Synthesis of semifluorinated block copolymers containing poly(ε-caprolactone) by the combination of ATRP and enzymatic ROP in scCO₂

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SUPPORTING INFORMATION

![IR spectra](image)

**Figure S1.** IR spectra of a) PCL-Br macroinitiator, b) PFOMA homopolymer and c) diblock copolymer PFOMA-₇-PCL.
General procedure for the ATRP of FOMA with PCL-Br macroinitiator in toluene. PCL-Br was weighed into a 25 mL two necked round-bottom flask with a magnetic stirrer bar wherein CuBr and bipy were subsequently added. The flask was then deoxygenated by five consecutive argon/vacuum cycles and kept under continuous argon flow. Degassed toluene was added to the flask and the mixture was stirred to dissolve all the components. Degassed FOMA was added to the flask by a syringe and the mixture was heated to 80 °C. Initially a homogeneous brown solution was observed. However, the polymerization led to a phase separation during the reaction once stirring was discontinued. The reaction was stopped after 16 h. The reaction mixture was dissolved in chloroform and the solution passed through an alumina column to remove the ATRP catalyst. The product was precipitated in cold methanol and analysed by GPC and 1H-NMR. The NMR spectra showed the peaks for PFOMA and PCL-Br.

Figure S2. GPC traces for (a) the bromine endcapped macroinitiator PCL-Br and (b) after ATRP of FOMA using PCL-Br as macroinitiator. Note that the product obtained after polymerization of FOMA showed a very broad molecular weight distribution, which is consistent with block copolymer PFOMA-b-PCL and unreacted PCL-Br homopolymer.