Electronic Supporting Information

From epoxide to cyclodithiocarbonate telechelic polycyclooctene through chain-transfer ring-opening metathesis polymerization (ROMP): precursors to non-isocyanate polyurethanes (NIPUs)

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Synthesis of the bis(oxiran-2-ylmethyl) maleate CTA (4).

General procedure for the chemical modification of PCOE epoxide into dithiocarbonate chain-end groups.

Scheme S1. Attempted ROMP/CM of COE catalyzed by G2 in the presence of DTA-Ac.

Scheme S2. Tandem ROMP/CM/RCM of COE catalyzed by Grubbs' second generation catalyst G2 in the presence of a monofunctional epoxide alkene CTA 1 or 2, showing the possible polymers (FG: glycidyl (meth)acrylate functional group; DF: α,ω -difunctional, MF: α -monofunctional, IMF: isomerized α -monofunctional, LNF: linear non-functional, ILNF: isomerized linear non-functional, CNF: cyclic non-functional).

Scheme S3. Proposed mechanism for the tandem ROMP/CM and concomitant RCM, isomerization (ISOM) and self-metathesis (SM) reactions possibly occurring during the polymerization of a COE mediated by **G2** Ru-alkylidene catalyst and a monofunctionalized alkene CTA, illustrating the formation of all possible polymers.

Scheme S4. Proposed mechanism for the tandem ROMP/CM/RCM of COE catalyzed by Grubbs' second generation catalyst G2 in the presence of symmetrical functionalized alkene CTAs 3–6, showing all the possible polymers (FG: glycidyl functional group; DF: α , ω -difunctional, CNF: cyclic non-functional).

Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of DTC-Ac.

Figure S2. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of DTC-Ac.

Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 2.

Figure S4. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of **2**.

Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 4.

Figure S6. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of 4.

Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 6.

Figure S8. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of 6.

Figure S9. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1** in THF showing IMF PCOE (Table 1, entry 1) (* stands for residual solvent).

Figure S10. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1** in THF showing IMF PCOE (Table 1, entry 1) (* stands for residual grease).

Figure S11. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1**/BZQ, showing MF PCOE (Table 1, entry 6).

Figure S12. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of G2/CTA 1/BZQ showing MF PCOE (Table 1, entry 6).

Figure S13. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 1.

Figure S14. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of **1**.

Figure S15. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of **3**. (* stands for residual water)

Figure S16. ¹³C{¹H} NMR spectrum (100 MHz,CDCl₃, 25 °C) of 3.

Figure S17. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 5.

Figure S18. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of 5.

Figure S19. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/DTC-Ac in THF at 40 °C for 2 h with $[COE]_0/[DTC-Ac]_0/[G2]_0 = 1000:10:1.$

Table S1. Polymerization of COE catalyzed by **G2** in the presence of DTC-OH and DTC-Ac CTAs in THF at 40 °C.

Figure S20. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **1** in THF (Table 1, entry 2).

Figure S21. ¹³C{¹H} NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **1** in THF(Table 1, entry 2).

Figure S22. SEC trace of the polymer sample prepared by polymerization of COE in the presence of G2/CTA 1 in THF (Table 1, entry 2).

Figure S23. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **2** in CH₂Cl₂ (Table 1, entry 8).

Table S2. Polymerization of COE catalyzed by **G2** using CTA **1** and **2** in CH₂Cl₂ at 40 °C for 24 h.^a

Figure S24. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **3** (Table 2, entry 6) (* residual water).

Figure S25. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **3** (Table 2, entry 6).

Figure S26. SEC trace of the polymer sample prepared by polymerization of COE in the presence of G2/CTA 3 in THF (Table 2, entry 3).

Figure S27. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **4** showing DF and possibly CNF PCOEs (Table 2, entry 15).

Figure S28. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of G2/CTA 5 (Table 2, entry 18).

Figure S29. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **5** (Table 2, entry 18).

