

Synthesis of new biodegradable clicking polyesters *via* tricomponent step-growth polymerization

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Introduction

Thanks to mild reaction conditions, functional group tolerance and quantitative yields click reactions are extensively used for the synthesis of a variety of polymer constructs including functionalized polymers and biopolymers, block copolymers, cyclic polymers, etc., “Click chemistry” (CC) is a rapidly growing field of research. Surprisingly, there are only few papers on the application of CC in step-growth polymerization (SGP) as a chain propagation reaction, and, to our best knowledge, there are no examples of the synthesis of biodegradable polymers such as aliphatic polyesters (PEs), polyamides and poly(ester amide)s via CC.

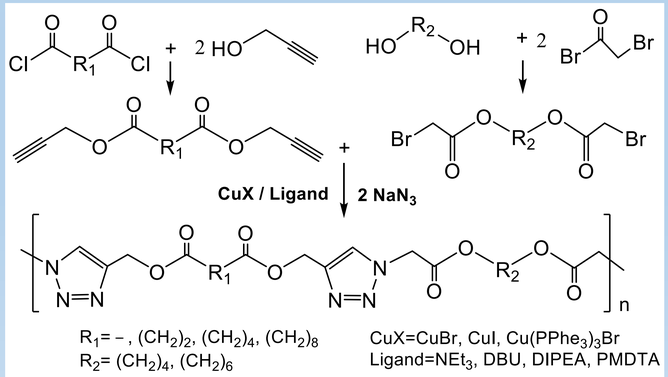
Research goal

Synthesis and characterization of new biodegradable “clicking” polyesters on the basis of non-toxic building blocks such as fatty diols and dicarboxylic acids using click chemistry-based step-growth polymerization.

Methods

The present study is the first attempt of the synthesis of new biodegradable “clicking” polyesters on the basis of non-toxic building blocks such as fatty diols and dicarboxylic acids using click chemistry-based SGP. Among a variety of click reactions we have selected copper(I) catalyzed alkyne–azide 1,3-cycloaddition reaction due to availability of starting reagents for obtaining suitable monomers leading to the formation of 1,2,3-triazole cycles. It is expected that the insertion of 1,2,3-triazole groups in the PEs backbone can, firstly, improve their thermal characteristics; secondly, a weak basicity of 1,2,3-triazole cycle can catalytically influence their non-specific hydrolysis (biodegradation), and, finally, the possibility of quaternization of 1,2,3-triazole cycles using halo-alkyls opens a way to positively charged systems - either water soluble polymers or cross-linked hydrogels both promising for various biomedical applications.

Synthesis of the new PEs has been carried out on the basis of di-propargyl esters of dicarboxylic acids and di-(bromo-acetic acid)-alkylene diesters in the presence of sodium azide *via* tricomponent *in situ* click reaction (Scheme 1).

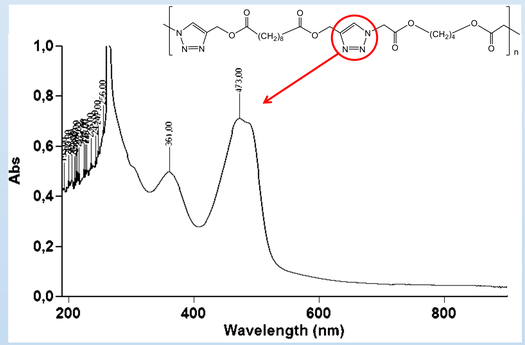


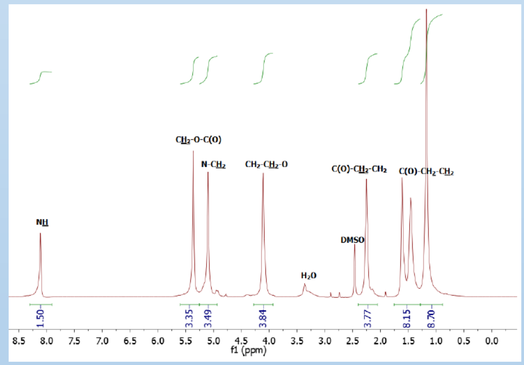
Scheme 1. Synthesis of clicking polyesters

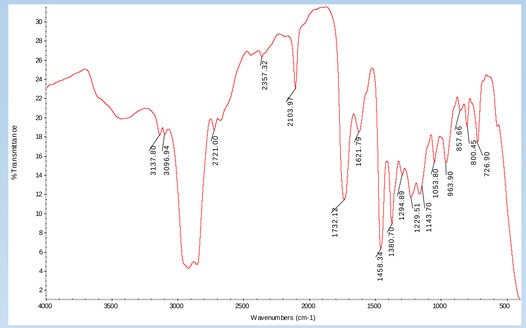
Results

Optimal reaction parameters (catalyst, solvent, solution concentration, reaction temperature, etc.) for the new click SGP have been established and the resulting PEs have been characterized by FTIR, NMR, GPC, viscosimetry and DSC.

New biodegradable “clicking” polyesters with molecular weight (*Mw*) up to 73,000 Da has been obtained *via* the new click SGP reaction.







Optimal parameters for the new “click” SGP:

- solvent - *N*-Methyl-2-pirrolidone
- catalyst – CuI,
- catalyst’s activator (ligand) – NEt_3
- monomer concentration – 0.6 mol/L
- duration of bis-azide formation step – 3 h
- duration of SGP – 15 h
- temperature of bis-azide formation step – room temperature
- temperature of SGP – O^0 C

Conclusions & Outlooks

The obtained PEs could be of interest for various biomedical applications. Furthermore, the possibility of quaternization of 1,2,3-triazole cycles using halo-alkyls opens a way to positively charged systems - either water soluble polymers or cross-linked hydrogels both promising for various biomedical applications.

The established optimal conditions of the click SGP reaction will be applied to the synthesis of other classes of clicking polymers such as regular aliphatic poly(ester amide)s and amino acid based poly(ester amide)s promising for biomedical applications as biodegradable biomaterials.

References

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