



Short communication

Crosslinking of poly(vinylpyrrolidone) activated by electrogenerated hydroxyl radicals: A first step towards a simple and cheap synthetic route of nanogel vectors



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ABSTRACT

A facile electrosynthesis route for the preparation of polymer nanogels based on the in situ production of hydroxyl radicals is reported for the first time. Electro-Fenton process with continuous H₂O₂ electrogeneration and Fe²⁺ regeneration performs better than electro-oxidation with a boron-doped diamond or dimensionally stable anode for promoting crosslinking of poly(vinylpyrrolidone).

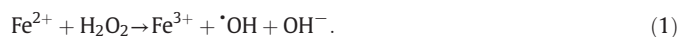
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1. Introduction

Polymer nanogels have been proposed as nanovectors to deliver drug molecules in living tissues under targeted and controlled release conditions [1,2]. They can be fabricated by surfactant-assisted polymerization of hydrophilic monomers in the presence of crosslinking agents but, toxicity of residual monomer, initiator and surfactant may impede their use in biomedicine [3]. A clean approach to prepare high purity nanogels is based on high energy irradiation of aqueous solutions of preformed polymers to generate free radicals onto the macromolecules [4,5]. Nanogels can be obtained by enhancing intramolecular combination of active centres using dilute polymer solutions exposed to ionizing radiation at relatively high doses per pulse [4]. Nanogels of poly(acrylic acid), carboxy-methylcellulose and poly(vinylpyrrolidone) (PVP) have been prepared by this method [6–10]. However, the need of special facilities for material processing limits its large-scale applicability [11].

The main effect of ionizing radiation in aqueous media is the volumetric generation of hydroxyl radicals ([•]OH) that can abstract H atoms to yield macroradicals [4,5]. Prompted by this consideration, several authors

have reported simpler, cheaper methods to produce [•]OH in water. A plausible route is based on Fenton's reaction chemistry at pH 2.8:



PVP nanogels have been prepared by crosslinking linear macromolecules in hexadecyltrimethylammonium bromide reverse micelles [12]. The accumulation of [•]OH in Fenton systems can be greatly enhanced upon use of UVA radiation and thus, photo-Fenton reaction has been used to generate PVP and polyethyleneimine nanogels [13–15]. Such processes require simpler set-ups than e-beam irradiation but, due the utilization of high concentrations of iron salts (up to 10 mM), the product purification becomes complex since residual concentration of metals must be very low for biomedical applications. On the other hand, the electrochemical advanced oxidation technologies allow the electrogeneration of different kinds of hydroxyl radicals on site, i.e., adsorbed on the anode surface (Eq. (2)) or free in the solution bulk (Eq. (1)), as demonstrated for the abatement of organic pollutants [16,17].



This study assesses the performance of three electrochemical approaches characterized by the different nature and reactivity of

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generated hydroxyl radicals: 1) electro-oxidation (EO) upon electrogeneration of physisorbed radicals at boron-doped diamond (BDD); 2) EO upon electrogeneration of chemisorbed active oxygen at a dimensionally stable anode (DSA); and 3) electrogeneration of homogeneous $\cdot\text{OH}$ by electro-Fenton (EF) process.

In contrast to chemical Fenton methods, much lower concentrations of iron ions (up to two orders of magnitude) are necessary to activate the generation of $\cdot\text{OH}$ in EF, thanks to the continuous cathodic reduction of Fe(III) (Eq. (3)) that sustains the catalytic process. Furthermore, the in situ electrogeneration of H_2O_2 (Eq. (4)) prevents its dangerous and costly handling [17,18].



The aim of our investigation is to provide the proof of concept that at least one of the aforementioned electrochemical routes can be used to change the architecture of linear PVP chains promoting the fabrication of nanogels by intra/intermolecular crosslinking and controlled oxidation/degradation with limited mineralization.

2. Materials and methods

PVP K60 ($M_n = 1.6 \times 10^5 \text{ g mol}^{-1}$, 45 wt.%, Aldrich) was used as received. A carbon-PTFE air-diffusion electrode (ADE) from E-TEK was used as the cathode in EF to electrogenerate H_2O_2 from pure O_2 gas, whereas Ni was used as cathode in EO. A Ti/IrO₂-Ta₂O₅ (DSA) plate and a BDD thin film supported on Nb, both from ElectroCell AB, were used as anodes. The exposed surface area of all electrodes was 3 cm². All potential values are referred to SCE.

