Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

ε-Thionocaprolactone: an accessible monomer for preparation of degradable poly(vinyl esters) by radical ring-opening polymerization

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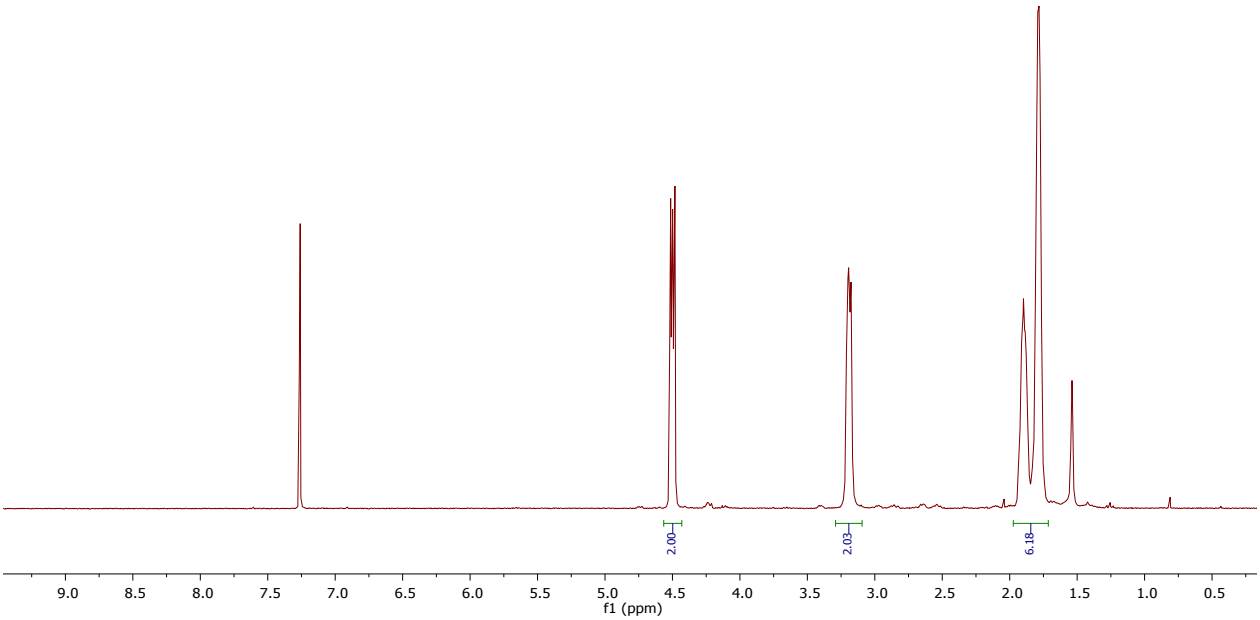

Figure S1. ^{1}H NMR ($CDCl_3$) of TCL

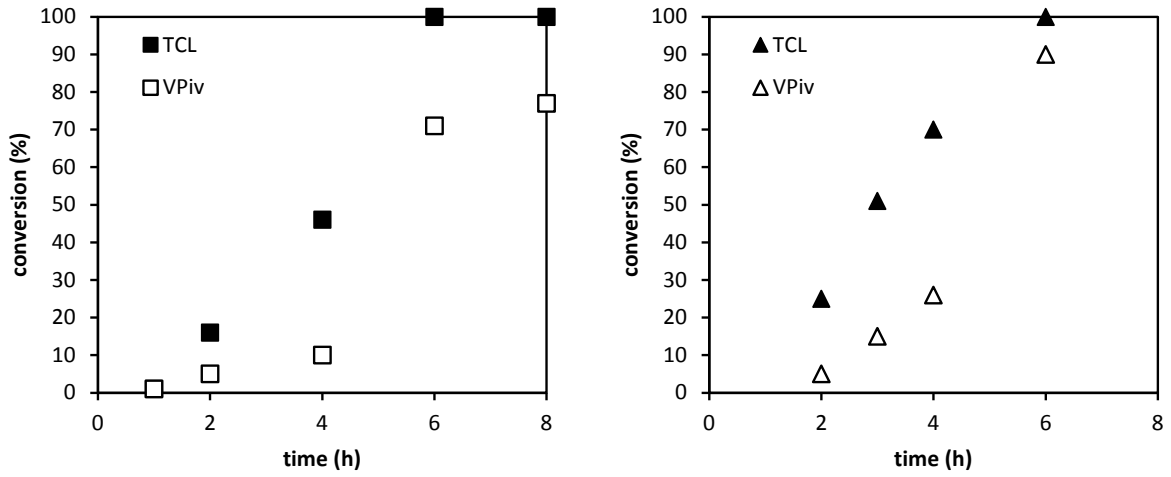

Figure S2. VPiv/TCL, conventional (a) and RAFT (b) polymerizations, conversion vs time**.**

Table S1. RAFT bulk copolymerization of VAc and TCL (90/10 mol. %) mediated by xanthate XA1 at 70°C. $[AIBN]_0$=5.5 mmol L^{-1}, $[XA1]_0$=10.2 mmol L^{-1}, $[VAc]_0$=0.95 mol L^{-1}, $[TCL]_0$=0.11 mol L^{-1}.

