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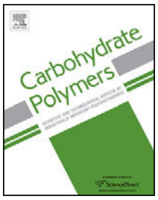

Imidazolyl derivative of chitosan with high substitution degree: Synthesis, characterization and sorption properties

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ABSTRACT

A method of synthesis of chitosan imidazolyl derivative – N-(5-methyl-4-imidazolyl)methylchitosan (IM-chitosan) with high degree of substitution (DS) via reaction with 5-methyl-4-imidazolylmethanol has been developed. This method enables one to obtain polymers with the DS up to 1.35 with simultaneous cross-linkage of the matrix. The chemical structure of the obtained IM-chitosan was characterized by FT-IR, ^{13}C and ^{15}N NMR spectroscopies. It was shown that cross-linkage of IM-chitosans occurred due to formation of N-glucoside derivatives. Sorption capacities of IM-chitosans toward transition metal ions have an extremal dependence on DS, which is less pronounced for Ag(I) ions in comparison with Cu(II) and Ni(II) ions. The decrease of sorption capacities for derivatives with DS 0.5–1.0 is attributed to steric hindrances for ion-binding due to increased stiffness of the polymer matrix at high DS as a result of cross-linking. Sorption capacities of IM-chitosans toward noble metal ions in 0.1 M HCl gradually increase with DS, since higher swelling polymers in acidic media eliminates negative effect of cross-linking on availability of sorption sites.

1. Introduction

Development of chitosan functionalization methods allows, on the one hand, expansion of chitosan application (El Kadib, 2015; Guibal, Vincent, & Navarro, 2014; Muzzarelli, 2011; Vinsova & Vavrikova, 2011), and on the other hand, investigation of peculiarities of polymers transformation in known organic chemical reactions in comparison with reactivity of low molecular weight compounds (Bratskaya et al., 2013; Kurita, 2006; Pestov, Zhuravlev, & Yatluk, 2007; Skorik, Pestov, Kodess, & Yatluk, 2012). Nowadays, fabrication and application of promising imidazolyl derivatives of chitosan is under investigated, first of all, due to low commercial availability of affordable and suitable functionalization reagents.

Thus, usage of imidazolecarboxaldehyde with subsequent reduction of the imine with sodium borohydride yields IM-chitosans with DS up to 0.3 (Muzzarelli, Greco, Busilacchi, Sollazzo, & Gigante, 2012). Further investigations targeted to increase DS and optimization of synthesis conditions have not been carried out yet. We earlier developed a new method of 4-imidazolylmethylchitosan synthesis using nonconventional substitution reaction (Pestov, Bratskaya, Azarova, & Yatluk, 2012), however, DS of IM-chitosan was also limited to 0.3 due to heterogeneous conditions of the chemical reaction. 1-vinylimidazole, which is, at first sight, a convenient functionalization reagent with similar to vinylpyridines structure, was used for chitosan functionalization in (Ahamed, Mbianda, Mulaba-Bafubiandi, & Marjanovic, 2013); however, incorrect interpretation of ^{1}H NMR spectra casts doubts on the possibility of such reaction and yield of the desired product that was confirmed in our experimental investigations using the suggested approach.

The most efficient reagents used up to now for introduction of imidazolyl fragments are chloromethyl derivatives. In one of the first reported examples of 4-chloromethylimidazole application as functionalization reagent, the authors did not report appropriate proofs to the product structure and did not investigate influence of the reaction conditions on the composition of the yielded polymer (Hu, Fang, Gao, & Wang, 2006). Later we have studied peculiarities of chitosan functionalization using this type of reagents (Pestov et al., 2014) and obtained IM-chitosans with DS up to 0.8. We have also shown that such modification resulted in formation of IM-chitosans insoluble in the full pH range (Pestov et al., 2014). The necessity and feasibility of fabrication of polymers with

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various functionalization degrees are topical, since many functional properties of the polymers significantly depend on DS (Bratskaya, Pestov, Yatluk, & Avramenko, 2009; Bratskaya, Ustinov, Azarova, & Pestov, 2011; Bratskaya et al., 2012; Liu, Guan, Yang, Li, & Yao, 2001; Molochnikov, Pestov, Zabolotskaya, & Yatluk, 2008; Petrova, Neudachina, Mekhaev, & Pestov, 2014).

This work describes the closing stage of systematic investigations on imidazolylmethylation of chitosan using chloromethylimidazoles targeted to the synthesis of the highly substituted derivatives and elucidation of the factors leading to macromolecules cross-linkage.

2. Experimental

2.1. Materials and methods

Chitosan was purchased from JSC "Sonat" (Moscow, Russia). The degree of acetylation (DA) was determined by ^{1}H NMR spectroscopy to be 0.18; average molecular weight of 2.5×10^5 Da was measured using viscometry according to Gamzazade et al. (1985). 4-Chloromethyl-5-methylimidazole hydrochloride was prepared as described in (Turner, Huebner, & Scholz, 1949). All other chemicals were of analytical grade and used without further purification.

The C, H, N-elemental composition was determined by "Perkin Elmer" Elemental Analyzer. Degree of substitution (DS) was calculated from element analysis data using the formula: $DS = (C/N - 2DA - 6)/(4 - 2C/N)$, where C/N is the molar ratio of carbon/nitrogen in the product.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer using the Diffuse Reflectance Sampling Accessory (DRA). Thermograms were registered using a Metter Toledo thermogravimetric analyzer.