Table S3. CS₂ functionalization of PCOE-GA₂ in the presence of LiBr at 40 °C in THF for 17 h.

Figure S30. ¹H NMR monitoring (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by reaction of diepoxide telechelic PCOE (PCOE-GA₂) with CS₂ in the presence of 1 equiv. of LiBr for 11 h, showing the conversion of PCOE-GA₂ into PCOE-DTC₂ (Table S3, entry 3). **Figure S31.** ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of a PCOE-DTC₂ sample prepared by reaction of PCOE-GA₂ with CS₂ in the presence of LiBr (Table S3, entry 5).

Figure S32. FTIR spectrum of a PCOE-DTC₂ sample prepared by reaction of PCOE-GA₂ with CS₂ in the presence of LiBr (Table S3, entry 5).

Figure S33. DSC trace (second heating cycle) of the PCOE-DTC₂ sample prepared by reaction of PCOE-GA₂ with CS₂ in the presence of LiBr (Table 3, entry 4).

Figure S34. DSC trace (second heating cycle) of the PCOE-GA₂ sample (Table 3, entry 4).

Figure S35. DSC trace (second heating cycle) of the NIPU sample prepared by reaction of PCOE-DTC₂ with JEFFAMINE EDR-148 in the presence of ethyl acrylate at 23 °C for 24 h in CH₂Cl₂ (Table 3, entry 3).

Figure S36. Thermal degradation profiles of PCOE-DTC₂ (in red) and resulting NIPU sample prepared by reaction of PCOE-DTC₂ with JEFFAMINE EDR-148 in the presence of ethyl acrylate at 23 °C for 24 h in CH₂Cl₂ (in black, Table 3, entry 3).

Synthesis of the bis(oxiran-2-ylmethyl) maleate CTA (4). CTA 4 was synthesized according to the previously reported procedure.⁷³ ¹H NMR (400 MHz; CDCl₃, 25 °C): δ (ppm) 2.66 (m, 2H, OCH₂CHCH₂OC(O)), 2.86 (t, J = 5 Hz, 2H, OCH₂CHCH₂OC(O)), 3.26 (m, 2H, OCH₂CHCH₂OC(O)), 4.02 (dd, J = 5, 12 Hz, 2H, OCH₂CHCH₂OC(O)), 4.54 (dd, J = 3, 12 Hz, 2H, OCH₂CHCH₂OC(O)), 6.31 (s, 2H, CHC(O)) (Figure S5). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 44.7 OCH₂CHCH₂OC(O), 49.1 OCH₂CHCH₂OC(O), 66.0 OCH₂CHCH₂OC(O), 129.9 CHC(O), 164.8 OCH₂CHCH₂OC(O) (Figure S6). HRMS (ESI): C₁₀H₁₂O₆Na [M+Na]⁺: calcd 251.05316; found 251.0531.

General procedure for the chemical modification of PCOE epoxide into dithiocarbonate chain-end groups. To a solution of PCOE-GA₂ (1 equiv., 0.8 g, 0.05 mmol) and lithium bromide (1 equiv., 0.043 g, 0.05 mmol) in THF (10 mL), carbon disulfide (2.2 equiv., 0.015 mL, 0.23 mmol) was added dropwise, and the resulting solution was heated to 40 °C while stirring. After 17 h, it was concentrated under reduced pressure. The recovered residue was precipitated in methanol three times. The solution was filtered and the precipitate was dried under vacuum to give the awaited dithiocarbonate end-functionalized polymer. The isolated PCOE-DTC₂ was characterized by ¹H, ¹³C {¹H} NMR, FTIR, MALDI-ToF mass spectrometry and DSC, analyses (Figures 1–3, S32–S33).



Scheme S1. Attempted ROMP/CM of COE catalyzed by G2 in the presence of DTA-Ac.



