

Supplementary

α,ω -Epoxide, Oxetane and Dithiocarbonate Telechelic Copolyolefins: Access by Ring-Opening Metathesis/Cross-Metathesis Polymerization (ROMP/CM) of Cycloolefins in the Presence of Functional Symmetric Chain-Transfer Agents

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Table, Schemes and Figures captions

Table S1. NMR and FTIR spectroscopic characteristics of the α,ω -diepoxide telechelic P(NB-*co*-CDT) prepolymers and the resulting α,ω -bis(dithiocarbonate) P(NB-*co*-CDT) analogues.

Figure S1. ORTEP representation of the molecular solid-state structure of CTA **2**. Ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Figure S2. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 25 °C) of CTA **2**; (*: residual solvents δ (ppm) 3.31 H₂O, 1.25, 4.20 ethanol).

Figure S3. ¹³C{¹H} NMR spectrum (100 MHz, DMSO-*d*₆, 25 °C) of CTA **2**; (*: residual solvents δ (ppm) 13.9; 61.1 diethylether; 18.6, 56.1 ethanol).

Figure S4. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 25 °C) of CTA **3**; (*: residual solvent δ (ppm) 3.31 H₂O).

Figure S5. ¹³C{¹H} NMR spectrum (100 MHz, DMSO-*d*₆, 25 °C) of CTA **3**.

Figure S6. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the copolymer sample prepared by ROMP/CM of COE/NB (50:50) in the presence of G2/CTA **1** in CH₂Cl₂ (Table 2, entry 1). (*: residual solvents: δ (ppm) 1.59 H₂O, 0.07 grease).

Figure S7. ¹³C NMR spectrum (125 MHz, CDCl₃, 25 °C) of the copolymer sample prepared by ROMP/CM of COE/NB (50:50) in the presence of G2/CTA **1** (Table 2, entry 1). (*: residual solvents: δ (ppm) 1.2 grease).

Figure S8. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of the copolymer sample prepared by ROMP/CM of NB/CDT (50:50) in the presence of **HG2**/CTA **1** in CH_2Cl_2 (Table 3, entry 3). (*: residual solvents: δ (ppm) 1.53 H_2O , 0.07 grease).

Figure S9. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of the copolymer sample prepared by ROMP/CM of NB/CDT (50:50) in the presence of **HG2**/CTA **1** in THF (Table 3, entry 4), a) after dialysis in THF, and b) before dialysis in THF (*: residual solvents: δ (ppm) 1.53 H_2O , 0.07 grease).

Figure S10. ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of the copolymer sample prepared by ROMP/CM of NB/CDT (50:50) in the presence of **HG2**/CTA **1** in THF (Table 3, entry 4) (δ (ppm) 0.07 grease).

Figure S11. 2D COSY ^1H – ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of the copolymer sample prepared by ROMP/CM of NB/CDT (50:50) in the presence of **G2**/CTA **3** (Table 3, entry 8).

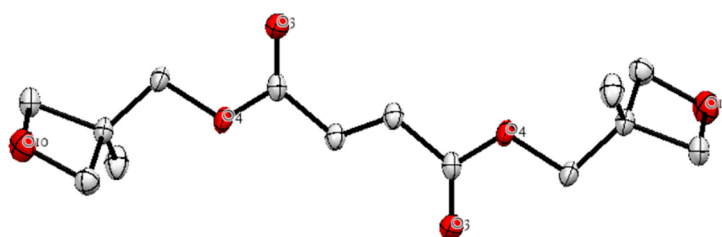
Figure S11. 2D COSY ^1H – ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of the copolymer sample prepared by ROMP/CM of NB/CDT (50:50) in the presence of **G2**/CTA **3** (Table 3, entry 6).

Figure S12. FTIR spectrum of the α,ω -bis(dithiocarbonate) P(NB-*co*-CDT) copolymer sample prepared by dithiocarbonatation of the α,ω -diepoxide telechelic P(NB-*co*-CDT) prepolymer (Table 4, entry 1).

Figure S13. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of the CNF copolymer isolated from the α,ω -bis(dithiocarbonate) P(NB-*co*-CDT) crude copolymers. (*: δ (ppm) 0.07 residual grease) (Table 4, entry 1).

Table S1. NMR and FTIR spectroscopic characteristics of the α,ω -diepoxide telechelic P(NB-*co*-CDT) prepolymers and the resulting α,ω -bis(dithiocarbonate) P(NB-*co*-CDT) analogues.

