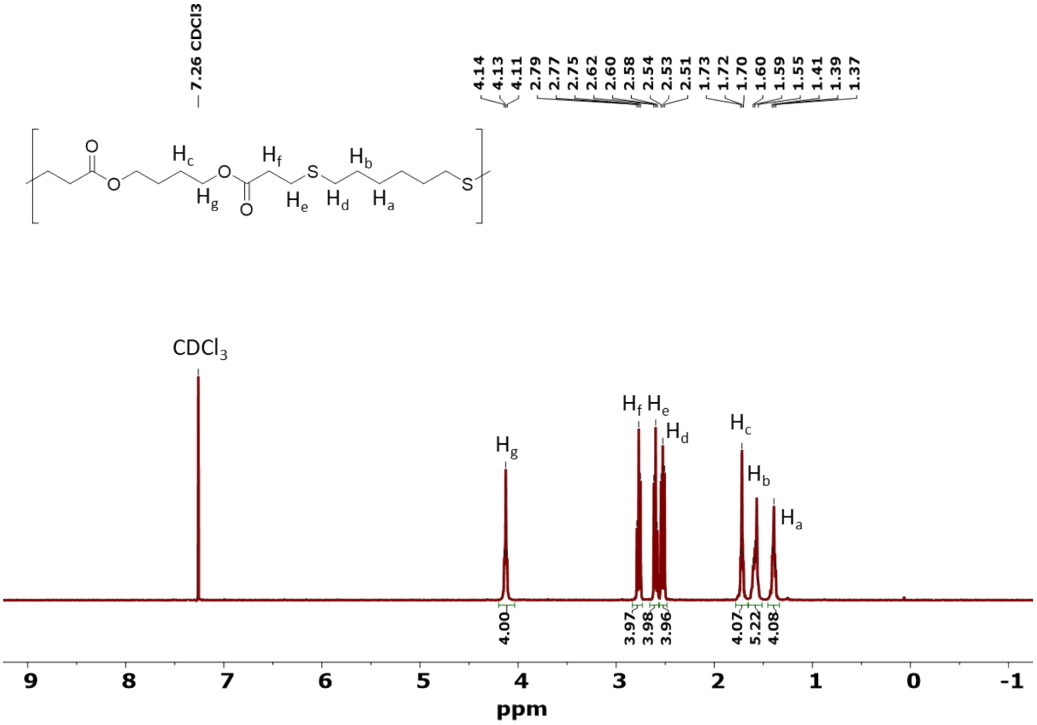

Figure S11 ^{1}H NMR spectrum of **BD-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

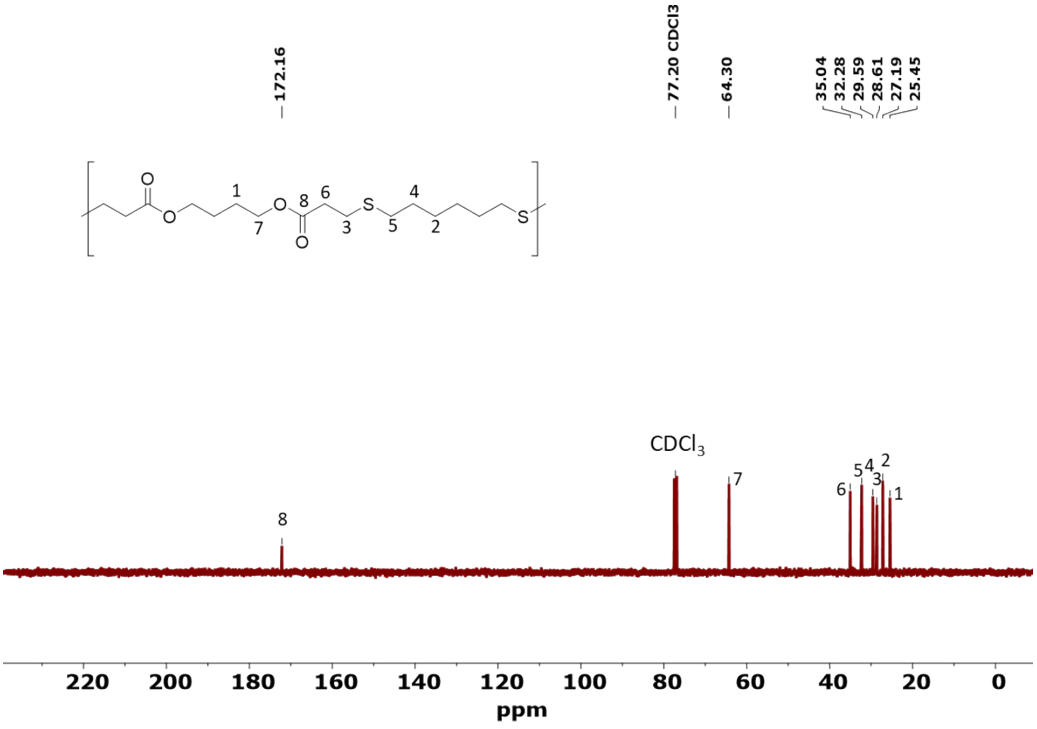

Figure S12 ^{13}C NMR spectrum of **BD-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

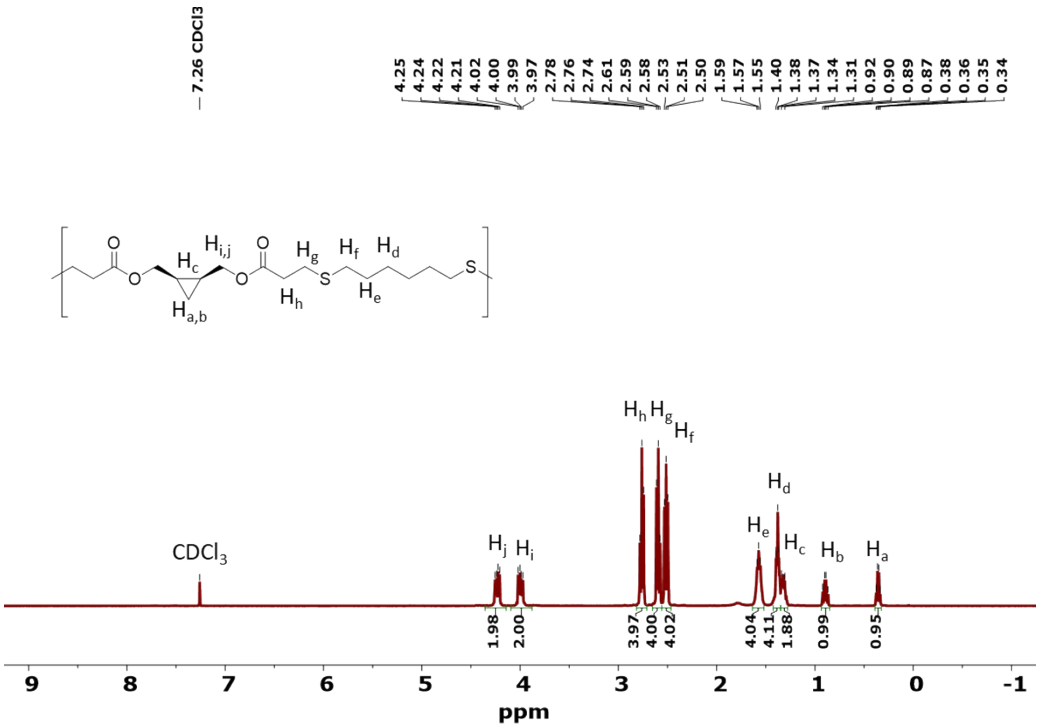

Figure S13 ^{1}H NMR spectrum of **Cy**(*cis*)-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

