

Functional aliphatic polyesters by click chemistry in supercritical carbon dioxide

B. Grignard, S. Schmeits, R. Riva, P. Lecomte, C. Detrembleur, C. Jérôme

Center for Education and Research on Macromolecules

University of Liège, Sart-Tilman, B6a, 4000 Liège

Introduction

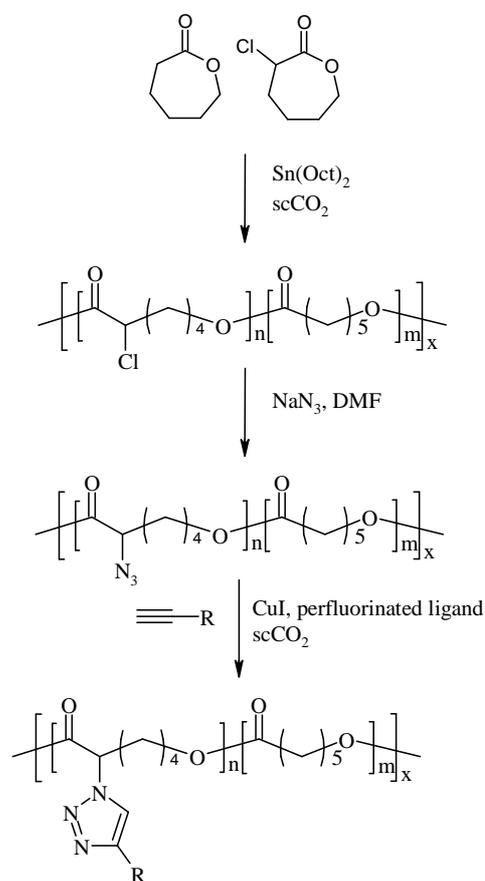
Functional aliphatic polyesters are materials that deserve potential applications in the biomedical and packaging fields. Recently, the combination of the ring-opening polymerization of lactones and “click” copper-catalyzed Huisgen’s [3+2] cycloaddition (CuAAC) has been demonstrated to be a very efficient strategy for the functionalization of poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA) in organic medium. The “Click” reaction typically occurs in organic solvents (THF or DMF), at a relatively low temperature (35°C) within short reaction time (2 hours), and no significant degradation of the polyester chains is detected. This strategy was implemented in previous works to graft alkynes substituted by different functional groups, such as hydroxyl, tertiary amines, acrylates or ammonium salts onto azide-functionalized PCL and was successfully extended to the preparation of graft copolymers, either by the grafting of ω -alkyne-PEO onto azide-functionalized aliphatic PLA or PCL (“grafting onto” technique) or by the grafting of an ATRP initiator followed by the polymerization of vinyl monomers, such as styrene (“grafting from” technique)¹. In this work, novel conditions were implemented for the “click” reaction in order to avoid the use of organic solvents and to limit the amount of catalyst remnants in functionalized aliphatic polyesters. Toward this end, it was found that the functionalization by “click” chemistry can be efficiently carried out in supercritical carbon dioxide rather than in THF or DMF. Even though aliphatic polyesters are insoluble in this medium, it will be shown that the functionalization of those polymers by “click” chemistry is quantitative after a very short reaction time (30 minutes) and at a low pressure (100 bar). Interestingly enough, no degradation was observed after the reaction as a result of the very mild reaction conditions. Last but not least, the copper catalyst was easily removed by supercritical fluid extraction leading to a very low content of residual copper in the final copolyester.

Materials and Methods

Typical CuAAC reaction. Poly(α N₃ ϵ CL-co- ϵ CL) (1 eq. of azide, Mn = 10000 g/mol, 30mol% of α N₃ ϵ CL) was introduced into a 35ml high pressure cell in the presence of 1.2 eq of alkyne, 0.1 eq of CuI and 0.1 eq of the perfluorinated ligand. The vessel was then equilibrated at 40°C for 3h at 300 bar. After the reaction goes to completion, a sample was picked out from the reaction medium for SEC characterization and the final product was dissolved in THF before precipitation in heptane and dried overnight under vacuum at room temperature.

