Novel Elastic Rubbers from CO_2-based Polycarbonates

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Supporting Information

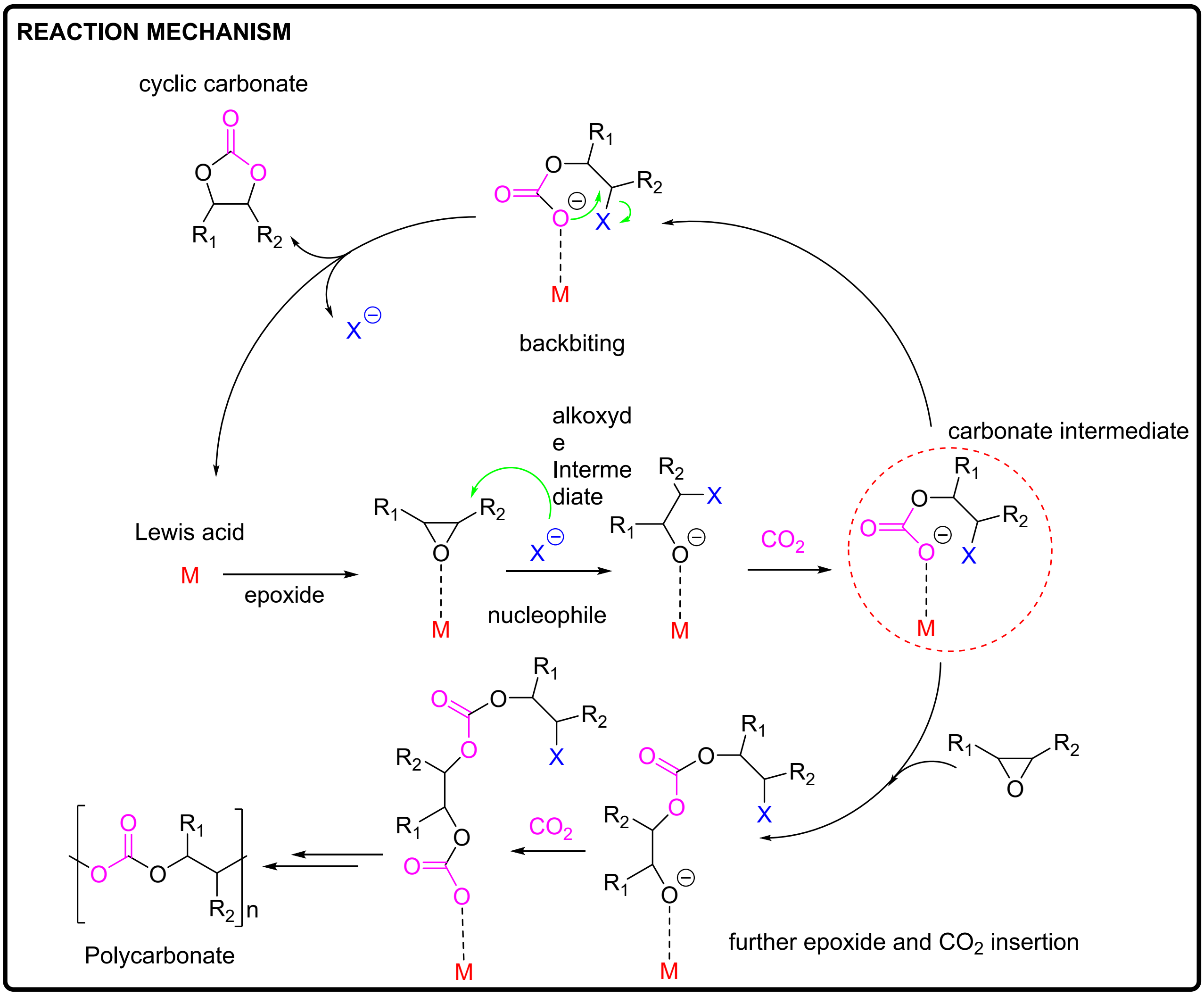


Figure S1. Proposed reaction mechanism for the coupling reaction between carbon dioxide and epoxides.

High-throughput reactor

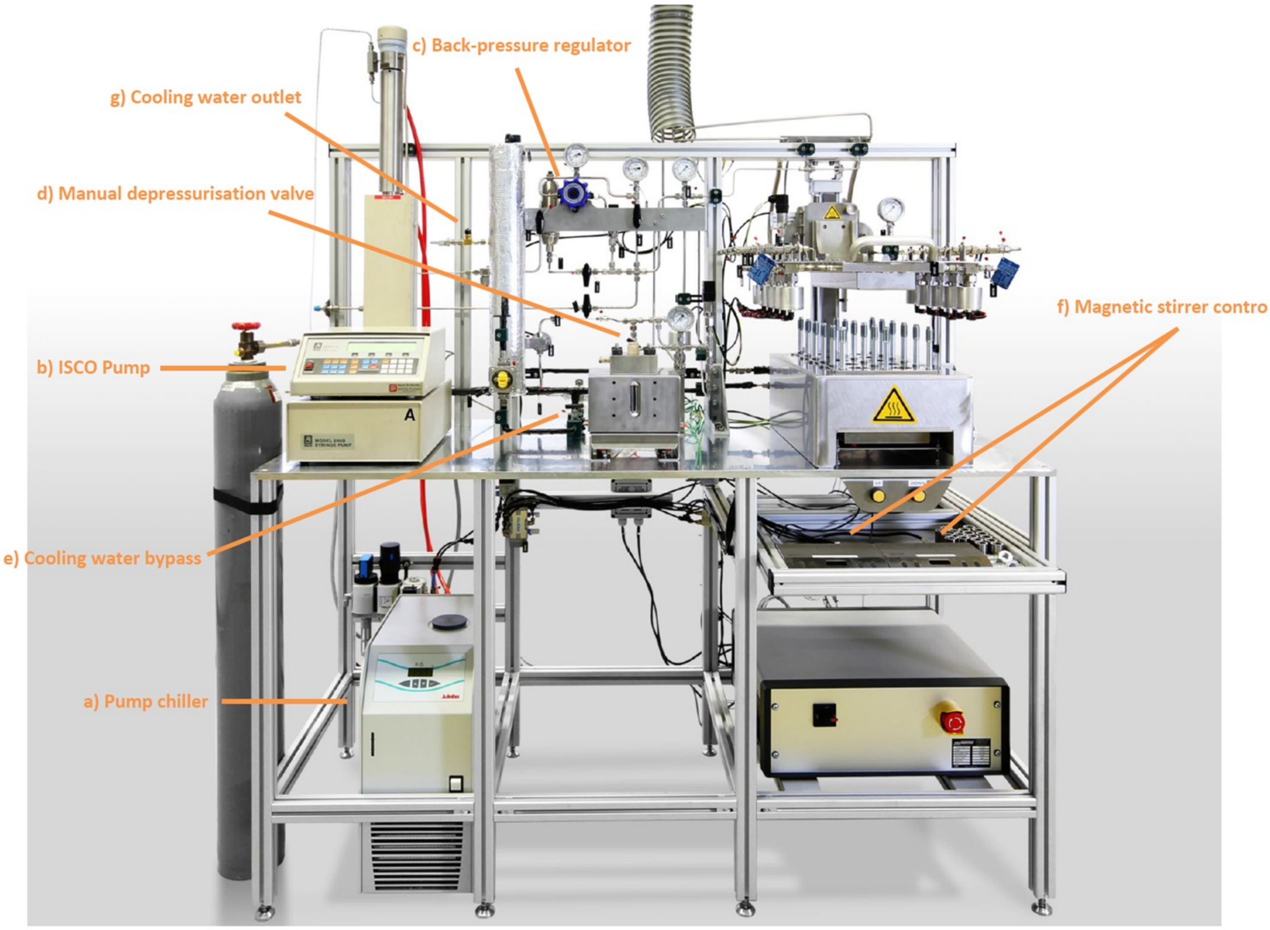


Figure S2. High-throughput unit used to perform the reactions with CO_2.

Duplicate and triplicate tests for the copolymerisation and terpolymerisation reactions

Table S1. Repeated copolymerisation and terpolymerisation tests showing the degree of reproducibility.

Entry	Long alkyl chain epoxide	Unsaturated epoxide	Epoxides ratio	Conv %[a]	Sel %[b]	PC:EL
1	1,2-epoxyhexane		100:0	95	93	82:18
2	1,2-epoxyhexane		100:0	96	89	73:27
3	1,2-epoxyoctane		100:0	99	81	89:11
4	1,2-epoxydecane		100:0	83	93	86:14
5	1,2-epoxydodecane		100:0	93	85	86:14
6	1,2-epoxydodecane	AGE	95:5	95/>99	96	92:8
7	1,2-epoxydodecane	AGE	80:20	90/95	97	95:5
8	1,2-epoxydodecane	AGE	80:20	98/99	98	92:8
	1,2-epoxydodecane	AGE	80:20	98/>99	98	89:11
9	1,2-epoxydodecane	AGE	50:50	99/>99	99	90:10
10		AGE	0:100	99	99	>99:00
11		AGE	0:100	99	99	>99:00
12	1,2-epoxydecane	AGE	95:05	97/>99	98	93:7
13	1,2-epoxydecane	AGE	95:5	94/>99	97	94:6
14	1,2-epoxydecane	AGE	80:20	93/97	96	93:7
15	1,2-epoxydecane	AGE	80:20	93/98	99	90:10
	1,2-epoxydecane	AGE	80:20	95/99	98	88:12
	1,2-epoxydecane	AGE	80:20	>99/>99	>99	93:7
16	1,2-epoxydecane	AGE	50:50	97/95	>99	85:15
17	1,2-epoxydecane	AGE	95:05	97/>99	98	93:7
18	1,2-epoxyoctane	AGE	80:20	98/>99	97	91:9
	1,2-epoxyoctane	AGE	80:20	>99/>99	99	93:7
19	1,2-epoxyoctane	AGE	95:5	>99/>99	98	93:7
20	1,2-epoxyoctane	AGE	50:50	>99/99	>99	88:12
21	1,2-epoxyhexane	AGE	80:20	99/>99	97	94:6
22	1,2-epoxyhexane	AGE	95:5	>99/>99	97	93:7
23	1,2-epoxyhexane	AGE	50:50	>99/>99	>99	92:8

All the tests were performed by adding 30 mmol of epoxide(s), 3 mmol of mesitylene (IS), 0.5 mol % of Al complex and 0.25 mol % of PPNCl (2:1 ratio). The reactions were all performed at 80 bar, 45 °C for 24h. [a] Conversion of the epoxide. [b] Selectivity of the reaction towards the synthesis of PC over CC.

NMR and FT-IR characterisation of the products of the copolymerisations and terpolymerisations involving AGE and 1,2-epoxyhexane

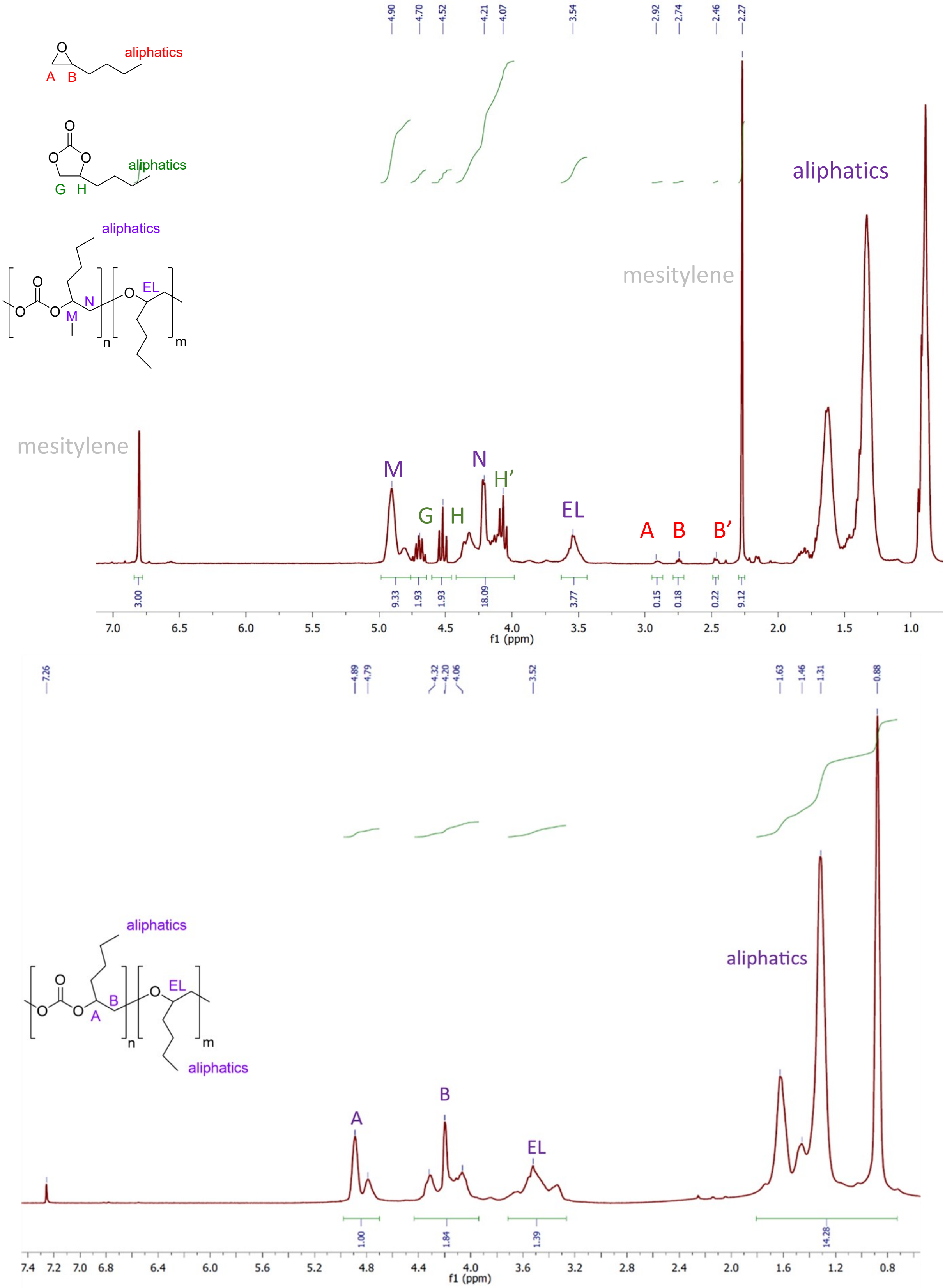
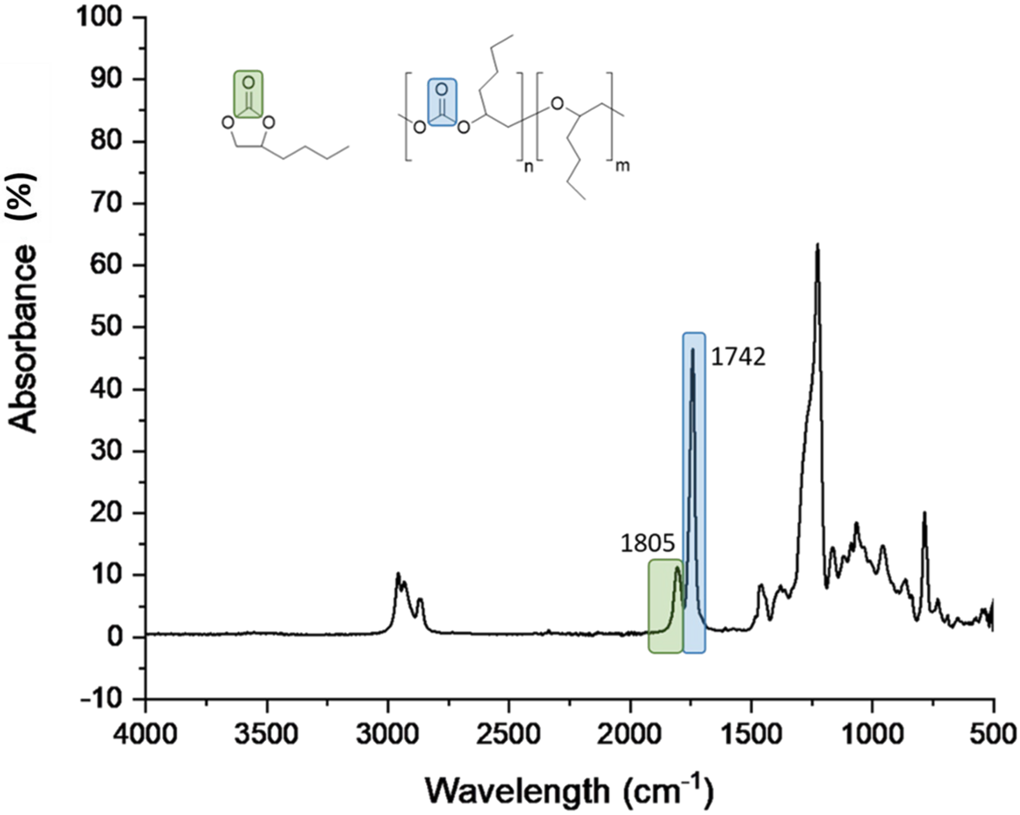


Figure S3. [1]H NMR spectrum of the crude mixture after the copolymerisation of 1,2-epoxyhexane with CO_2 (top) and of the purified polycarbonate (bottom).