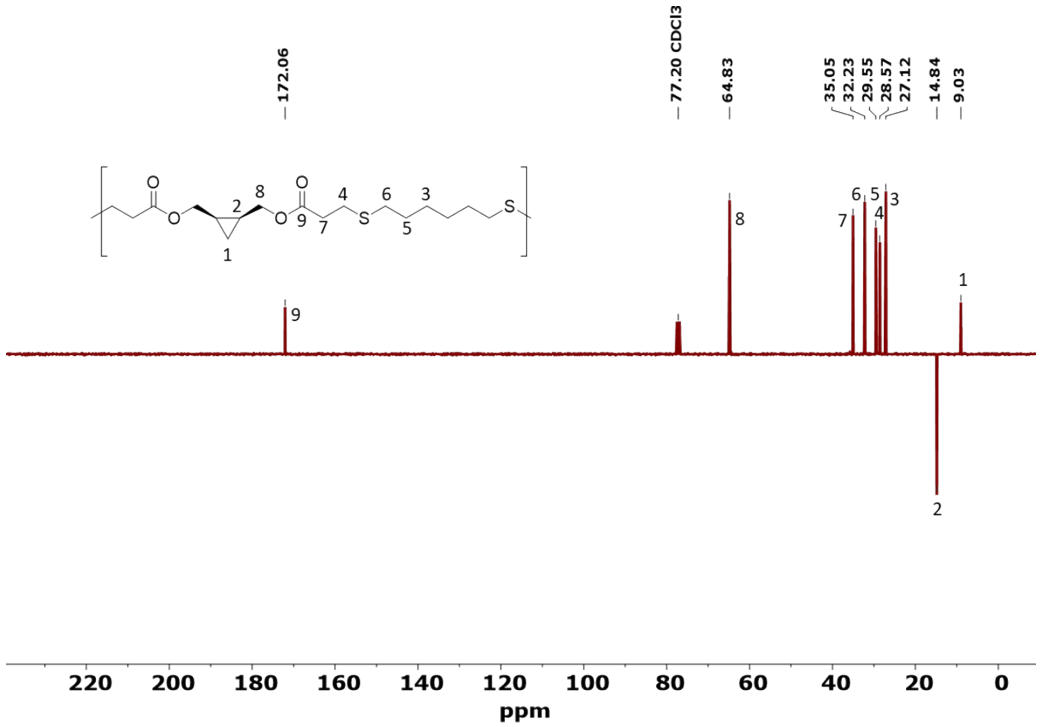

Figure S14 ^{13}C NMR spectrum of **Cy**(*cis*)-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

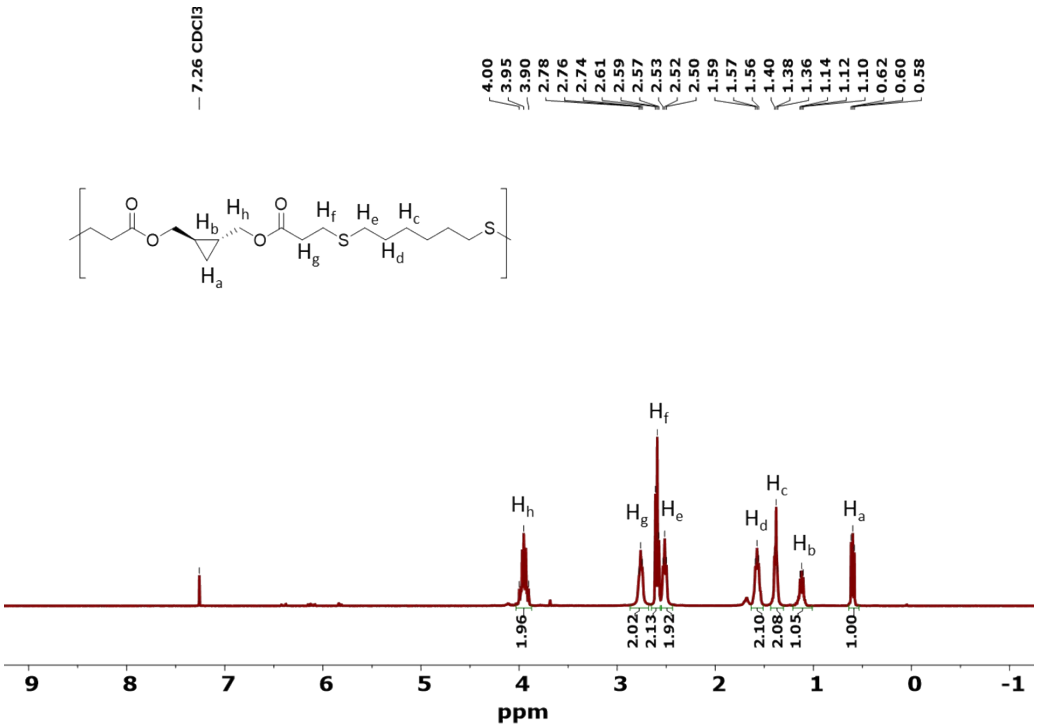

Figure S15 ^{1}H NMR spectrum of **Cy**(*trans*)-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

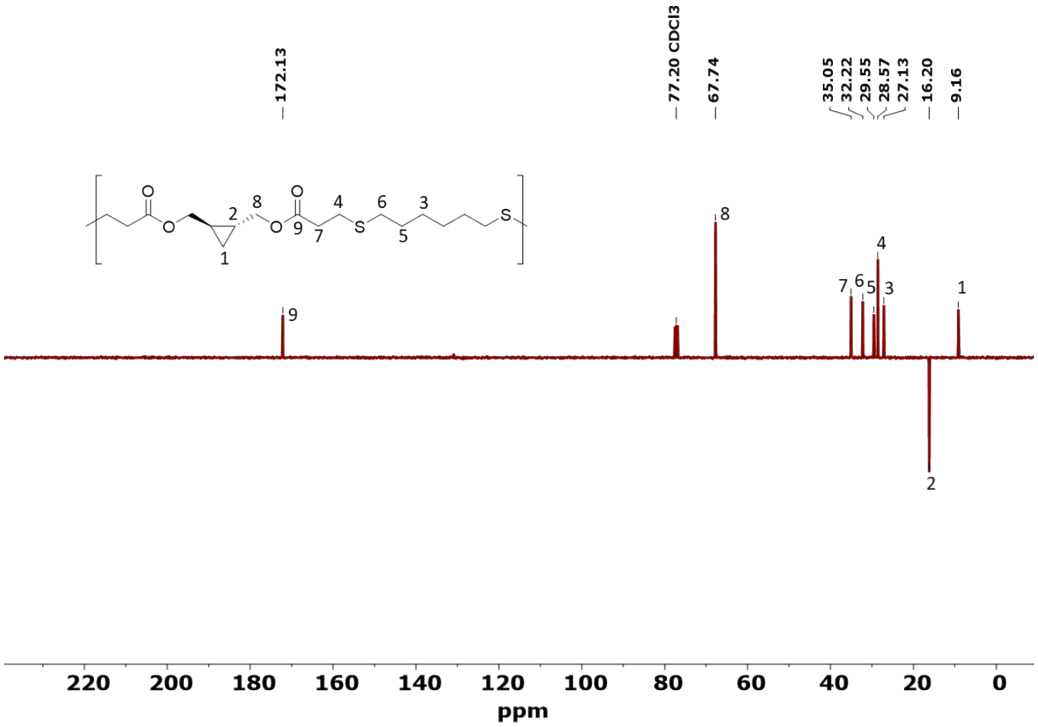

Figure S16 ^{13}C NMR spectrum of **Cy**(*trans*)-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

