New copolymers with triazole pendant groups: Synthesis, characterization and their application to remove heavy metals

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Abstract

Copolymers obtained from polyvinyl alcohol (PVA) containing substituted triazole pendant groups were synthesized via “click” reactions. The chemical structures of the new copolymers with hydroxyl methyl (PVATPHM) or protected galactosyl groups (PVATPGal) as substituents were characterized by spectroscopical analysis (FTIR, 13C NMR, and 1H NMR spectroscopies) as well as the thermal properties were analyzed by TGA and DSC techniques. Interactions studies with heavy metals, ions such as Cd²⁺, Zn²⁺, Hg²⁺, and Cu²⁺, in aqueous solutions were carried out. Ion sorption was evaluated taking into account pH, time, and concentration. Results of competitive selectivity assays were also analyzed. PVATPHM was capable to remove all the analyzed metal ions in different experimental conditions. Furthermore, the PVATPGal showed excellent capacity for lead removal with maximum adsorption capacity at pH 1.0 and the heavy metal can be desorbed using ethylenediaminetetraacetic acid.

Introduction

PVA is a versatile polymer that can suffer chemical modification or physical interactions that lead to new materials with improved properties, for example, Vega et al. have reported stiff gels by PVA and Congo red interaction that can be used as hydraulic fracturing liquids [1]. Moreover, attempt was made to prepare an interpenetrated network hydrogel microsphere by using PVA and locust bean gum for oral controlled drug delivery [2]. Such modification may provide PVA with pendant functional groups or graft polymer chains, and thus expand their applications in different fields. The typical PVA chemical modification includes esterification, etherification or acetalization of the hydroxyl groups [3]. On the other hand, the azide/alkyne ‘click’ reaction [4] is a recent re-discovery of a reaction fulfilling many requirements for the affixation of ligands onto polymers by post-modification processes, which include: often quantitative yields, a high tolerance of functional groups, an insensitivity of the reaction to solvents, irrespective of their protic/aprotic or polar/non-polar character, and reactions at various types of interfaces interfaces [5,6]. This methodology is appropriate to obtain five members heterocyclic rings, particularly 1,2,3-triazole. Yacıgi et al. [7] used a convergent strategy to obtain chromophoric pendant groups incorporated to the modified PVA.

It is well known the ability to coordinate metal ions of the N-heterocyclic groups [8,9]. For example, the strong coordination of tetrazole, triazole, and its derivatives to metal ions makes them attractive ligands, and because of that they were used as bridging ligands in coordination chemistry [10,11].

The presence of heavy metal ions in the environment is one of the major concerns due to their toxicity to many life forms. They are introduced into the environment during industrial processes, refining of ores, mining, disposal of industrial and domestic waters, etc. Pollution in water concern to worldwide due the toxic effect on humans hence it needs the immediate attention of researchers and environmentalists [12,13]. Polymer resins and hydrogels bearing electron donor groups have the ability to bind metal cations [15-20]. Mercury is generally considered to be one of the most toxic metals found in the environment [21] and that is why the discharge limit of waste water streams has been fixed by law in very small values.

In search of new materials capable of capturing heavy metals, in previous works we reported the chemical modification of an industrial polymer capable to remove copper from an aqueous solution [22,23]. Therefore, the aim of this work is to synthesize new copolymers from PVA, containing triazole pendant groups, and evaluate their capacity as heavy metal ions removal agents.

Experimental

Materials

Poly(vinyl alcohol), “click” reaction, triazole, heavy metal removal

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The treatment of PVA-Ts (260 mg, 4.3 mmol) with NaN₃ (279 mg, 4.3 mmol) in DMF (anhydrous) during 48 h at 65 °C in Ar atmosphere, lead to a copolymer with some azide as pendant groups (PVA-N₃). Then, the reaction was precipitated into excess ethyl ether, filtered, sonicated in ethyl alcohol (1 h) and filtered again. Finally, the obtained solid was dried under vacuum pump at 40 °C. The new copolymer obtained was completed to carbon of these groups.

In order to perform ‘click’ reaction, PVA-N₃ (250 mg) was mixed with propargyl alcohol (0.05 mL) in 5 mL of DMF. The reaction was carried out at room temperature for 70 h. A freshly prepared aqueous solution of sodium ascorbate (68 mg, 0.34 mmol) was employed as reaction catalyst. Then, a solution of copper sulfate aqueous (1%) pentahydrate (17 mg, 0.068 mmol) was added. When the reaction finished, it was precipitated into ethyl alcohol (excess), filtered, and dried under vacuum. The new copolymers with triazolic rings (PVATPHM) were obtained and near-quantitative functionalization was achieved.

Synthesis of copolymer with galactosyl derivative substituent of 1,2,3-triazolyl as pendant groups (PVATPGal): A similar procedure applied to obtain PVATPHM was used to synthesize PVATPGal. In this case, PVAN₃ reacted with 1,2,3,4-di-O-isopropylidene-6-O-(2-propynyl)-α-D-galactopyranose [24] as dipolarophile. PVATPGal was quantitatively obtained.

