

Polystyrene-supported triazoles for metal ions extraction: Synthesis and evaluation



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ABSTRACT

In order to prepare substituted polymers bearing functional groups to chelate metals for their application in extraction and/or depollution applications, Merrifield polymer was transformed into the known azidomethyl polystyrene. Click-chemistry based on copper (I)-catalyzed Huisgen's reaction was then used to form polymer-grafted 1,4-triazoles using a variety of synthesized substituted alkynes. These polymer-supported triazoles were then used to extract metals (Cd, Fe, Mg, Ni and Co) from aqueous solutions. A comparative study of metal extractions by these supported triazoles was made between the starting azidomethyl polystyrene and two natural clays taken from the Gafsa area (South-West Tunisia). Raw and purified clays from two Gafsa sites were found to extract metals quite well with almost no selectivity, except for lower fixations of cadmium and magnesium. The synthesized polymers were found to extract all metals with lower efficiencies than the clays. However, one of the polymer-supported triazole was found to extract selectively cadmium with a high efficiency, reaching the levels of the natural clays.

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1. Introduction

Solid–liquid extraction of metals and contaminants is a long-time known field that has gained interest during the past year, thanks to the greener approaches to chemistry and better control of industrial effluents for obvious ecological reasons. Many substrates can be used for the removal of pollutants that range from natural clays and other minerals, human made zeolites and ceramics, to functionalized polymers. Ion-exchange polymers, as an example, are known for a long time [1–3].

The polymers can be more hydrophilic [4–7] or hydrophobic [8,9] in nature, depending of the desired application [10–14]. Polymers substituted by chelating entities, ionic or not, have found new applications in supported catalysis as well as for the depollution, or purification, by their ability to interact with different metals [15–20].

Based on the experience of both our laboratories, we became interested by the comparison between engineered polymers and natural clays for such purposes [21–31]. The preparation of the desired polymers was based on the concept of “click-chemistry” using especially the copper(I)-catalyzed Huisgen's cycloaddition (“copper (I)-catalyzed azide/alkyne cycloaddition” or CuAAC) in this field [32–37]. The basic idea was to graft on an azided polymer a set of functionalized alkynes using such a reaction [38–41]. The formed 1,4-triazole units in this approach (“triazole design”), as well as the appendages on this heterocycle (“pendant design”), or both (“integrated design”), can participate in the chelation of metals; alone or with other subunits on the polymer network (Fig. 1) [42,43].

We thus present in this article the preparation of some polymer-supported triazoles starting from Merrifield resin (chloromethylated polystyrene), followed by its transformation in azido derivative and CuAAC with selected alkynes. These polymers were then used to extract metals salts (Mg^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cd^{2+}) from aqueous solutions. Extraction results were compared to those obtained with natural clays from the Gafsa area (Tunisia).

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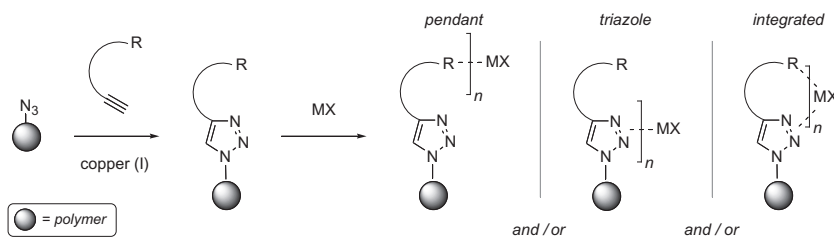


Fig. 1. General scheme for the preparation of triazolic polymers and possible chelation ways (pendant, triazole and integrated designs).

2. Experimental

2.1. Materials and apparatus

2.1.1. Materials

Merrifield polymer (chloromethylated poly-styrene-co-divinylbenzene (1%), 100–200 mesh, $2.1 \text{ mmol Cl g}^{-1}$) was purchased from Fluka (France), washed alternatively three times with methanol and methylene chloride (10 mL g^{-1}) and dried before use. Acyl chlorides (99%), propionic acid (95%), propargyl amine (98%), substituted anilines, *N,N*-dimethyl-aminopyridine (DMAP) (99%), *N,N'*-dicyclohexylcarbodiimide (DCC) (99%), triethyl and diisopropylethyl (DIPEA) amines (99%), phenylacetylene (99%), methyl propiolate (97%), sodium azide (99%) and copper (I) iodide (98%) were provided by Sigma–Aldrich (France) and used without further purification. Methylene chloride and dimethylsulfoxide (DMSO) were bought from SDS-Carlo-Erba (France) and used as received. Tetrahydrofuran (THF) was from the same source but distilled from benzophenone ketyl under nitrogen prior to use. $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (98%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (98%) were produced by Fluka (France) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99%) by Panreac Quimica SA (Barcelona, Spain), and used as such. Samples of clays from Gafsa were collected on two sites (Jebel Es Sath and Jebel Sehib) and used raw or purified accordingly to the method described in the experimental part.