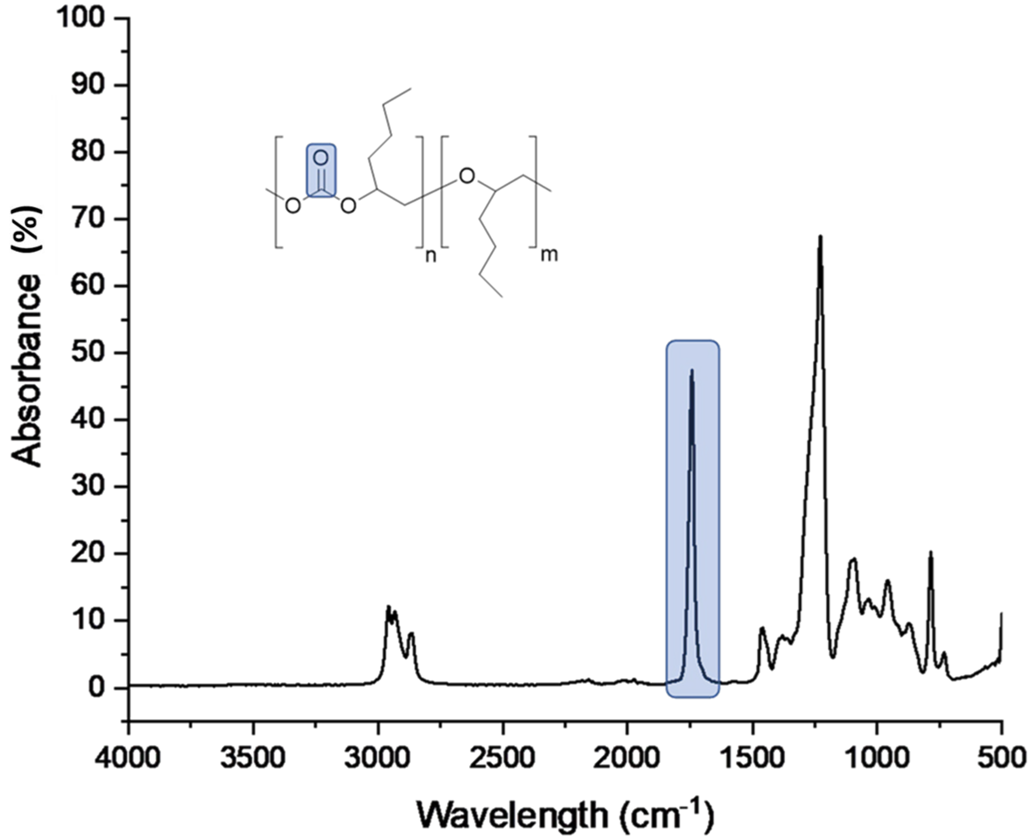


Figure S4. FT-IR spectrum of the crude mixture after the copolymerisation of 1,2-epoxyhexane with CO_2 (top) and of the purified polycarbonate (bottom).

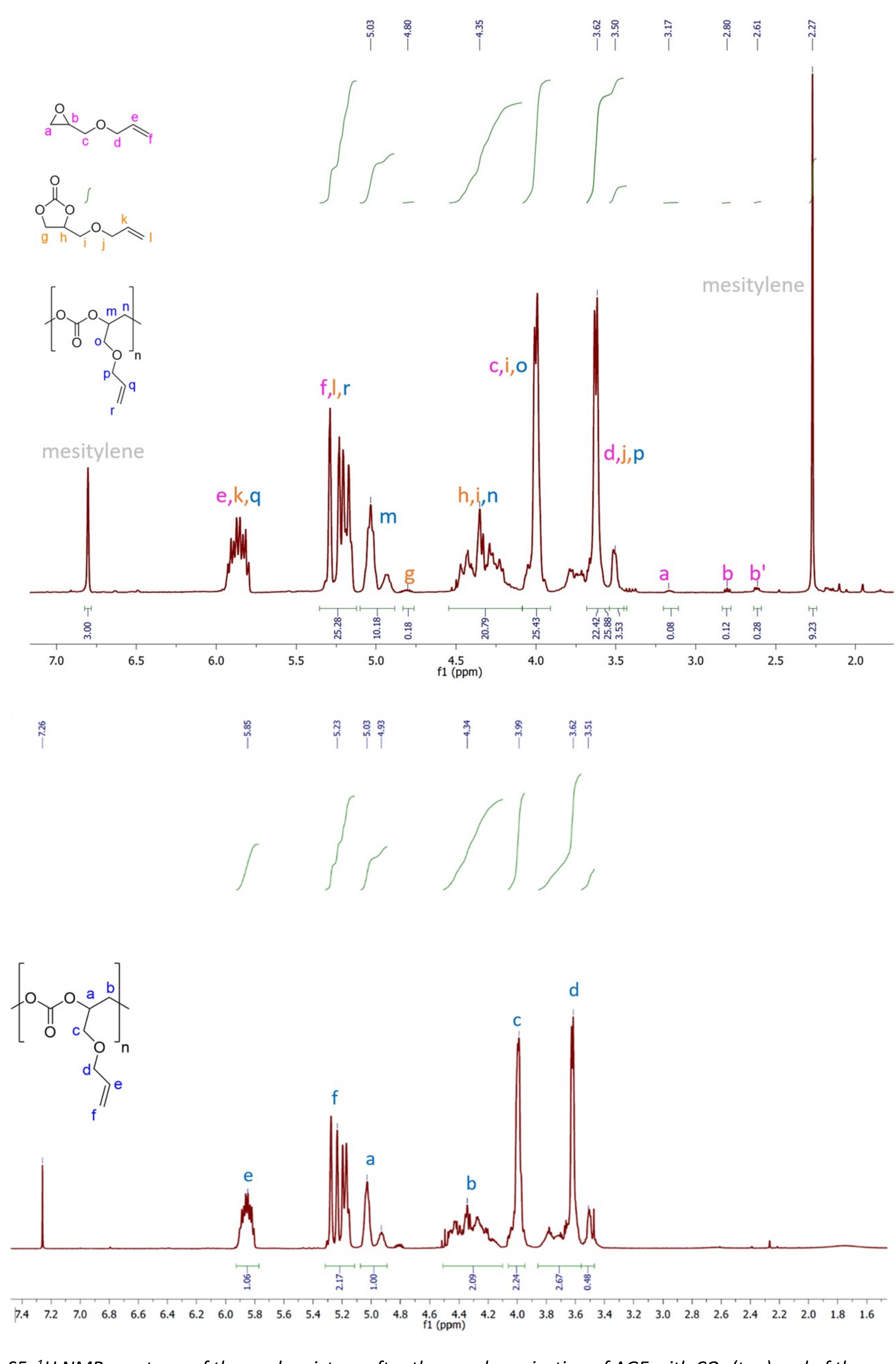
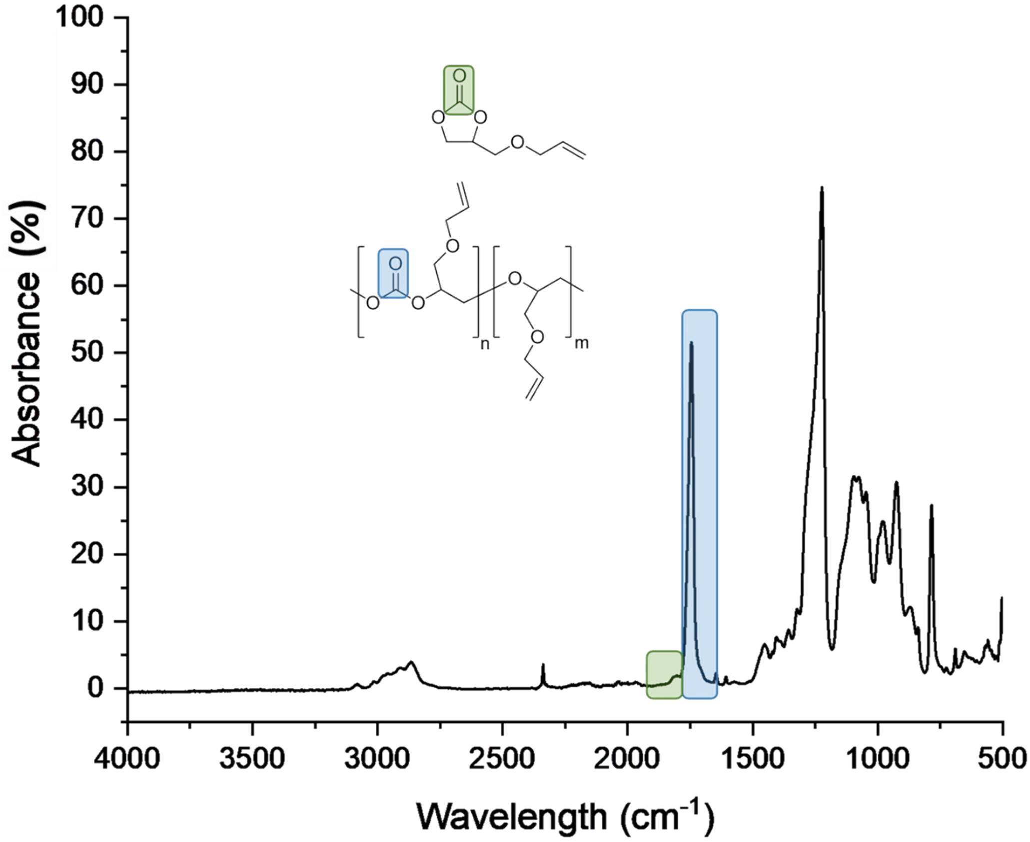


Figure S5. ^{1}H NMR spectrum of the crude mixture after the copolymerisation of AGE with CO_2 (top) and of the purified polycarbonate (bottom).



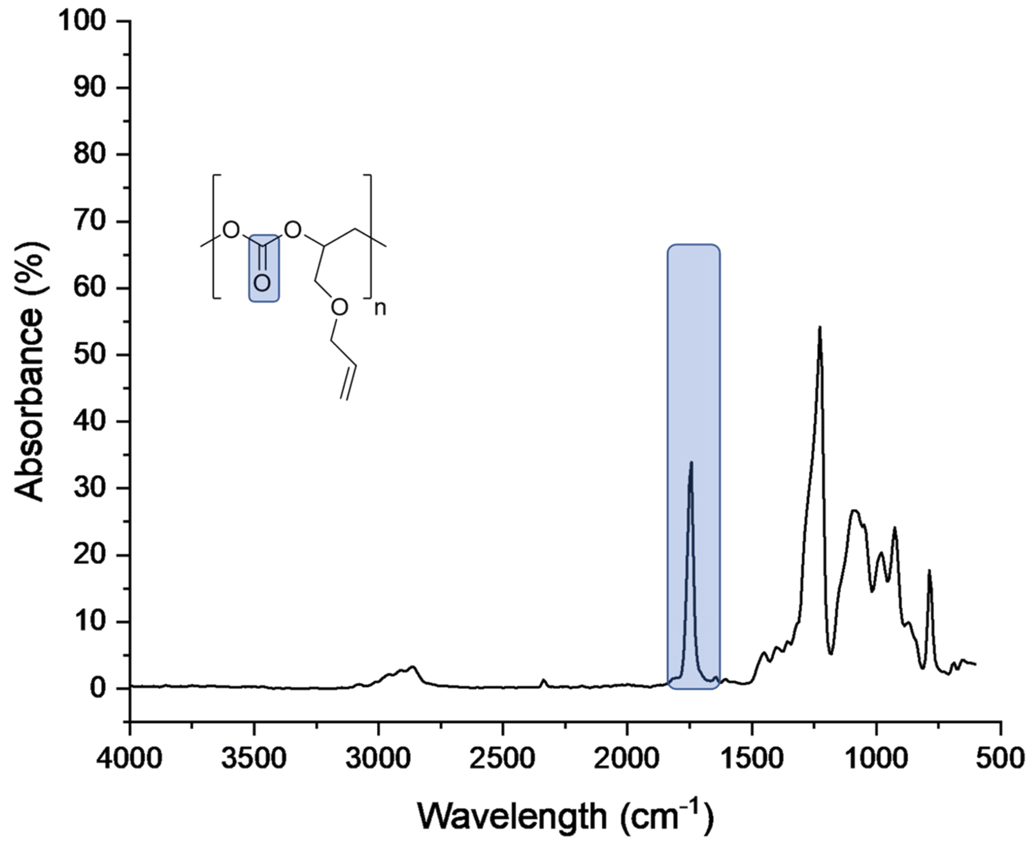
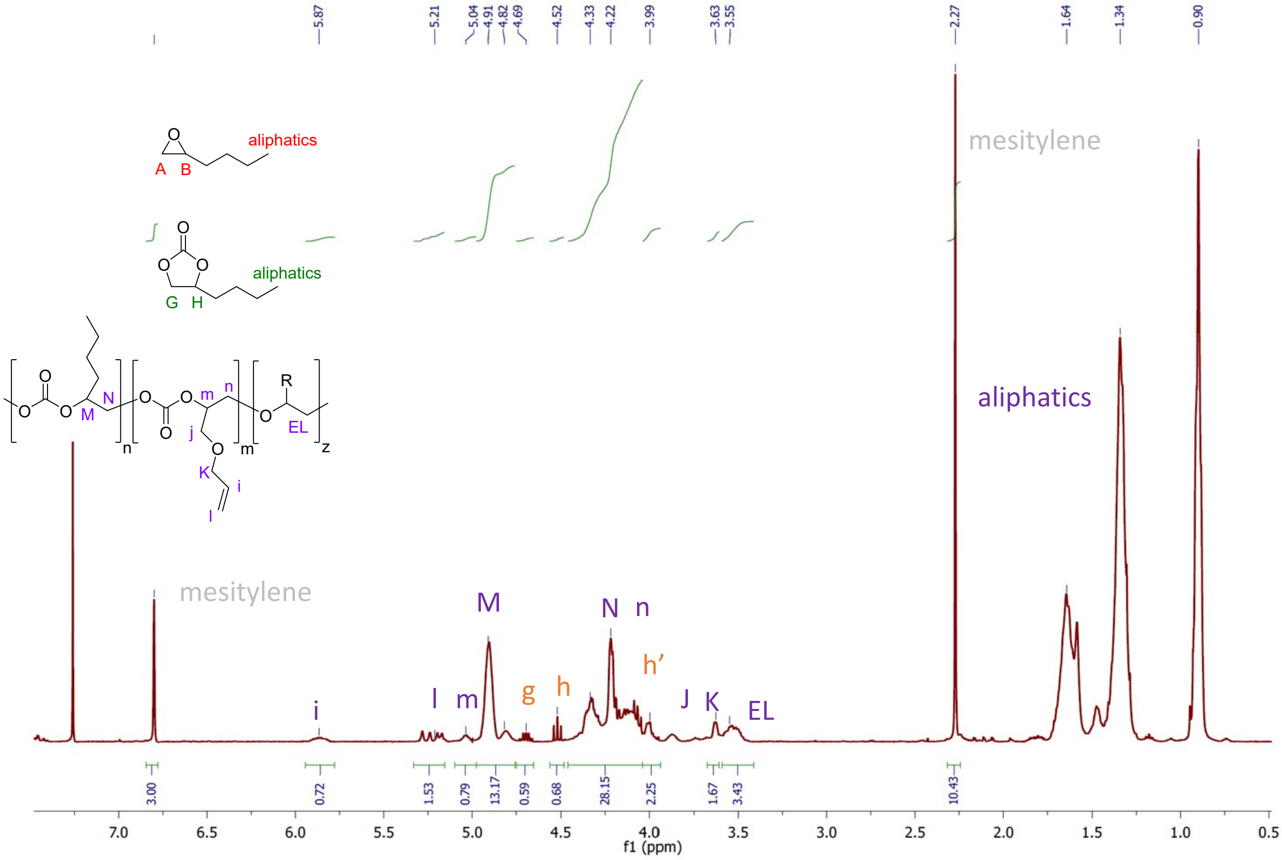


Figure S6. FT-IR spectrum of the crude mixture after the copolymerisation of AGE with CO_2 (top) and of the purified polycarbonate (bottom).



