

**Ethylene Carbonate/Cyclic Ester Random Copolymers Synthesized by Ring-Opening
Polymerization**

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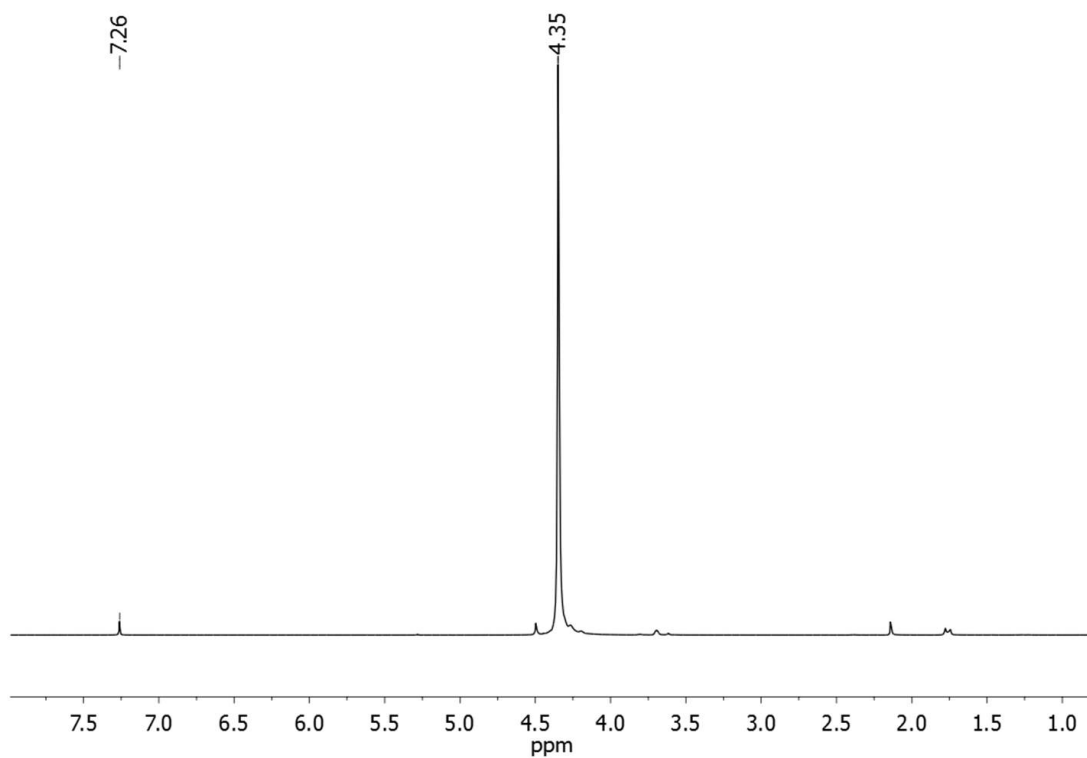


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3 , 23 °C) of a commercial PEC ($M_n = 250\,000$ g.mol $^{-1}$, $D_M = 1.9$) prepared from CO_2 /ethylene oxide copolymerization.