For the electrosyntheses of nanogels, fresh PVP aqueous solutions were stirred overnight, filtered with 0.22 μm nylon filters under vacuum and, after deaeration with N_2 for 30 min, stored in opaque, sealed glass bottles. The electrolyses were performed in an undivided glass cell under magnetic stirring, using 50 mL of PVP solution with 50 mM Na_2SO_4 as supporting electrolyte. In EO, N_2 was fed into the solution during the experiments. EF trials were performed at pH 2.8 in the presence of 1.0 mM of FeSO_4 as catalyst. An Amel 2053 potentiostat/galvanostat was employed to operate at constant current. Galvanostatic conditions were preferred in order to control the rate of generation of hydroxyl radicals during the whole duration of the electrolyses. Samples were filtered with 1.22 μm cellulose acetate syringe filters. The mineralization of solutions was monitored from their total organic carbon (TOC) decay determined on a Shimadzu LCSH analyser. The hydrodynamic radius (R_h) of polymer chains dispersion was measured after each electrolysis by dynamic light scattering (DLS) using a Brookhaven Instruments BI200-SM goniometer and compared with that of untreated linear PVP ($28 \pm 9 \text{ nm}$) [19]. DLS data were analyzed according to the method of cumulants [20]. For gel permeation chromatography (GPC) and FTIR analyses, the samples were dialyzed using distilled water for 96 h and employing cellulose acetate membranes (12,000 Da cutoff, Aldrich). GPC analyses of filtered samples were carried out with an Agilent 1100 Series HPLC equipped with two Shodex columns (804 and 806, Phenomenex) in series, using a solution of 3 mM NaN_3 as mobile phase and an RI detector at 35 °C. FTIR spectra were recorded on a Perkin-Elmer Spectrum 400.

3. Results and discussion

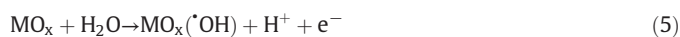
Hydroxyl radicals were first electrogenerated by using BDD, a “non-active” anode producing $\cdot\text{OH}$ as quasi-free radicals (i.e., physisorbed) [21,22]. BDD presents a low adsorption of species, high corrosion stability, high efficiency in oxidation processes and very efficient generation of quasi-free $\cdot\text{OH}$ [16]. The latter aspect is particularly relevant, since it has been observed that the weaker the interaction

between $\cdot\text{OH}$ and the anode surface, the higher the O_2 -overpotential and the chemical reactivity towards the oxidation of organic molecules [23]. Therefore, in the presence of organics, $\cdot\text{OH}$ formed from Eq. (2) can cause their partial or total oxidation, which in the case of preformed polymers like PVP could entail crosslinking to yield nanogels of interest.

A first series of experiments was performed at 5 mA cm⁻², thus reaching an anode potential of 2.5 – 2.6 V, which is high enough to activate the water oxidation while minimizing the oxygen evolution.

When experiments with different duration (251 and 900 s) and PVP concentration (0.25 or 0.50 wt.%) were performed (Table 1, entries 1–3), TOC measurements indicated that no incineration of PVP chains occurred probably due to the low charge passage as compared to that needed for total mineralization. However, none of these trials caused a significant change of PVP R_h , plausibly due to the low amount of radicals generated on the polymer chains. Aiming to stimulate the polymer modification, some experiments were performed under a higher current passage (Table 1, entries 4 and 5). Working at 10 mA cm⁻² for 1800 s (entry 4), which corresponds to 54.0 C of charge passed and accounts for 1.5% of that needed for the total mineralization of PVP chains, the R_h still remained unchanged. Furthermore, a small TOC abatement, of the same order of magnitude of that expected on the basis of the charge passed for PVP mineralization was found, which means that $\cdot\text{OH}$ generated at BDD can abstract H atoms from PVP, although in a useless manner for our purpose since they seem to promote mineralization. This was confirmed when trials were made at 50 mA cm⁻² for 26,013 s (entry 5), with a charge that corresponds to that for total mineralization. In this case, it was not possible to obtain a clean DLS signal, which can be explained by the significant degradation of the macromolecules as suggested by the drastic TOC decay.

The EO approach was then tested using an “active” anode like DSA that allows the formation of chemisorbed active oxygen (Eqs. (5) and (6)). In the absence of enough amounts of organic molecules, this oxidant may evolve towards oxygen [16].



Ti/IrO₂-Ta₂O₅ was chosen as optimal DSA since iridium oxide is known to yield chemisorbed active oxygen and, in combination with Ta oxides, presents a good stability [24]. As shown in Table 1 (entries 6–8), no remarkable changes of R_h and TOC content were observed working at low j for different time periods, meaning that the operation conditions were too mild to alter the polymer chains. Conversely, when the electrolyses were performed at 50 mA cm⁻² with a charge corresponding to that required for total mineralization (entry 9), a significant increase of R_h was achieved, which can be explained by the existence of intermolecular crosslinking promoted under the action of MO_{x+1} that create radical centres on independent PVP chains as they reach the anode. In contrast to BDD (entry 5), TOC content did not undergo a relevant decrease, thus showing that “active” anodes may allow the modification of polymers without causing their mineralization. However, a massive anodic generation of O_2 gas was observed because mass transport limitations impede the arrival of enough organic molecules to react with MO_{x+1} , which then partly evolves to O_2 . To minimize the gas evolution, some electrolyses were performed at a very low j (3 mA cm⁻²) with similar duration. Quite interestingly, analogous results in terms of R_h and TOC content were obtained.

A radically different approach is offered by the EF process, which is usually based on the electrogeneration of H_2O_2 in aqueous solution via Eq. (4) at massive or gas-diffusion carbonaceous cathodes [17]. Completely free $\cdot\text{OH}$ in the bulk are formed in this method via Fenton's reaction (1), whose different nature and space distribution can plausibly lead to a more advantageous modification of the PVP chains. High current densities (33.3 mA cm⁻²) were always used in EF to ensure

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