¹ H NMR	(δ ppm)	2.67; 2.86; 3.24; 3.98; 4.45 (A61)					3.59; 4.49; 5.37		
(400 MHz, 23 °C, CDCl ₃)	Assignments	a ; a ; b ; c ; c					a'; c' ; b'		
	Integrations	1	1	1	1	1	2	2	- ^b
Figure S9						Figure 5			
¹³ C{ ¹ H} NMR	(δ ppm)	38.2 ; 49.6 ; 64.9 ; 166.6					210.9 ; 166.0 ; 87.7 ; 53.6 ; 31.0		
(100 MHz, 23 °C, CDCl ₃)	Assignments	a ; b ; c ; d					g' ; d' ; b'		
							; c' ; a'		
Figure S10						Figure 6			
FTIR	(σ cm ⁻¹)	-					1190 (νC=S) ; 1519 (νC=O)		
						Figure S13			



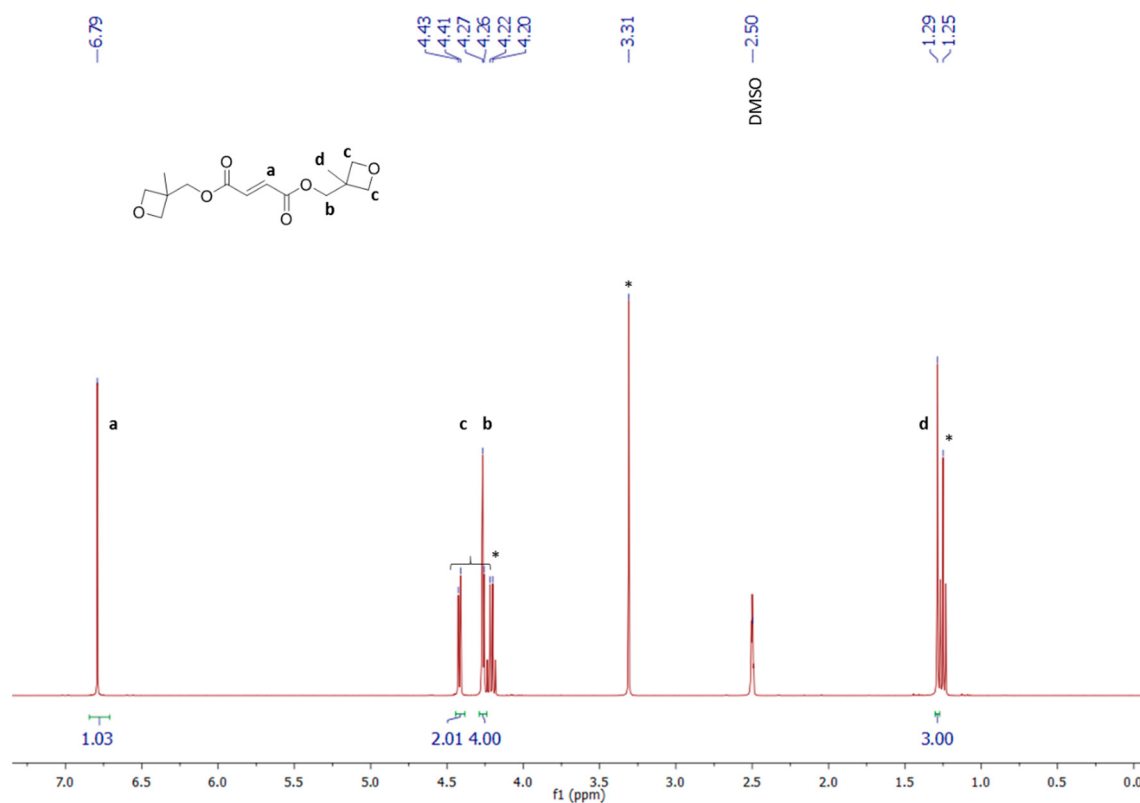


Figure S2. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 25 °C) of CTA 2; (*: residual solvents δ (ppm) 3.31 H₂O, 1.25, 4.20 ethanol).