Results and Discussion

The strategy that was proposed for the synthesis of functional aliphatic polyesters relies first on the random ring-opening copolymerization of α -chloro- ϵ -caprolactone (α -Cl- ϵ -CL) and ϵ -caprolactone (ϵ -CL) in scCO₂ using tin ethyl hexanoate as a catalyst. In a second step, the chlorinated groups of the random copolymers were substituted by NaN₃ into azido functions before grafting functional alkynes using a CO₂-soluble copper(I) catalyst (Scheme 1). This strategy was described in one of our very recent paper.²



R = CH₂OH, CH₂N(Me)₂, ethynylpyrene, ATRP initiator
Scheme 1: synthesis of functional aliphatic polyesters: general strategy

The random copolymerization of α -chloro- ϵ -caprolactone and ϵ -caprolactone, initiated by benzylic alcohol with tin ethylhexanoate as a catalyst was first realized in supercritical carbon dioxide using a [α -Cl- ϵ -CL]/[ϵ -CL]/[initiator]/[catalyst] molar ratio ~ [30]/[140]/[1]/[1] at 80°C and 260 bar. After 96h, the total monomer conversion, determined gravimetrically was high (~ 80%) and the experimental molecular weight as well as the [α -

Cl- ϵ -CL]/[ϵ -CL] molar ratio were in good agreement with the theoretical values. In a second step, the chlorinated groups of the random copolymers were substituted by 1.1 eq. of NaN₃ into azido functions at a room temperature (24h). However, due to the insolubility of the azido salt in scCO₂, this reaction was realized in DMF. After the purification of the azido-functional aliphatic polyester, the grafting of prop-2-yn-1-ol onto poly(α N₃ ϵ CL-co- ϵ CL) (30 mol% of α N₃ ϵ CL) was first tested in scCO₂ by introducing 1g of poly(ϵ CL-co- α N₃ ϵ CL) (M_n =10000 g/mol, 30mol% of α N₃CL) in a 35ml high pressure cell in the presence of prop-2-yn-1-ol (1.2 eq compared to α N₃ ϵ CL), CuI ([Cu]/[alkyne] = 0.1) and a perfluorinated aminoligand ([Cu]/[ligand] = 1) that is already soluble at a room temperature in liquid CO₂ (80 bars). The CuAAC reaction in scCO₂ was then optimized by changing the pressure, the amount of the catalyst and the reaction time. From these results, the quantitative grafting of prop-2-yn-1-ol was achieved in 30 minutes at 100 bars and 35°C even though PCL is not soluble in this medium. Those excellent results result from the high mass transport properties of scCO₂, so that the catalyst as well as the alkyne were able to rapidly diffuse inside the plasticized polymer matrix. Next, the concept of the CuAAC reaction in supercritical carbon dioxide was successfully extended to the grafting of *N,N*-dimethylprop-2-yn-1-amine, ethynylpyrene or an alkyne functionalized ATRP initiator. Finally, as the presence of copper traces can involve toxicological or environmental problems, the copper catalyst that exhibits high solubility in scCO₂ was removed by supercritical fluid extraction leaving the functional aliphatic polyester with catalytic residues as low as 4% (determined by ICP).

Conclusions

In this communication, we have reported a very simple, very fast and very mild method for the functionalization of aliphatic polyesters based on the CuAAC reaction. The grafting of an alcohol, a tertiary amine, a chromophore group, and a polymerization initiator was successfully achieved at a very low temperature and pressure. Moreover, due to the mild reaction conditions, no degradation of the polymer was observed after the functionalization and, due to its high solubility, the copper catalyst was easily removed by supercritical fluid extraction, leaving polymers with catalyst residues lower than 4%.

References

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