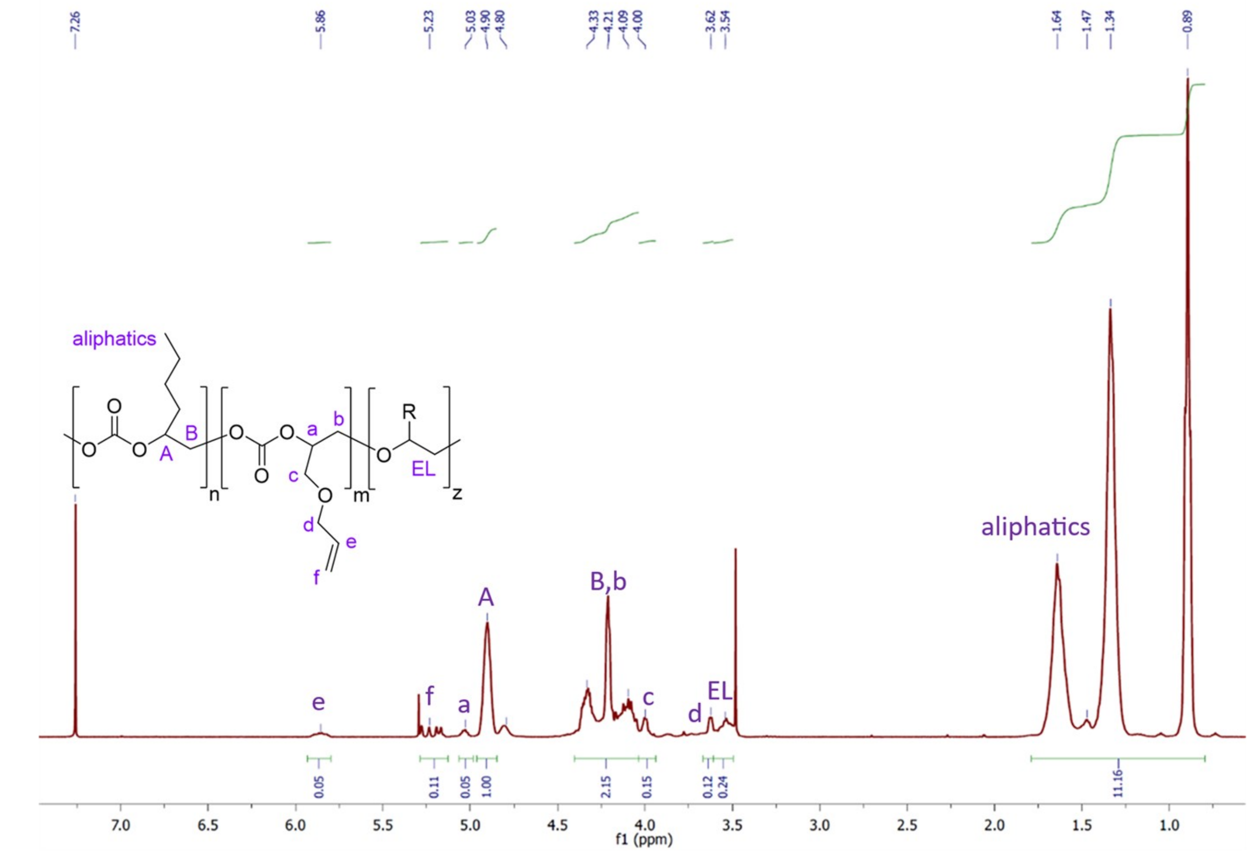
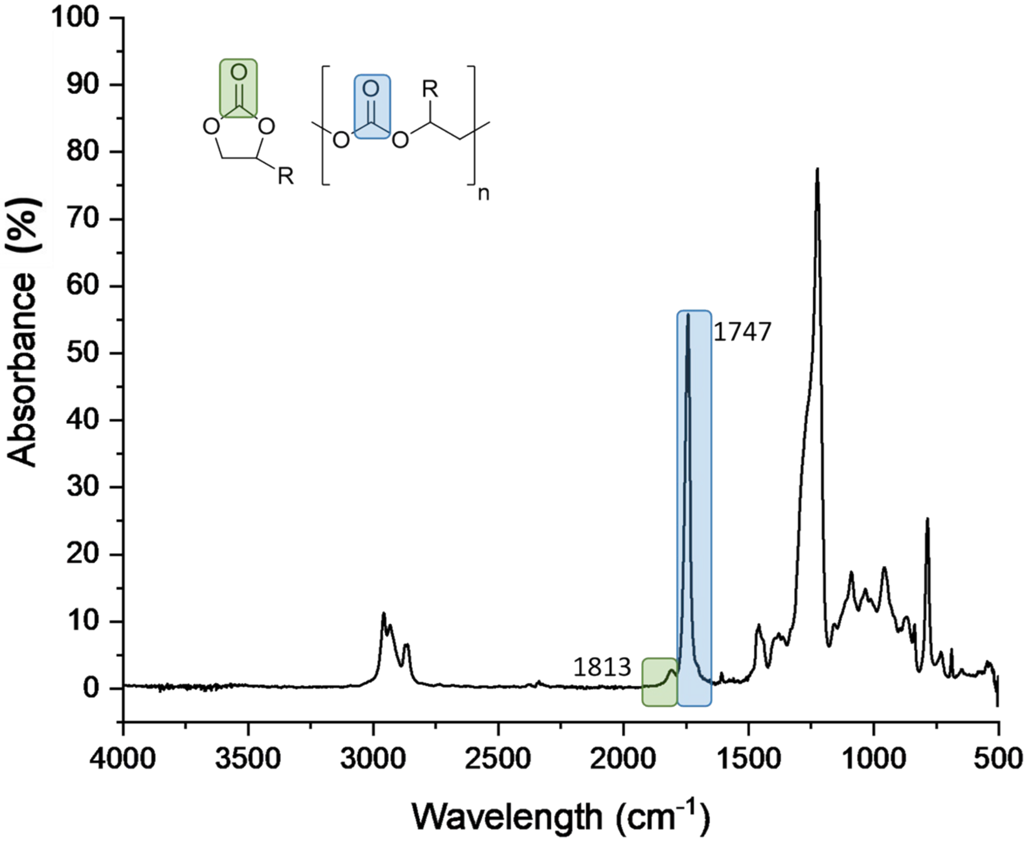


Figure S7. [1]H NMR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (95:5) with CO_2 (top) and of the purified polycarbonate (bottom).



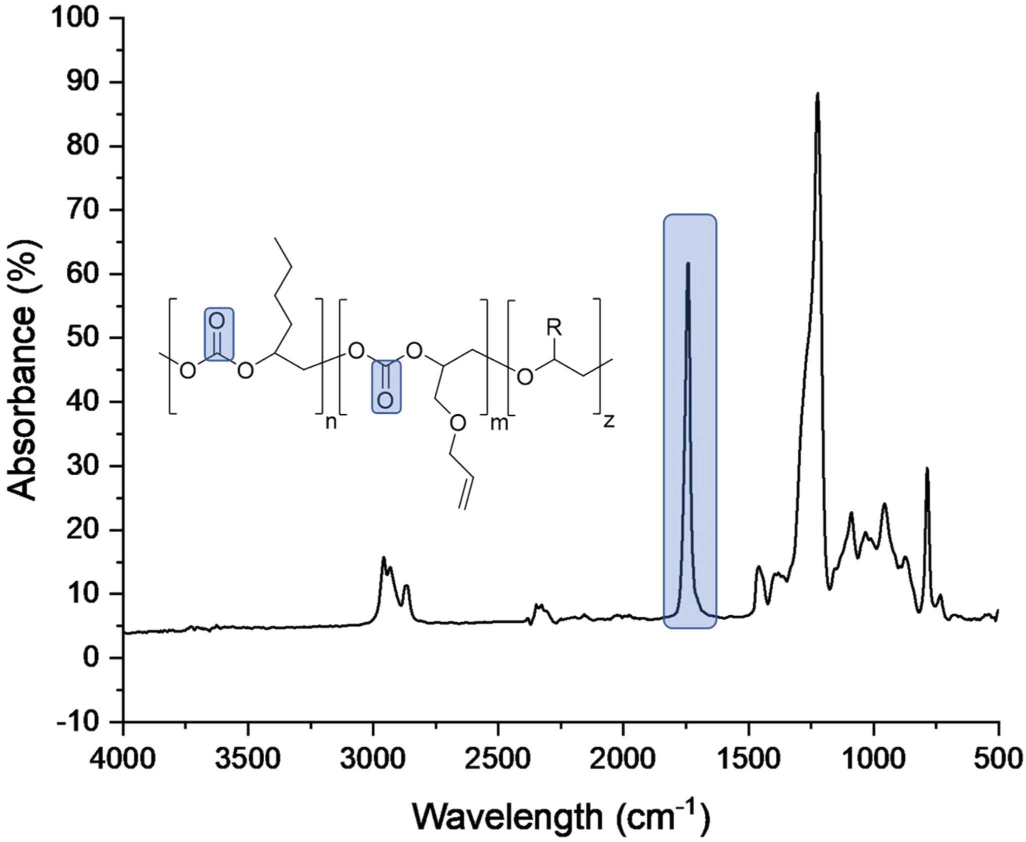
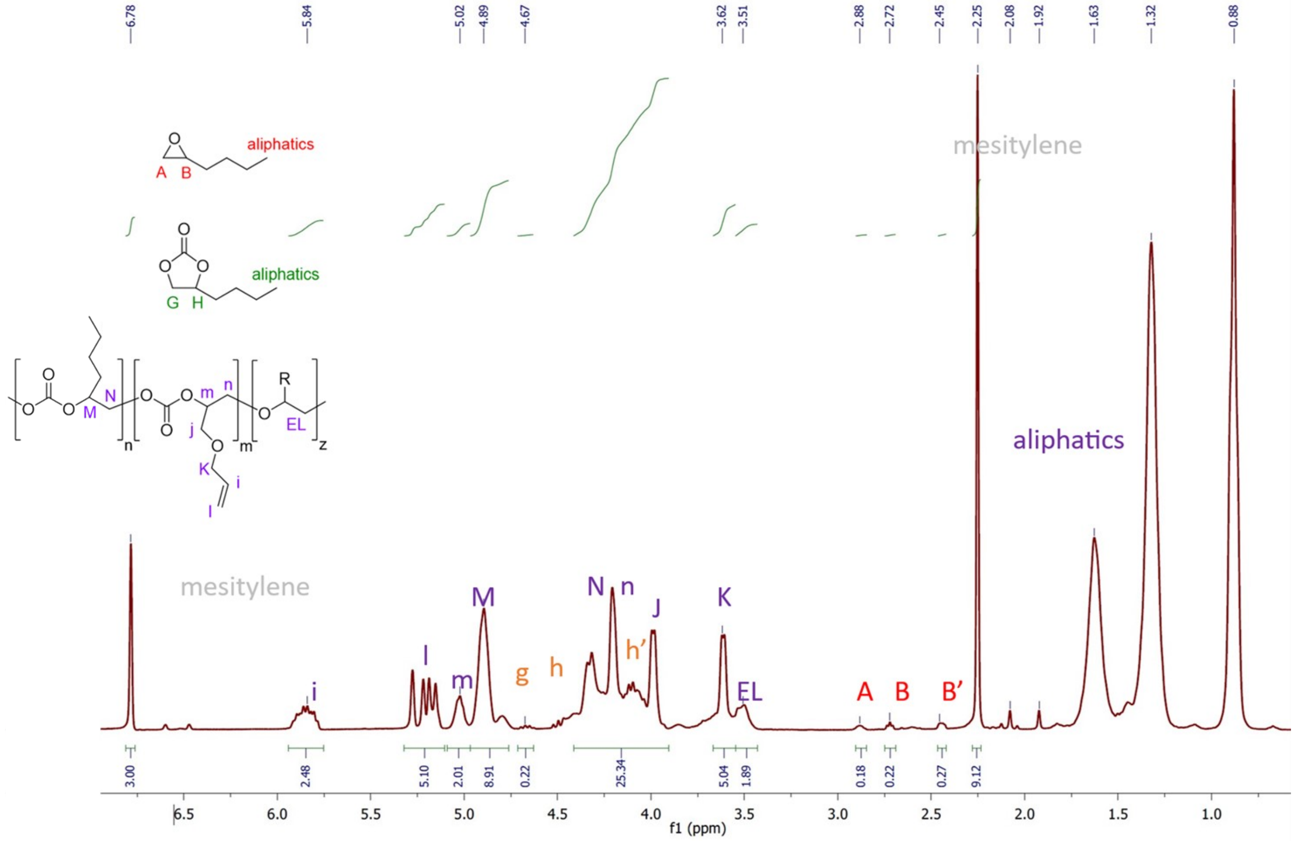


Figure S8. FT-IR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (95:5) with CO_2 (top) and of the purified polycarbonate (bottom).



