

Title:

Contribution of “click chemistry” to the macromolecular engineering of aliphatic polyesters

Abstract:

Nowadays, biodegradable and biocompatible aliphatic polyesters are widely used as environmentally friendly thermoplastics and biomaterials. Nevertheless, the absence of any pendant functional group is a severe limitation for the development of novel applications.

Recently, the expansion of the “click chemistry”, and more particularly the copper-mediated Huisgen's cycloaddition (CuAAC), marked a turning point for the design of new functional and grafted copolymers in macromolecular engineering. Indeed, this reaction between an organic azide and an alkyne is characterized by a high yield under mild conditions in relatively short reaction time, which is well-suited for polymer modifications or coupling reactions.

The chemical modification of aliphatic polyesters is sometimes a challenge because of their sensitivity to degradation, generally by hydrolysis, which limits the range of usable organic reactions. The very mild conditions of the CuAAC reaction made of this reaction a very powerful tool for the chemical modification of aliphatic polyesters. For this purpose, a PCL bearing azide groups was synthesized by ring-opening copolymerization of ϵ -caprolactone and α -chloro- ϵ -caprolactone (α Cl ϵ CL), followed by the substitution of the pendant chlorides into azides by simple reaction of the copolyester with sodium azide (Figure 1). Starting from this unique precursor, different functional PCLs were obtained by reaction of the PCL-azide with different alkynes substituted by various suitable functional groups. With this strategy, alcohols, tertiary amines, acrylates or ATRP initiators were quantitatively grafted onto PCL without any detectable degradation of the polyester chain. The grafting of an alkyne end-capped poly(ethylene oxide) (PEO) onto PCL-azide was also investigated with formation of the corresponding amphiphilic PCL-*g*-PEO copolymer, which may find an application in the biomedical field as a drug carrier.

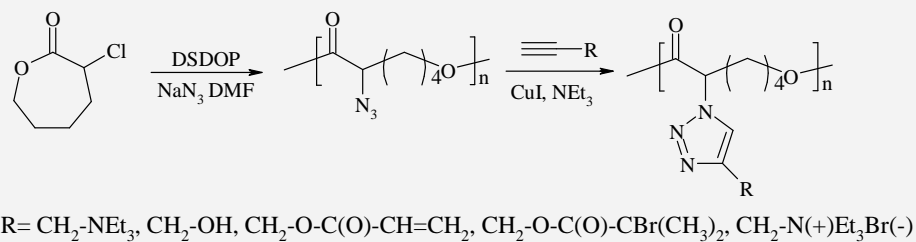


Figure 1

Moreover, the mildness of the CuAAC conditions allowed the chemical modification of more sensitive aliphatic polyesters, such as PLA. For this sake, our strategy was successfully extended to the chemical modification and grafting of poly(α Cl ϵ CL-co-LA) copolymers, again without degradation of the PLA backbone.

Finally, the CuAAC reaction was not only applied for the preparation of functional or grafted aliphatic polyesters but also for the design of new materials. The grafting of an ammonium salt is an efficient tool to render aliphatic polyesters anti-bacterial. The synthesis of partially biodegradable hydrogels and pH sensitive hydrogels was also investigated. More recently, the different strategies developed in this work were combined with the purpose to synthesize star-shaped amphiphilic copolymers with arms exclusively made up of aliphatic polyesters.