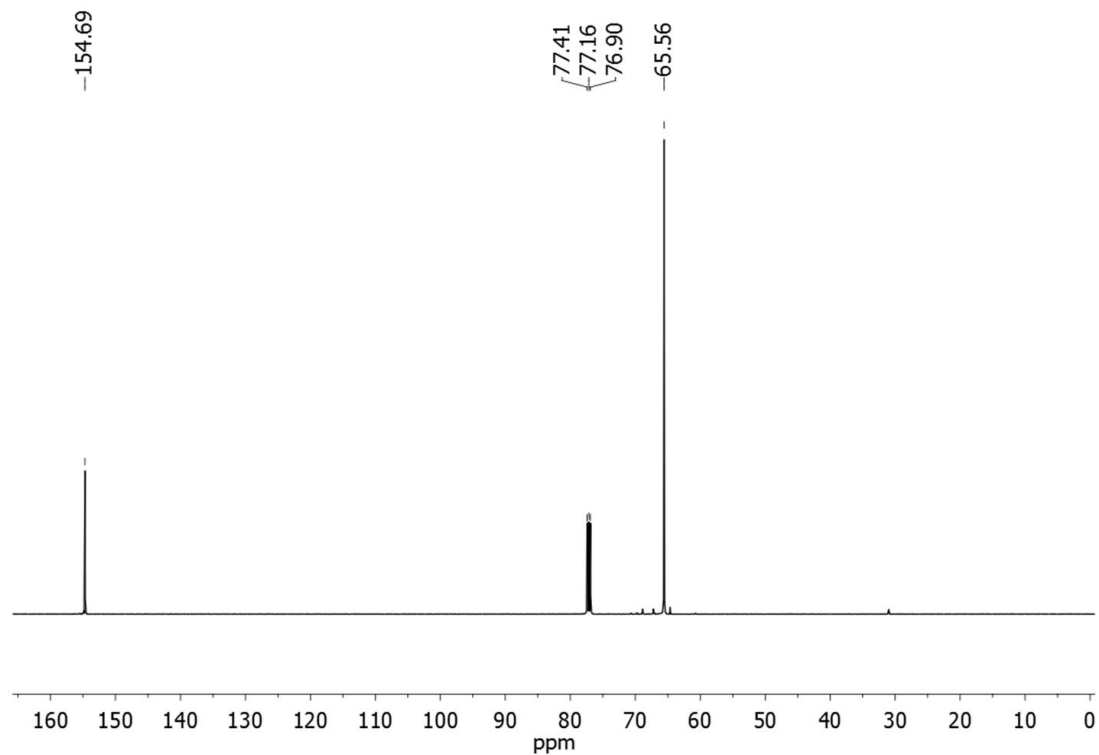


Figure S2. ^{13}C NMR spectrum (400 MHz, CDCl_3 , 23 °C) of a commercial PEC ($M_n = 250\,000$ g.mol $^{-1}$, $D_M = 1.9$) prepared from CO_2 /ethylene oxide copolymerization.

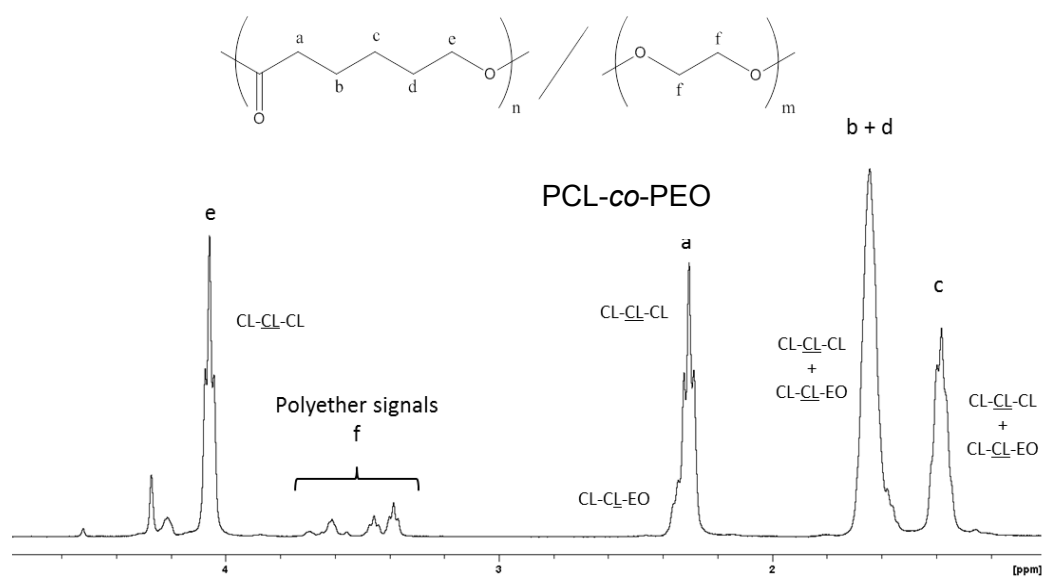


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a copolymer synthesized by copolymerization of EC/CL mediated by $\text{Al}(\text{OTf})_3/\text{BnOH}$ (Table 1, entry 12).