In Figure 1 is shown the synthetic pathway employed to obtain PVATPHM and PVATPGal.

Results and discussion

FTIR characterization

In Figure 2 are shown the FTIR spectra for PVA-N₃, PVATPHM, and PVATPGal. In the case of PVA-N₃ it can be seen the characteristic signal of the azide group at 2094 cm⁻¹ [7], which is very intense and shows the effective replacement of the tosyl groups. Regarding samples PVATPHM and PVATPGal the fingerprint area differs not only among themselves but also with respect to the precursor, in this case PVA-N₃. In PVATPHM and PVATPGal spectra, the effectiveness of click reactions could be confirmed by the absence of the characteristic band of the azide group. Indeed, it could be observed absorption bands between 1680-1690 cm⁻¹ (C=NC=). In particular, the PVATPGal spectrum shows a markedly increase of the relative intensity of the signal corresponding to CH stretching (2800 cm⁻¹) which is consistent with the incorporation of the protected galactosyl moiety.

NMR characterization

The 'H NMR spectrum of PVA-N₃ is in agreement with the results reported by Yagci et al. [7], where a signal at 4.02 ppm is due to –CHN₃.
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Figure 1. Synthetic pathway to obtain PVA-N3 and subsequent click reactions to obtain PVATPHM and PVATPGal.

Figure 2. FTIR spectra for a) PV A-N3, PV ATPGal and c) PV ATPHM.

Figure 3 shows the 1H NMR (DMSO d 6) spectra for samples PVATPHM and PVATPGal, in which it could be observed the modifications of methyne protons neighboring substituent groups (azido, triazole derivatives). In the case of PVATPHM and PVATPGal methyne and methylene signals are observed at 3.2-3.8 ppm and at 1.3-1.6 ppm, respectively. In particular, in the PVATPGal spectrum a signal at 5.43 ppm is an evidence to confirm the presence of the carbohydrate residue. This signal corresponds to the anomeric protons of the carbohydrate and appears as a broad signal due to wide variations in its chemical environment, indicating that the click reaction had occurred.

The 13C NMR spectra analyzed confirmed the modifications and are shown in Figure 4. In the spectrum (DMSO d 6) of PVA-N3 it can be seen a signal at 56 ppm which corresponds to the carbon attached to the azide group. This signal is absent in PVATPHM and PVATPGal spectra. In PVATPGal spectrum signals at 90 ppm appeared due to the anomeric carbons of different arrangements involving galactose residues as triazole substituent. Also, methyl carbons of isopropylidene groups are observed between 23-27 ppm, meanwhile at 110 ppm appears the signal of quaternary carbons of this protected group. These signals can be considered as an evidence of effectiveness of click reaction. For all copolymers signals were observed between 120-130 ppm due to the aromatic carbons of the tosyl group.

Thermal characterization

Thermogravimetric analyses were done for PVA-N3, PVATPHM, and PVATPGal. The thermal stability for the new copolymers was higher than their precursor (PVA-Ts). For all the samples, the highest mass loss occurs at temperatures above 200°C (see Supplementary Data – TGA Table). Besides, DSC characterization was performed between 25 at 200, from these results (see Supplementary Data - TGA Figure) it can be seen that PVATPHM and PVATPGal does not show melting endothermic peak in the studied temperature range. These copolymers melt with decomposition at higher temperatures. However, glass transition temperatures (Tg) could be determinate, both samples have higher Tg values than their polymer precursor (PVAN3), this fact was probably due to the presence of the heterocyclic rings that enhance the chains interactions. Also, both PVATPHM and PVATPGal were more thermally stable (higher decomposition temperature) in comparison with their precursor (PVA-N3).

Applications as heavy metals removal

PVA-Ts: Since this is an intermediate in the synthesis copolymer and has the sulfur substituent groups, retention was tested only with Hg(II) at pH 1, since it is presumed that interaction with metal ions could occur only through the sulfur and it is well known that this has a high affinity for Hg(II). Test was made to determine the maximum retention capacity (MRC). Table 1 summarizes of the results.
From the results obtained in the study of retention capacity, it is observed that the PVA-Ts was saturated in the first contact assay, and then the retention rate dramatically decreased.

As was mentioned above, PVATPHM has a ring-triazole directly bonded to the polymer chain, which has a hydroxyl group as a substituent. Because it has suitable characteristics to coordinate with metal ions, assays were performed to study the effect of pH for retention of Cu(II), Cd(II), Zn(II), and Hg(II). All metal ions were tested at pH 1, 3, and 5, except Hg(II) which was tested only at pH 1 due to, at high concentrations like we used, at pH 2 the precipitation of the salt was observed. In Table 2 are shown the results for each of the metal ions at different pHs.

Due to the R (%) obtained for copper ion (II) was very low at pH 1 and higher than 70% at pH 3, these differences could be useful for releasing retention cycles according to the pH value allowing recovery the polymer. It was observed that the highest percentage of retention is obtained with the mercury ion (II) at pH 1, so it was decided to analyze the maximum retention capacity for such metal only. In Table 3 are shown the results for this last analysis.

