CONTRIBUTION OF 'CLICK CHEMISTRY' TO THE FUNCTIONALIZATION OF ALIPHATIC POLYESTERS

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For the last decade, a steadily increasing attention was paid to biodegradable and biocompatible aliphatic polyesters either as substitutes for non biodegradable polymers or in the field of biomedical applications. Nevertheless, the lack of pendent functional groups along polyester chains is a major limitation for many applications. This communication aims at reporting on a novel route to go a step further in the macromolecular engineering of aliphatic polyesters. Our strategy combines ring-opening polymerization and the most popular "click" reaction to date, e.g., the copper-catalyzed Huisgen's [3+2] cycloaddition of azides and alkynes. This "click" reaction is of wide scope, gives high yields with readily available starting materials. Interestingly enough, this reaction can be carried out under very mild conditions (35°C in THF), which are particularly advantageous to avoid polyester degradation. Consistently, different alkynes substituted by either a functional group, e. g., hydroxyl, tertiary amine, acrylate, ATRP initiator and quaternary ammonium salt or a polymer chain were efficiently cycloadded onto azide-containing poly(ε-caprolactone) (PCL) (Fig. 1) [1]. The grafting conditions are so mild that derivatization of an azide-containing copolyester of poly(lactide) (PLA) was also successfully carried out without degradation even tough this copolyester is more sensitive to degradation[2].

$$\begin{array}{c} CuI, \, NEt_3, \, THF \\ \hline = -R \, , \, 35^{\circ}C \\ X = CH_3 \, \text{and} \, y = 0 \quad Lactide \\ X = H \, \text{and} \, y = 4 \quad \epsilon\text{-caprolactone} \\ R \\ \hline R = CH_2OH, \, CH_2NMe_2, \, CH_2N(Et)_3Br, \, CH_2OC = OCH = CH_2, \, CH_2OC = OCBr(CH_3)_2, \, CH_2Me_2^{\dagger}C_8H_{17}Br \\ \end{array}$$

Figure 1

This strategy turned out to be very versatile to extend the range of available aliphatic polyesters and thus, to tailor their properties. Indeed, highly hydrophilic, hydrosoluble and amphiphilic polyesters were made available. The grafting of quaternary ammonium salts was carried out with an aim to impart antimicrobial activity to aliphatic polyesters. Last but not least, our strategy was extended to the preparation of pH-responsive amphiphilic polymer networks.

References

CH₂-CH₂-C(O)-O-PEO

- [1] Riva, R., Schmeits, S., Jérôme, Ch., Jérôme, R., Lecomte, Ph. *Macromolcules* **2007**, 40, 796-803.
- [2] Riva, R., Schmeits, S., Stoffelbach, F., Jérôme, Ch., Jérôme, R., Lecomte, Ph. *J. Chem. Soc.*, *Chem. Commun.* **2005**, 5334-5336.