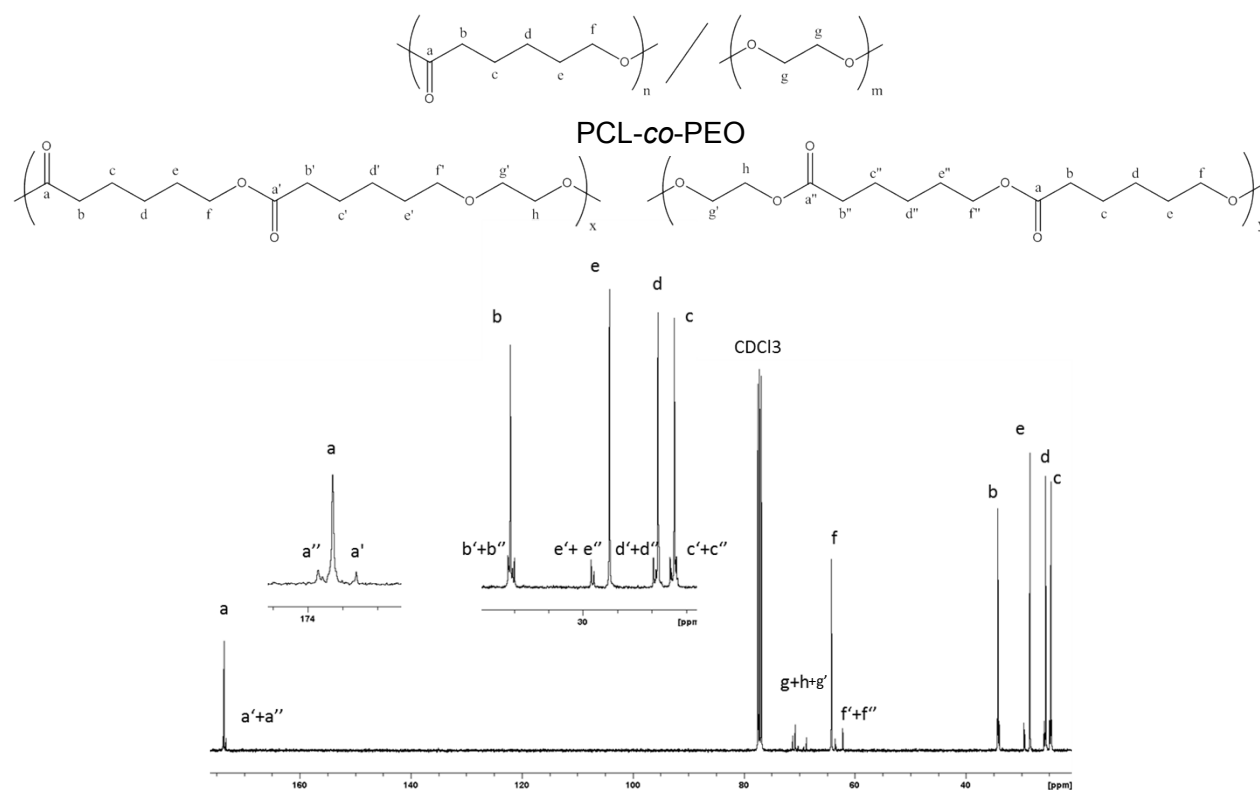


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 23 $^\circ\text{C}$) of a copolymer synthesized by copolymerization of EC/CL mediated by $\text{Al}(\text{OTf})_3/\text{BnOH}$ (Table 1, entry 12).

