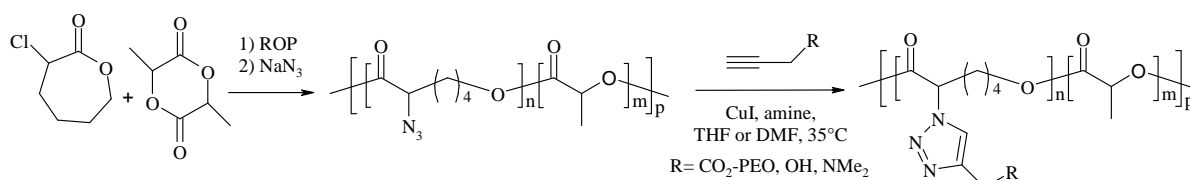


New developments in the functionalization of aliphatic polyesters by “click” copper-catalyzed azide-alkyne cycloaddition

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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. Our strategy aiming at functionalizing aliphatic polyesters relies on the “click” copper-catalyzed cycloaddition (CuAAC) of alkynes duly substituted by functional groups or even chains onto PCL bearing pendant azides.^{1,2} The aliphatic polyesters bearing pendant azides have been very efficiently synthesized by a straightforward approach, which relies on the ring-opening copolymerization of α Cl ϵ CL (or γ Br ϵ CL) and ϵ CL (or lactide) followed by reaction with sodium azide to convert pendant chlorides or bromides into azides.



The alternative reported by Emrick et al. is based on the CuAAC reaction of azides substituted by any functional group onto copolyesters of poly(ϵ -caprolactone) bearing pendant alkynes.³ Interestingly enough, Emrick et al. carried out the CuAAC reaction in water at 80°C . Unfortunately, it turned out, at least in our hands, that these conditions can not be extended to the derivatization of more sensitive aliphatic polyesters because degradation was then unavoidable. Nevertheless, we found out that degradation can be minimized whenever the CuAAC reaction is carried out in an organic solvent at lower temperature. Typically, the CuAAC reaction was carried out in DMF or THF at 35°C . Recently, it was shown that supercritical carbon dioxide can be used as a more environmentally friendly solvent than DMF or THF.

The contamination by catalytic residues of aliphatic polyesters functionalized by the CuAAC reaction is a severe limitation in view of future applications, especially in the biomedical field. In the last part of this talk, a special attention will be paid on our current efforts to get rid of copper residues.

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3. B. Parrish, R.B. Breitenkamp, T. Emrick, *PEG- and peptide-grafted aliphatic polyesters by click chemistry*, J. Am. Chem. Soc., **127**, 7404 (2005).