Entry	Time h	$Conv_{TCL}$[a]	$Conv_{VAc}$[a]	F_{TCL}[a]	M_n[b] kg mol^{-1}	$M_{n,th}$[c] kg mol^{-1}	$Đ$[b]
1[e]	6	1	0.85	0.12	22.8 (35.1)[d]		2.84
2	1	0.17	0.03	0.38	0.2	0.66	2.7
3	2	0.27	0.09	0.25	0.8	1.25	2.6
4	3	0.51	0.20	0.22	1.4	2.41	2.3
5	4	0.69	0.29	0.21	2.0	3.33	2.2
6	5	0.83	0.41	0.18	2.7	4.42	2.1
7	6	0.93	0.57	0.15	3.6	5.76	2.2
8	7	0.98	0.69	0.14	6.0	6.73	1.54
9	16	1	0.93	0.11	7.5	8.57	1.61

[a] Determined by ^{1}H NMR

[b] Determined by SEC in DMF +10 mmol LiBr with PSt calibration

[c] $M_{n\,th} = ([TCL]_0/[XA1]_0) \times conversion(TCL) \times M_w(TCL) + ([VA]_0/[XA1]_0) \times conversion(VAc) \times M_w(M) + M_w(XA1)$

[d]Determined by SEC-RI-MALS in DMF+10 mmol LiBr (dn/dc=0.046 mL g^{-1}).

[e] RAFT-free control experiment

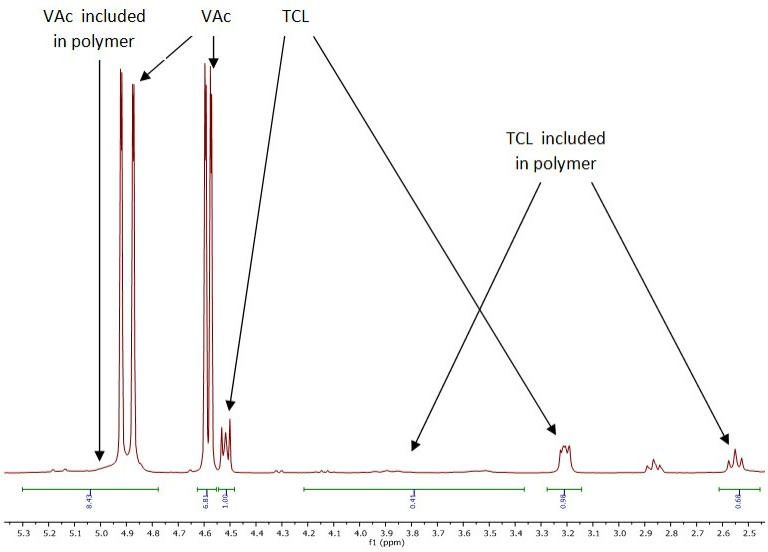

Figure S3. ^{1}H NMR ($CDCl_3$) of VAc/TCL (90/10) crude mixture after polymerization. VAc and TCL conversions (X) were determined from the following equations:

$$X_{VAc} = \frac{\int_{4.80}^{5.30} CH^{polymer+monomer} - \int_{4.55}^{4.63} CH^{monomer}}{\int_{4.80}^{5.30} CH^{polymer+monomer}}$$

$$X_{TCL} = \frac{\int_{3.40}^{4.20} CH_2^{closed\ TCl} + \int_{2.45}^{2.60} CH_2^{opened\ TCl}}{\int_{4.48}^{4.55} CH_2^{monomer\ TCl} + \int_{3.40}^{4.20} CH_2^{closed\ TCl} + \int_{2.45}^{2.60} CH_2^{opened\ TCl}}$$

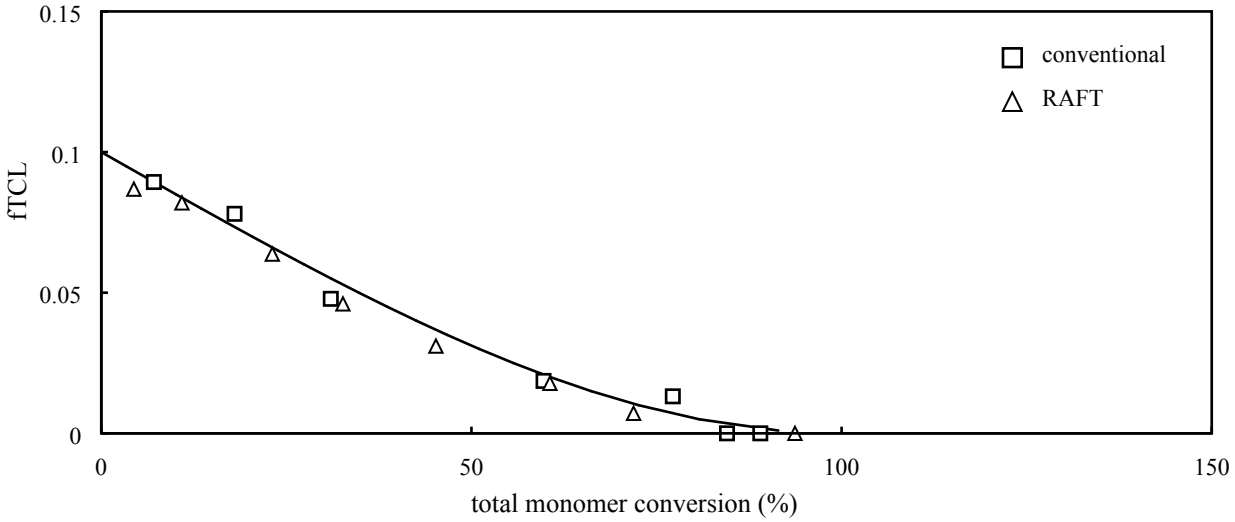

Figure S4. Copolymerization kinetics of vinyl acetate and TCL (f_{TCL} = 0.1). Evolution of f_{TCL} with total monomer conversion under RAFT and conventional radical conditions. Line represents terminal model prediction for r_{TCL} = 3, r_{VAc} = 0.3

Table S2. Effect of XA1 concentration in RAFT bulk copolymerization of VPiv and TCL (90/10 mol. %) at 70°C. $[AIBN]_0$= 71 mmol L^{-1}, $[VPiv]_0$= 6.4 mol L^{-1}, $[TCL]_0$= 0.71 mol L^{-1}.