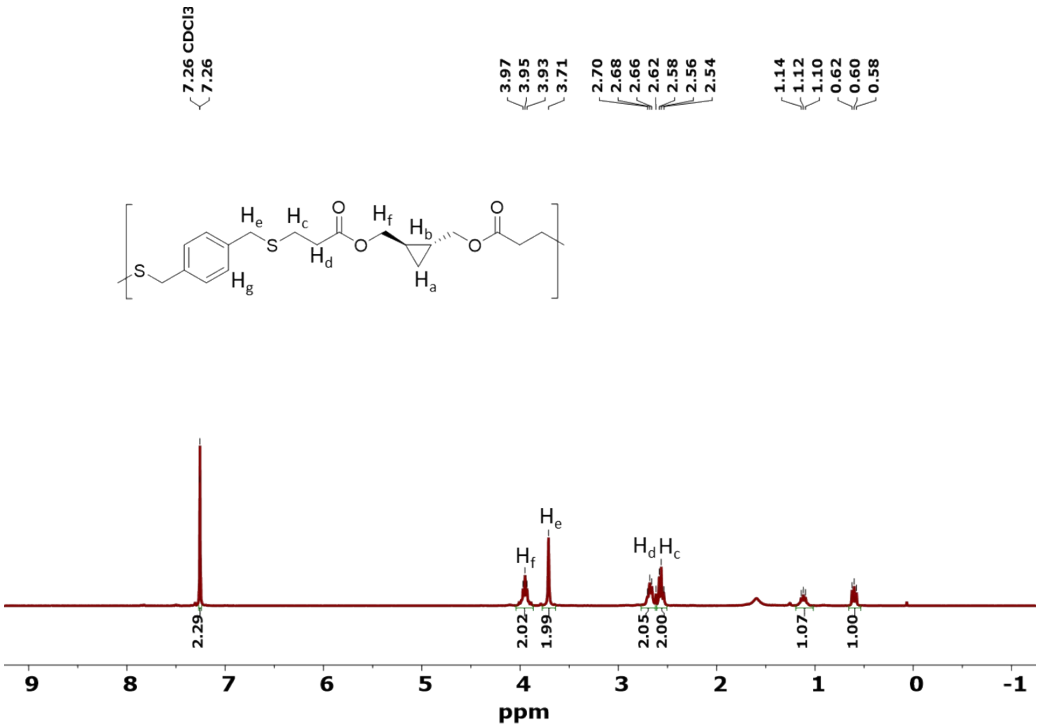

Figure S17 ^{1}H NMR spectrum of **Cy**(*trans*)-*co*-**BDT** in $CDCl_3$ (400 MHz, 298 K)

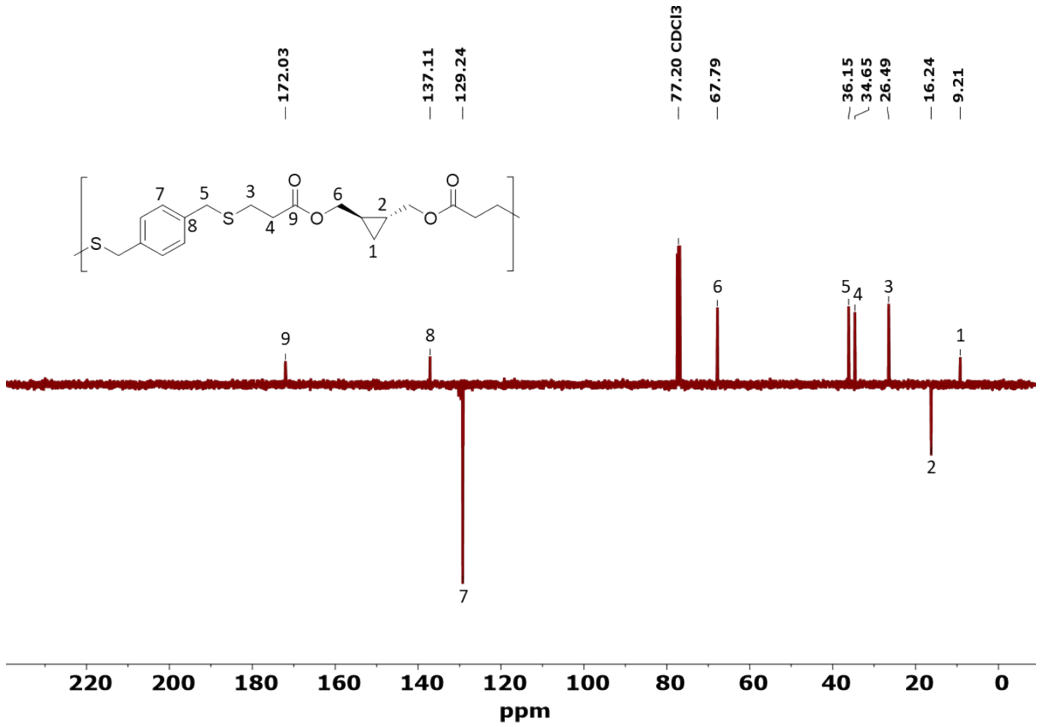

Figure S18 ^{13}C NMR spectrum of **Cy**(*trans*)-*co*-**BDT** in $CDCl_3$ (400 MHz, 298 K)

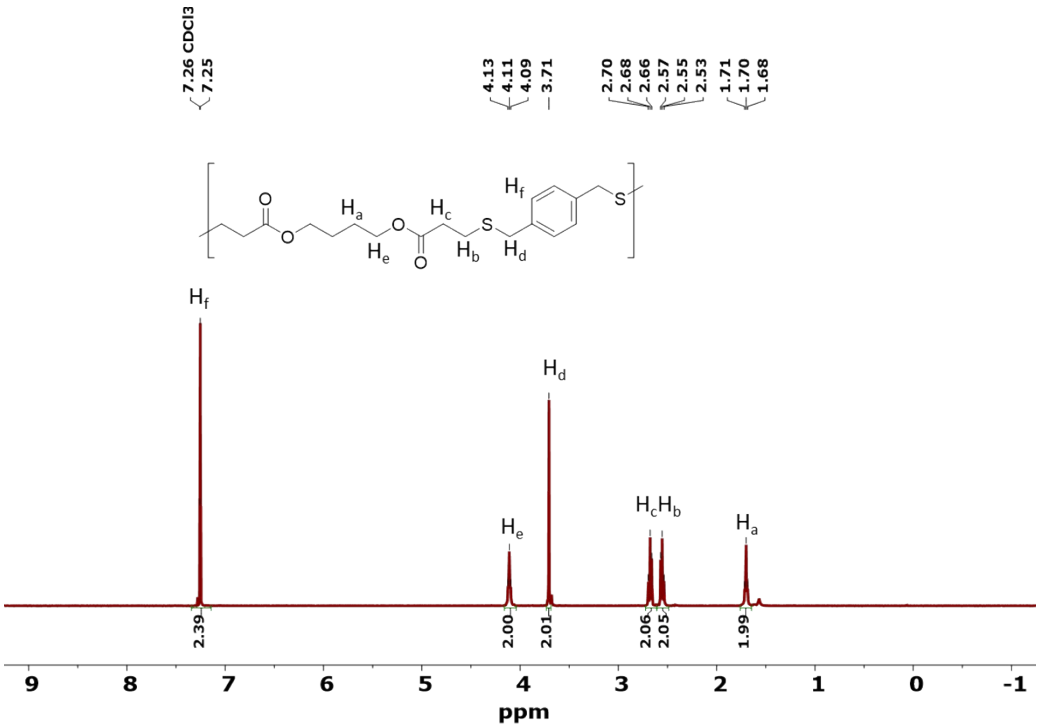

Figure S19 ^{1}H NMR spectrum of **BD-*co*-BDT** in $CDCl_3$ (400 MHz, 298 K)