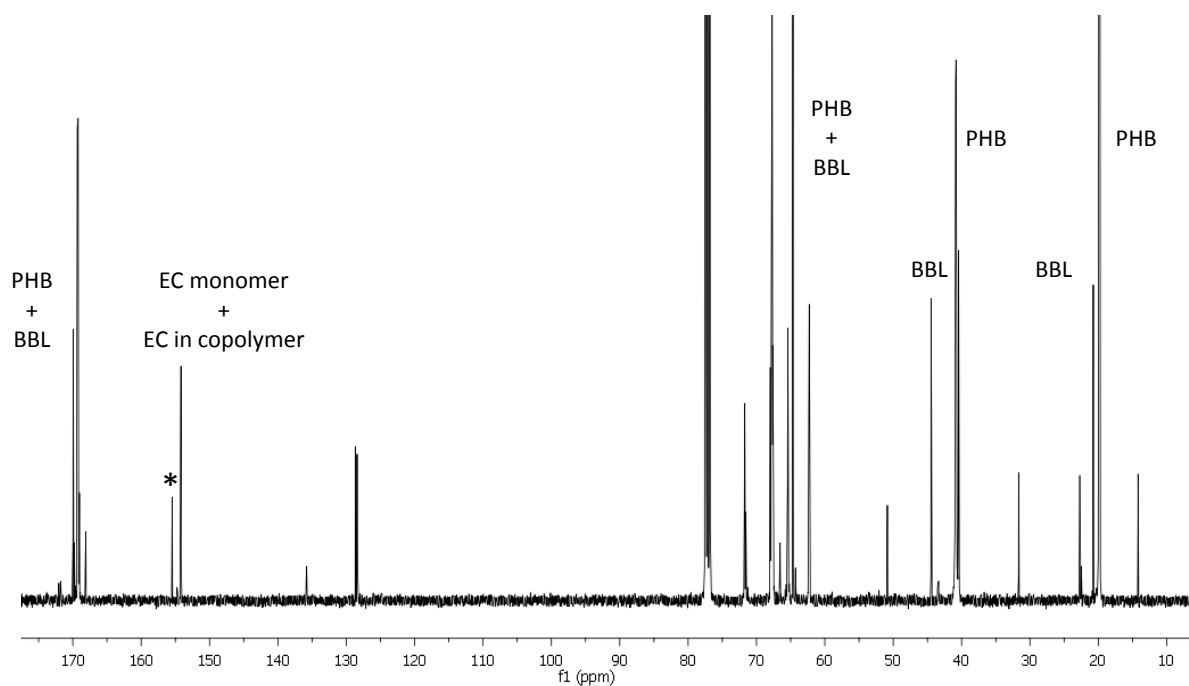


Figure S5. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 23 °C) of a P(EC-*co*-BL) synthesized from [(NNO)ZnEt] and featuring 26 mol% of inserted EC (Table 1, entry 4) (* stands for residual EC).