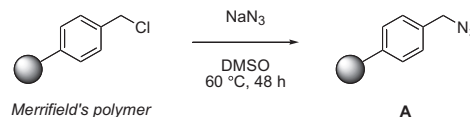
2.1.2. Apparatus

Characterizations were made as described below. Melting points (mp) were measured on a “Original Kofler” apparatus ($43 \text{ cm} \times 14 \text{ cm}$, 50–260 °C, 100 W, Fisher Scientific Bioblock, France). Infrared analysis using the attenuated total reflectance technique (ATR/FTIR) was made on a Nicolet FTIR 200 spectrophotometer (Thermo Scientific, France). Nuclear magnetic resonance spectroscopy (NMR) was recorded on a Bruker Avance 300 WB spectrometer (Bruker, France) at 300 MHz for the proton spectra (^1H) and 75.5 MHz for the carbon spectra (^{13}C). Differential scanning calorimetry (DSC) was performed on a Setaram DSC 131 (France). X-ray diffraction (XRD) was recorded on a Thermo Scientific ARL 9900 XRF (France). The amount of remaining metal ions in solution was evaluated by atomic absorption spectroscopy (AAS) analysis on a Perkin–Elmer Analyst 200 (France). Elemental analysis of N was performed by using Perkin Elmer Analyzer CHN Series II 2400 (France). The DTA and TGA were obtained with a Setaram SETSY-1750 (France).

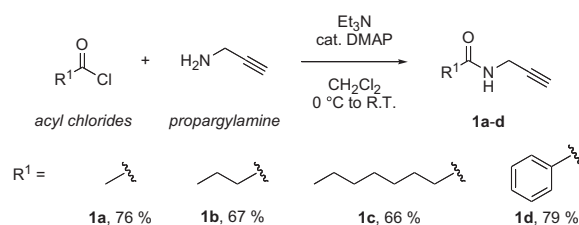
2.2. Organic syntheses

2.2.1. Syntheses of azidomethyl polystyrene (A) and substituted alkynes (1a–d, 2a–d)

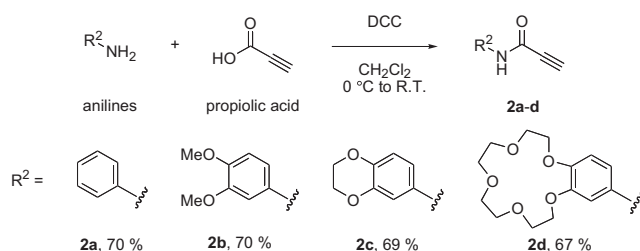
Organic syntheses (Schemes 1–3, Section 3.1) were conducted under Nitrogen, otherwise stated, using standard methods and procedures. Characterizations were made as described below. Melting points (mp) were measured on a Kofler apparatus after calibration around the observed fusion of the product. Infrared



Scheme 1. Preparation of azido methyl polystyrene (A) from Merrifield resin.



Scheme 2. Synthesis of alkynes 1a–d from acyl chlorides and propargylamine.



Scheme 3. Synthesis of alkynes 2a–d from anilines and propiolic acid.

analysis using the attenuated total reflectance technique (ATR/FTIR) was recorded using pure samples between 4000 and 400 cm^{-1} . Only the main and relevant absorption bands are indicated as vibrations (ν) and angular deformations (δ). Nuclear magnetic resonance spectroscopy (NMR) was recorded in deuteriochloroform (CDCl_3) or deuterated dimethylsulfoxide ($\text{DMSO}-d_6$) with calibration onto the residual ^1H signal of the solvent. Chemical shifts (δ) are indicated after calibration on the residual undeuterated solvent peak in part per million (ppm) and as follow: s (singlet), d (doublet), t (triplet), sex (sextuplet), m (multiplet). Coupling constants (J) are given in Hz.

2.2.1.1. Synthesis of azidomethyl polystyrene (A). The polymer A was prepared according to literature [44]. Merrifield polymer ($2.1 \text{ mmol Cl g}^{-1}$, 10 g, 21 mmol Cl) was suspended in 100 ml DMSO and 6.82 g NaN_3 (105 mmol, 5 eq.) were added. The reaction mixture was slowly magnetically stirred at 60 °C for 48 h. The cooled mixture was filtered on sintered glass and washed 3 times with DMSO (60 mL) and finally dried under vacuum at 60 °C for 48 h. The isolated polymer isolated weighted 10.097 g. The substitution yield, calculated by weight increase and ATR/FTIR (data not shown) was 50%. Substitution was calculated with the results

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