



Cellulose supported poly(amidoxime) copper complex for Click reaction



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ABSTRACT

A highly active poly(amidoxime) copper complex was prepared by the surface modification of kenaf cellulose through graft copolymerization and subsequent amidoximation. The prepared copper complex was characterized by IR, FESEM, TEM, XPS, EDX and ICP-AES analyses. The copper complex was applied to the Click reaction of organic azides and alkynes as well as one-pot three-component reactions in presence of sodium ascorbate to give the corresponding cycloaddition products in up to 96% yield. The complex was easy to recover and reused six times without significance loss of its activity.

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1. Introduction

The Cu(I) catalyzed 1,3-dipolar cycloaddition leading to regio-selective 1,4-disubstituted-1,2,3-triazoles has received widespread attention since its discovery by Sharpless and his co-workers (Rostovtsev et al., 2002; Huisgen et al., 1967; Tornøe et al., 2002). 1,2,3-Triazoles are an important class of heterocyclic compounds that received significant attention from many pharmaceutical and organic chemists. The broad applicability and high atom efficiency of this reaction stimulates an increasing interest for a wide range of synthetic applications. Triazoles are found to possess wide applications in several research fields like synthetic organic chemistry (Wacharasindhu et al., 2009; Liu et al., 2008; Verma et al., 2007), biological chemistry (Genin et al., 2000), medicinal chemistry (Manetsch et al., 2004; Whiting et al., 2006; Wang et al., 2006) and material chemistry (Nandivada et al., 2007; Ye et al., 2007). Furthermore, these class of compounds are used as dyes, corrosion inhibition, photostabilizers, and photographic materials (Lee et al., 2007; Xia et al., 2006). Copper catalyzed synthesis of triazole is followed by Huisgen 1,3-dipolar cycloaddition reaction between azide and alkyne which is also known as Click reaction (Huisgen,

1989; Totobenazara and Burke, 2015; Tasca et al., 2015; Brien et al., 2015; Vidal and Álvarez, 2014). Different copper sources have been described for this cycloaddition reaction, including copper nanoparticles (Pathigoolla et al., 2013; Jumde et al., 2015; Albadi et al., 2012), copper on charcoal (Lipshutz and Taft, 2006), Cu(II)/Cu(0) comproportionation (Appukkuttan et al., 2004), mixed Cu/Cu-oxide nanoparticles (Huisgen, 1963; Pachón et al., 2005; Molteni et al., 2006), *in-situ* reduction of Cu(II) salts to Cu(I) salts (Bock et al., 2006; Kim et al., 2010; Wang et al., 2010). The major disadvantages associated with these homogeneous copper catalysts are the difficulties to recover and reuse for successive reaction cycles and the possibility of metal contamination of the desired product. To overcome these serious issues, various solid-supports like zeolites (Chassaing et al., 2007), polymers (Girard et al., 2006; Roy et al., 2013; Yamada et al., 2012), non-magnetic and magnetic supported Cu(I) (Fernandez et al., 2010), and silica (Miao and Wang, 2008; Roy et al., 2014) have been employed to synthesis of the corresponding heterogeneous catalysts by immobilizing active metal ions onto the solid supports. In recent years scientists are searching more environmentally friendly and sustainable resources and processes. In this aspect, cellulose is the most common biopolymer, which is widely abundant in nature. The development of a renewable and biodegradable resources has growing interest because bio-based materials and composites could be a promising solution both in terms of environmental and performances. Thus,

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natural celluloses would be highly attractive candidates to explore the solid support of catalysts (Clark and Macquarrie, 2002; Guibal, 2005). Cellulose has interesting features for example, high adsorption capacity, stability, physical and chemical versatility makes them attractive to use as supports. Cellulose can be chemically modified to attain sufficient structural strength and effective chelating ligands can be introduced onto the cellulose backbone, which can be coordinated with metal ions (O'Connell et al., 2008; Dahou et al., 2010; Rahman et al., 2016a, 2016b). Recently, alginate (Wei et al., 2004), gelatin (Zhang et al., 2001), starch (Huang et al., 2002) and chitosan (Quignard et al., 2000) derivatives have been utilized as supports for catalytic applications. Herein we report the isolation and characterizations of kenaf cellulose and further modified with poly(acrylonitrile) through graft copolymerization. The poly(acrylonitrile) was converted into poly(-amidoxime) chelating ligand by hydroximation process. The resulting cellulose supported poly(amidoxime) ligand smoothly bonded with copper Cu(II) (Yong et al., 2012; Lutfor et al., 2014) salt which efficiently promoted Click reaction of organic azides and alkynes as well as one-pot three-component reaction in presence of 5 mol% of sodium ascorbate under mild condition. The easy preparation of the chelating ligand, outstanding activity of copper complex, long shelf life and stability toward water, makes it an ideal system for the synthesis of triazoles in water.