Entry	$[XA1]_0$ mol L^{-1}	Time h	X_{TCL}[a]	X_{VPiv}[a]	F_{TCL}[a]	M_n[b] kg mol^{-1}	$M_{n,\ th}$[c] kg mol^{-1}	$Đ$[b]
1[d]	0	8	1	0.77	0.13	35.5		2.6
2	0.038	7	1	0.95	0.10	15.6	23.3	1.87
3	0.076	7	1	0.95	0.10	11.2	11.6	1.70
4	0.156	6	1	0.90	0.11	5.5	5.8	1.49

[a] Determined by ^{1}H NMR.

[b] Determined by SEC in THF with PMMA calibration

[c] $M_{n\ th}$ = M_w(XA1) + ($[VPiv]_0/[XA1]_0$) × $Conv_{VPiv}$ × M_w(VPiv) +($[TCL]_0/[XA1]_0$) × $Conv_{TCL}$ × M_w(TCL).

[d] 2-mercaptopropionic acid ethyl ester *O*-ethyl dithiocarbonate[1] RAFT agent was used instead of XA1.

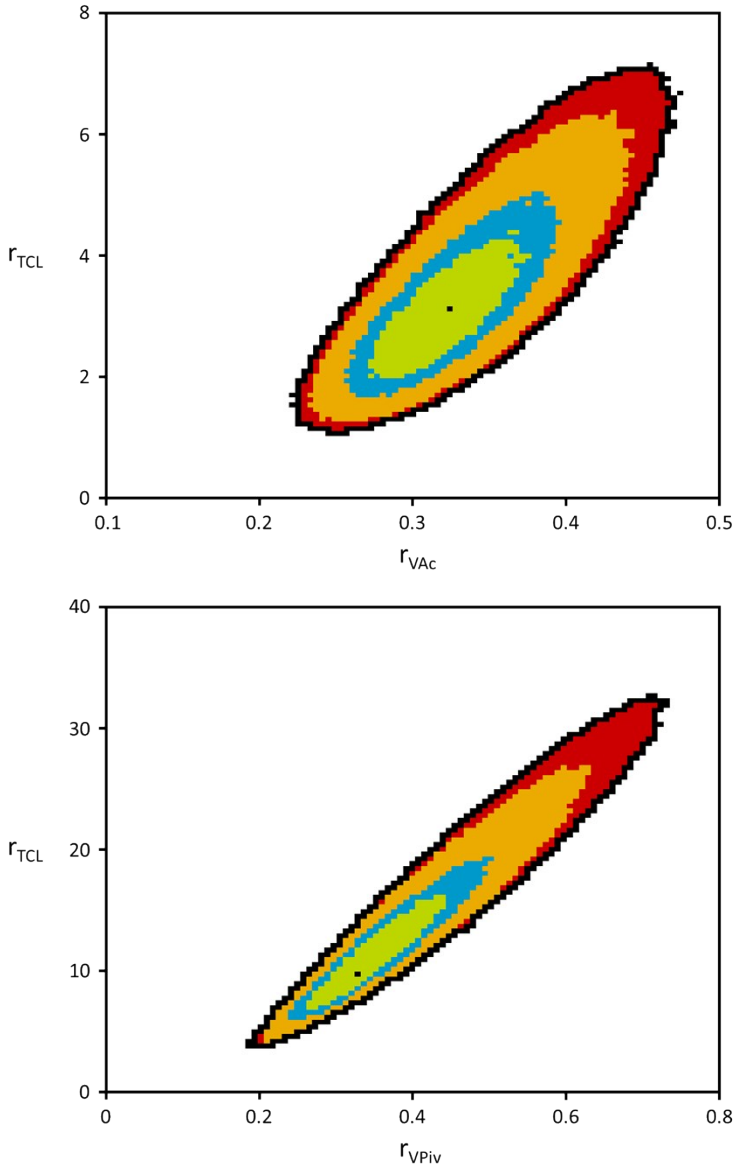

Figure S5. 95% joint confidence regions for r_{VAc}/r_{TCL} (top) and r_{VPiv}/r_{TCL} (bottom). Internal contours represent 90%, 70% and 50% joint confidence regions. Point estimates are (3.0, 0.32) (r_{TCL}, r_{VAc}) and (9.6, 0.33) (r_{TCL}, r_{VPiv}).