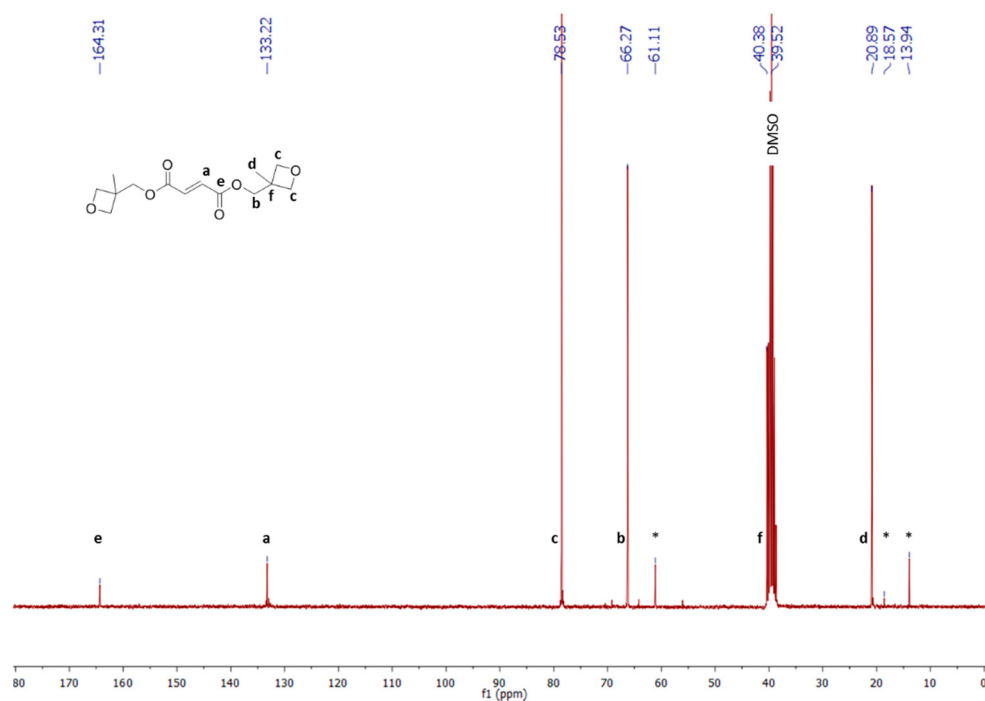


Figure S3. ¹³C{¹H} NMR spectrum (100 MHz, DMSO-*d*₆, 25 °C) of CTA 2; (*: residual solvents δ (ppm) 13.9; 61.1 diethylether; 18.6, 56.1 ethanol).

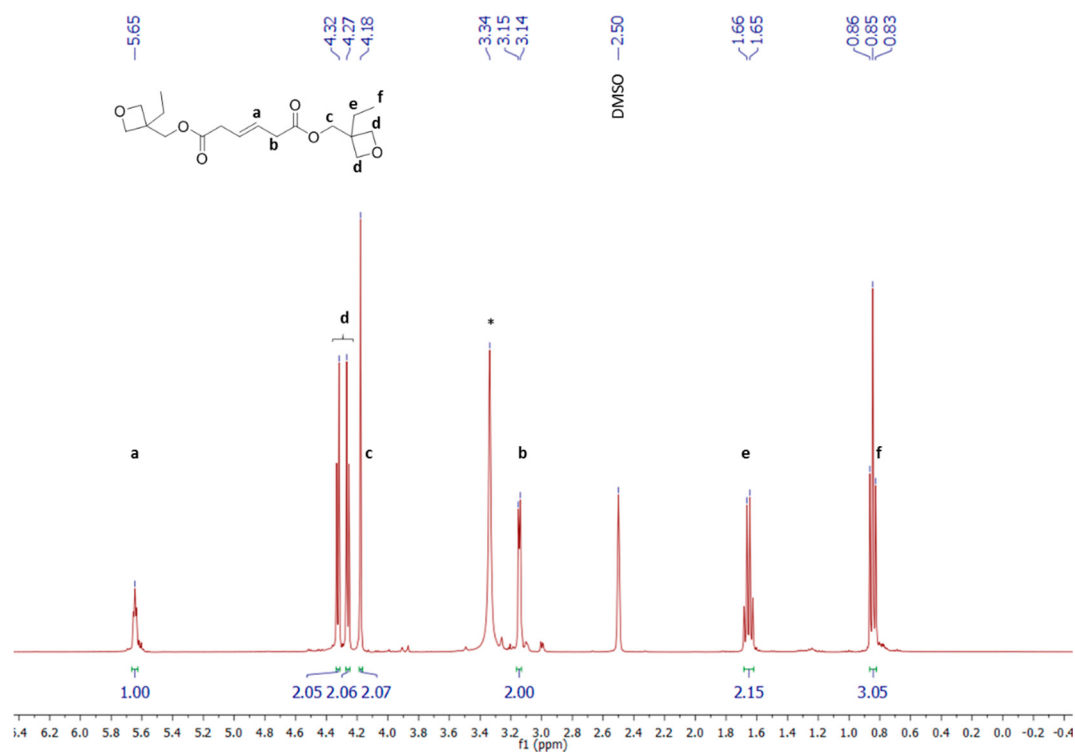


Figure S4. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$, 25 °C) of CTA 3; (*: residual solvent δ (ppm) 3.31 H_2O).