Solid state ^{13}C and ^{15}N NMR spectra were recorded using the method of cross polarization with rotation at the magic angle (CP/MAS) on spectrometer Bruker AVANCE-500, with rotor diameter of 4 mm, rotation frequency of 5000 Hz. High resolution ^{1}H NMR spectra of polymers were recorded on a Bruker AVANCE-500 spectrometer at 70 °C to increase the solubility of samples and obtain better spectral resolution. Samples were dissolved in D_2O/DCl (concentration 10 mg/ml), sodium 3-(trimethylsilyl)-1-propanesulfonate was used as an internal standard. Suppression of the solvent signal during the spectrum recording was realized by the "presaturation" technique.

2.2. Preparation of IM-chitosan

The typical procedure of the polymer transformation was as follows: a mixture of 0.83 g (0.005 mol) of chitosan, 2.5 g (0.015 mol) of 4-chloromethyl-5-methylimidazole hydrochloride, and 40 mL of dimethyl sulfoxide (DMSO) was stirred at 80 °C for 10 min; then 7 mL (0.05 mol) of trimethylamine (Et_3N) was added, and the mixture was stirred for an additional 10 h at the same temperature. After cooling, 100 mL of acetone was added to the reaction mixture, and the precipitate was filtered off, washed with 2% NaOH solution and then with water to neutral reaction, afterwards the product was dried at the room temperature to constant weight. Yield of the product was 1.2 g with DS = 1.35.

2.3. Sorption experiment

Sorption properties of IM-chitosan with DS = 1.35 toward ions of noble metals were investigated from solutions of $H[AuCl_4]$, $H_2[PdCl_4]$ and $H_2[PtCl_6]$ in 0.1 M HCl, and 1 M HCl. The sorption of transition metal ions (Cu(II), Ag(I), and Ni(II)) was studied from solutions of metal nitrates in 1 M NH_4NO_3 at pH 5.3. The solid:liquid ratio in sorption experiments was set to 1:1000, the contact time was 18 h. The adsorbed amounts were calculated using the difference in initial and equilibrium concentrations of metal ions in the solutions determined by the atomic absorption spectroscopy (AAS) using a Solaar M6 (Thermo, USA) device. At least three replicates were made to assure results reproducibility.

Table 1
Conditions of imidazolylmethylation of chitosan with 4-chloromethyl-5-methylimidazole hydrochloride (CMI) and degree of substitution (DS) of obtained products (80 °C, 10 h).

Entry	Molar ratio chitosan:CMI:Et_3N	Solvent	Chitosan concentration in suspension (%)	DS
1	1:1:2	DMSO	2	0.54
2	1:2:7		2	0.78
3	1:2.5:8.5		2	1.02
4	1:3:10		2	1.35
5	1:2:5		10	0.24
6	1:2:5	1% solution LiI in DMSO	10	0.89

3. Results and discussion

3.1. Preparation of IM-chitosan

We have earlier found that 4-chloromethyl-5-methylimidazole was the most effective reagent for the synthesis of chitosan imidazolyl derivatives (Scheme 1) (Pestov et al., 2014). The reaction passes, when dimethyl sulfoxide is used as a solvent, and chitosan concentration in suspension does not exceed 4%. Varying modification conditions enable one to obtain polymer with DS up to 0.8, which is simultaneously cross-linked, since reaction products with DS above 0.3 is swellable but not soluble in acidic solutions.

New experimental investigations presented here on chitosan transformation in this reaction (Scheme 1) make possible enhancement of chitosan modification efficiency and obtaining IM-chitosan with high degrees of substitution.

As follows from the data shown in Table 1, consecutive increase of molar excess of reagent to chitosan leads to the monotonous increase of DS up to 1.0 and higher (Table 1, entries 1–4). The increase of reagent: chitosan ratio above 4:1 is unreasonable, since under these conditions 4-chloromethyl-5-methylimidazole is inefficiently consumed in the reaction without significant increase of product DS, in a similar way as we have demonstrated for other chitosan functionalization reactions (Bratskaya et al., 2012, 2013; Pestov et al., 2007; Petrova et al., 2014; Skorik et al., 2012).

Chitosan is not soluble but swellable in dimethyl sulfoxide, thus, the modification reaction occurs under heterogeneous conditions, and the increase of polymer concentration in the reaction suspension leads to DS lowering (Table 1, entries 2 and 5). Using previously discovered capability of chitosan to dissolve in solutions of alkali and earth-alkali metals iodides (Pestov, Kodess, Matochkina, & Yatluk, 2011), the reaction was carried out in the presence of lithium iodide (Table 1, entry 6). One can see, addition of solubilizing inorganic salt increases the efficiency of chitosan modification (Table 1, entries 5 and 6). Most likely, lithium iodide facilitates chitosan swelling and partial dissolution that enhances the polymer reactivity.

Thus, to obtain IM-chitosan with high DS, one shall use derivatives of 4-chloromethylimidazole as a functionalization reagent and dimethyl sulfoxide as a solvent. Variation of 4-chloromethylimidazole mole excess to chitosan allows obtaining desired functionalization degree.