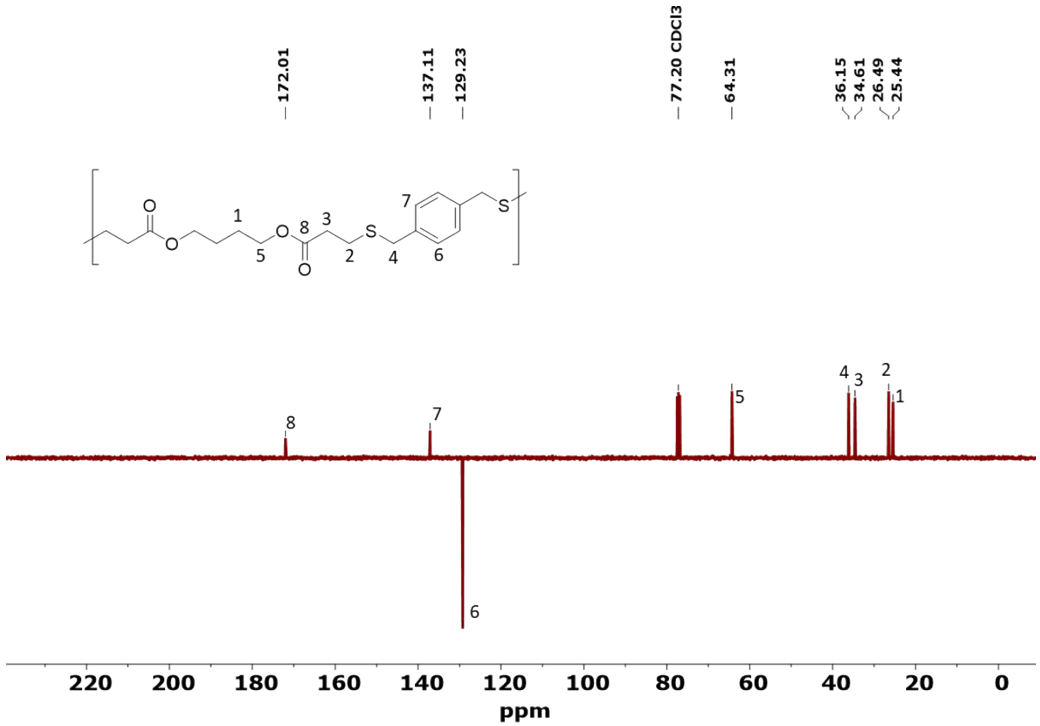

Figure S20 ^{13}C NMR spectrum of **BD-*co*-BDT** in $CDCl_3$ (400 MHz, 298 K)

NMR spectra of copolymers

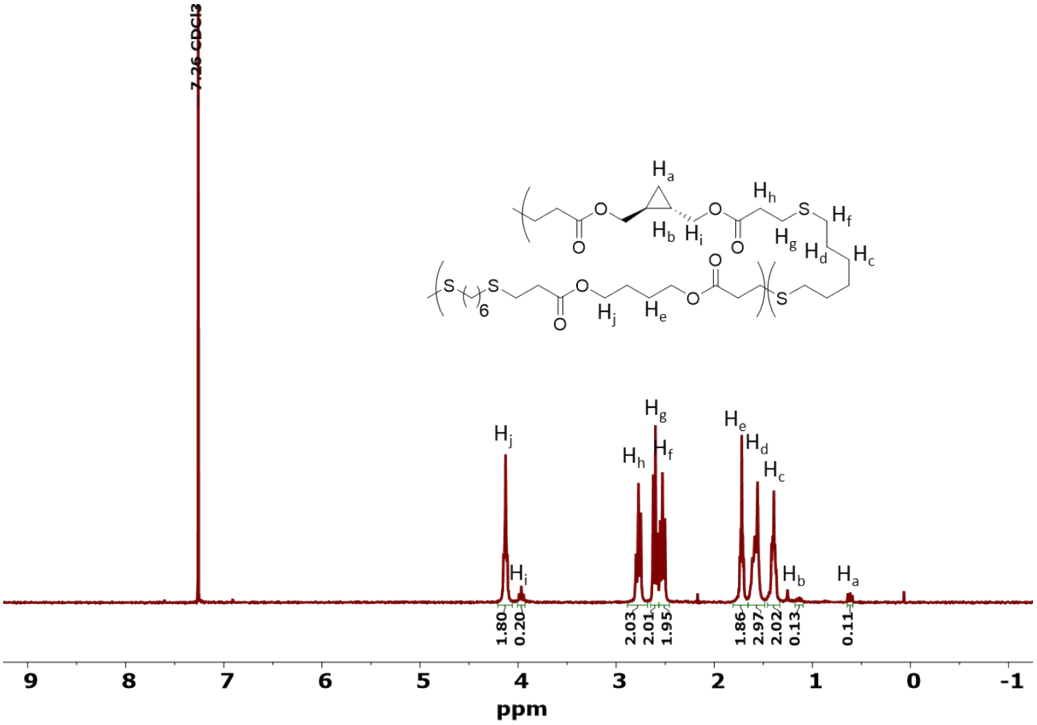

Figure S21 ^{1}H NMR spectrum of **BD$_{90}$Cy(*trans*)$_{10}$-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

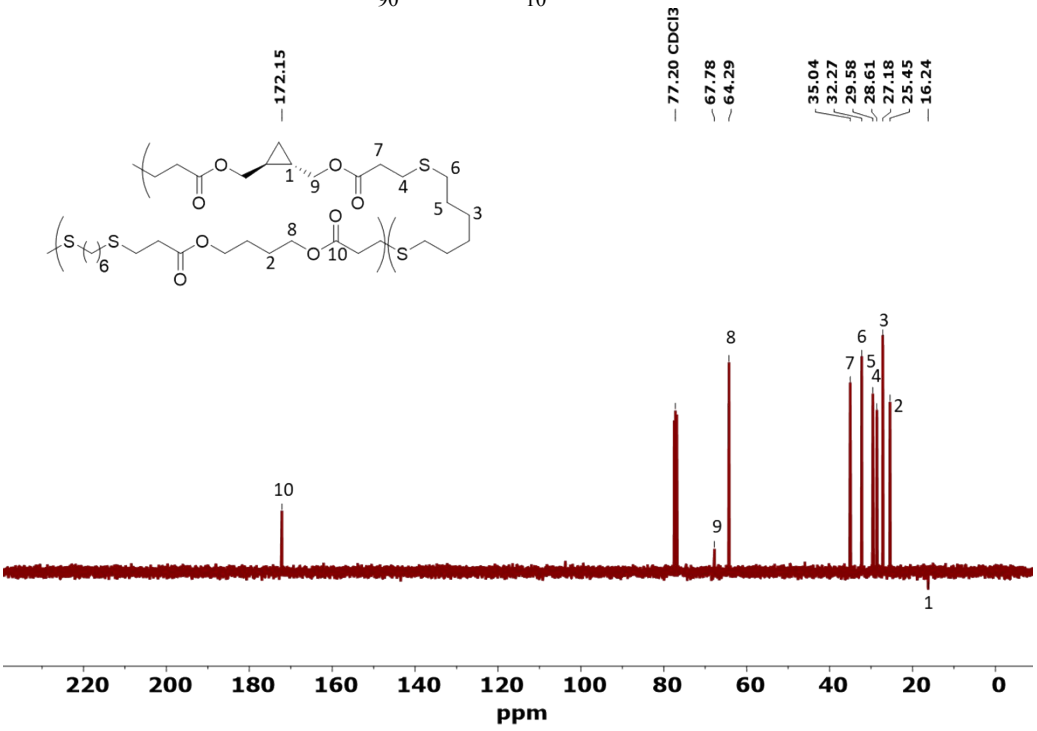

Figure S22 ^{13}C NMR spectrum of **BD$_{90}$Cy(*trans*)$_{10}$-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