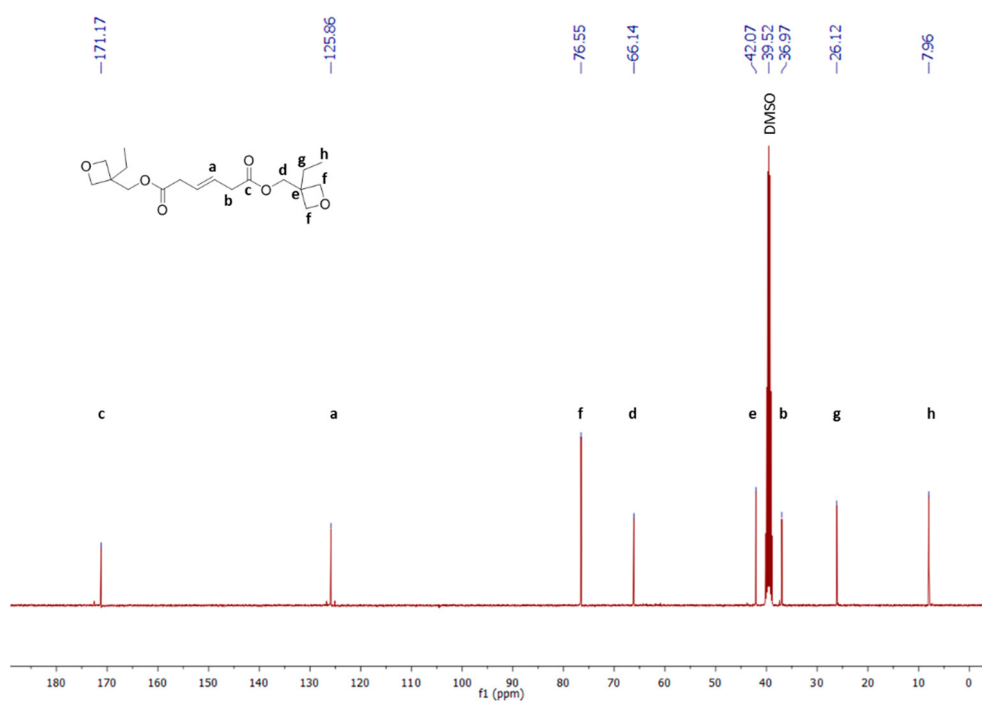


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, $\text{DMSO}-d_6$, 25 °C) of CTA 3.

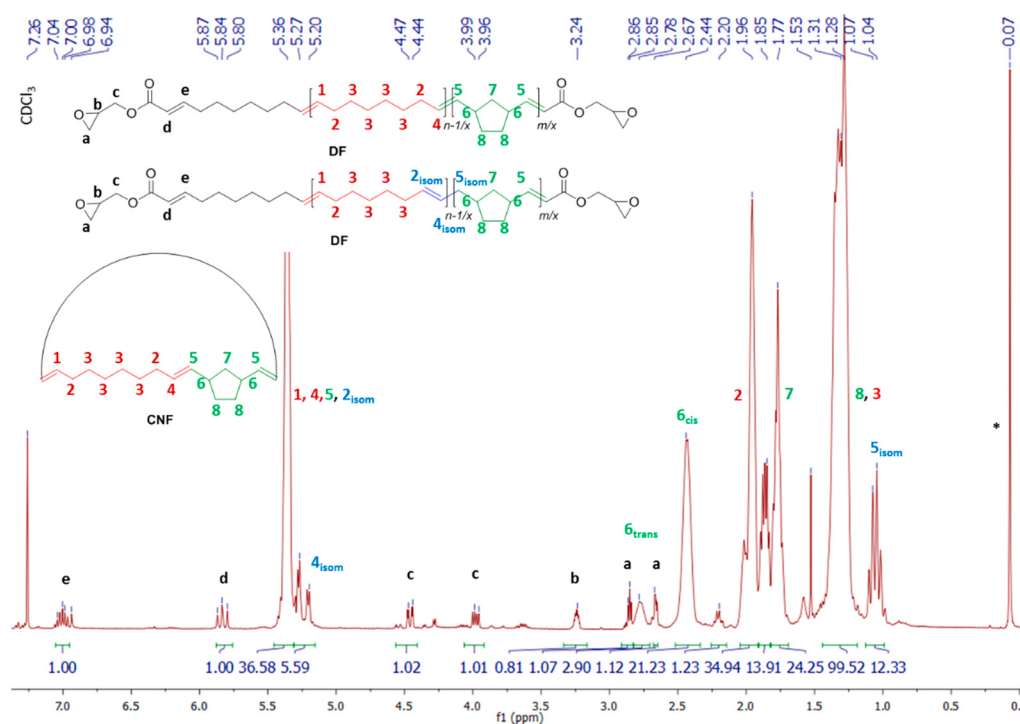


Figure S6. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a copolymer sample prepared by ROMP/CM of COE/NB (50:50) in the presence of **G2**/CTA **1** in CH_2Cl_2 (Table 2, entry 1). (*: residual solvents: δ (ppm) 1.59 H_2O , 0.07 grease).

