

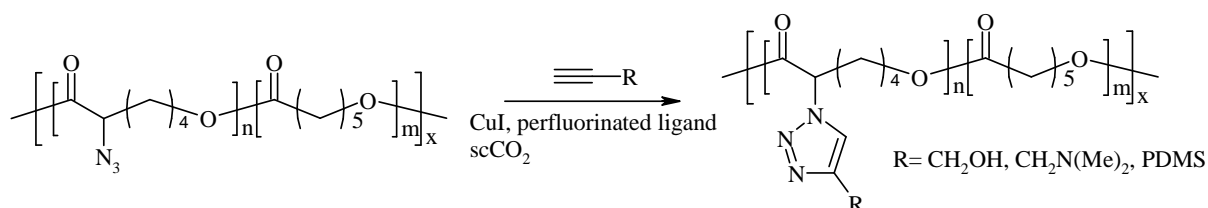
FUNCTIONALIZATION OF ALIPHATIC POLYESTERS BY “CLICK CHEMISTRY” IN SUPERCRITICAL CARBON DIOXIDE

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The combination of ring-opening polymerization of lactones and “click” copper-catalyzed Huisgen’s [3+2] cycloaddition is known to be a very efficient strategy for the functionalization of poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA). Whenever the “click” reaction occurs in an organic solvent (THF or DMF), at relatively low temperature (35°C) and within short reaction time (2 hours), no significant degradation of 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 PCL¹. Moreover, this approach was previously extended to the synthesis of grafted copolymers, either by the grafting of ω -alkyne-PEO onto azide-functionalized aliphatic PLA or PCL (“grafting onto” technique) either by grafting of an ATRP initiator followed by the polymerization of vinyl monomers, such as styrene (“grafting from” technique).

These functionalized aliphatic polyesters are promising materials for the development of new biomedical devices. 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. For that sake, it turned out necessary to synthesize a perfluorinated polyamine in order to solubilize the catalyst in supercritical carbon dioxide².



Aliphatic polyesters are not soluble in supercritical carbon dioxide. Nevertheless, even under heterogeneous conditions, the functionalization of aliphatic polyesters by “click” chemistry is quantitative. Interestingly enough, no degradation was observed. 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.

References

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2. B. Grignard, S. Schmeits, R. Riva, C. Detrembleur, Ph. Lecomte and Ch. Jérôme, *Green Chemistry*, 2009, submitted for publication