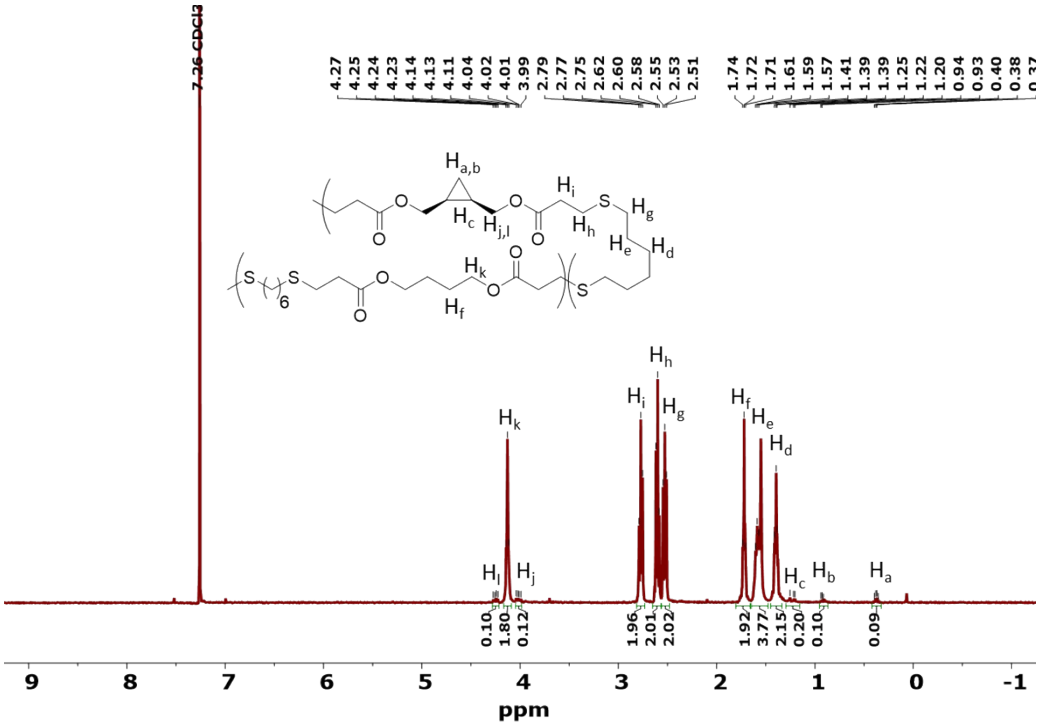

Figure S23 ^{1}H NMR spectrum of **BD$_{90}$Cy(*cis*)$_{10}$-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

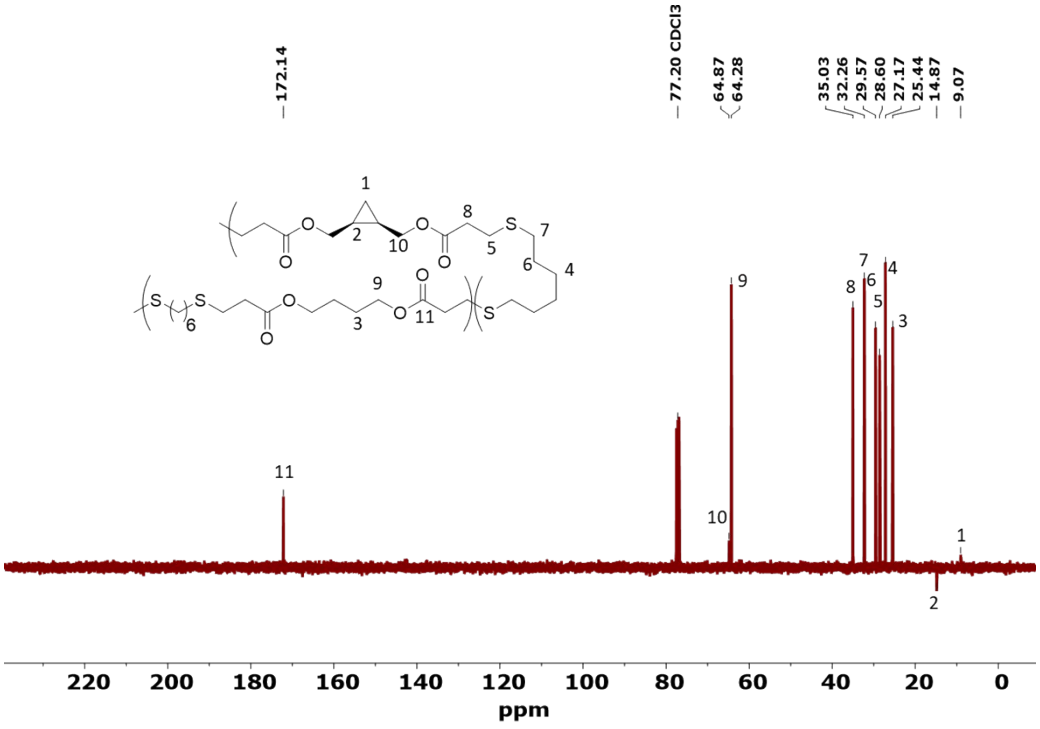

Figure S24 ^{13}C NMR spectrum of **BD$_{90}$Cy(*cis*)$_{10}$-*co*-HDT** in $CDCl_3$ (400 MHz, 298 K)

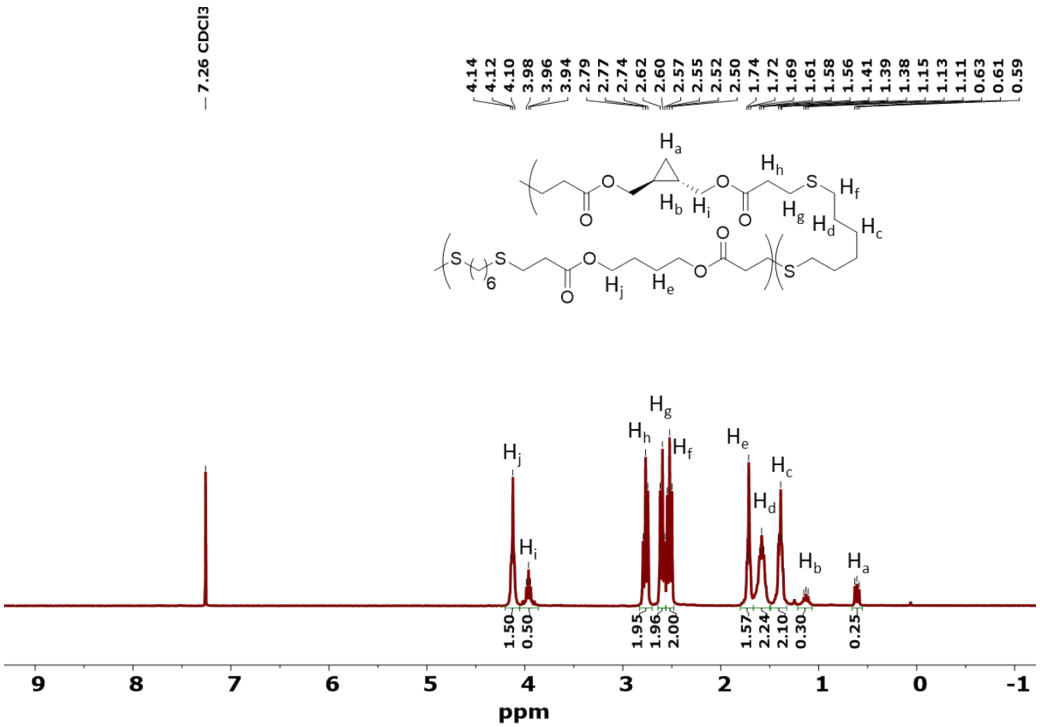

Figure S25 ^{1}H NMR spectrum of **BD**$_{75}$**Cy**(*trans*)$_{25}$-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