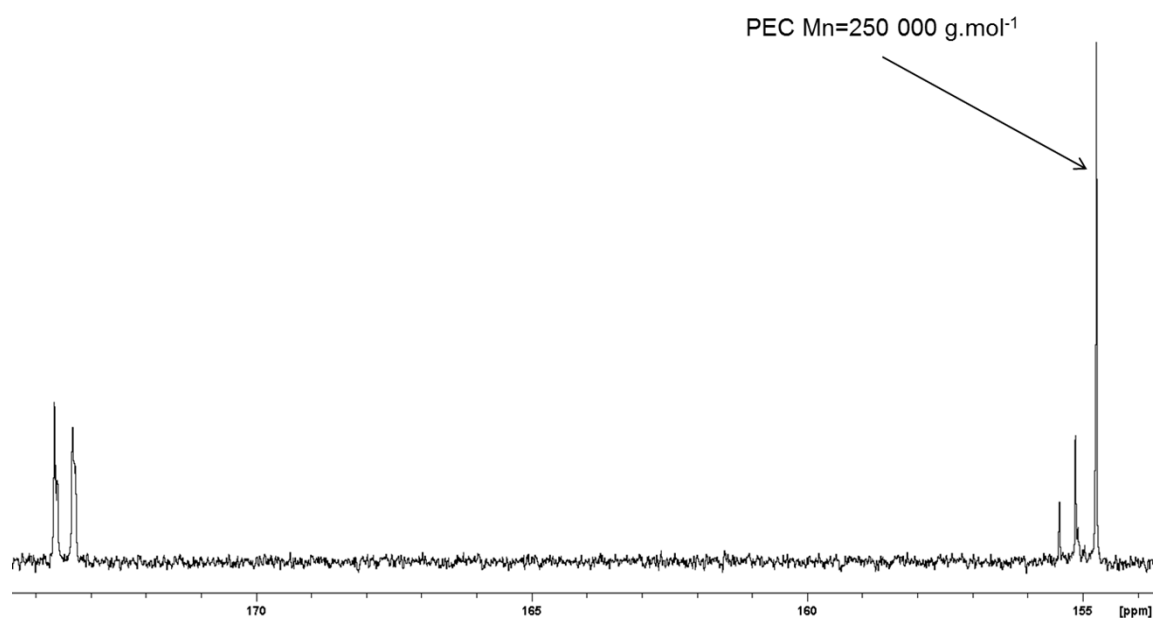


Figure S6. Carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 23 °C) of a mixture of a P(CL-*co*-EC) featuring 28 mol% of inserted EC (Table 1, entry 14) and a commercial PEC ($M_n = 250\,000\text{ g.mol}^{-1}$, $D_M = 1.9$ prepared from CO_2 /ethylene oxide copolymerization).

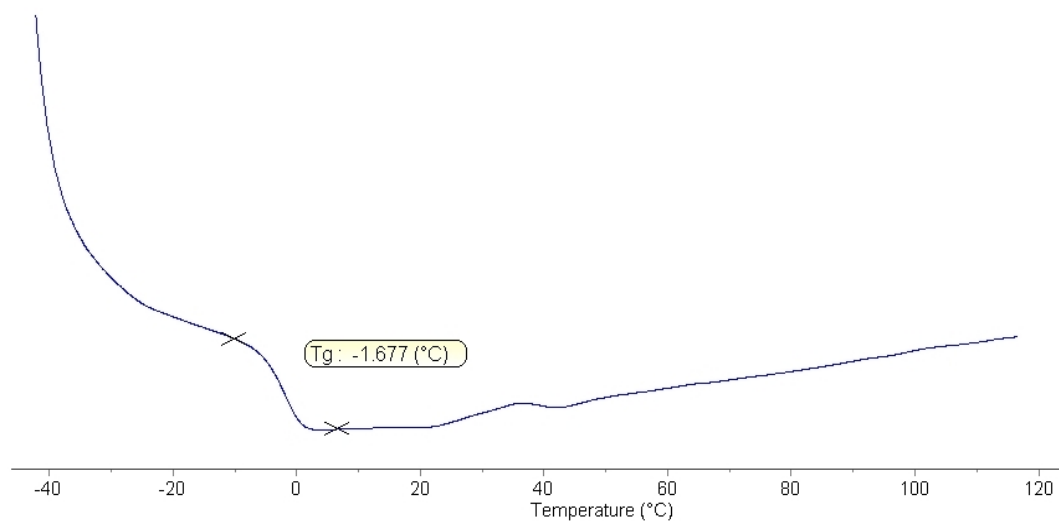


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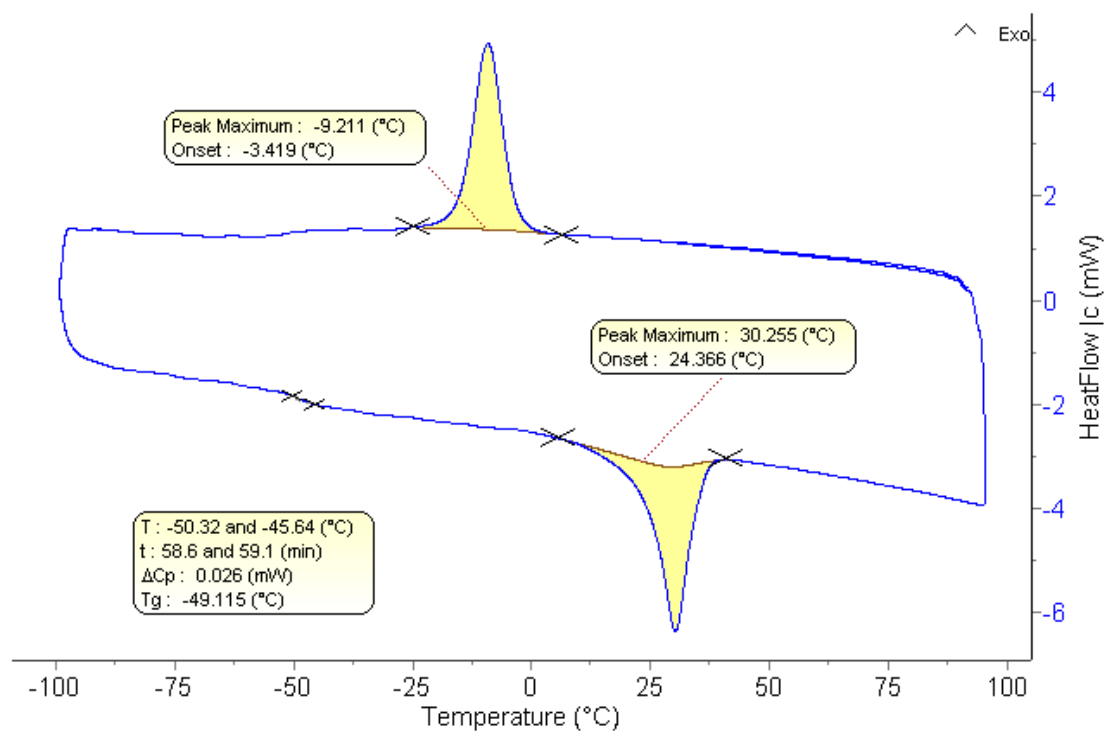