**PVATPGal**: PVATPGal has a triazole ring directly attached to the hydrocarbon chain of the polymer, which in turn is substituted with a galactose residue. Then, it was decided to study the effect of pH for retention of the metallic ions Cu (II), Cd (II), Zn (II) and Hg (II). The obtained results are shown in Table 4.

From this analysis, it was observed that the mercury ion (II) is highly removed by the polymer PVATPGal. For this reason, it was decided to develop the following studies on the interaction of this polymer with the metal ion Hg(II) that led to describe in detail the coordination:

**Determination of the MRC of Hg(II) for the PVATPGal**

It was observed that the highest retention percent was obtained with the mercury ion (II) at pH 1, so it was decided to analyze the maximum retention capacity for this metal (see Table 5).

From this analysis, it could be seen that PVATPGal has its maximum retention on the first contact, then the polymer saturates and the retention rate decreases about 50% compared to the first one.

**Influence of Hg(II) concentration in retention with PVATPGal**

Different solutions were prepared from Hg (II), which had the following molar ratios with respect to the repetitive unit of the PVATPGal triazole groups (PVA-Gal: Hg (II)): (20:0.1), (20:0.5), (20:1), (20:1.5). All the results obtained are summarized in Table 6.

![Figure 5. DSC results for PVA-Ts, PVATPGal, and PVATPHM.](image-url)
The results of this analysis revealed that, the percentage of retention depends on the molar ratio polymer:metal ion, in this particular in this case it was found that the optimal molar ratio for the retention concentration of Hg(II) was PVATPGal:Hg(II) (20:1).

**Influence of the contact time on the interaction Hg(II) with PVATPGal**

The influence of contact time on the interaction of Hg(II) at pH 1 with a molar ratio (PVATPGal:Hg(II)) (20:1) was analyzed. Considering the results obtained (Table 6), it is important to note that after 15 min of constant retention higher than 90 % was obtained, so the interaction between the polymer and metal ion occurred fast and effectively. Also, it could be concluded that optimal contact time which allow the highest retention of Hg(II) at the studied conditions was 60 minutes.

**Competitive selectivity in a ternary mixture**

To evaluate the kind of selective retention of mercury (II) versus Cd (II) and Zn (II) a competitive selectivity assay was performed. We used a molar ratio of 20:1 of polymer to the total of metal ions moles.

The pH of the solution was 1 and the contact time was 1 hour. The results are shown on Table 6.

After the competitive assay selectivity, it was observed that the mercury ion remains the most retained, however the retention percent decreased in comparison to the result obtained with the pure solution of this salt (see Table 4).

**Elution**

The first assay to evaluate the reusability of the polymer is the determination of optimal eluent that allows the regeneration of the active sites of the polymer. For this purpose, a sample of PVATPGal loaded with Hg(II) (0.97 mg) was eluted with two solutions with different characteristics: ethylenediaminetetraacetic acid (EDTA) and sodium carbonate, both at a concentration of 0.5 M. The results after contacting the sample, with each of the separate eluent for an hour with continuous stirring in a thermostatic bath at room temperature, showed that the recovery percent obtained with sodium carbonate was 32.1 meanwhile with EDTA it was 95.7%. After this analysis, it could be concluded that EDTA was an appropriate eluent to remove Hg(II) from PVATPGal, which is essential to evaluate charge and discharge cycles.

In summary, from all these results it can be concluded that PVA Ts: retains Hg(II) at pH 1 and the copolymer saturation occurred at first trial of contact. PVATPHM showed higher retention percent for Hg (II) at pH 1, and would be useful with Cu(II) to release retention cycles. Finally, PVATPGal has the highest retention percent for Hg(II) at pH 1. Also, this copolymer showed selectivity for Hg(II) at this pH under non-competitive and competitive conditions, which was easily eluted with 0.5 M EDTA at a percentage higher than 95%. The optimum conditions of retention were a molar ratio (PVA-Gal: Hg(II)) of (20:1) and 60 min of contact time.

**Conclusions**

“Click” reactions had been successfully extended to macromolecules, particularly for PVA modification. The synthetic strategies applied led to novel copolymers with heterocyclic side groups attached to the polymer backbone with quantitative yields. In turn, these heterocycles could present in their structure carbohydrate or hydroxymethyl groups as substituents.

The new copolymers as well as their precursors were fully characterized by spectroscopical and thermal characterizations, from these analyses are can conclude that none of them present decomposition below 200°C.

It is important to remark that all the copolymers have the ability of removing the analyzed heavy metal ions. However, PVATPGal showed the highest retention level for mercury ion under competitive and non-competitive conditions. Furthermore, the mercury adsorbed in PVATPGal structure could be eluted with EDTA solution of 0.5 M, and the copolymer be reused after treatment.

The copolymer containing triazolic rings with galactose residue showed promising results as resin for the cleaning of water contaminated with mercury.

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