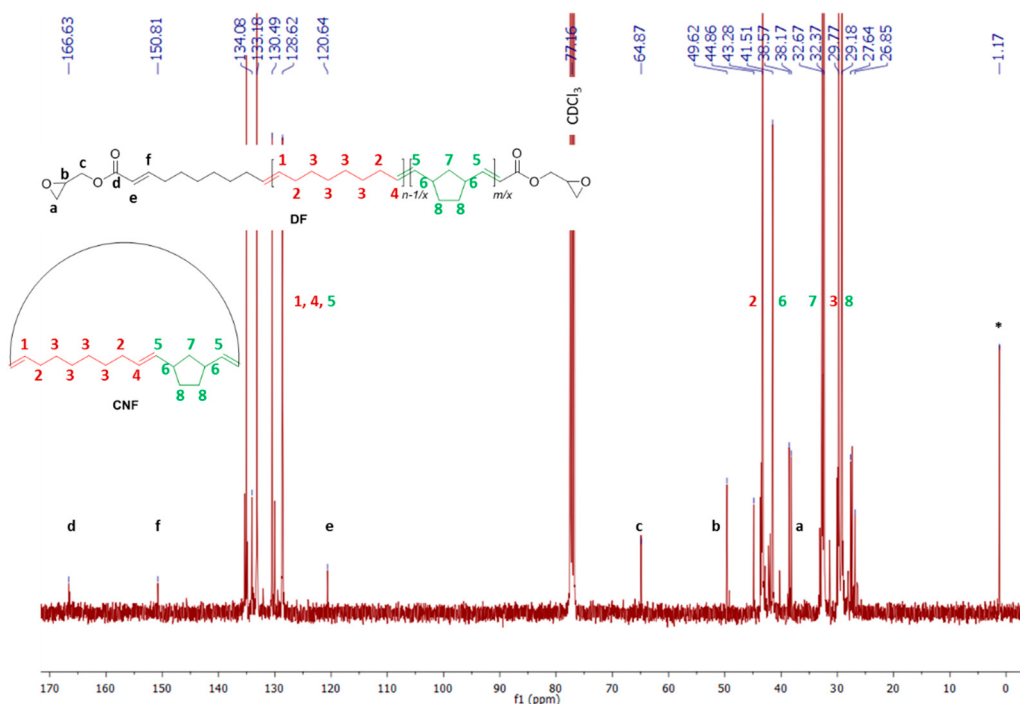


Figure S7. ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a copolymer sample prepared by ROMP/CM of COE/NB (50:50) in the presence of **G2**/CTA **1** (Table 2, entry 1). (*: residual solvents: δ (ppm) 1.2 grease).