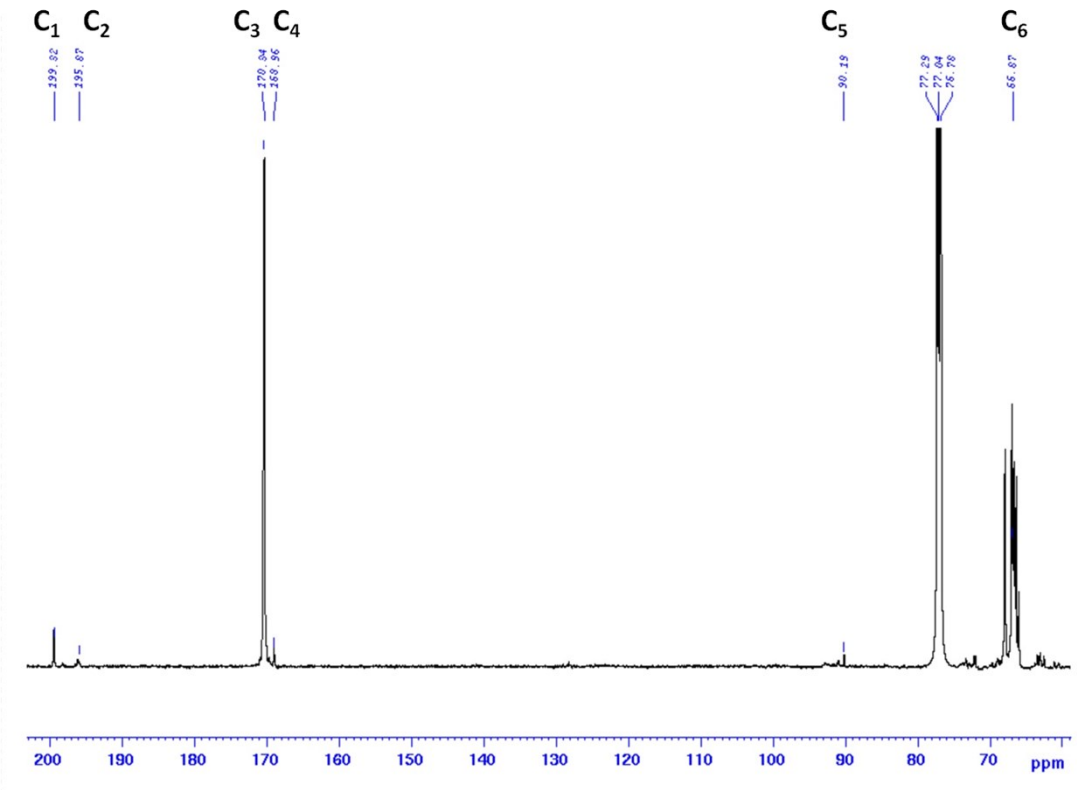

Figure S6. ^{13}C NMR ($CDCl_3$) of a TCL-VAc copolymer (Table S1 entry 1) and identifications of main signals.

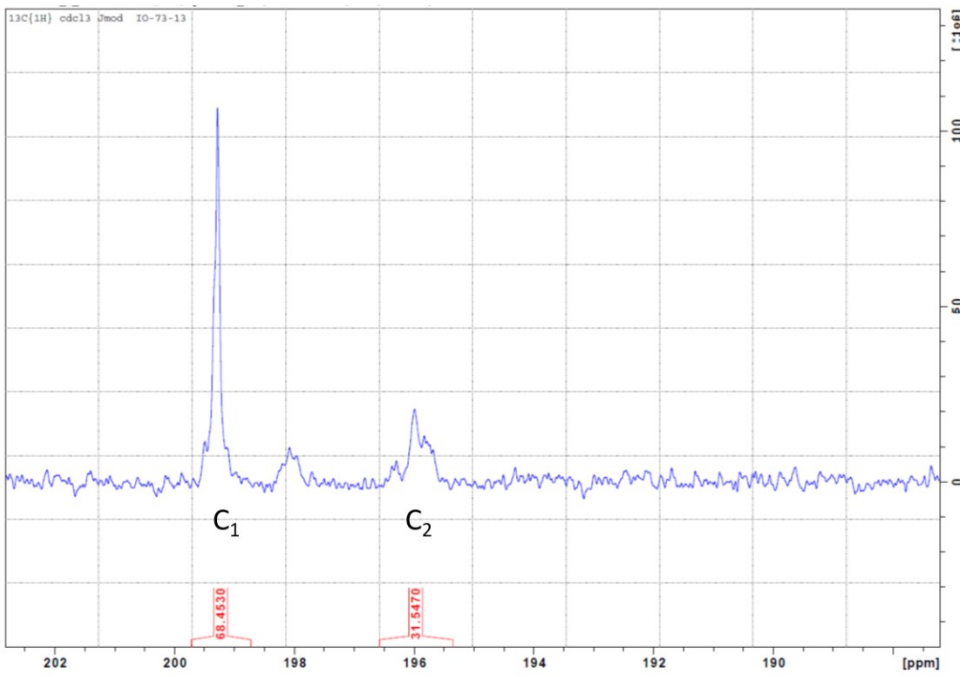

Figure S7. ^{13}C NMR ($CDCl_3$) in the region of TCL carbonyl groups in the polymer (Table S1 entry 1).

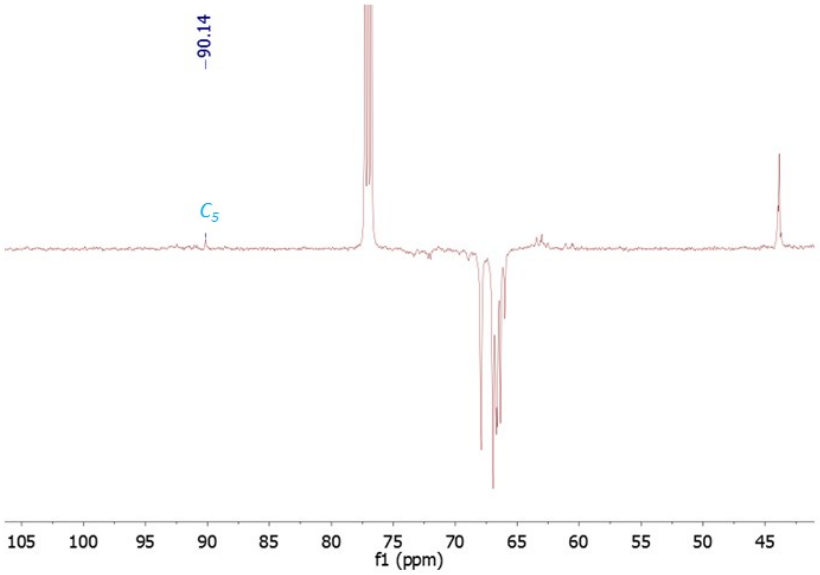

Figure S8. ^{13}C j-mod NMR ($CDCl_3$). Signal **C_5** in the polymer (Table S1 entry 1).