Figure S8. DSC trace of a P(EC-*co*-VL) featuring 13 mol% of EC (Table 1, entry 7).

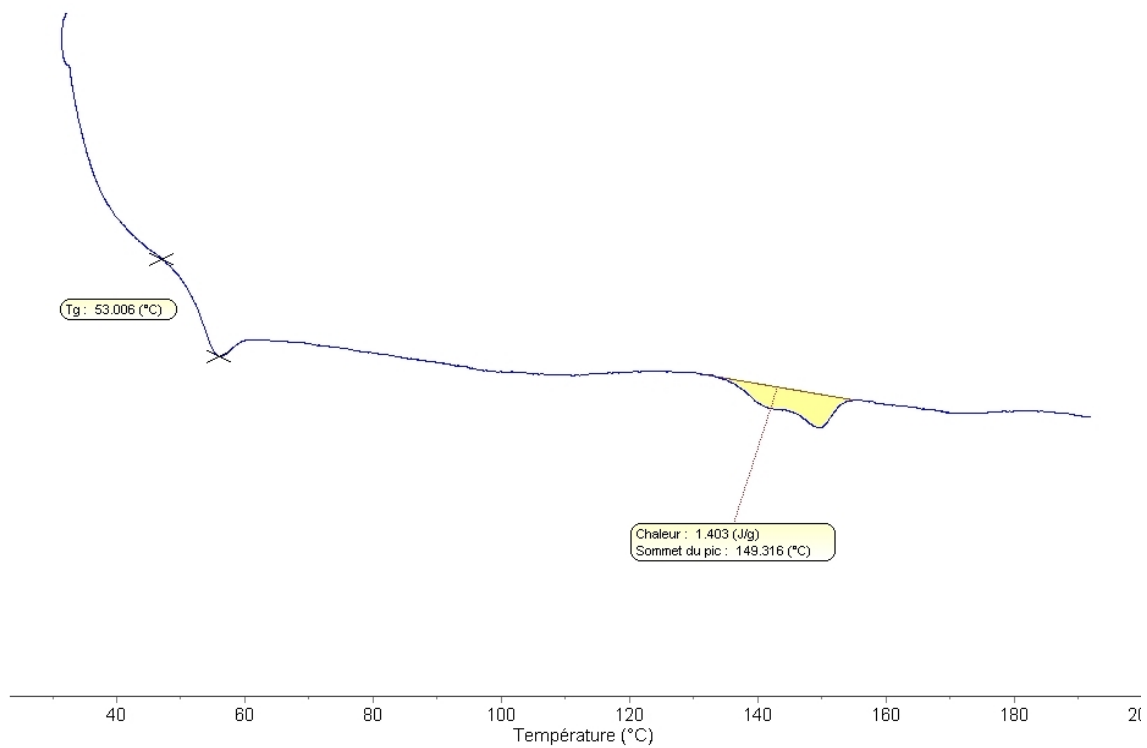


Figure S9. DSC trace of a P(EC-co-LLA) featuring 9 mol% of EC (Table 2, entry 5).