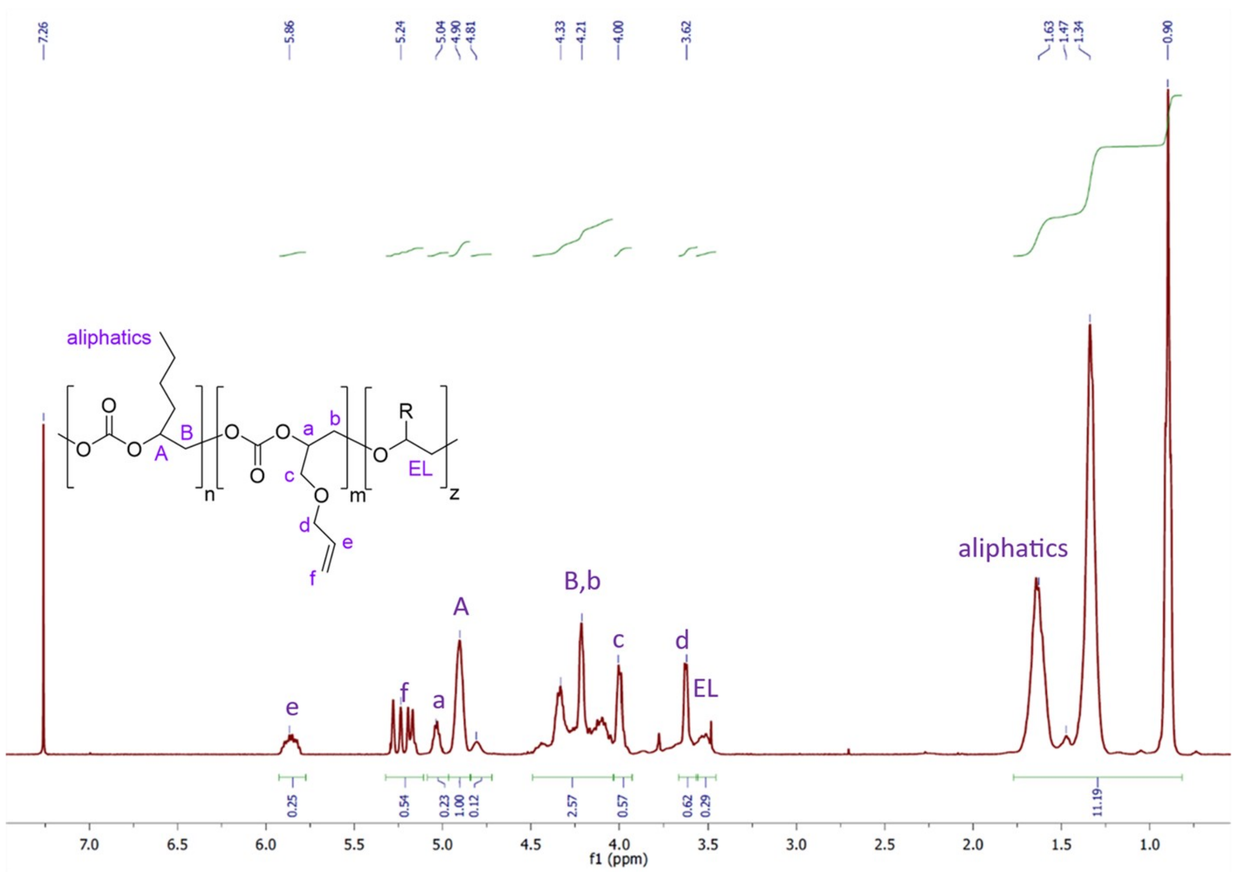
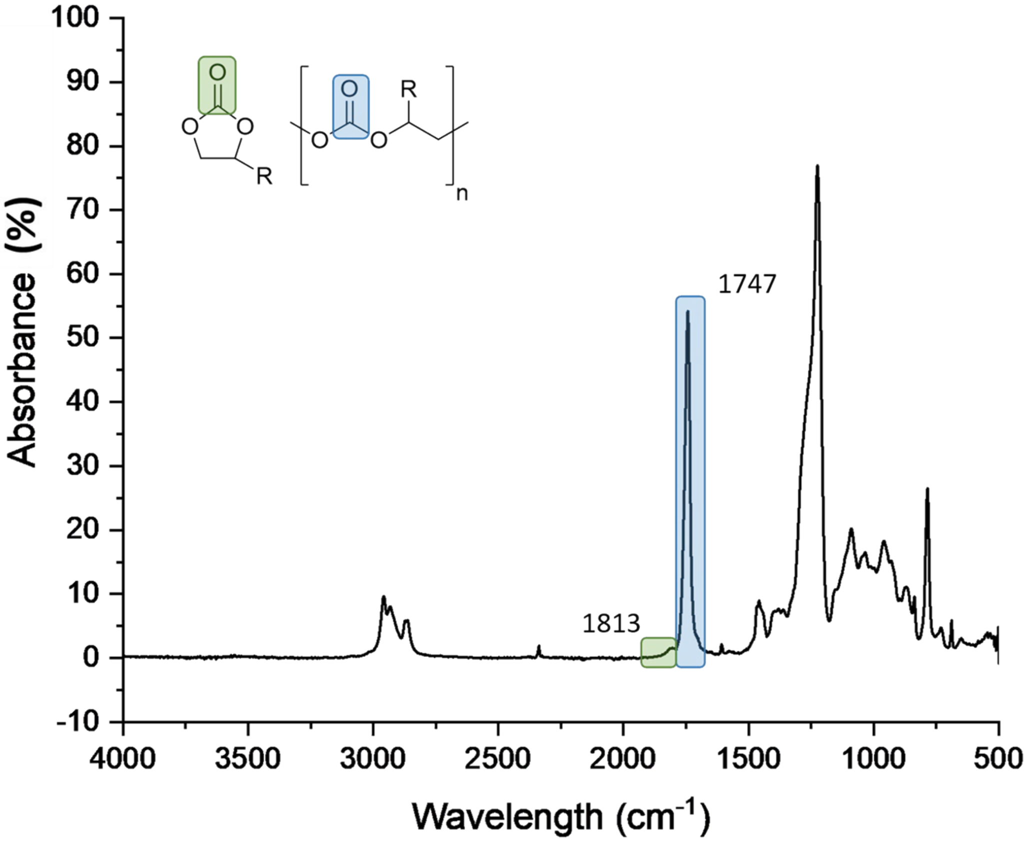


Figure S9. [1]H NMR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (80:20) with CO_2 (top) and of the purified polycarbonate (bottom).



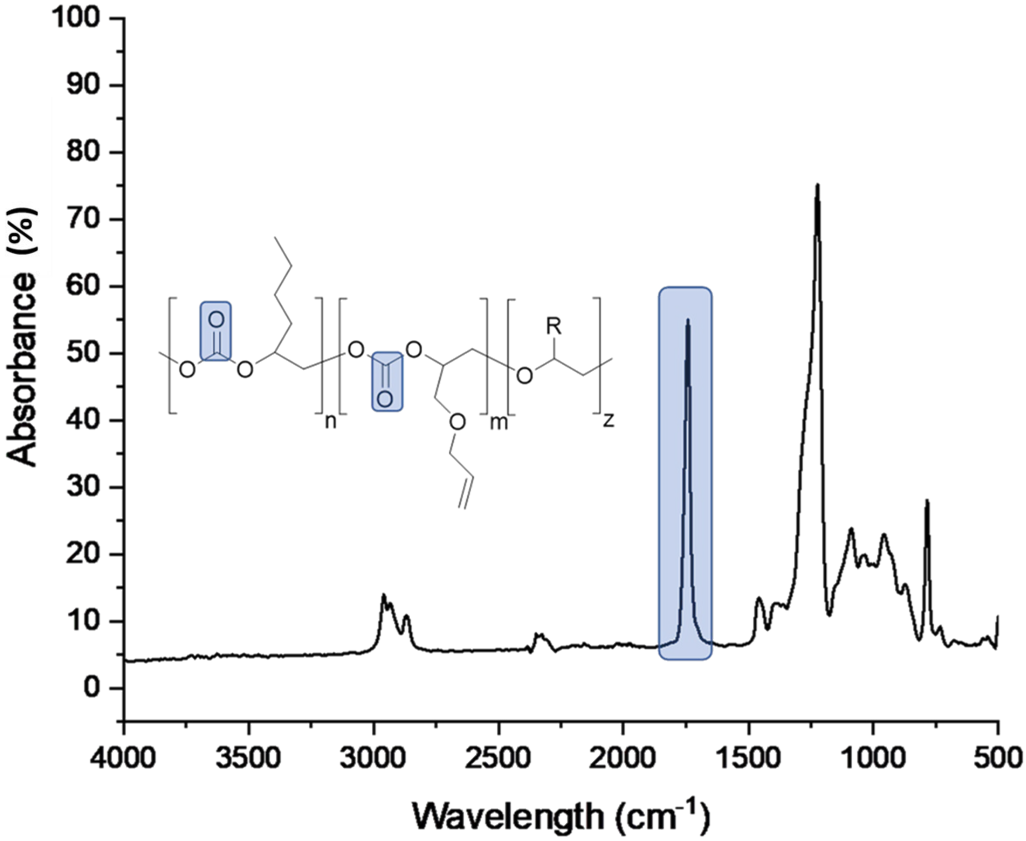
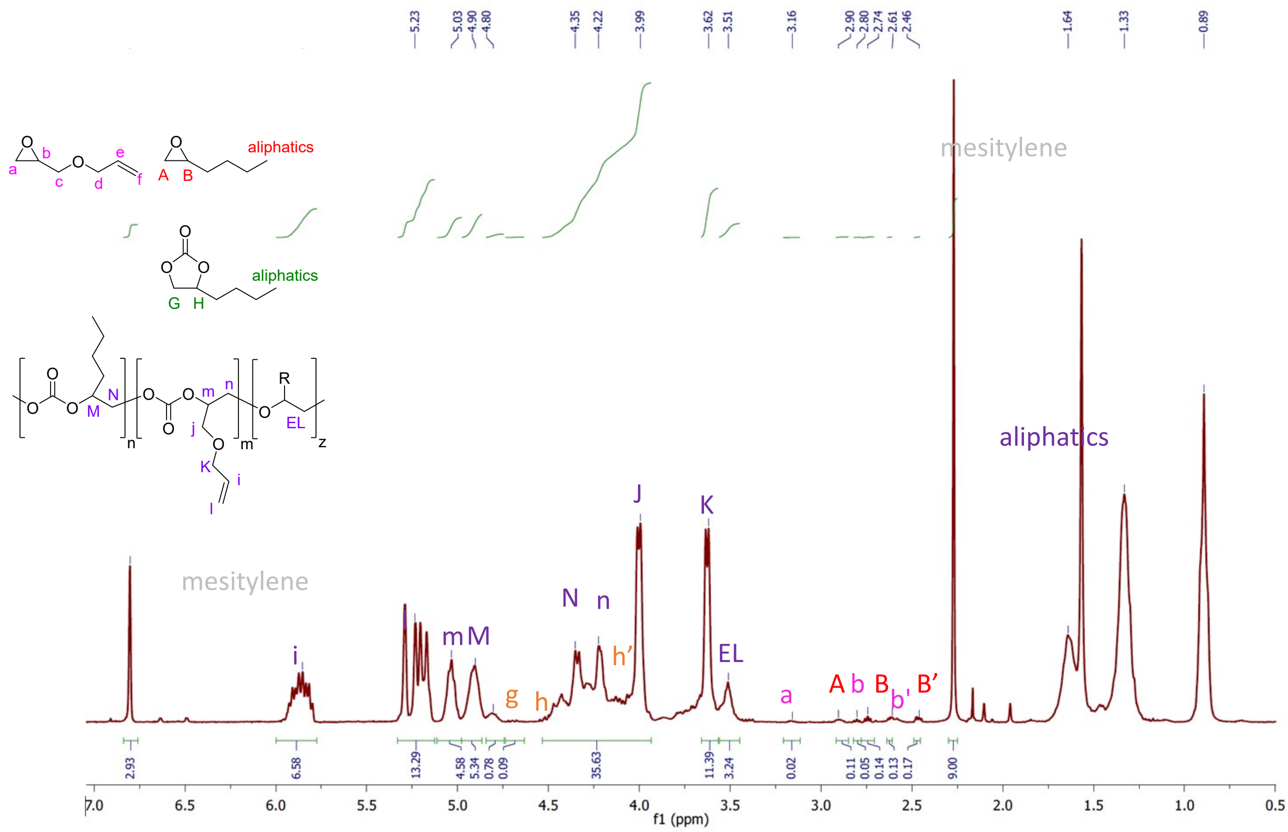


Figure S10. FT-IR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (80:20) with CO_2 (top) and of the purified polycarbonate (bottom).



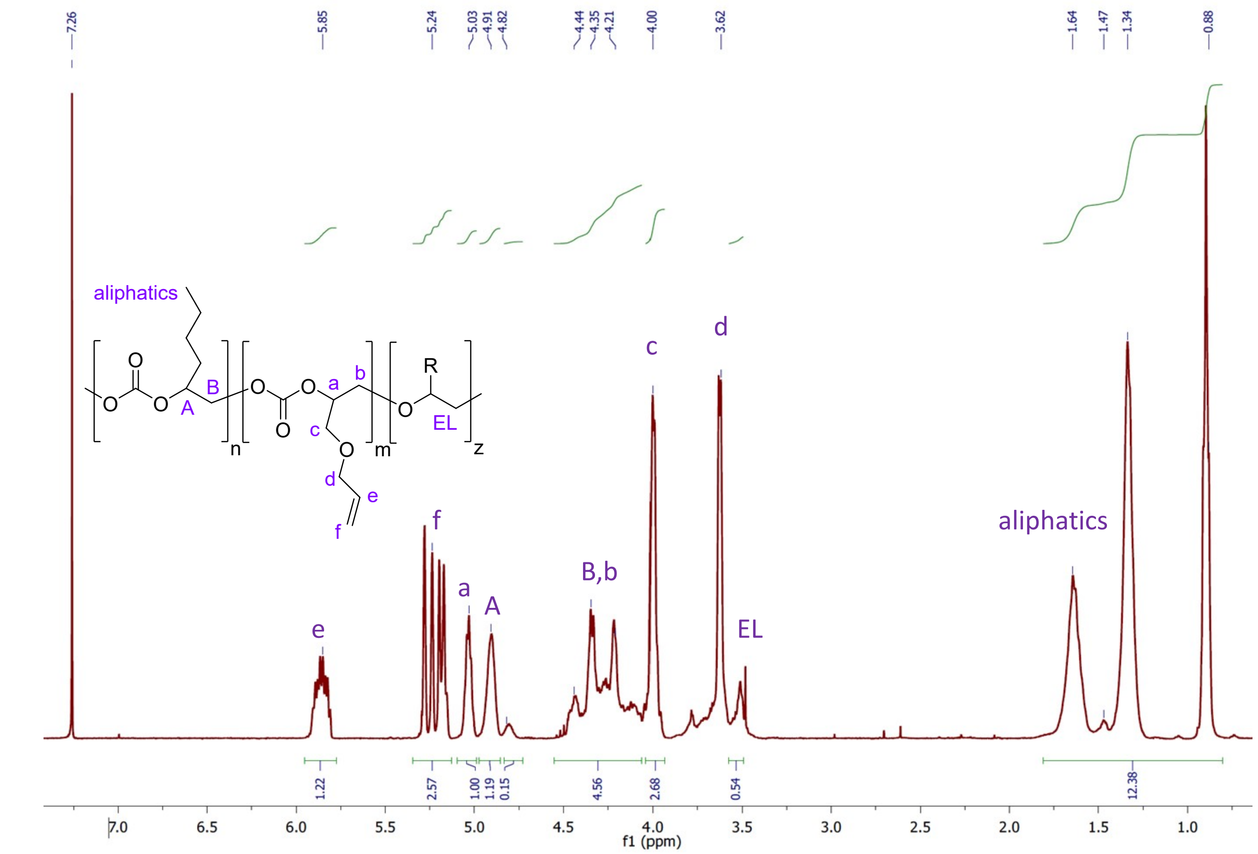
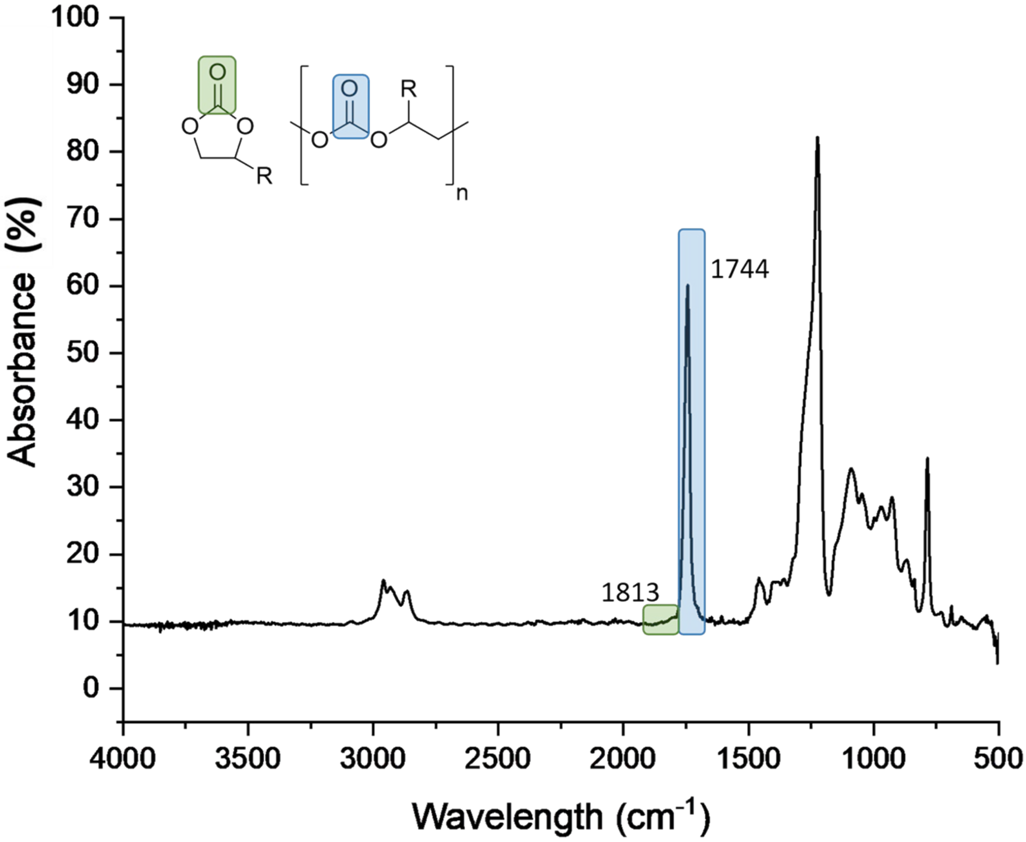


Figure S11. [1]H NMR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (50:50) with CO_2 (top) and of the purified polycarbonate (bottom).