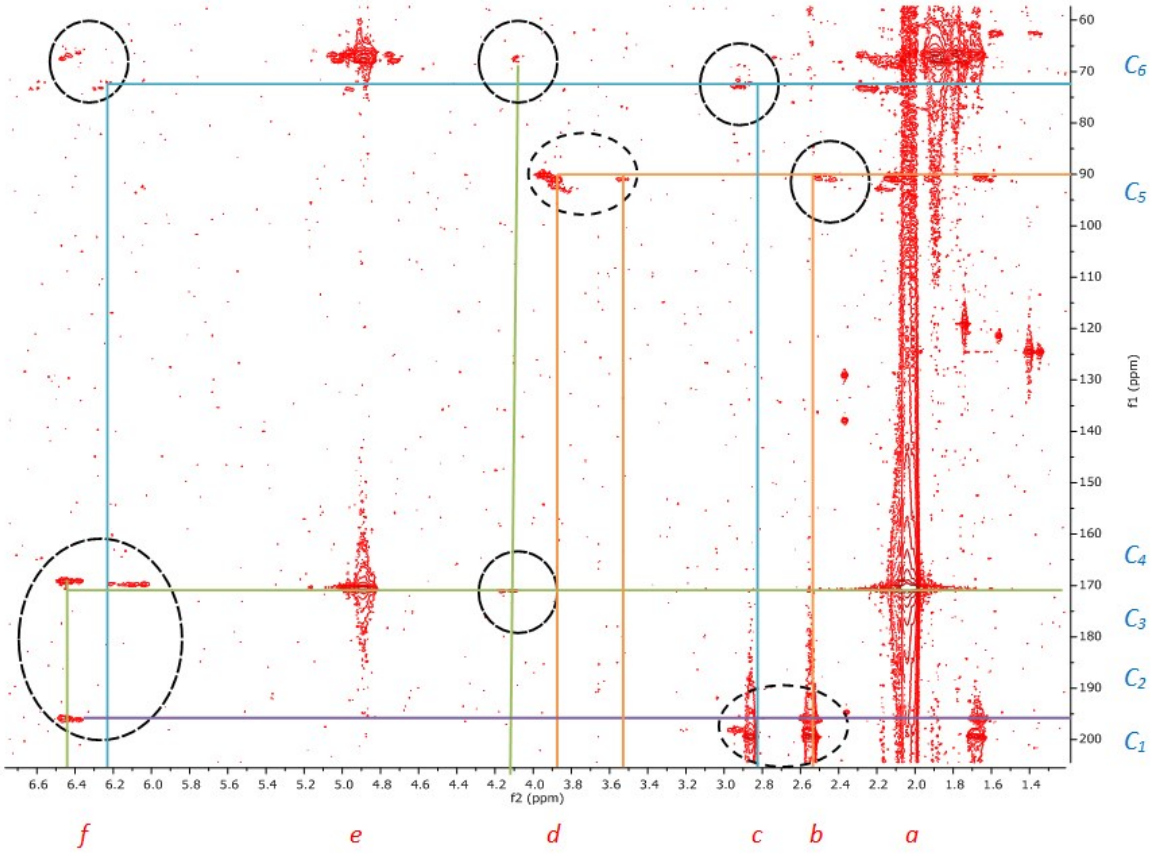

Figure S9. HMBC 2D NMR of a copolymer TCL-VAc copolymer (Table S1 entry 1), In circles are the main correlation plots.