Scheme S2. Tandem ROMP/CM/RCM of COE catalyzed by Grubbs' second generation catalyst G2 in the presence of a monofunctional epoxide alkene CTA 1 or 2, showing the possible polymers (FG: glycidyl (meth)acrylate functional group; DF: α,ω -difunctional, MF: α -monofunctional, IMF: isomerized α -monofunctional, LNF: linear non-functional, ILNF: isomerized linear non-functional, CNF: cyclic non-functional).



Scheme S3. Proposed mechanism for the tandem ROMP/CM and concomitant RCM, isomerization (ISOM) and self-metathesis (SM) reactions possibly occurring during the polymerization of a COE mediated by **G2** Ru-alkylidene catalyst and a monofunctionalized alkene CTA, illustrating the formation of all possible polymers.



Scheme S4. Proposed mechanism for the tandem ROMP/CM/RCM of COE catalyzed by Grubbs' second generation catalyst G2 in the presence of symmetrical functionalized alkene CTAs 3–6, showing all the possible polymers (FG: glycidyl functional group; DF: α , ω -difunctional, CNF: cyclic non-functional).

In the presence of a symmetrical difunctional alkene CTA such as 3-6, the overall mechanism is a simpler process as depicted in Scheme S4. As with monofunctional CTAs (Scheme S3), the first step is proposed to involve CM of the ruthenium-alkylidene catalyst with the, in this latter case, CTA featuring two functional groups, giving the functionalized metal-carbene alkylidene species (1), while the initial Ru catalyst bearing a phenyl group (2) may directly proceed to the next step (Scheme S4a). For the sake of clarity, the active catalyst with either a phenyl (1) or CTA-functional group (2) group is noted as species (*i*) with FG =

functional group from the CTA or Ph (Scheme S4a). The ensuing ROMP of COE would then generate the active linear polymer end-capped by FG and the Ru metal center (*ii*, *iii*) (Scheme S4b). At this stage, competitive CM and RCM would lead to DF and CNF PCOEs, respectively. CM between *ii/iii* and the CTA would directly result in DF (Scheme S4c). Also, backbiting from *ii* or *iii*, i.e. the coordinative cyclization of the alkene terminus onto Ru (RCM), would generate CNF (Scheme S4d), while CNF could undergo a CM with the ruthenium-alkylidene *i* to regenerate *ii/iii* (Scheme S4e).



Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of DTC-Ac.



Figure S2. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of DTC-Ac.



Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 2.



Figure S4. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of 2.



Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 4.



Figure S6. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of 4.



Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 6.



Figure S8. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, CDCl₃, 25 °C) of 6.



Figure S9. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1** in THF showing IMF PCOE (Table 1, entry 1) (*, \blacklozenge stand for residual solvents and unidentified impurities).



prepared by ROMP/CM of COE in the presence of **G2**/CTA **1** in THF showing IMF PCOE (Table 1, entry 1) (* stands for residual grease).



Figure S11. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1**/BZQ, showing MF PCOE (Table 1, entry 6) (* stands for residual water and grease).



Figure S12. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **1**/BZQ showing MF PCOE (Table 1, entry 6).



Figure S13. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 1.



Figure S14. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of **1**.



Figure S15. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of **3**. (* stands for residual water)



Figure S16. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz,CDCl₃, 25 °C) of 3.



Figure S17. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 5.



Figure S18. ¹³C{¹H} NMR spectrum (100 MHz, CDCl₃, 25 °C) of **5**.