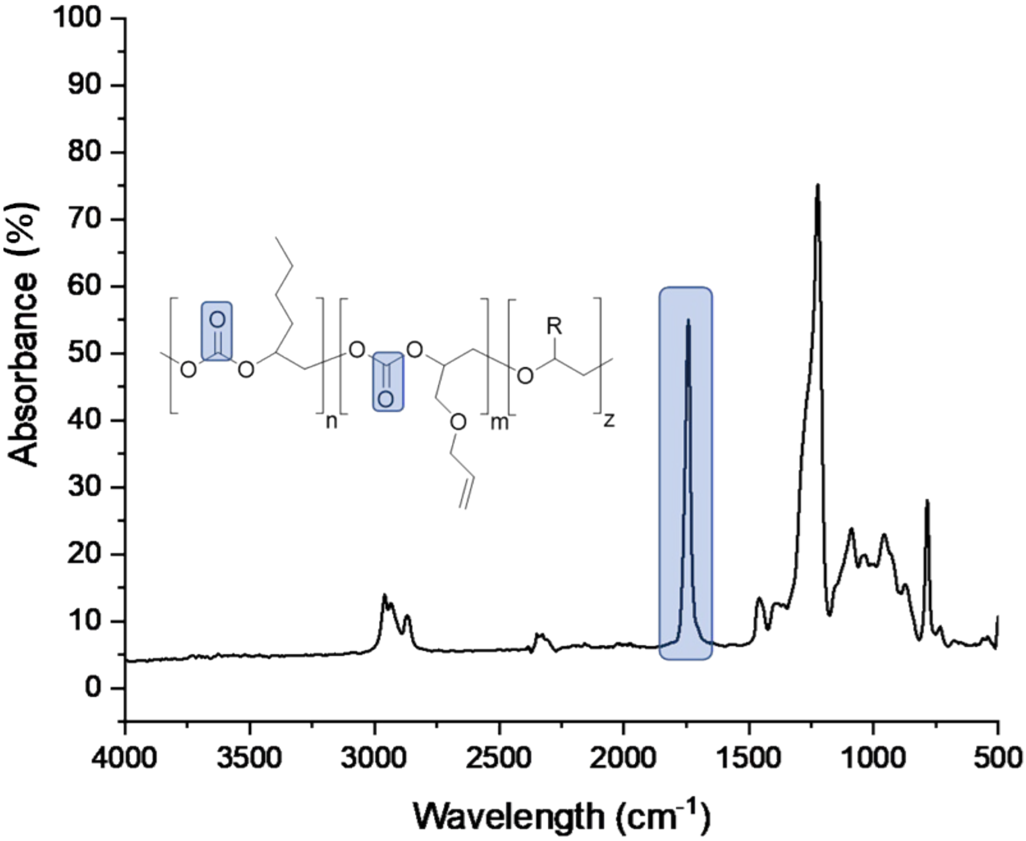


Figure S12. FT-IR spectrum of the crude mixture after the terpolymerisation of 1,2-epoxyhexane and AGE (50:50) with CO_2 (top) and of the purified polycarbonate (bottom).

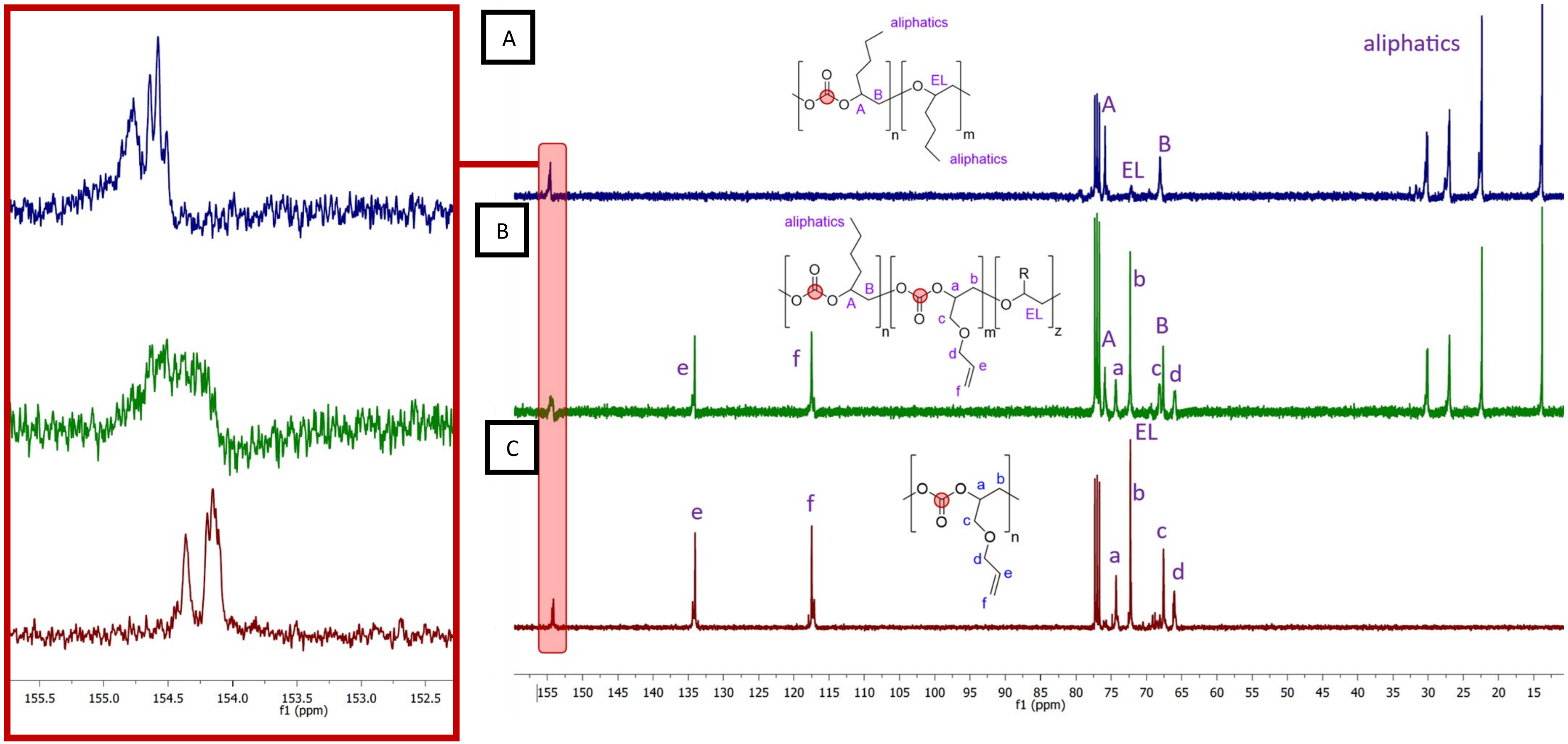
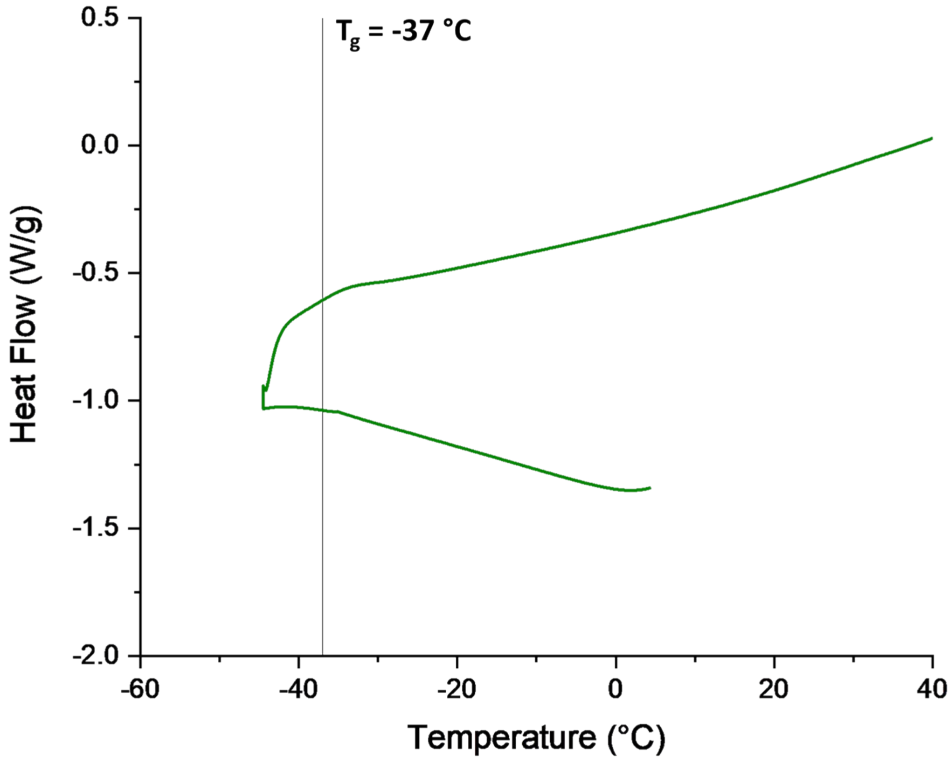


Figure S13. [13]C NMR spectra of: (A) polycarbonate copolymer of 1,2-epoxyhexane, in blue; (B) polycarbonate terpolymer of 1,2-epoxyhexane:AGE = 50:50, in green; and (C) polycarbonate copolymer of AGE, in red. The region of the signals of PC carbonyls is highlighted in burgundy red. On the left: zoom-in of the carbonate signals of the three samples; no preferantial polymerisation regiochemistry was observed in the terpolymerisation (random terpolymer, in green).

DSC analysis



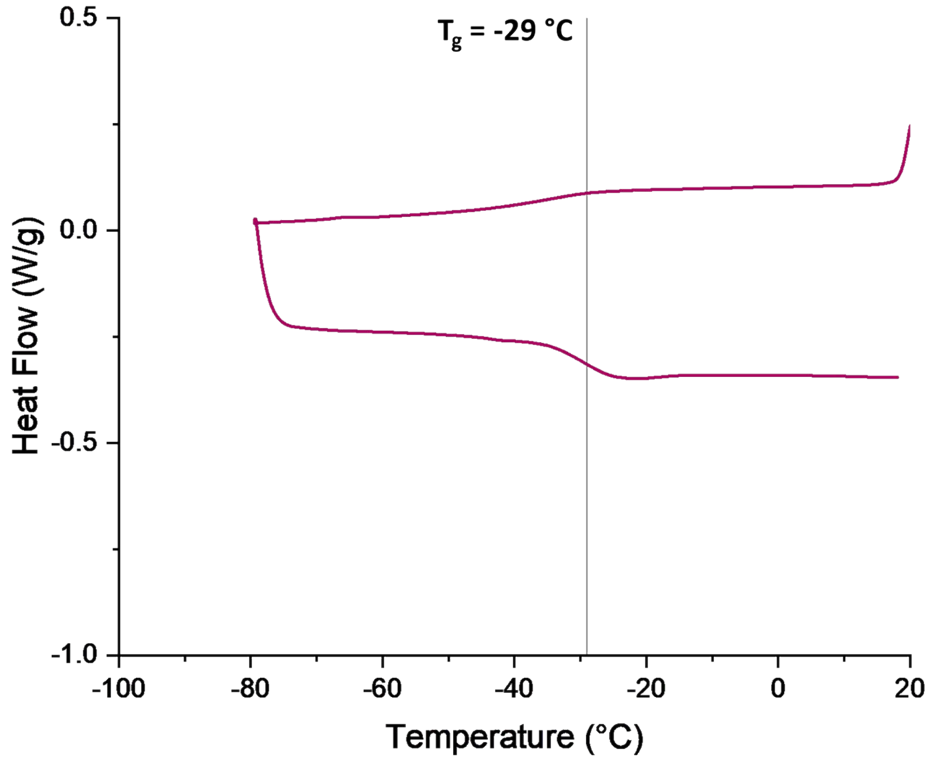


Figure S14. DSC curve of AGE polycarbonate (copolymer).
T_g determined from the heating branch (top).

Figure S15. DSC curve of 1,2-epoxyhexane polycarbonate (copolymer).
T_g determined from the heating branch (bottom).

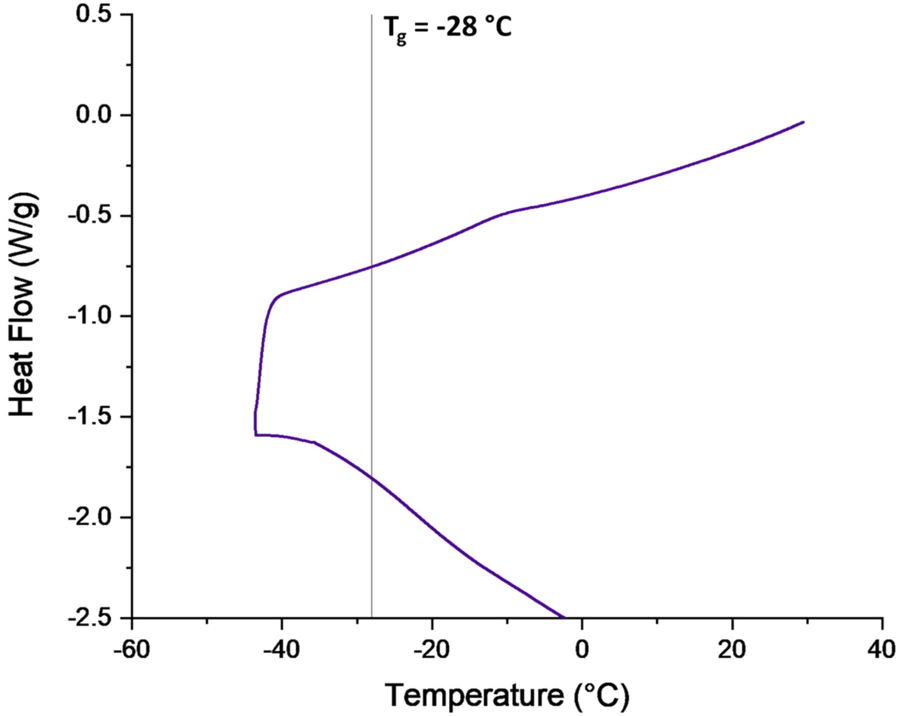


Figure S16. DSC curve of 1,2-epoxyoctane polycarbonate (copolymer). T_g determined from the heating branch (top).