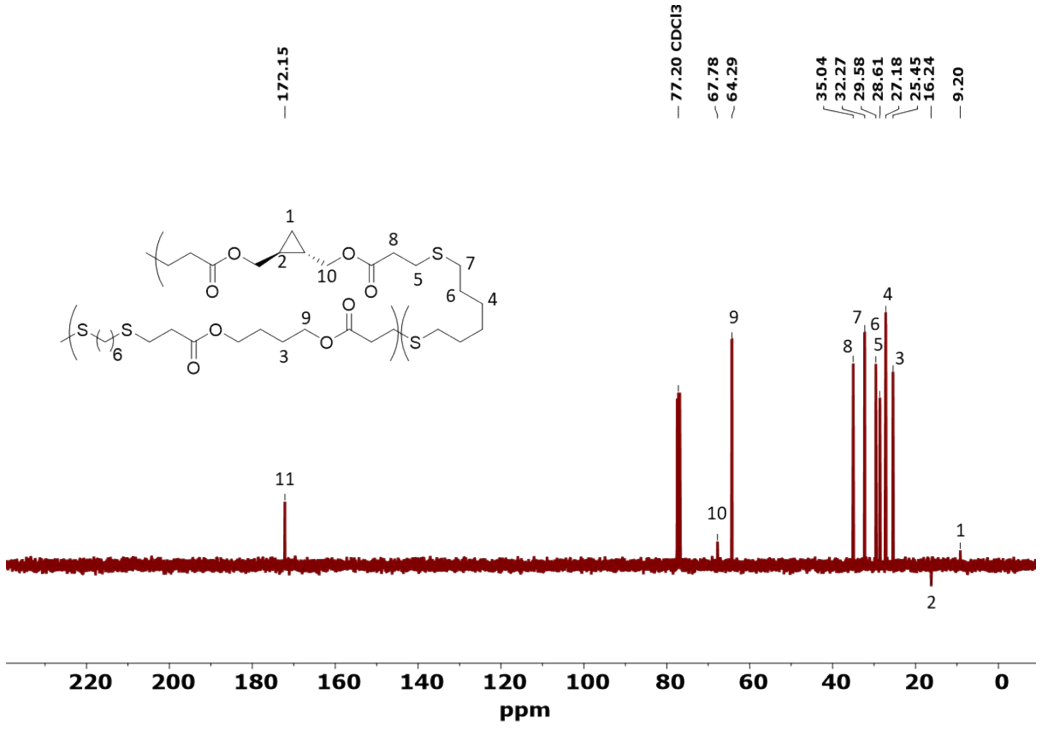

Figure S26 ^{13}C NMR spectrum of **BD**$_{75}$**Cy**(*trans*)$_{25}$-*co*-**HDT** in $CDCl_3$ (400 MHz, 298 K)

SEC chromatograms of Homopolymers

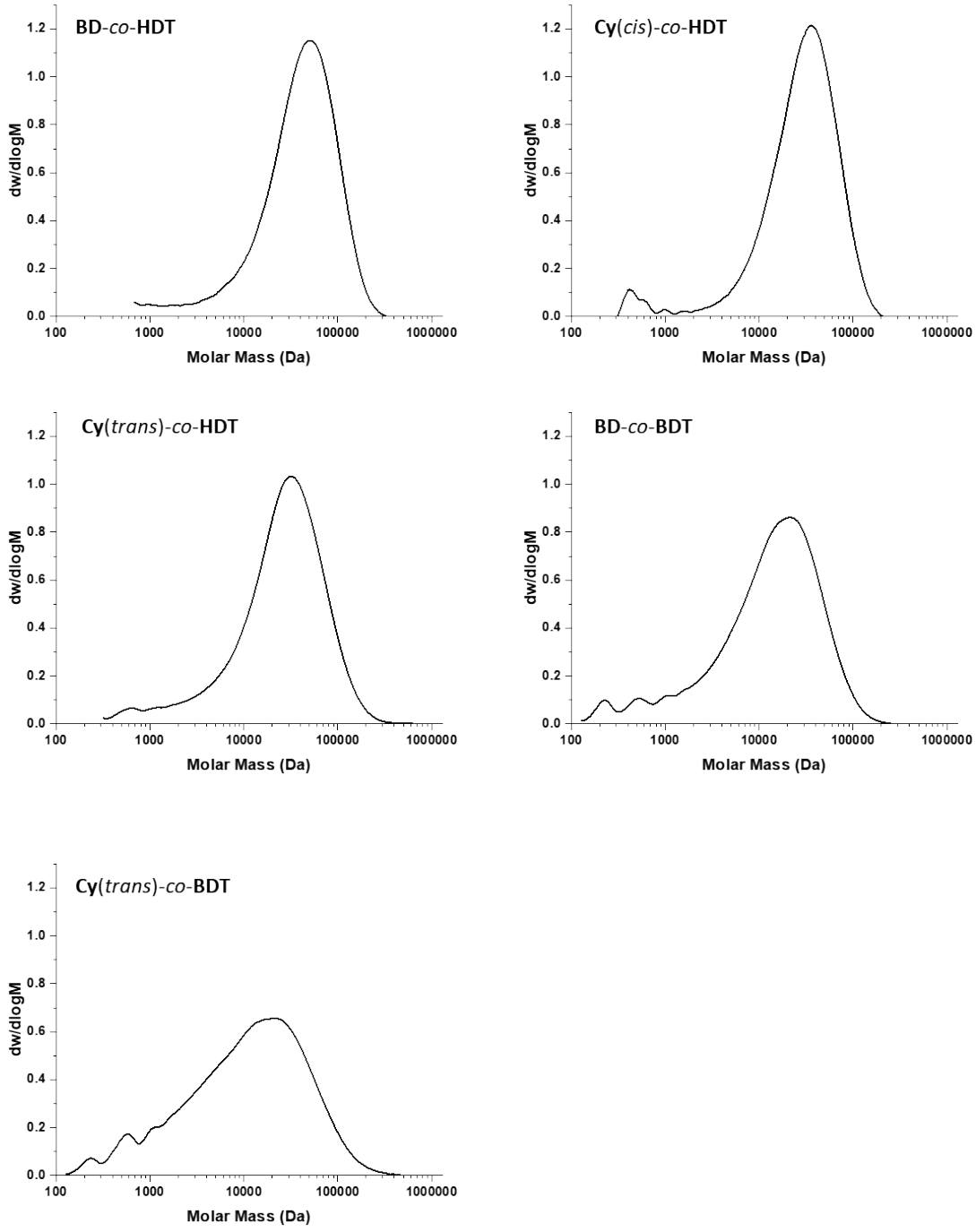

Figure S27 SEC chromatograms of homopolymers calculated against polystyrene standards in THF + 2% v/v NEt_3.