2. Experimental

2.1. General information

1. All manipulations were done under atmospheric conditions if otherwise noted. Reagents and solvents were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system as a Milli-Q grade. CuSO₄ was purchased from Aldrich Chemical Industries, Ltd. ¹H NMR (500 MHz), ¹³C NMR (125 MHz) spectra were measured with a BRUKER-500 spectrometer, Central laboratory, University Malaysia Pahang. The ¹H NMR chemical shifts were reported relative to tetra methylsilane (TMS, 0.00 ppm). The ¹³C NMR chemical shifts were reported relative to CDCl₃ (77.0 ppm). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Shimadzu ICPS-8100 equipment by the central laboratory, University Malaysia Pahang. XPS spectra were measured with a Scanning X-ray Microprobe PHI Quantera II, MIMOS, Kuala Lumpur, Malaysia. FESEM and EDX were measure with JSM-7800F, Central laboratory, University Malaysia Pahang. TLC analysis was performed on Merck silica gel 60 F 254. Column chromatography was carried out on silica gel (Wakogel C-200).

2.2. Materials

Kenaf plants were obtained from National Kenaf and Tobacco Board at Kuantan, Pahang, Malaysia. Kenaf bark was cut into small size (2 cm long average). The raw bark (100 g) was boiled with 17% NaOH (600 mL) and glacial acetic acid (600 mL) for 4 h and 2 h and washed with distil water respectively. The raw kenaf cellulose was bleached with hydrogen peroxide (400 mL) and 7% NaOH (300 mL), washed with distilled water (500 mL) several times and oven dried at 60 °C before use. Acrylonitrile monomer purchased from Aldrich and it was passed through a column filled with chromatographic grade activated alumina to remove the inhibitor. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich), methanol (Merck), sulfuric acid (Lab Scan), metal salts and other analytical grade reagents were used without purification.

2.3. Synthesis of poly(acrylonitrile) 1

A 1L three-neck round bottomed flask was charged with 6 g of kenaf cellulose in 600 mL distilled water and it was kept for overnight. The mixture was heated at 55 °C and 2.1 mL of diluted sulfuric acid (50%) and 1.8 g of CAN were added to the reaction flask under N₂ atmosphere. After 20 min, 16 mL acrylonitrile (purified monomer) was added in the cellulose suspension and stirred for another 2 h. The work-up procedure for the graft polymer was carried out according to our previous report (Yong et al., 2012; Lutfor et al., 2014).

2.4. Synthesis of poly(amidoxime) ligand 2

The preparation of the hydroxylamine solution is described in our previous work (Yong et al., 2012; Lutfor et al., 2014). Poly(-acrylonitrile) grafted kenaf cellulose **1** (10 g) was placed into a two-neck round bottom flask fixed with a stirrer, condenser and thermostat water bath. The prepared hydroxylamine solution was then added to the flask and the hydroximation reaction was carried out at 70 °C for 6 h.

2.5. Preparation of the poly(amidoxime) copper complex 3

An aqueous solution of CuSO₄·5H₂O (250 mg, in 10 mL H₂O) was added into a stirred mixture of 1 g poly(amidoxime) ligand **2** in 50 mL of water at room temperature. The blue color CuSO₄ was immediately turned into green color and the mixture was stirred for 1 h at room temperature. The reaction mixture was filtrated and washed by excess amount of ammonium chloride, water, MeOH and dried at 60 °C for 1 h. The ICP-AES analysis showed that 0.5 mmol of copper was coordinated with 1.0 g poly(amidoxime) ligand **2**.

2.6. General procedure for one-pot three-component Click reaction

A 5 mL glass vessel was charged with **3** (1 mg, 0.05 mol%), alkyne (1.1 mmol), sodium azide (1.1 mmol), and the corresponding aryl halide (1 mmol) in 2 mL 5% of sodium ascorbate. The reaction mixture was stirred at 80 °C for 3 h during which time the colorless triazoles were precipitated. The color of the copper complex **3** was changed blue to lite yellow which indicated that the *in-situ* formation of Cu(I) ion in presence of sodium ascorbate (Yamada et al., 2012). The reaction mixture was diluted with EtOAc and the insoluble **3** was recovered by filtration. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 2 mL), dried over MgSO₄, and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. The crude product was purified by silica gel column chromatography (EtOAc/hexane).

2.7. General procedure for Click reaction of azides and terminal alkynes

The experimental procedure was followed according to one-pot three-component reaction using alkyne (1.1 mmol) and alkyl or aryl azide (1 mmol) for 2.5 h.

2.7.1. 1-Benzyl-4-phenyl-1H-1,2,3-triazole (**6a**)

¹H NMR (500 MHz, CDCl₃) δ = 5.56 (s, 2 H), 7.26–7.37 (m, 3 H), 7.32–7.43 (m, 5 H), 7.67 (s, 1 H), 7.82 (d, *J* = 8.6 Hz, 2 H); ¹³C NMR (125 MHz, CDCl₃) 54.1, 119.2, 125.4, 128.1, 128.2, 128.6, 129.2, 130.4, 134.5, 148.1. MS-EI, *m/z* 235 (M⁺).

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