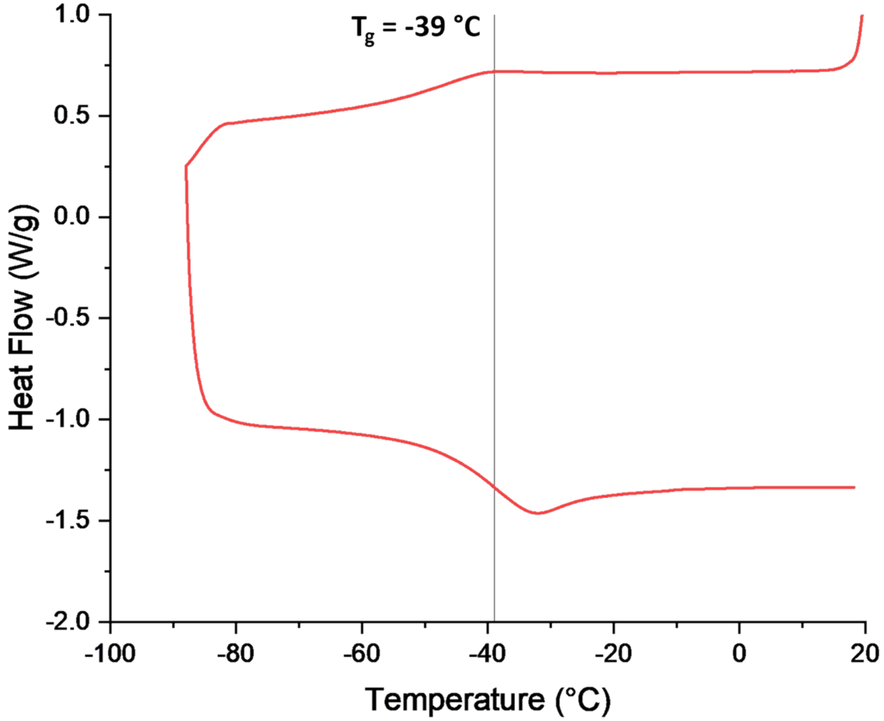


Figure S17. DSC curve of 1,2-epoxydecane polycarbonate (copolymer). T_g determined from the heating branch (bottom).

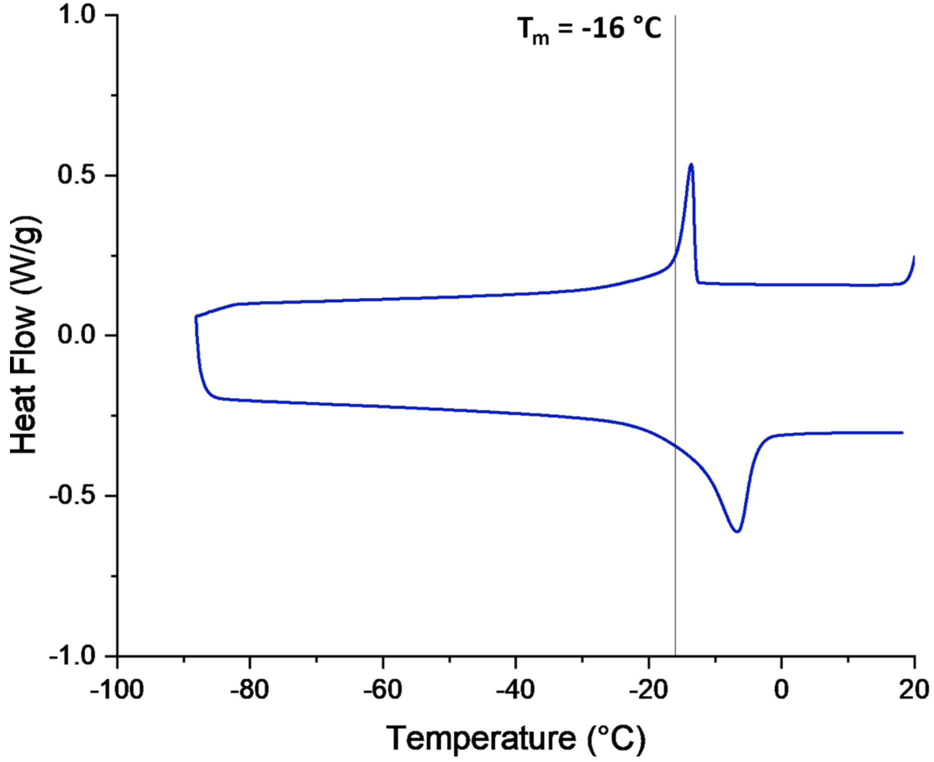


Figure S18. DSC curve of 1,2-epoxydodecane polycarbonate (copolymer). T_m determined from the heating branch (bottom).

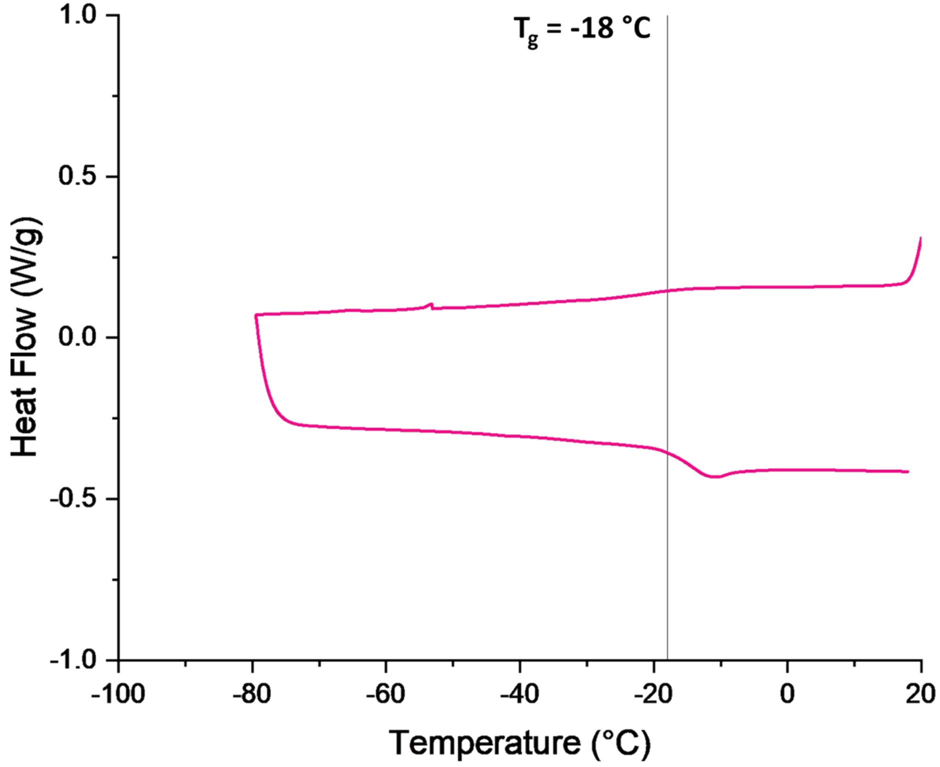


Figure S19. DSC curve of 1,2-epoxyhexane:AGE = 95:5 polycarbonate (terpolymer). T_g determined from the heating branch (bottom).

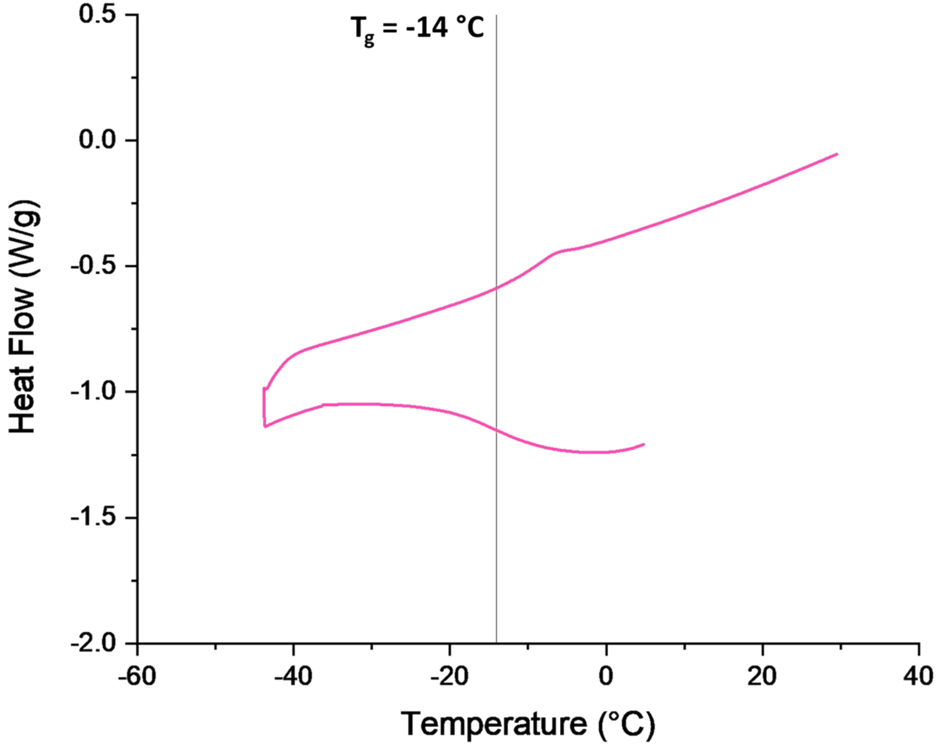


Figure S20. DSC curve of 1,2-epoxyhexane:AGE = 80:20 polycarbonate (terpolymer).
T_g determined from the heating branch (top).

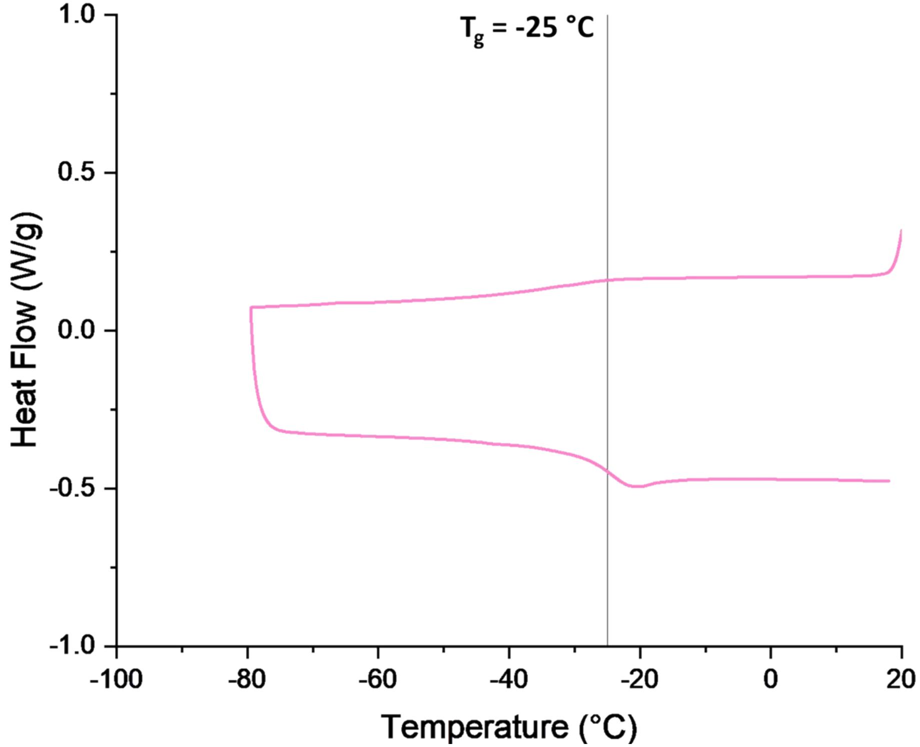


Figure S21. DSC curve of 1,2-epoxyhexane:AGE = 50:50 polycarbonate (terpolymer).
T_g determined from the heating branch (bottom).

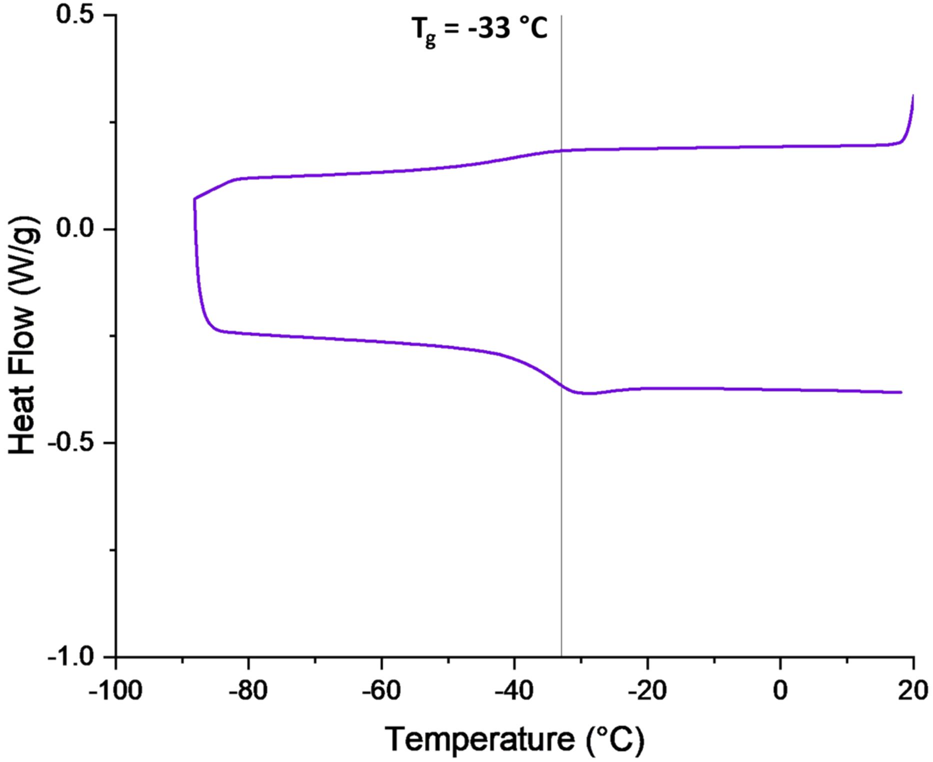


Figure S22. DSC curve of 1,2-epoxyoctane:AGE = 95:5 polycarbonate (terpolymer). T_g determined from the heating branch (bottom).

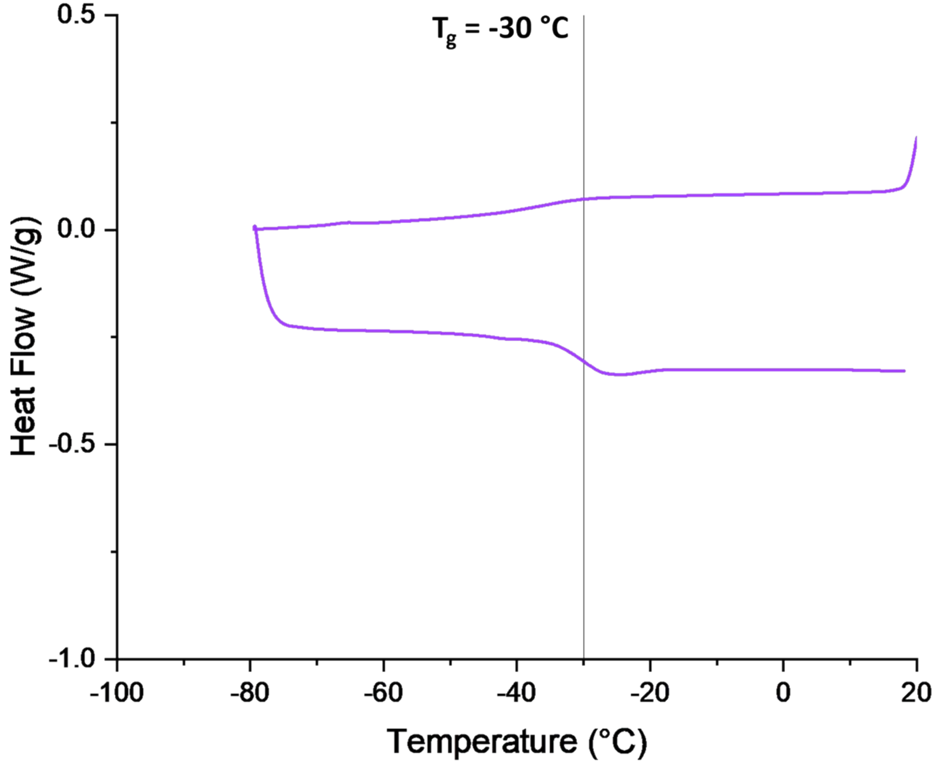


Figure S23. DSC curve of 1,2-epoxyoctane:AGE = 80:20 polycarbonate (terpolymer). T_g determined from the heating branch (bottom).