SEC chromatograms of Copolymers

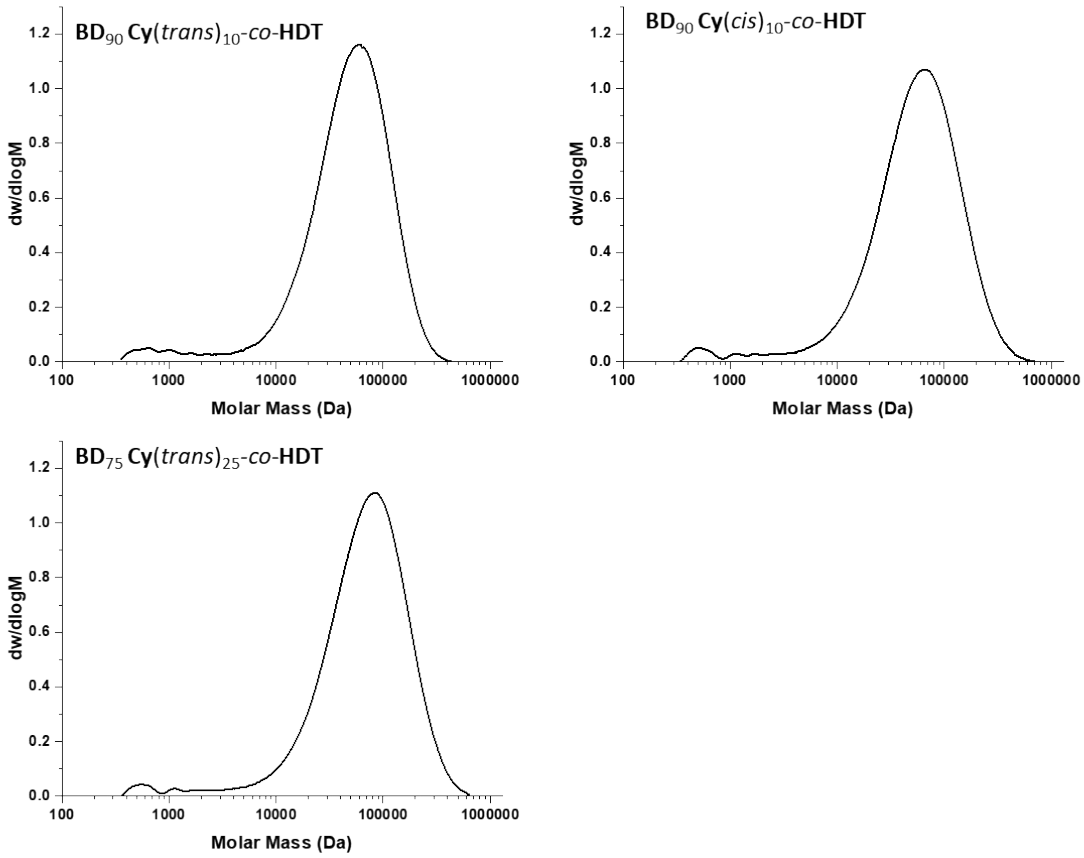

Figure S28 SEC chromatograms of Copolymers calculated against polystyrene standards in THF + 2% v/v NEt_3.

DSC thermograms of Homopolymers

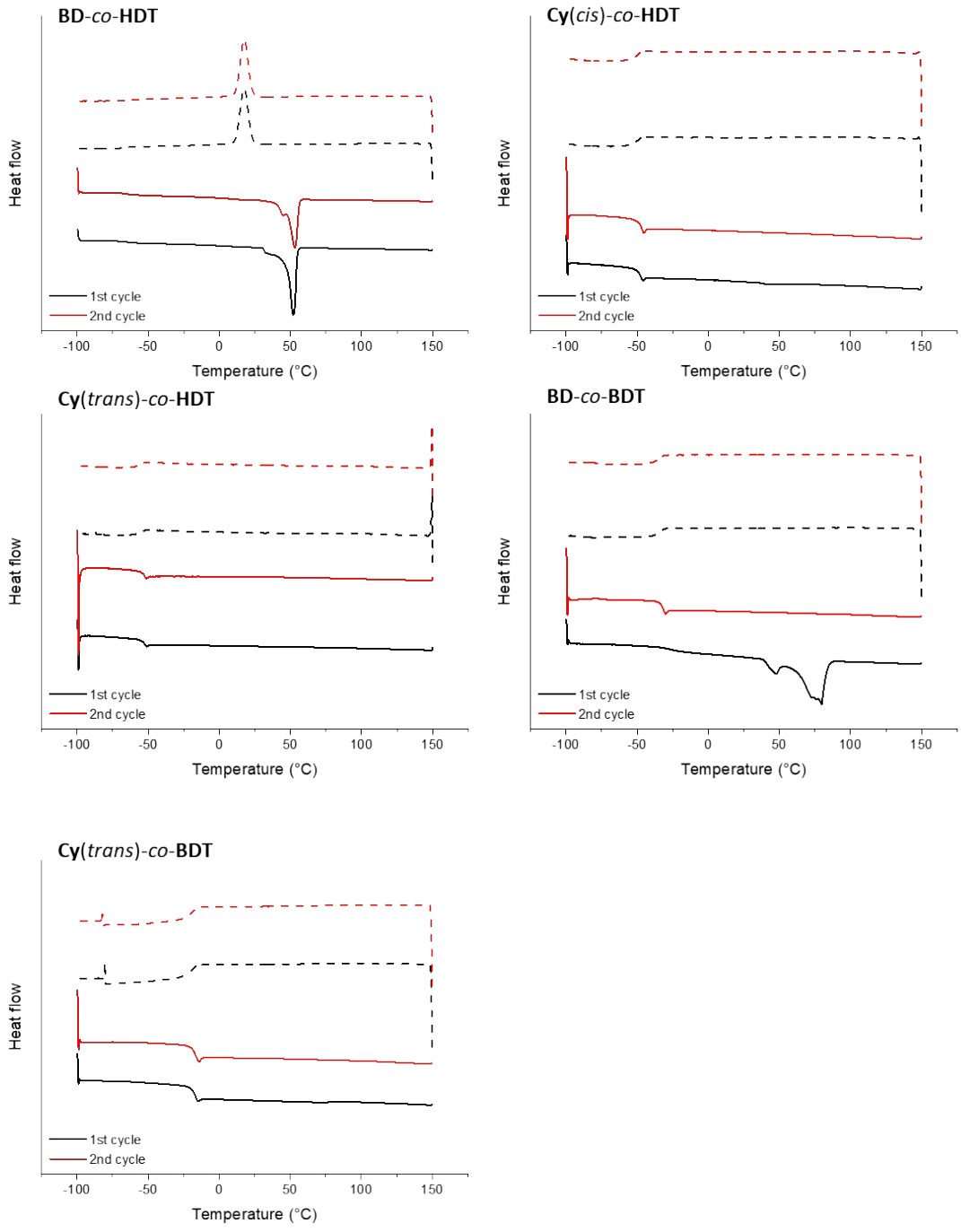

Figure S29 DSC thermograms of Homopolymers 10 K·min^{-1} heating and cooling rate.