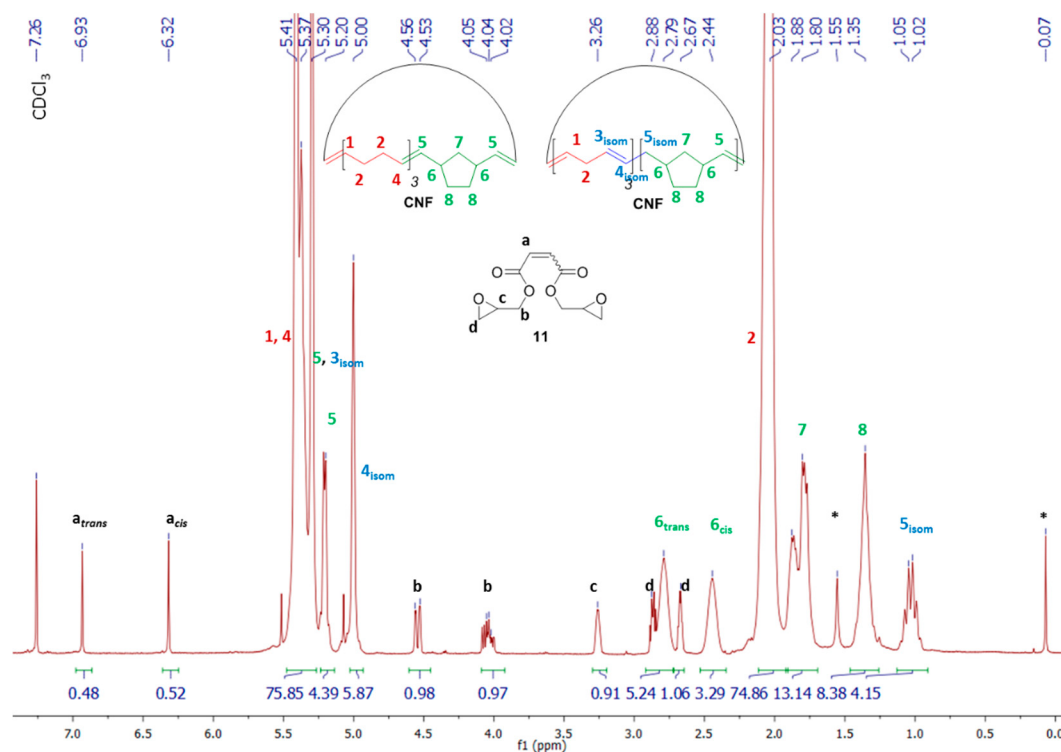


Figure S8. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a copolymer sample prepared by ROMP/CM of NB/CDT (50:50 mol/mol) in the presence of HG2/CTA **1** in CH_2Cl_2 (Table 3, entry 3). (*: residual solvents: δ (ppm) 1.53 H_2O , 0.07 grease).

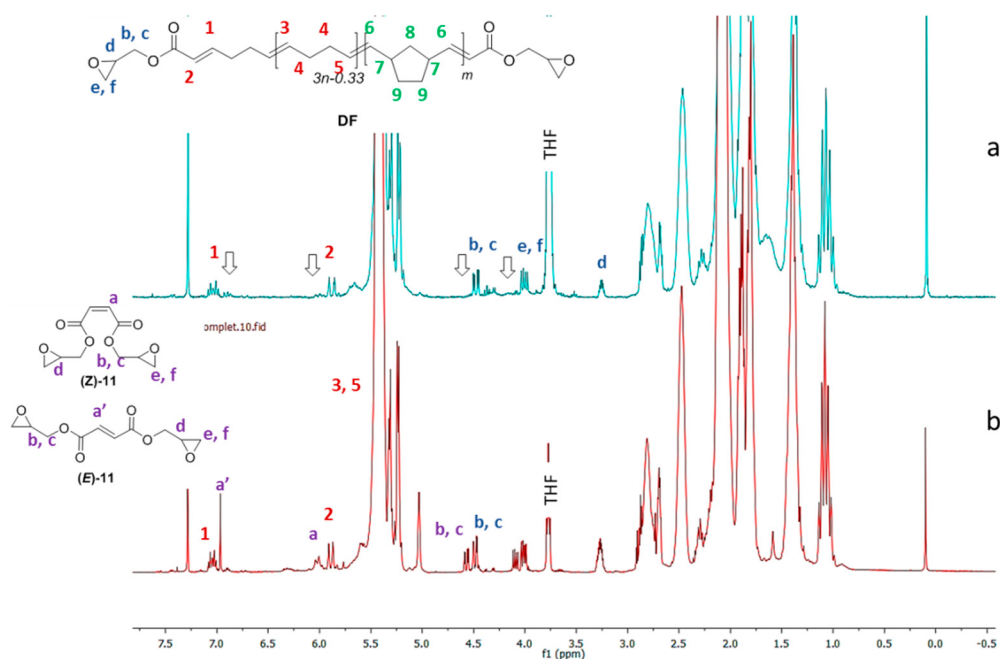


Figure S9. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a copolymer sample prepared by ROMP/CM of NB/CDT (50:50 mol/mol) in the presence of HG2/CTA **1** in THF (Table 3, entry 4), a) after dialysis in THF, and b) before dialysis in THF (*: residual solvents: δ (ppm) 1.53 H_2O , 0.07 grease).