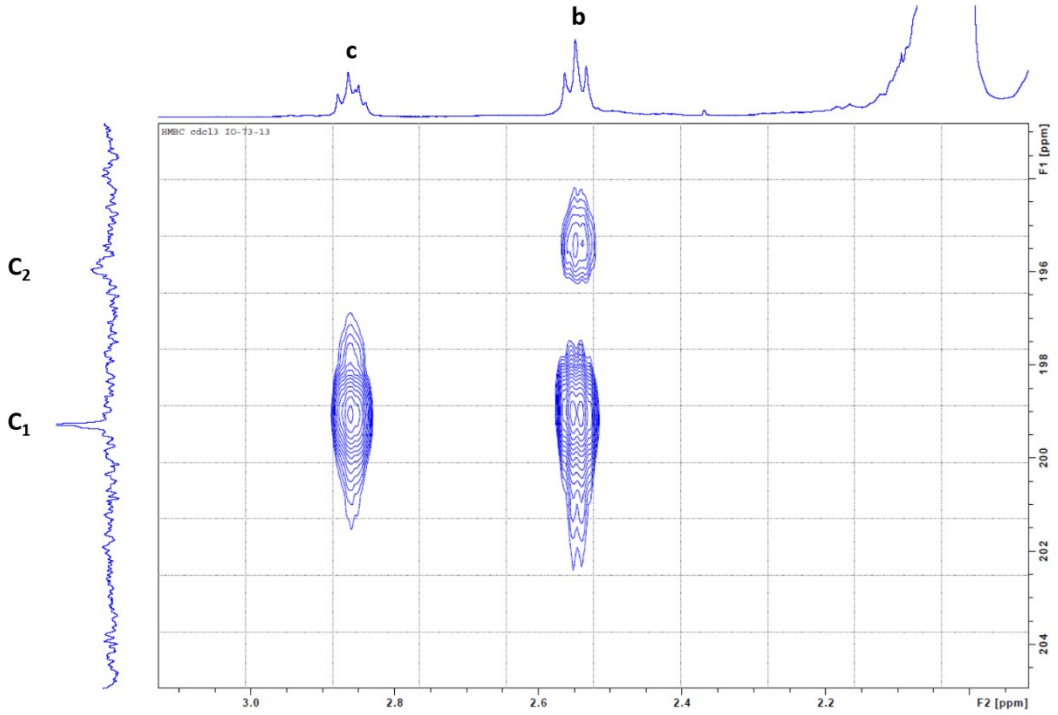

Figure S10. $^{1}H/^{13}C$ 2D NMR HMBC ($CDCl_3$). Correlation ***c*-C_1** and ***b*-C_1/C_2** in the copolymer (Table S1 entry 1).

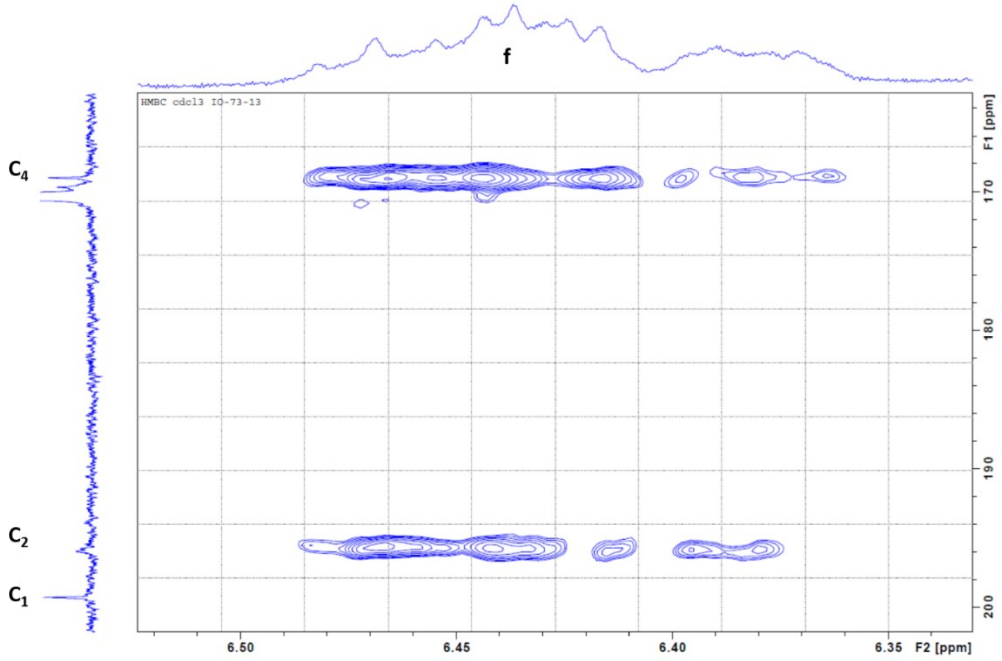

Figure S11. $^{1}H/^{13}C$ 2D NMR HMBC ($CDCl_3$). Correlation ***f*-C_2/C_4** in the copolymer (Table S1 entry 1).

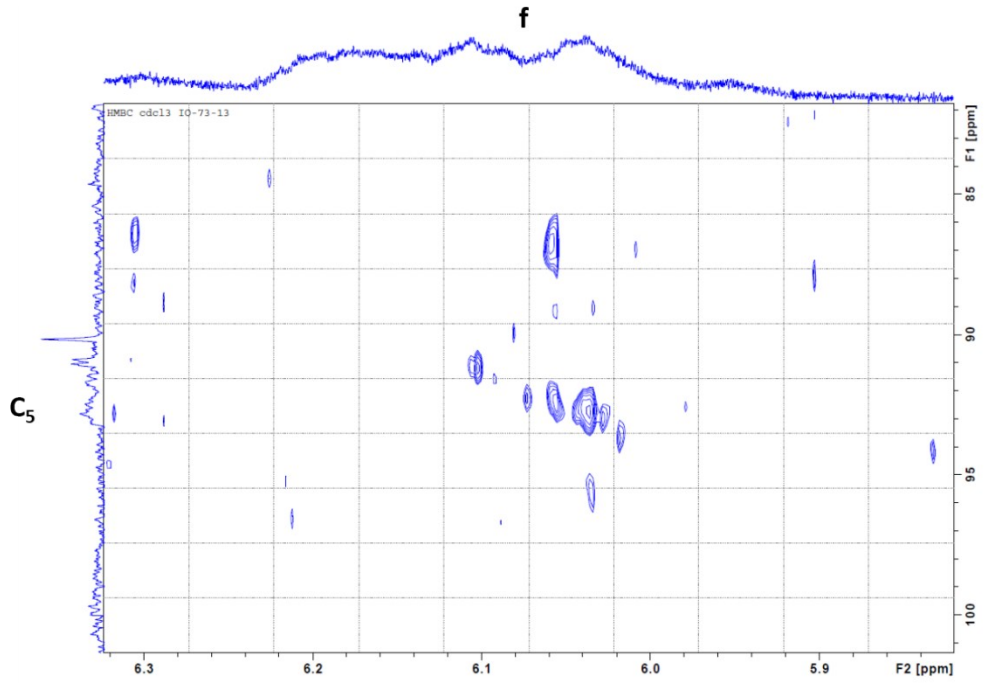

Figure S12. $^{1}H/^{13}C$ 2D NMR HMBC ($CDCl_3$). Correlation **f-C_5** in the copolymer (Table S1 entry 1).