Figure S19. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of G2/DTC-Ac in THF at 40 °C for 2 h with $[COE]_0/[DTC-Ac]_0/[G2]_0 = 1000:10:1.$

Table S1. Polymerization of COE catalyzed by G2 in the presence of DTC-Ac and 5CC-Ac

CTAs in	THF	at 40	°C.
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Entry	[COE] ₀ /[DTC-Ac] ₀ / [5CC-Ac] ₀ /[G2] ₀ ^a	Conv. 5CC-Ac (%)	MF ^b (mol%)	IMF ^b (mol%)	DF ^b (mol%)	M _{n,theo} ^c (g.mol ⁻¹)	$M_{n,NMR}^{d}$ (g.mol ⁻¹)	$M_{ m n,sec}^{e}$ (g.mol ⁻¹)	Ðме
1	1000:0:20:1	100	0	100	0	5 510	8 000	15 200	2.39
2	1000:10:20:1	50	100	0	0	11 200	10 100	17 300	2.26
3	2000:40:70:1	0	0	0	0	220 200 ^f	-		-

^{*a*} General conditions: Catalyst = 5.9 µmol, [COE + CTA]₀ = 1.8 mol.L⁻¹; COE and CTA conversion observed by ¹H NMR analysis = 100% for COE and 0% for DTC-Ac respectively. ^{*b*} Relative molar ratio as determined by ¹H NMR analysis of MF = α -functional PCOE ; IMF = α -functional isomerized PCOE; DF = α , ω -difunctional PCOE (Scheme S2). ^{*c*} Theoretical molar mass value calculated from $M_{n,theo} = \{DF\% \times ([COE]_0 \times Conv.coe) \times M_{COE} / (\frac{1}{2} [CTA]_0 \times Conv.cTA)\} + \{(MF\% + IMF\%) \times ([COE]_0 \times Conv.coe \times M_{COE}) / ([CTA]_0 \times Conv.cTA)\} + M_{CTA}, with <math>M_{COE} = 110 \text{ g.mol}^{-1}, M_{DTC-Ac} = 204 \text{ g.mol}^{-1}, M_{SCC-Ac} = 172 \text{ g.mol}^{-1}, on the basis of the formation of only MF, IMF and DF without taking into account any LNF, CNF and ILNF. ^{$ *d*} Experimental molar mass value determined by ¹H NMR analysis (refer to the Experimental Section).^{*e* $} Number-average molar mass (<math>M_{n,SEC}$) and dispersity ($D_M = M_w/M_n$) values determined by SEC vs polystyrene standards (uncorrected M_n values) in THF at 30 °C. ^{*f*} Theoretical molar mass value calculated from $M_{n,theo} = [COE]_0 / [G2]_0 \times Conv.coe \times M_{COE}$, with $M_{COE} = 110 \text{ g.mol}^{-1}$, on the basis of the formation of only LNF and CNF PCOE.



Figure S20. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **1** in THF (Table 1, entry 2).



Figure S21. ¹³C{¹H} NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample

prepared by polymerization of COE in the presence of G2/CTA 1 in THF(Table 1, entry 2).



Figure S22. SEC trace of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **1** in THF (Table 1, entry 2).



Figure S23. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **2** in CH₂Cl₂ (Table 1, entry 8).

 Table S2. Polymerization of COE catalyzed by G2 using CTA 1 and 2 in CH₂Cl₂ at 40 °C for

 24 h.^a

Entry	[COE] ₀ /[2] ₀ / [1] ₀ /[G2] ₀ ^a	\mathbf{MF}^{b}	IMF ^b	DF ^b	$M_{n,theo}{}^{c}$	$M_{n,NMR}^{d}$	
		(mol%)	(mol%)	(mol%)	(g.mol ⁻¹)	(g.mol ⁻¹)	
1	2000:50:54	0	100	0	4500	5900	
2	2000:80:20	0	100	0	11 100	11 400	
3	2000:20:80	0	100	0	2800	2900	