DSC thermograms of Copolymers

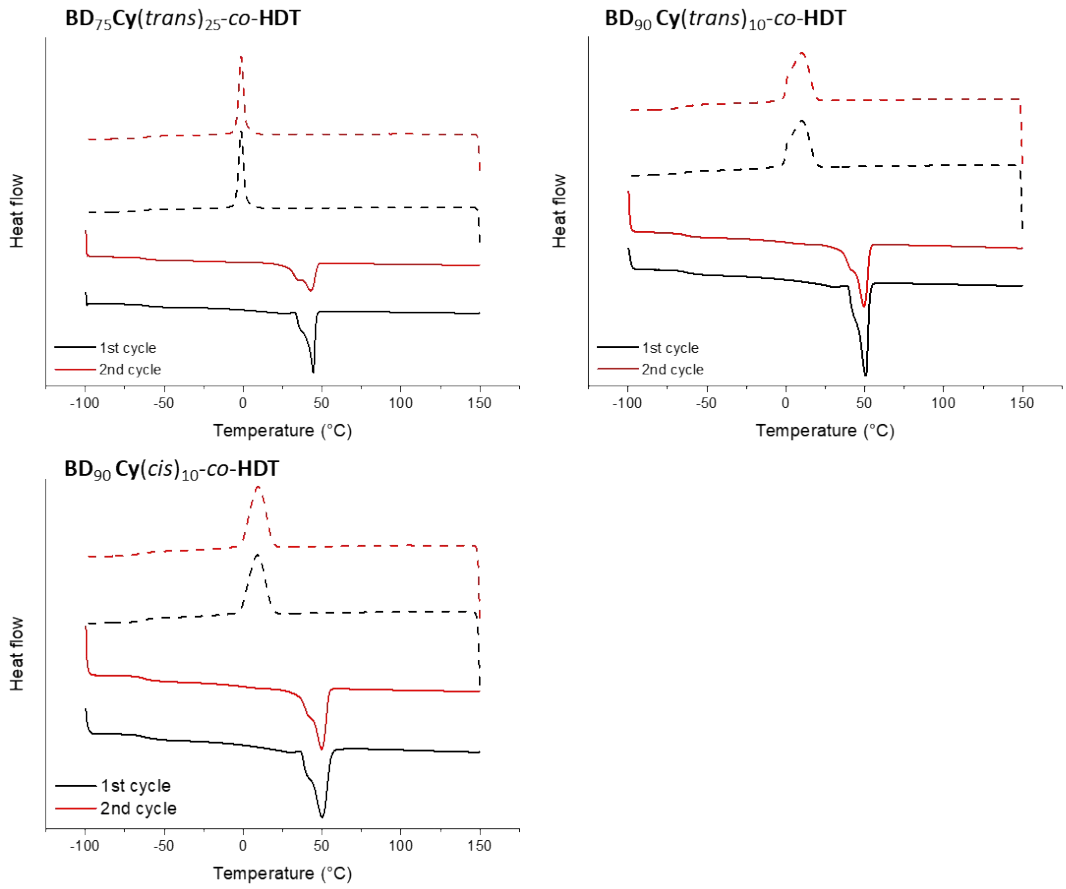

Figure S30 DSC thermograms of Copolymers 10 K·min^{-1} heating and cooling rate

Tensile stress *vs* strain Curves

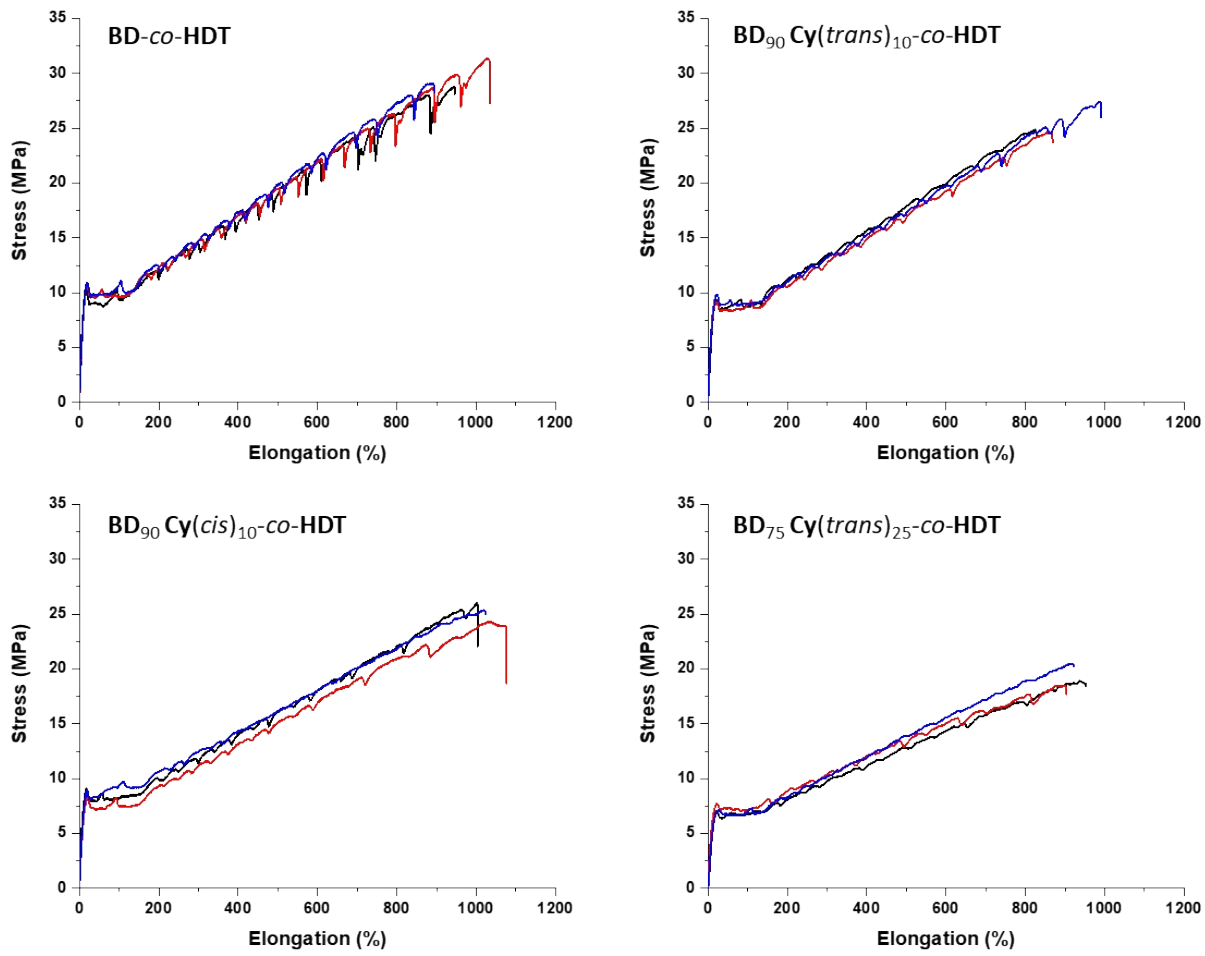

Figure S31 Stress *vs* strain tensile curves of 2 day annealed polyester films

Thermogravimetric analysis (TGA)

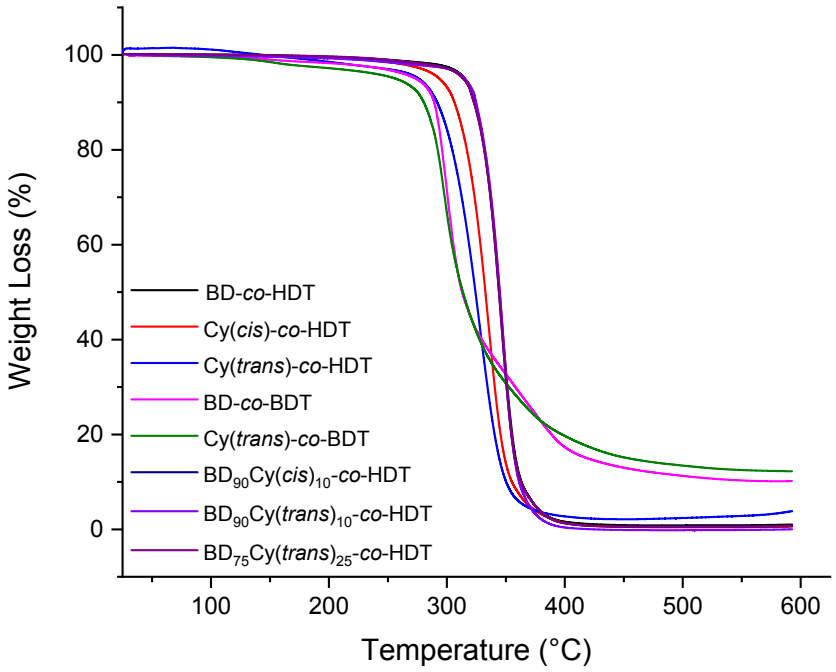

Figure S32 Thermogravimetric analysis of polymers at a 10 $K \cdot min^{-1}$

Sample	M_w (kDa)	$Đ$	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	E (MPa)ǂ	UTS (MPa)ǂ	ε_b (%)ǂ	U_T (MJm^{-3})ǂ
BD-*co*-HDT	52.7	3.13	-66	52	17	-64.0	105±13	30±2	952±72	180±20
Cy(*cis*)-*co*-HDT	37.4	4.08	-47	-	-	-	-	-	-	-
Cy(*trans*)-*co*-HDT	38.0	4.30	-52	-	-	-	-	-	-	-
BD-*co*-BDT	22.0	7.78	-27	80	-	-58.7	-	-	-	-
Cy(*trans*)-*co*-BDT	23.5	6.58	-17	-	-	-	-	-	-	-
Cy(*cis*)$_{10}$BD$_{90}$-*co*-HDT	76.9	4.62	-63	50	9	-53.3	87±2	25±1	1028±31	167±1
Cy(*trans*)$_{10}$BD$_{90}$-*co*-HDT	63.5	4.28	-64	51	10	-55.0	81±4	26±2	890±84	147±22
Cy(*trans*)$_{25}$BD$_{75}$-*co*-HDT	91.8	4.54	-62	44	-2	-50.0	60±10	19±1	920±26	117±4

Table S1 Summary of the reported thermomechanical properties for all polyesters. ǂ Uncertainty taken as standard deviation (n=3).