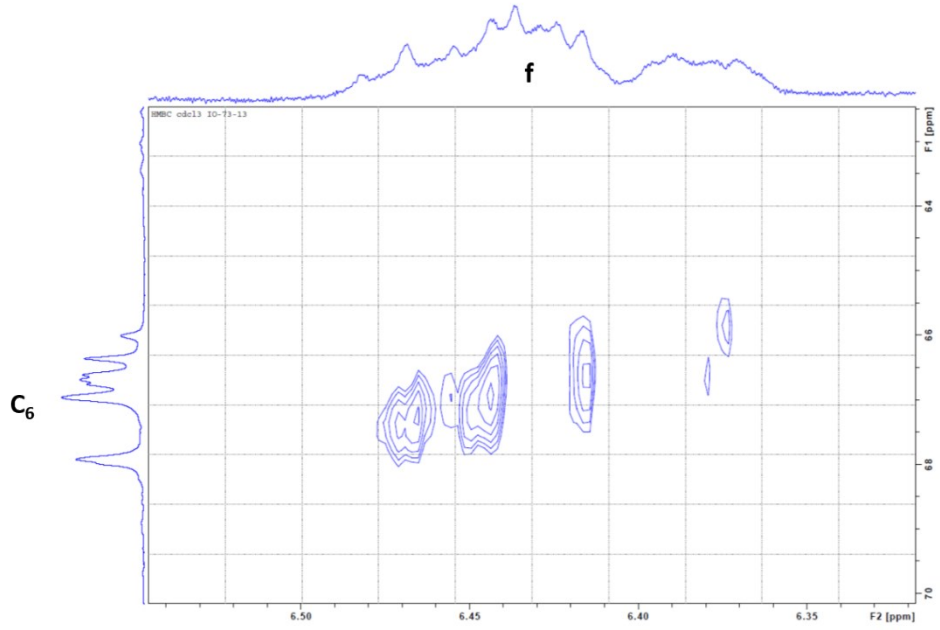

Figure S13. $^{1}H/^{13}C$ 2D NMR HMBC ($CDCl_3$). Correlation **f-C_6** in the copolymer (Table S1 entry 1).

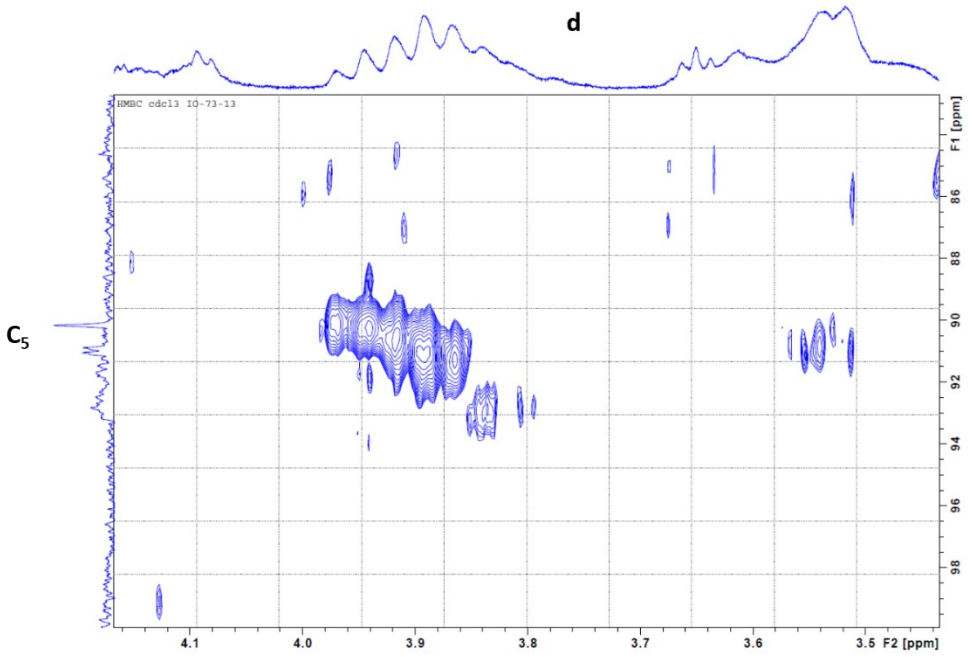

Figure S14. $^{1}H/^{13}C$ 2D NMR HMBC ($CDCl_3$). Correlation **d-C_5** in the copolymer (Table S1 entry 1).

