



# Integration of graft copolymerization and ring-opening reaction: A mild and effective preparation strategy for “clickable” cellulose fibers

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## ABSTRACT

A mild and effective strategy to prepare alkynyl-functionalized cellulose fibers (A-CFs) and azido-functionalized cellulose fibers (N<sub>3</sub>-CFs) was presented. Epoxy-cellulose fibers (Epoxy-CFs), graft copolymerization products of cellulose fibers (CFs) and glycidyl methacrylate (GMA), were prepared using cerium ammonium nitrate (CAN) as initiator. Epoxy groups content of Epoxy-CFs were as high as 2.5 mmol/g. Introduction of alkynyl/azido groups into Epoxy-CFs were achieved through ring-opening reactions of epoxy groups with propargylamine (PgAm) and sodium azide (NaN<sub>3</sub>), respectively. Under appropriate conditions, A-CFs with alkynyl groups of 0.57 mmol/g and N<sub>3</sub>-CFs with azido groups of 0.35 mmol/g were obtained. Click reactivities of A-CFs, N<sub>3</sub>-CFs and Epoxy-CFs were verified by Cu(I) catalyzed alkyne-azido cycloaddition (CuAAC) and thiol-epoxy click reactions. A-CFs, N<sub>3</sub>-CFs, Epoxy-CFs and their clicked products were characterized by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS).

## 1. Introduction

Cellulose as a kind of green and sustainable polysaccharide has many advantages such as non-toxicity, inexpensiveness, degradability and flexibility. However, some intractable challenges still remain. Physical and/or chemical modifications of cellulose are commonly designed to overcome inherent drawbacks of this most abundant polysaccharide in nature such as insolubility, poor dimension stability and hydrophilicity, or to impart novel properties such as antimicrobial activity, fluorescence and thermosensitivity (Guan, Xiao, Sullivan, & Zheng, 2007; Ye, Xiong, & Sun, 2012; Zhang, Xu, Wu, Zhang, & Zhuo, 2009). Cellulose-based functional materials are attracting more and more attention in advanced fields. Investigations on such aspects are driven by increasing environment concerns and demands for advanced materials derived from renewable resources.

The concept of click chemistry proposed by Sharpless et al in 2001 as an efficient and environmentally friendly approach has high selectivity, high yield and high tolerance towards oxygen and water and also works at ambient temperature (Kolb, Finn, & Sharpless, 2001). The first investigation on the design of cellulose derivatives through click reaction was reported by Liebert, Hänsch, and Heinze (2006), closely followed by Hafrén et al (Hafrén, Zou, & Córdova, 2006). Click chemistry has several reaction types, including Cu(I)-catalyzed alkyne-azide 1,3-dipolar cycloaddition (CuAAC), strain promoted azide-alkyne

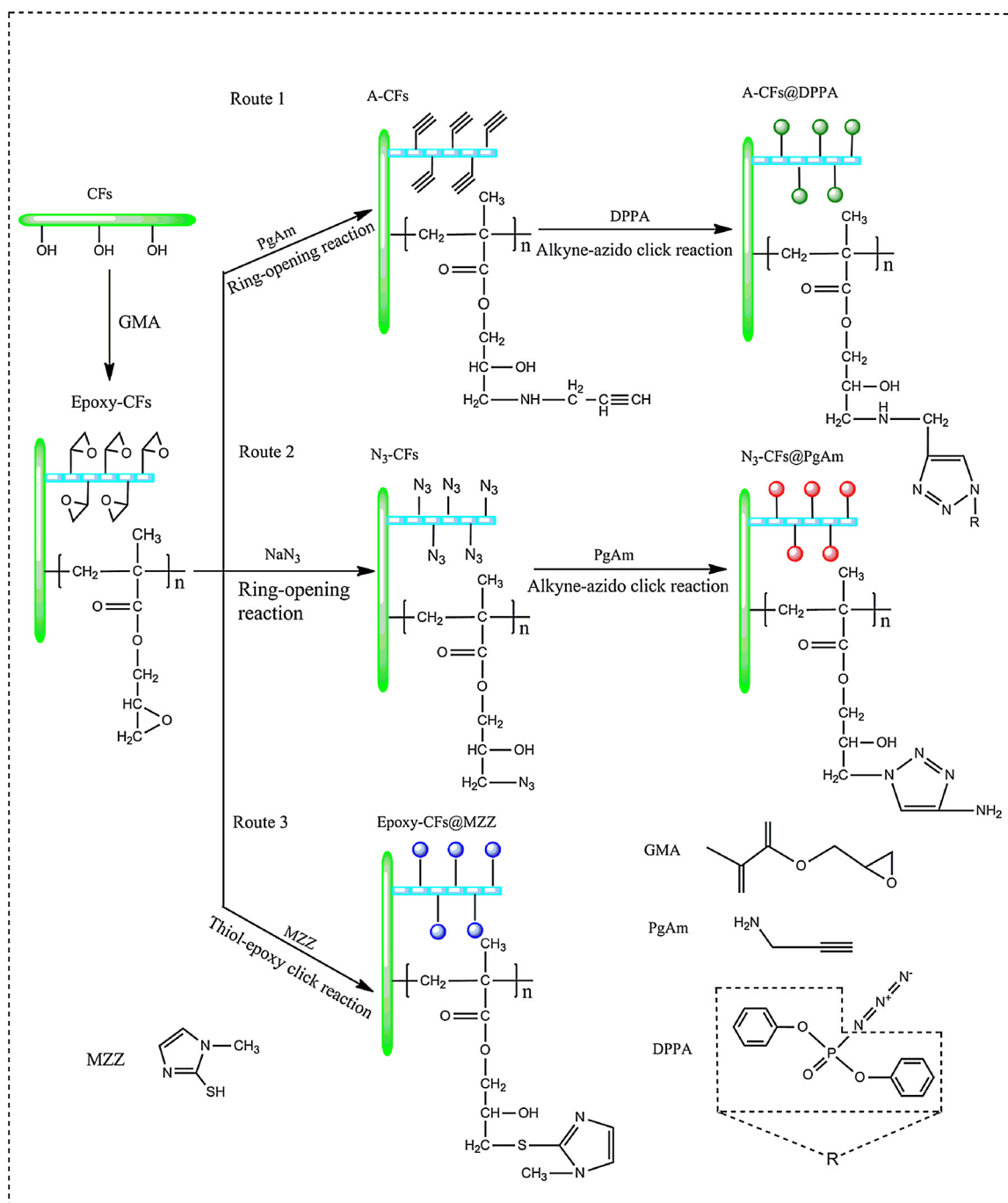
cycloadditions (SPAACs), Diels-Alder reaction and photo-initiated thiol-ene radical reaction (Agard, Prescher, & Bertozzi, 2004; Bock, Hiemstra, & van Maarseveen, 2006; Meng & Edgar, 2016). In addition, various alternative methods such as thiol-Michael addition reaction and thiol-epoxy click reaction have also been presented (Anseth & Klok, 2016; Jin, Heath, & Torkelson, 2015).