^{*a*} General conditions: Catalyst = 5.9 µmol, $[COE + CTA]_0 = 1.8 \text{ mol.L}^{-1}$; COE and CTA conversion observed by ¹H NMR analysis = 100% for **1** and 100% and 0% for **2**, respectively. ^{*b*} Relative molar ratio as determined by ¹H NMR analysis of MF = α -functional PCOE ; IMF = α -functional isomerized PCOE; DF = α, ω -difunctional PCOE. ^{*c*} Theoretical molar mass value calculated from $M_{n,theo} = \{DF\% \times ([COE]_0 \times Conv._{COE}) \times M_{COE} / (!_2 [CTA]_0 \times Conv._{CTA})\} + \{(MF\% + IMF\%) \times ([COE]_0 \times Conv._{COE} \times M_{COE}) / ([CTA]_0 \times Conv._{CTA})\} + M_{CTA}$, with $M_{COE} = 110 \text{ g.mol}^{-1}$, $M_1 = 128 \text{ g.mol}^{-1}$, $M_2 = 142 \text{ g.mol}^{-1}$, on the basis of the formation of only MF, IMF and DF without taking into account any LNF, CNF and ILNF. ^{*d*} Experimental molar mass value determined by ¹H NMR analysis (refer to the Experimental Section).



Figure S24. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **3** (Table 2, entry 6) (* residual water).



Figure S25. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **3** (Table 2, entry 6).



Figure S26. SEC trace of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **3** in THF (Table 2, entry 3).



Figure S27. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **4** showing DF and possibly CNF PCOEs (Table 2, entry 15).



Figure S28. ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of **G2**/CTA **5** (Table 2, entry 18).



Figure S29. ¹³C{¹H} NMR spectrum (125 MHz, CDCl₃, 25 °C) of the polymer sample prepared by polymerization of COE in the presence of G2/CTA 5 (Table 2, entry 18).

Table S3. CS_2 functionalization of PCOE-GA₂ in the presence of LiBr at 40 °C in THF for 17 h.

Entry	[CS ₂] ₀ /[GA] ₀ ^a	[LiBr]0 ^b	Yield ^c (%)	% DTC function
1	0.5	0.25	0	-
2	0.75	0.5	0	-
3	1.1	0.5	100	100
4	1.1	0.5	100	100
5	1.1	1	100	100
6	1.1	1.5	0	-
7	1.1	2.0	0	
8	1.2	1.0	100	100
9	2.0	0.5	100	100

^a $[CS_2]_0/[GA]_0$ ratio corresponding to the number of CS_2 equiv. per epoxide function. ^b LiBr initial feed equivalent per epoxide function. ^c Yield of the GA conversion into DTC.



Figure S30. ¹H NMR monitoring (400 MHz, CDCl₃, 25 °C) of the polymer sample prepared by reaction of diepoxide telechelic PCOE (PCOE-GA₂) with CS₂ in the presence of 1 equiv. of LiBr for 11 h, showing the conversion of PCOE-GA₂ into PCOE-DTC₂ (Table S3, entry 3).



prepared by reaction of PCOE-GA2 with CS2 in the presence of LiBr (Table S3, entry 5).



Figure S32. FTIR spectrum of a PCOE-DTC₂ sample prepared by reaction of PCOE-GA₂ with CS₂ in the presence of LiBr (Table S3, entry 5).



Figure S33. DSC trace (second heating cycle) of the PCOE-DTC₂ sample prepared by reaction of PCOE-GA₂ with CS₂ in the presence of LiBr (Table 3, entry 4).



Figure S34. DSC trace (second heating cycle) of the PCOE-GA2 sample (Table 3, entry 4).



Figure S35. DSC trace (second heating cycle) of the NIPU sample prepared by reaction of PCOE-DTC₂ with JEFFAMINE EDR-148 in the presence of ethyl acrylate at 23 °C for 24 h in CH₂Cl₂ (Table 3, entry 3).



Figure S36. Thermal degradation profiles of PCOE-DTC₂ (in red) and resulting NIPU sample prepared by reaction of PCOE-DTC₂ with JEFFAMINE EDR-148 in the presence of ethyl acrylate at 23 °C for 24 h in CH₂Cl₂ (in black, Table 3, entry 3).