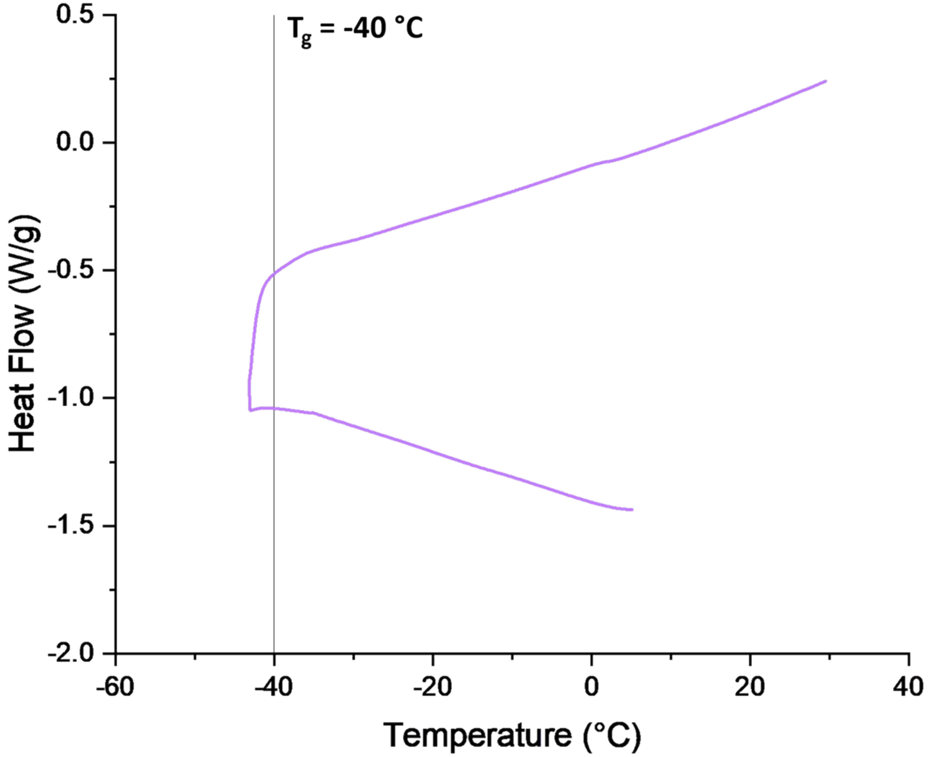


Figure S24. DSC curve of 1,2-epoxyoctane:AGE = 50:50 polycarbonate (terpolymer). T_g determined from the heating branch (top).

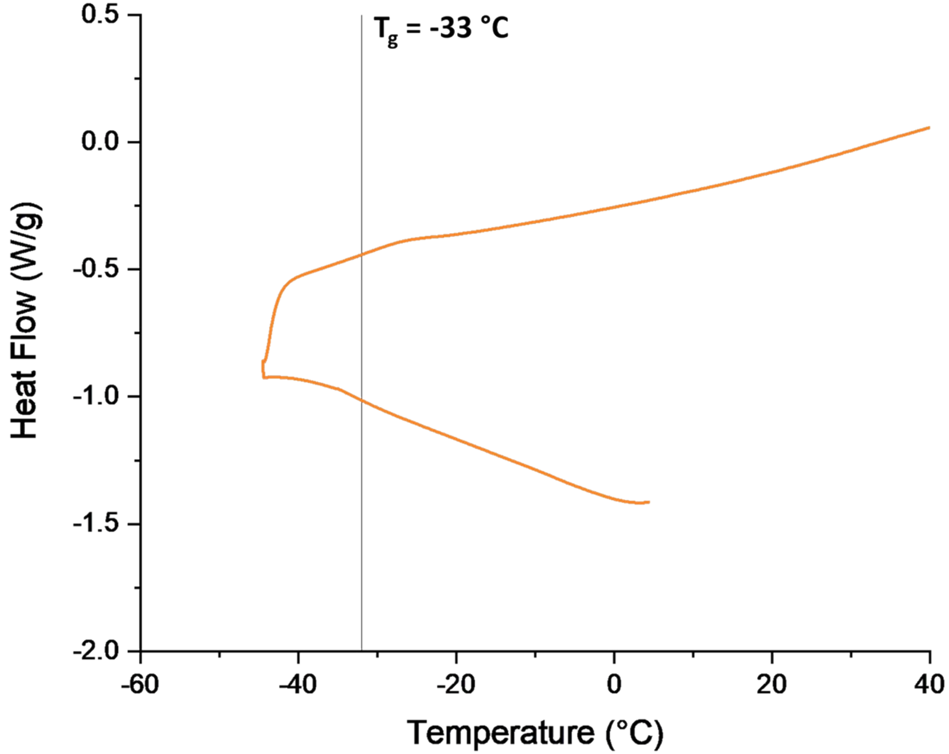


Figure S25. DSC curve of 1,2-epoxydecane:AGE = 95:5 polycarbonate (terpolymer). T_g determined from the heating branch (top).

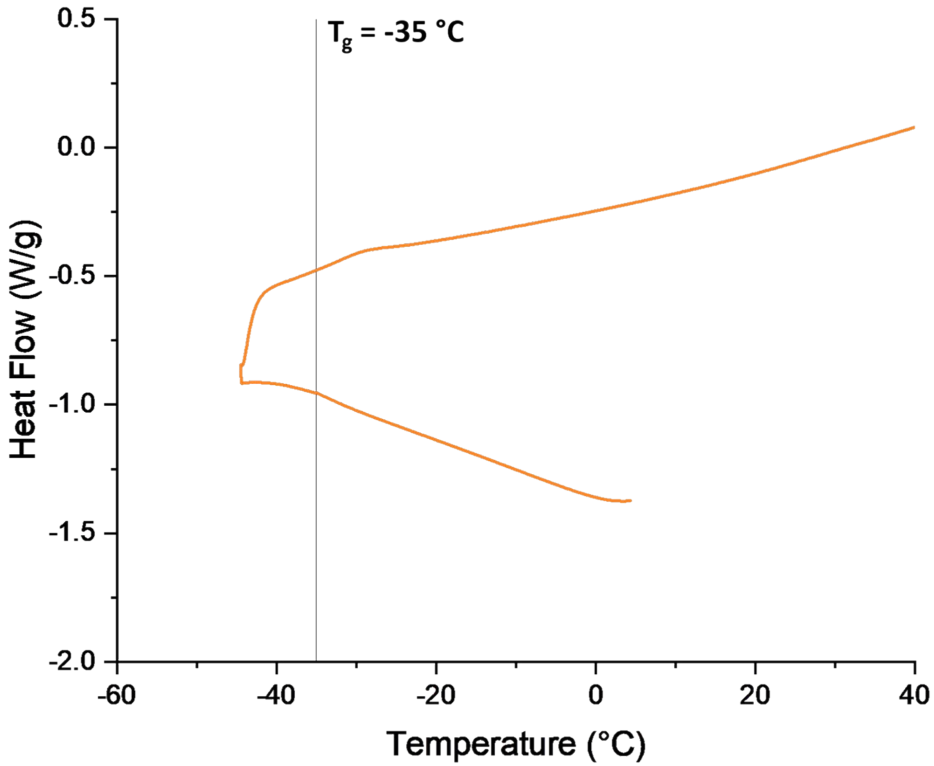


Figure S26. DSC curve of 1,2-epoxydecane:AGE = 80:20 polycarbonate (terpolymer). T_g determined from the heating branch (top).

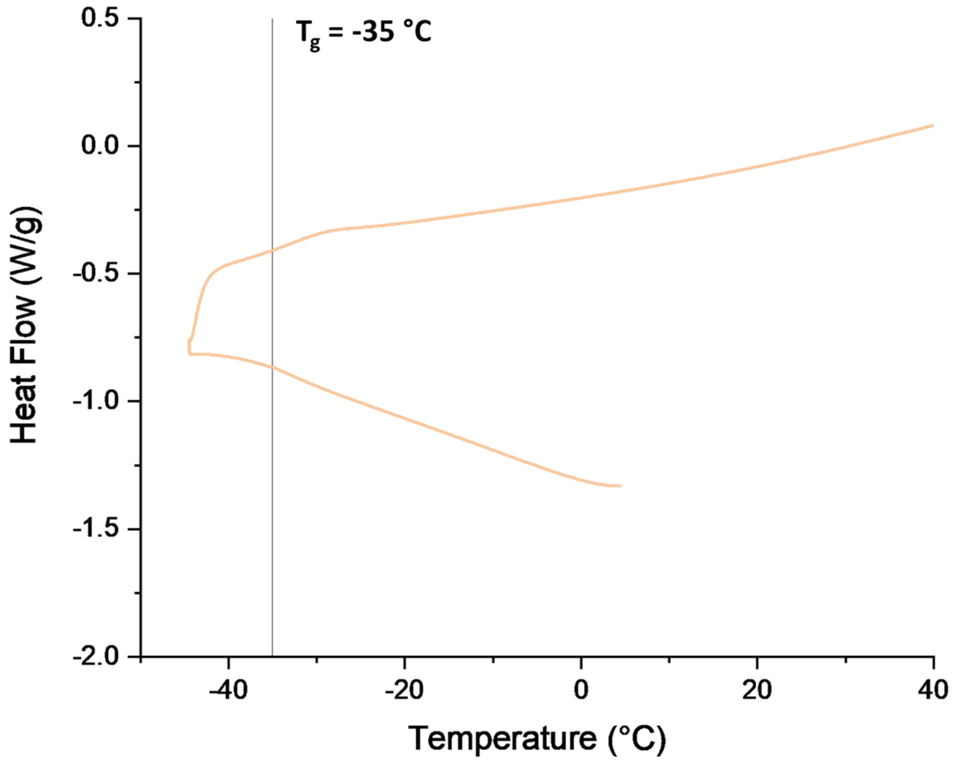


Figure S27. DSC curve of 1,2-epoxydecane:AGE = 50:50 polycarbonate (terpolymer). T_g determined from the heating branch (top).

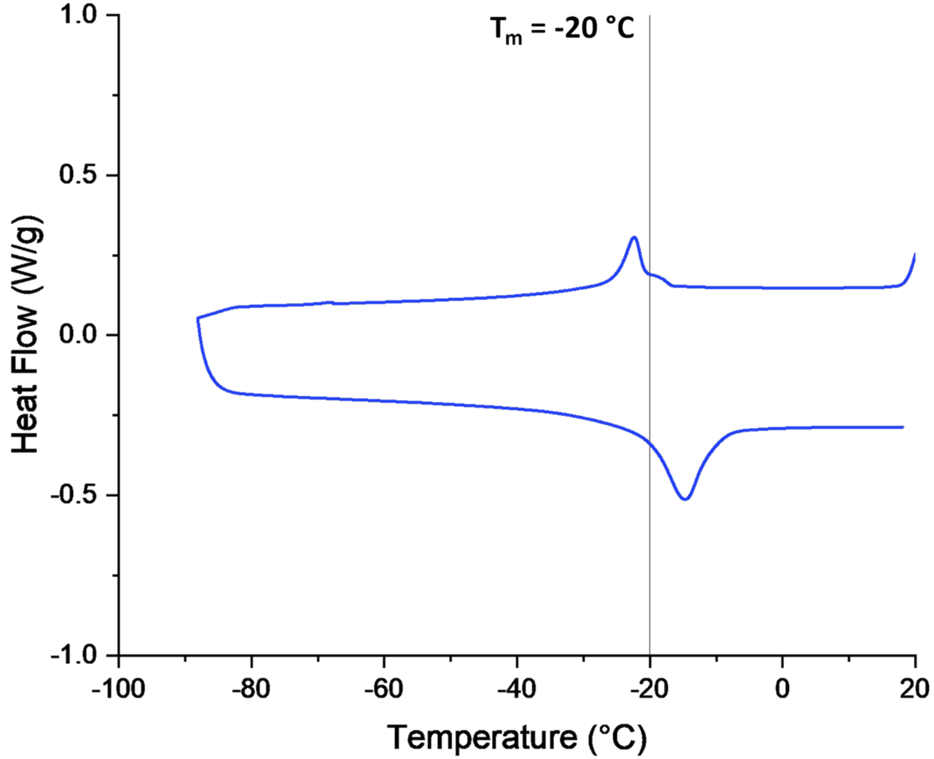


Figure S28. DSC curve of 1,2-epoxydodecane:AGE = 95:5 polycarbonate (terpolymer). T_m determined from the heating branch (bottom).

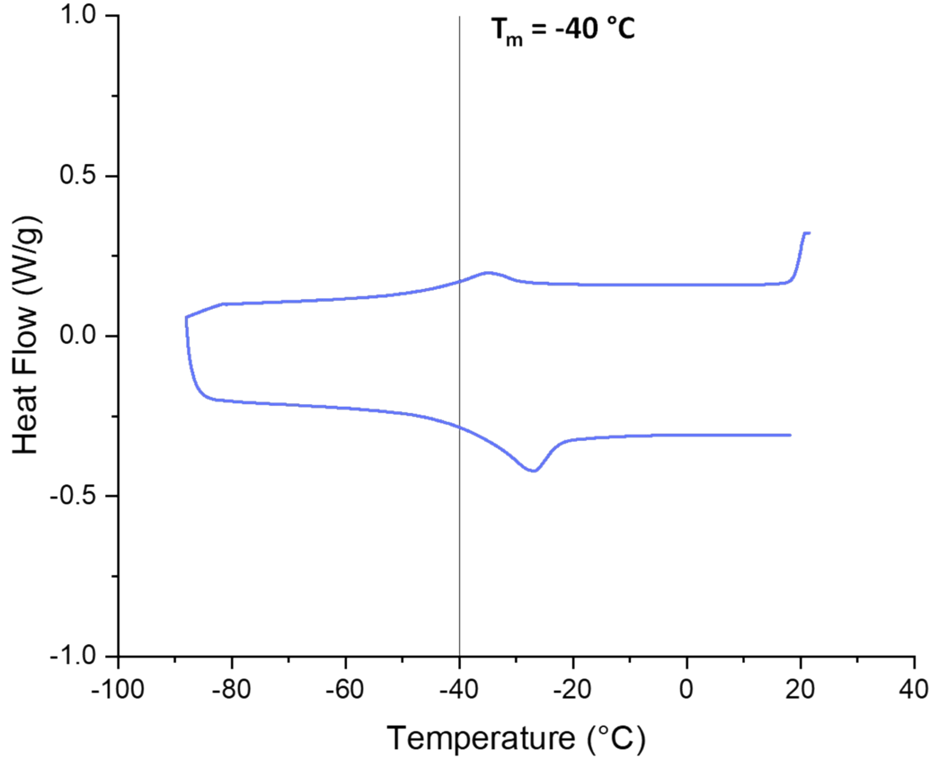


Figure S29. DSC curve of 1,2-epoxydodecane:AGE = 80:20 polycarbonate (terpolymer). T_m determined from the heating branch (bottom).

