Recent advances in the macromolecular engineering of aliphatic polyesters by ring-opening polymerization and click chemistry.

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Introduction

During the last decade, a wide range of biodegradable and biocompatible aliphatic polyesters have been synthesized by ring-opening polymerization (ROP) of lactides and lactones.[1] In parallel, extension of the "click" copper-mediated Huisgen 1,3-cycloaddition reaction of azides and alkynes to macromolecular chemistry has proved to be successful. [2,3] This lecture aims at reporting the recent progress made in our laboratory in the synthesis of new aliphatic polyesters by ring-opening polymerization and assistance of "click" chemistry.

Results and Discussion

PCL bearing pendent functional groups, e.g., amines, ammonium salts, acrylates, bromides, alcohols, were synthesized by copper-mediated Huisgen 1,3-cycloaddition of duly substituted alkyne and pendent azide groups of PCL (Figure 1). [4] This strategy is very versatile because a variety of functional aliphatic polyesters can be prepared from a single precursor.[5] "Click" cycloaddition is carried out under so mild experimental conditions (CuI, Et$_3$N, THF, 35°C) that no degredation is observed by SEC, [4] whenever very sensitive lactide containing copolyesters are derivatized.

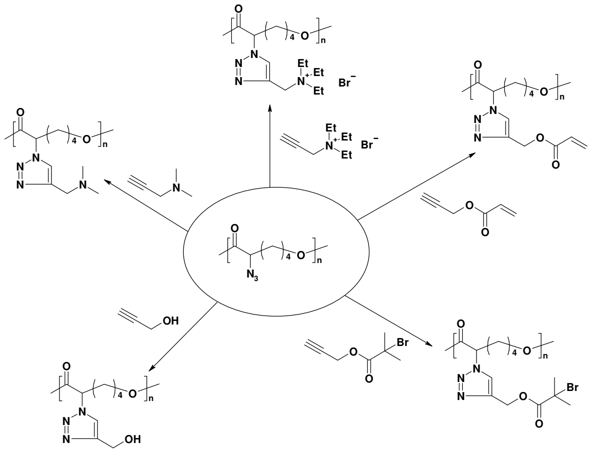

Figure 1 – Examples of reactive groups that can be attached to PCL by Huisgen 1,3-cycloaddition

Thi methodology was extended to the synthesis of graft copolymers (Figure 2).[4] Indeed, ω-alkyne-PEO was grafted onto PCL and polylactide (PLA) bearing azide substitutents with formation of amphiphilic PCL-g-PEO and PLA-g-PEO copolymers.

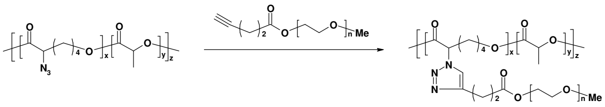

Figure 2 – Synthesis of PLA-g-PEO copolymer

Very recently, an original method was reported for the synthesis of macrocyclic polyesters by combination of ring-opening polymerization and intramolecular cross-linking.[6] This strategy was extended to the synthesis of novel tadpole-shaped copolymers composed of one polyester macrocycle onto which two polyester arms were grafted. The main steps were as follows (i) sequential ring-opening polymerization of εCL and approximatedly 15 units α-acrylic-ε-CL, initiated by DSDOP (ii) intramolecular photocross-linking of the acrylic double bonds (iii) resumption of the lactone polymerization. (figure 3)

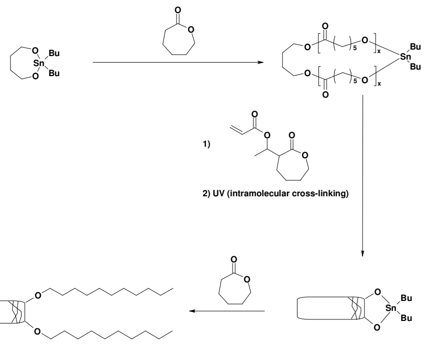

Figure 3 – Synthesis of novel tadpole-shaped copolymers with two grafted arms.

pH-sensitive amphiphilic networks were prepared in "one pot" by coupling N,N-dimethylamino-1-propyne onto poly(α-azide-ε-caprolactone) followed by "click" crosslinking with telechelic α,ω-alkyne-PEO (Figure 4)

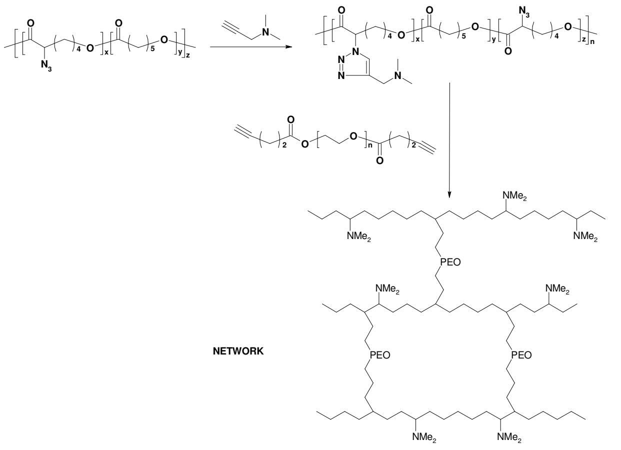

Figure 4 – Synthesis of pH-sensitive hydrogels.

Hyperbranched polymers were prepared by ring-opening polymerization of a ε-caprolactone substituted by an hydroxyl group, prepared by click coupling of butynol-1 with γ-azido-ε-caprolactone.

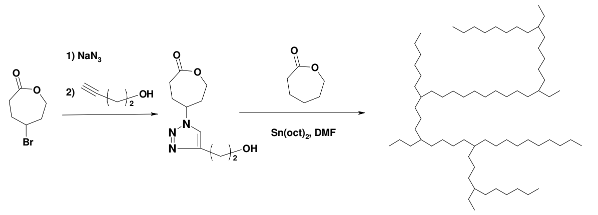

Figure 54 – Synthesis of hyperbranched copolymers.

Conclusion

Ring-opening polymerization and "click" Huisgen 1,3-cycloaddition are very efficient techniques for the synthesis of new aliphatic polyesters with diverse architectures, bearing or not functional groups. One main advantage of the "click" Huisgen 1,3-cycloaddition has to be found in the experimental conditions (CuI, Et_3N, THF, 35°C), which are mild enough to minimize polyester degradation, even of highly sensitive PLA.

References

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