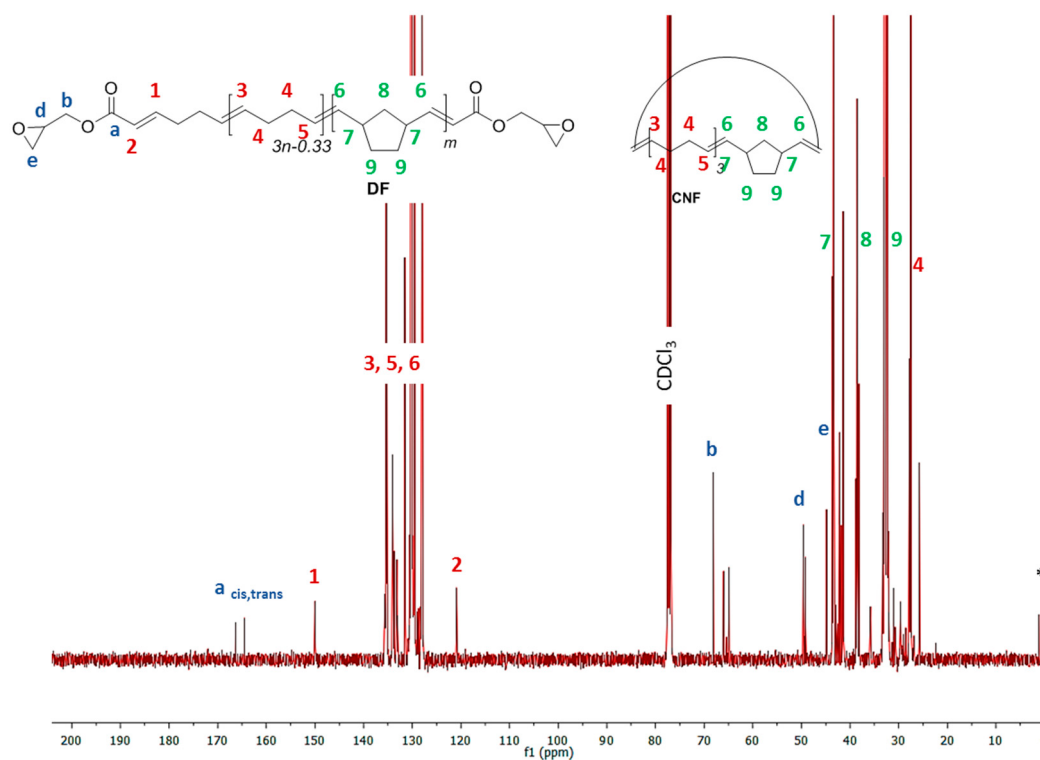


Figure S10. ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of a copolymer sample prepared by ROMP/CM of NB/CDT (50:50 mol/mol) in the presence of HG2/CTA 1 in THF (Table 3, entry 4) (δ (ppm) 0.07 grease).

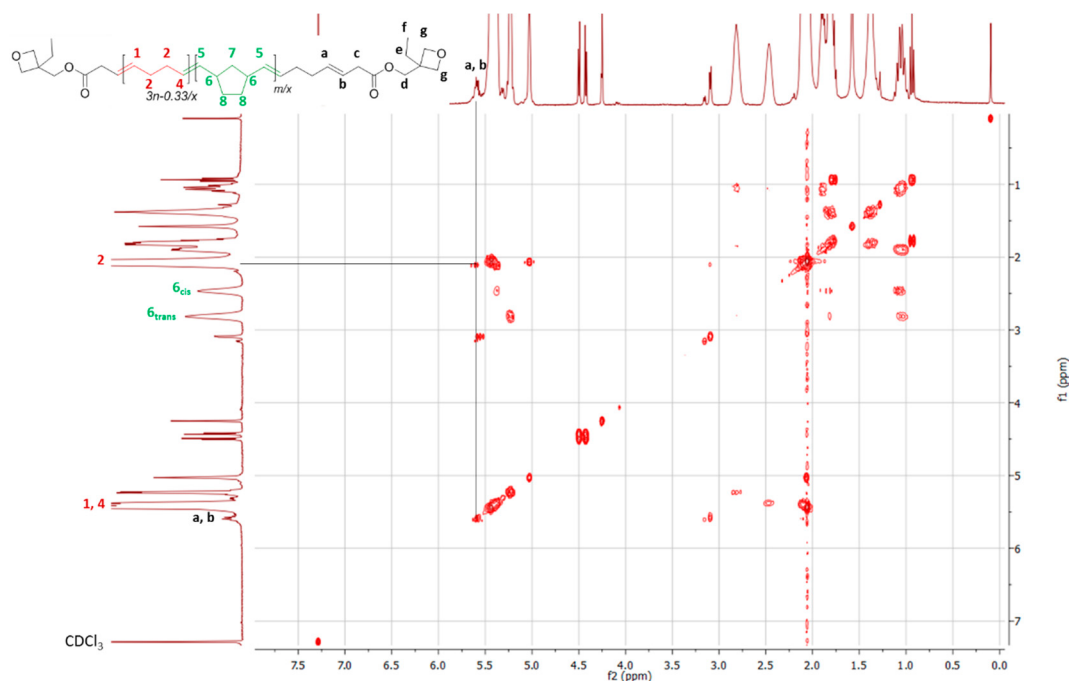


Figure S11. 2D COSY ^1H - ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of a copolymer sample prepared by ROMP/CM of NB/CDT (50:50 mol/mol) in the presence of G2/CTA 3 (Table 3, entry 8).