CuAAC is the most popular click reaction, although many more reactions are being classified as click chemistry. CuAAC is a powerful tool for introducing various functional molecules onto cellulose to prepare different cellulose-based functional materials. Preparing clickable cellulose, including alkynyl-bearing cellulose, alkynyl-functionalized cellulose, azido-bearing cellulose and azido-functionalized cellulose, is the first step in the preparation of cellulose-based functional materials via CuAAC (Nongbe et al., 2018; Xu, Spadiut, Araffljo, Nakhai, & Brumer, 2012).

Physical adsorption/deposition was feasible to impart cellulose click reactivity. For example, nanofibrillar cellulose (NFC) was heterogeneously modified by adsorbing propargyl- or azido-functionalized carboxymethyl cellulose and then clicking with the counterpart module (Junka et al., 2014). Similarly, the study on surface modification of cellulosic material by sequential adsorption and click reaction was reported (Filpponen et al., 2012). Recently, a new physical adsorption route to prepare alkyne-functionalized cellulose fibers (ACFs), i.e., in situ chemical oxidation polymerization of 3-ethynylaniline in presence

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**Scheme 1.** Schematic diagram of Epoxy-CFs, A-CFs and N<sub>3</sub>-CFs preparation and their click reaction.

of cellulose fibers (CFs), was also presented (Xiao, Ding, Song, Qian, & An, 2017).

Regarding chemical methods towards alkyne-bearing cellulose, direct chemical reactions include etherification and esterification (Faugeras, Elchinger, Brouillette, Montplaisir, & Zerrouki, 2012; Hafrén et al., 2006; Mangiante et al., 2013). It is well known that hydroxyl groups of cellulose could be turned into carboxyl or aldehyde groups under appropriate treatment conditions. Scientists then designed subsequent reactions towards clickable cellulose. For example, cellulose nanocrystals (CNCs) were firstly selectively oxidized by TEMPO to generate carboxylated CNCs, then propargyl-bearing CNCs were synthesized by amidation between the resultant carboxylated CNCs and propargyl amine under the catalysis of EDC/NHS to prepare photo-responsive CNCs via CuAAC click reaction (Filpponen, Sadeghifar, &

Argyropoulos, 2011). In our previous study, alkynylated CFs were synthesized by combining selective oxidation of cellulose fibers using NaIO<sub>4</sub> and Schiff base reaction with 3-ethynylaniline (Ding, Sun, Xiao, Qian, & An, 2017).

The other clickable cellulose modules for CuAAC are azido-bearing cellulose and azido-functionalized cellulosic materials. A classical method was substitution of hydrogen of hydroxyls by a good leaving group such as tosyl group (Liebert et al., 2006) then a nucleophilic displacement using NaN<sub>3</sub>. Based on this strategy, some cellulose-based functional materials were prepared (Elchinger, Montplaisir, & Zerrouki, 2012; Feese, Sadeghifar, Gracz, Argyropoulos, & Ghiladi, 2011; Parsamanesh & Tehrani, 2016; Ringot, Sol, Granet, & Krausz, 2009; Sadeghifar, Venditti, Jur, Gorga, & Pawlak, 2016). A combinational method, similar to that of alkynyl-bearing cellulose, is also applicable to

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