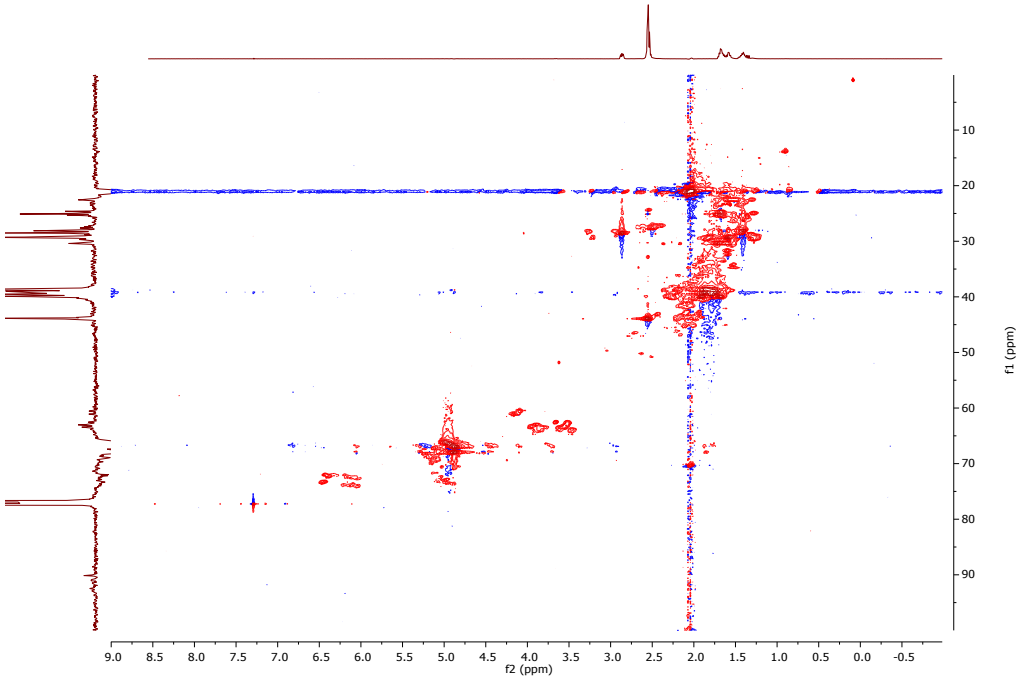

Figure S15. $^{1}H/^{13}C$ 2D NMR HSQC ($CDCl_3$) of TCL-VAc copolymer (Table S1 entry 1), no correlation in the region 80-100 ppm for ^{13}C NMR, meaning that signals (C_5) which appear correspond to quaternary carbon as in TCL_{closed}.

Table S3. Macromolecular characteristics of PVPiv and P(VPiv-*co*-TCL) used in the degradability study. Reaction temperature=70°C.

Entry	Polymer	$[Monomer]_0/[XA1]_0$	X_{TCL}[d]	X_{VPiv}[d]	F_{TCL}[d]	M_n[e] kg mol^{-1}	$M_{n,th}$[f] kg mol^{-1}	$Đ$[e]
1[a]	PVPiv	152	-	98	-	26.6	19.3	1.4
2[b,g]	P(VPiv-*co*-TCL)	183	0.93	0.93	0.1	8.0	23.0	1.8
3[c,g]	P(VPiv-*co*-TCL)	46.1	1	0.92	0.11	4.5	5.7	1.7

[a] in bulk. 0.5% mol. AIBN / VPiv. f_{TCL}=0.1.

[b] in 1,4-dioxane/ethyl acetate (80/20 w/w), 50 wt%. monomers in solution. 0.5% mol. AIBN / monomers t=24 h.

[C] in bulk. 2% mol. AIBN / VPiv. f_{TCL}=0.1, t= 18 h.

[d] Determined by ^{1}H NMR

[e] Determined by SEC in THF with PMMA calibration

[f] $M_{n\,th} = ([TCL]_0/[XA1]_0) \times conversion(TCL) \times M_w(TCL) + ([VP]_0/[XA1]_0) \times conversion(VP) \times M_w(M) + M_w(XA1)$..

[g] 2-mercaptopropionic acid ethyl ester *O*-ethyl dithiocarbonate[1] RAFT agent was used instead of XA1.

Table S4. Macromolecular characteristics of PVPiv and P(VPiv-*co*-TCL) before and after chemical degradation.

Entry	*Sample*	*Degradation*	M_n[a] kg mol^{-1}	$Đ$[a]
1	PVPiv	Before	26.6	1.40
		After	25.3	2.08
2[b]	P(VPiv-*co*-TCL)	Before	8.0	1.8
		After	0.4	4.76
3[b]	P(VPiv-*co*-TCL)	Before	4.5	1.70
		After	0.5	3.3

[a] Determined by SEC in THF with PMMA calibration

[b] 2-mercaptopropionic acid ethyl ester *O*-ethyl dithiocarbonate[1] RAFT agent was used instead of XA1.

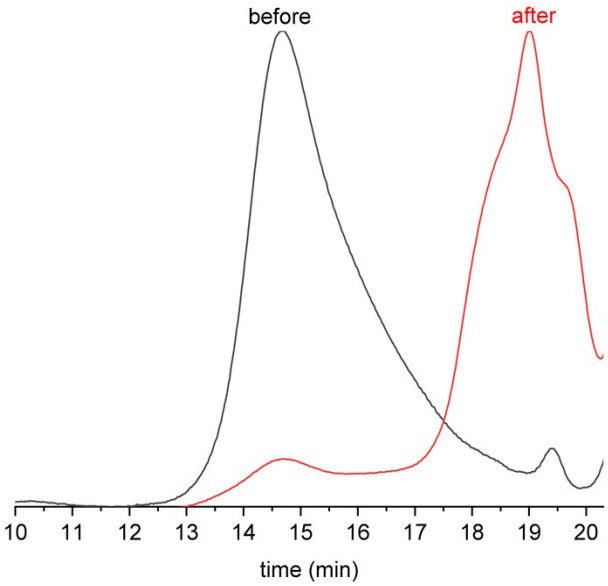

Figure S16. Comparison of SEC chromatograms of P(VPiv-*co*-TCL) before and after treatment with a large excess of isopropylamine (Table S4, entry 3). Chromatograms for entries 1 and 2 of Table S4 are illustrated in Figure 5 of the manuscript.

References

[1] M. Destarac, C. Brochon, J-M. Catala, A. Wilczewska, S.Z.Zard, *Macromol. Chem. Phys.* **2002,** *203*, 2281-2289.