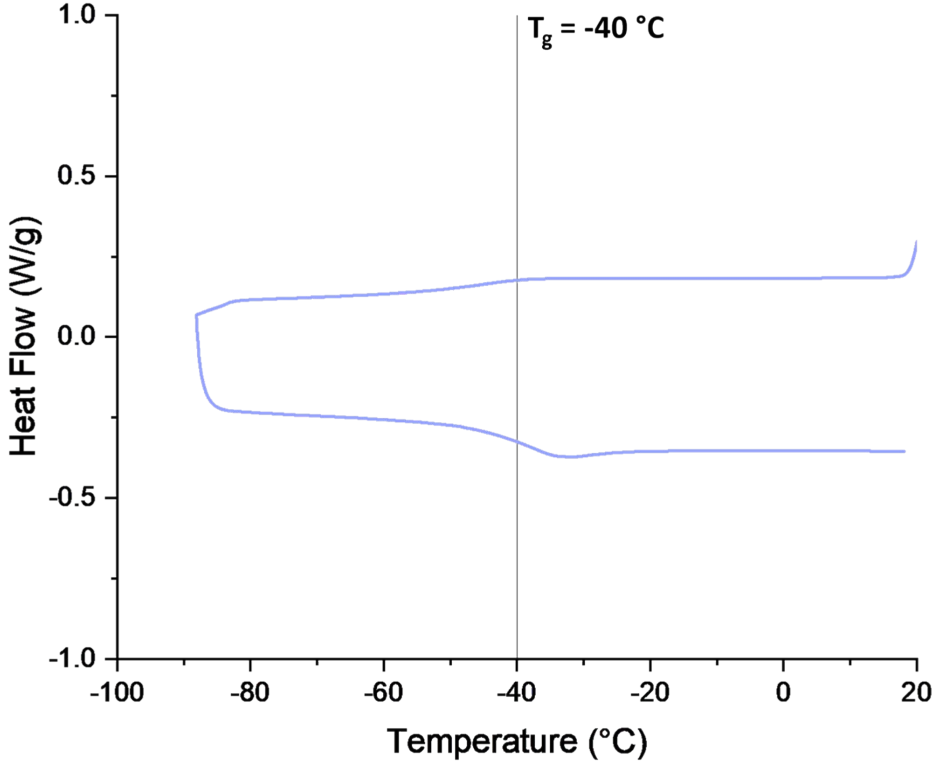


Figure S30. DSC curve of 1,2-epoxydodecane:AGE = 50:50 polycarbonate (terpolymer). T_g determined from the heating branch (bottom).

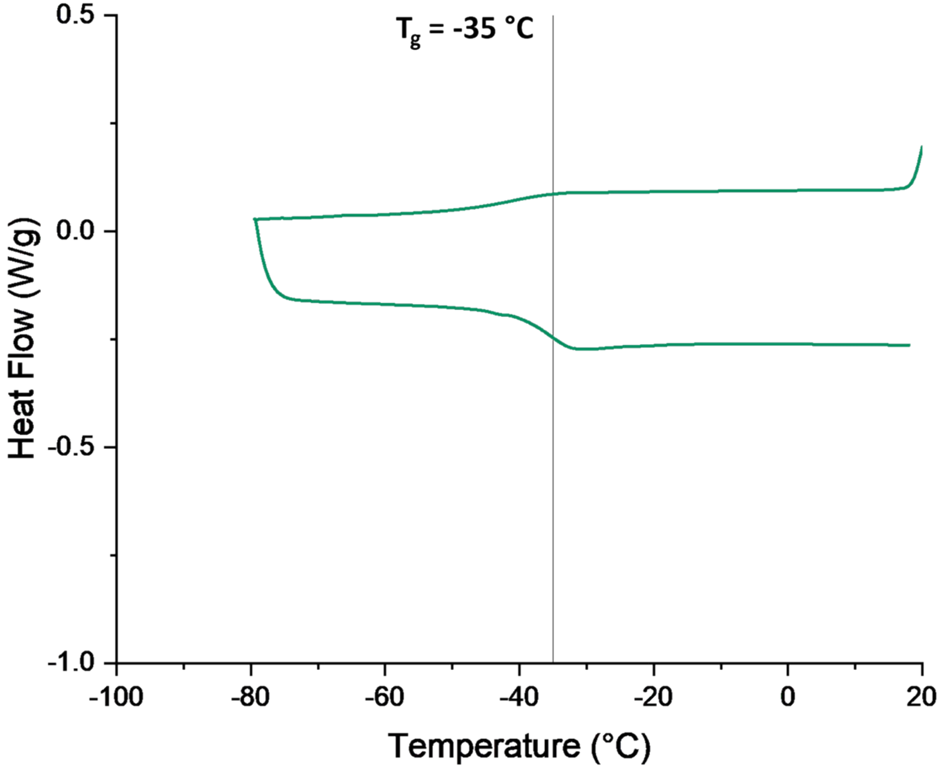


Figure S31. DSC curve of AGE polycarbonate (copolymer) prepared on large scale. T_g determined from the heating branch (bottom).

The vast majority of the examined polycarbonates showed a small and smooth change in the heat flow, which is consistent with a T_g peak.

DSC curves of polycarbonates synthesised from 1,2-epoxydodecane showed a T_m when [AGE] < 50. No T_g was detected in the analysed temperature range for these samples.

Molecular weight curves measured by GPC/SEC

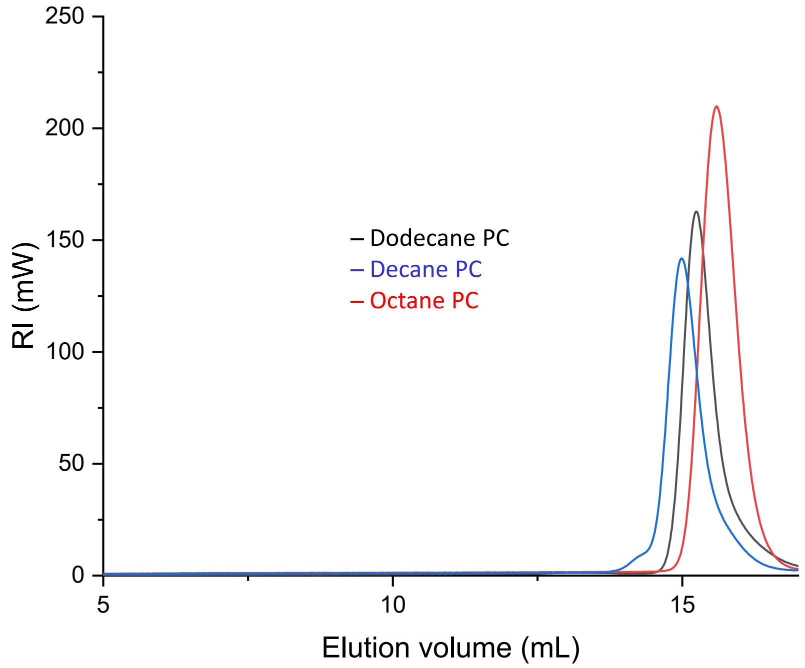


Figure S32. Examples of the monomodal GPC eluograms of the prepared copolymers: 1,2-epoxydodecane-based copolymer in black; 1,2-epoxydecane-based copolymer in blue; 1,2-epoxyoctane-based copolymer in red.

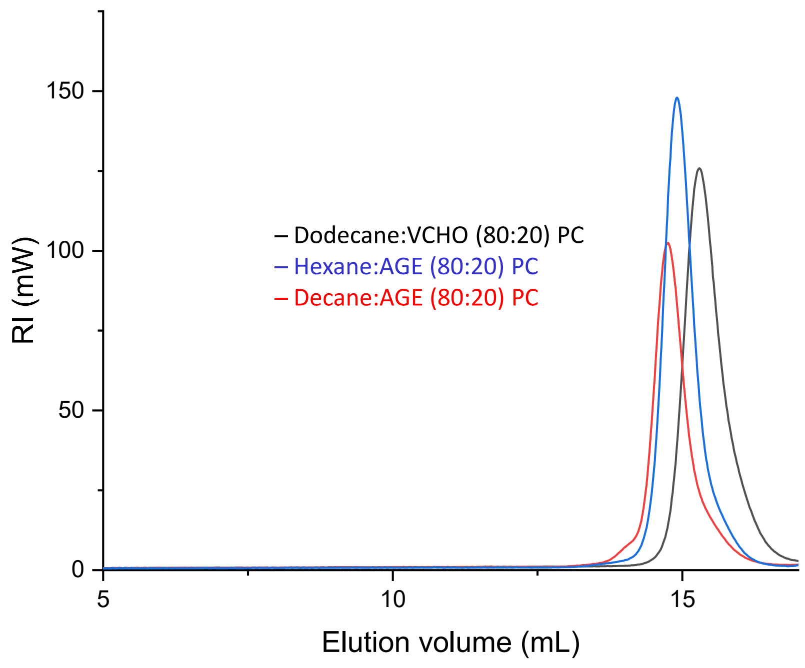


Figure S33. Examples of the monomodal GPC eluograms of the prepared terpolymers: 1,2-epoxydodecane:VCHO (80:20) terpolymer in black; 1,2-epoxyhexane:AGE (80:20) terpolymer in blue; 1,2-epoxydecane:AGE (80:20) terpolymer in red.

TGA

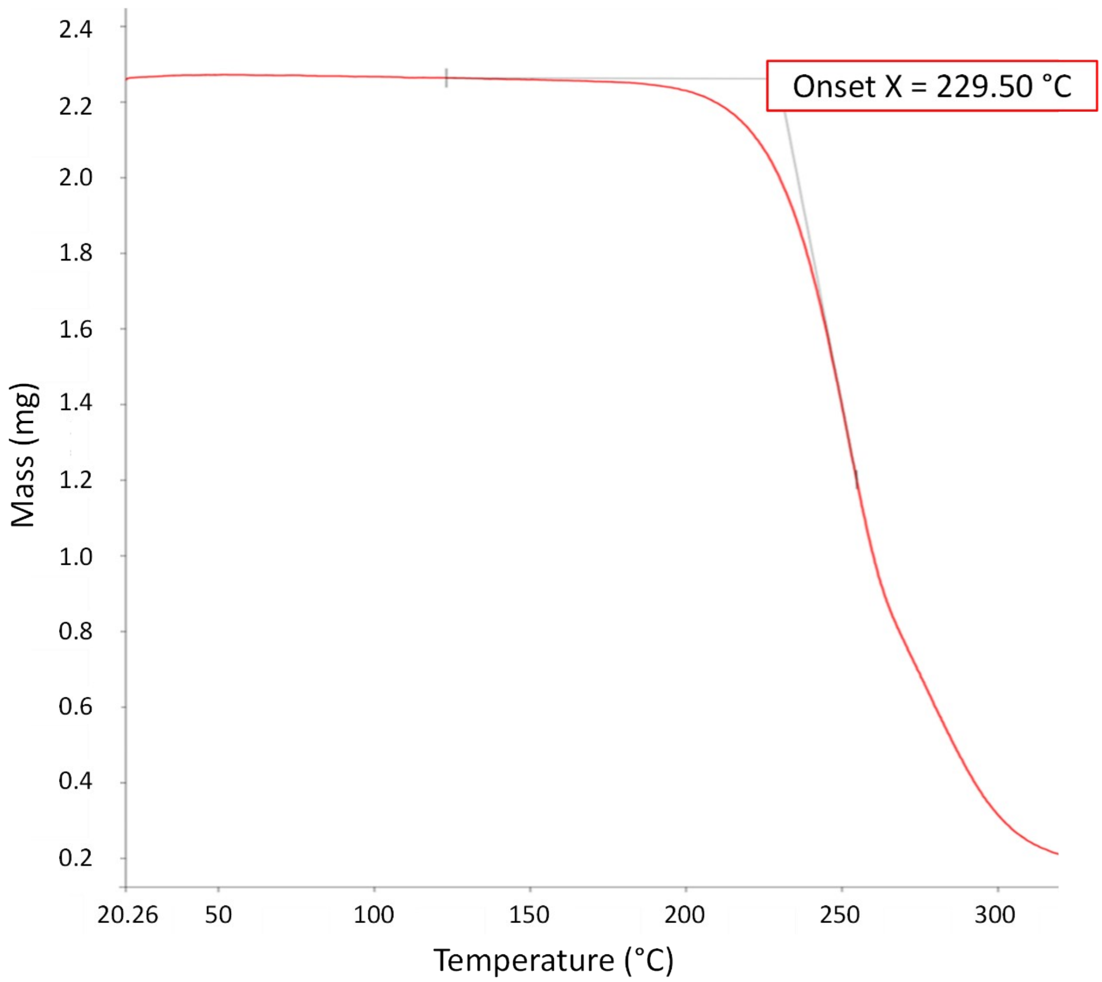


Figure S34. TGA of 1,2-epoxydecane:AGE = 80:20 polycarbonate (terpolymer). The temperature of the onset of the degradation was calculated as the intersection of the two tangents to the curve.

Peroxide curing: relationship between curing temperature and curing time

Table S2. DCP half degradation time and complete curing depending on the cross-linking temperature.

T (°C)	$t_{1/2}$ (min)	Full curing (min.) = 10 * $t_{1/2}$
130	75	750
140	25	250
150	8.8	88
160	3.2	32
170	1.23	12.3

Cross-linking setup

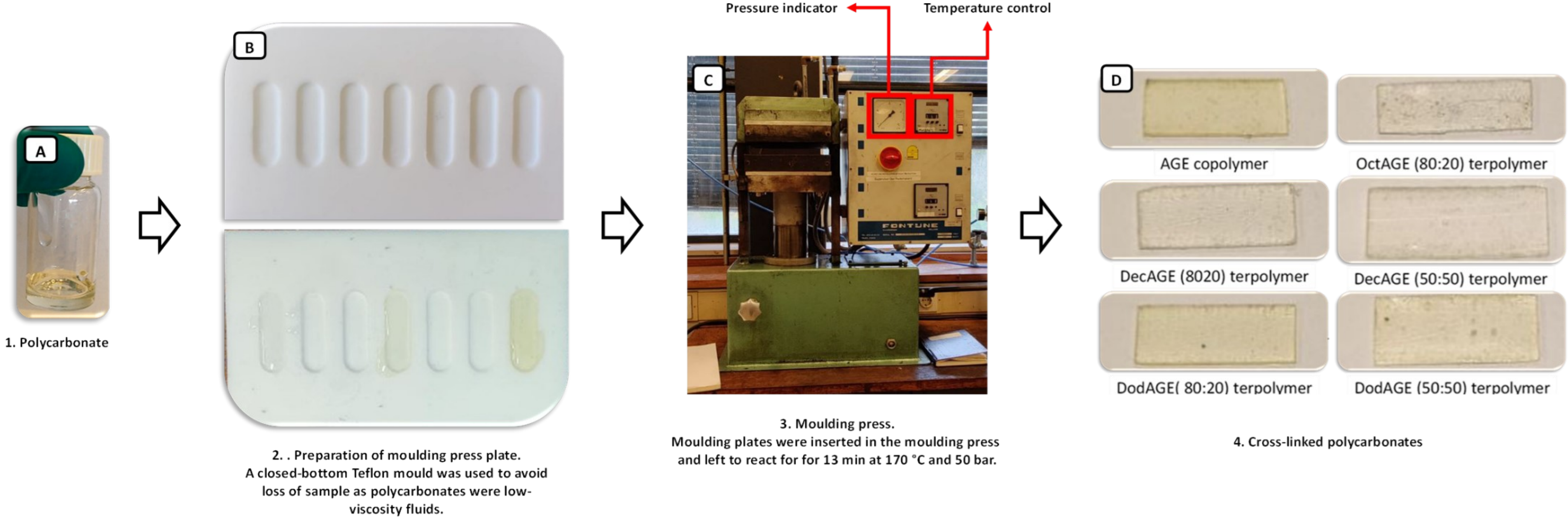


Figure S35. Cross-linking in a moulding press: (A) liquid polycarbonates before cross-linking; (B) a closed-bottom Teflon moulding plate to avoid polymers loss (the polycarbonates before cross-linking are low-viscosity fluids); (C) moulding press set-up; and (D) final cross-linked polycarbonates (solid).