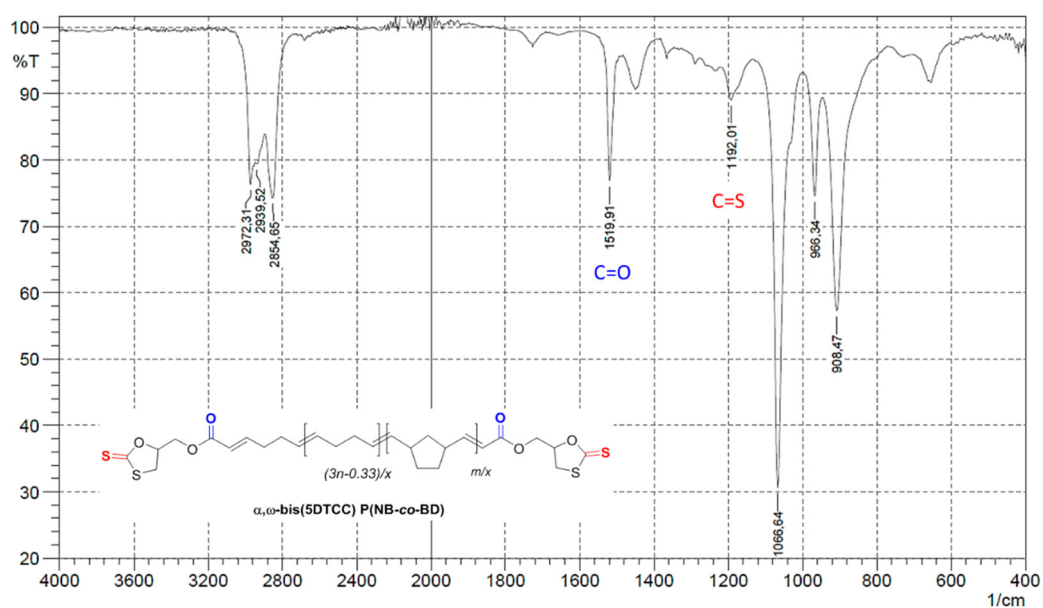


Figure S12. FTIR spectrum of an α,ω -bis(dithiocarbonate) P(NB-co-CDT) copolymer sample prepared by dithiocarbonation of an α,ω -diepoxide telechelic P(NB-co-CDT) prepolymer (Table 4, entry 1).

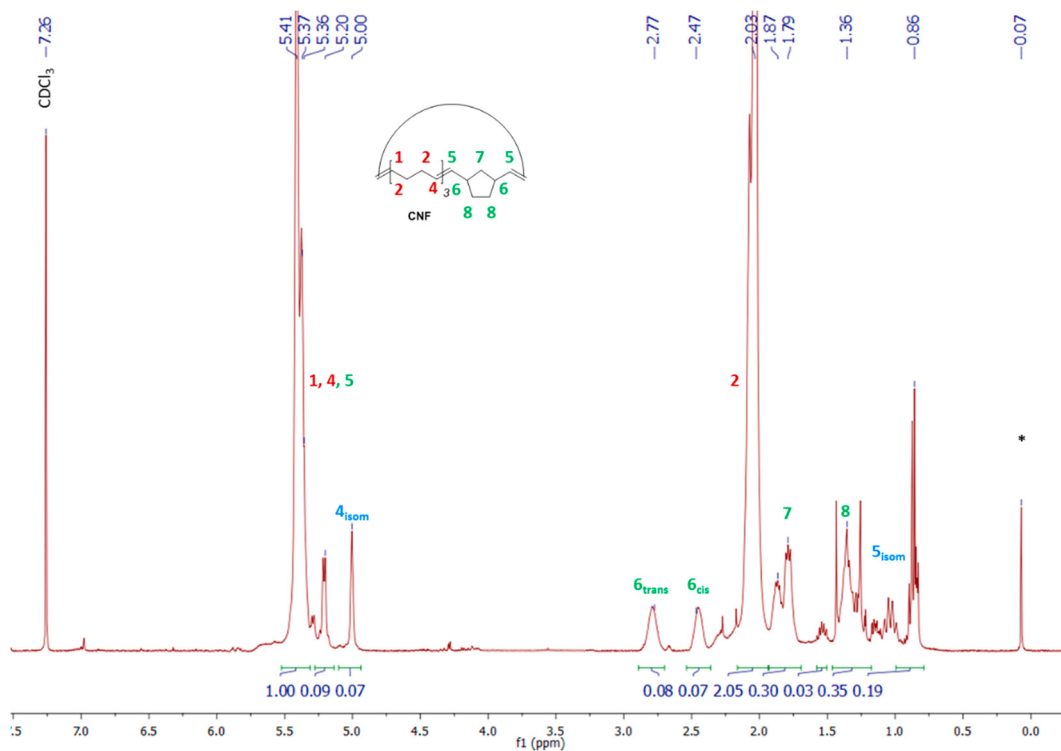


Figure S13. ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a CNF copolymer isolated from an α,ω -bis(dithiocarbonate) P(NB-co-CDT) crude copolymers. (*: δ (ppm) 0.07 residual grease) (Table 4, entry 1).

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