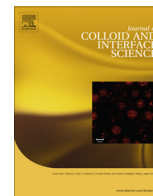




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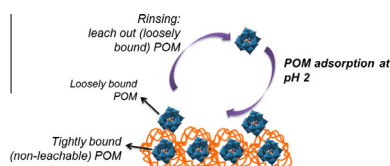
# In situ quartz crystal microbalance monitoring of the adsorption of polyoxometalate on a polyampholyte polymer matrix



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Hybridization of polyoxometalates (POMs) via an organic–inorganic association constitutes a new route to develop heterogeneous POM catalysts with tunable supramolecular architecture. As the structural stability of POMs is strongly influenced by the pH conditions, a quantitative understanding of the POMs–polymer association is important in practical applications. Herein, we use Quartz Crystal Microbalance (QCM) to systematically investigate the interactions of Keggin phosphotungstic acid POM with a polyampholyte polymer-coated QCM sensor as a function of pH. The mass of adsorbed POMs increases when pH decreases from 5.6 to 2, indicating that electrostatic forces play a major role in the formation of POM–polymer hybrids. This finding is complemented by AFM images that show an increase in the size of the hybrid entities from 5 to 12 nm as the pH decreases from 5.6 to 2. The POM adsorbed amount at a particular pH value reaches an equilibrium level with time. The hybrids further gain in adsorbed mass only when lowering the pH value of the POM solution. The hybrid structure formed above pH 2 shows resistance to leaching as indicated by the steady level of the adsorbed mass during a rinsing step with water. However, at pH 2, the rinsing step causes desorption of some weakly adsorbed POMs. It is shown that leached POMs can be re-adsorbed back into the polymer matrix during a second contact with a POM solution at pH 2. This adsorption–desorption cycles of POMs were successfully repeated. Our experiments shed light into the coexistence of tightly as well as loosely bound POMs in hybrid catalyst formed at pH 2. The loosely bound POMs can potentially act as homogeneous catalysts when desorbed. However, these leached POMs can be re-adsorbed back into the matrix, preserving the heterogeneous state of the catalyst. Our results show that QCM is a powerful technique to study in situ the dynamics of the adsorption of POMs on a polymer matrix under different pH conditions.

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## 1. Introduction

Polyoxometalates (POM) are oxoanionic clusters of early transition metals with well-defined molecular structure and properties. They have attracted growing interest in developing advanced functional materials owing to their plethora of tunable properties, as well as their ability to combine with organic moieties to form hybrid materials. These have opened up new avenues not only in

the field of supramolecular chemistry, but also in new materials technology [1,2]. Their tunable molecular architecture, charge density, strong redox capability, and electro- and photochemical properties, make that these molecular metal-oxide nano-clusters find emerging applications in diverse fields, such as magnetism [3–5], electronics [6], electro- and photochromic systems [7,8], medicine [9], molecular batteries [10] and catalysis [11–15].

POM anions are often hybridized in an organic matrix in order to improve their processability in device fabrication. The hybridization strategy essentially involves the association of POM anions with an organic matrix through either covalent [16] or non-covalent bonds [17]. The later approach may be applied with charged polymer matrices. The electrostatic interactions between POM and such polymers lead to a fast hybridization and, provided that the polymers have a supramolecular structure, allow a well-controlled assembly of POM with multifunctional properties e.g. thermo- and photoresponsive properties [18], dielectric property [16], and catalytic activity [15]. In catalysis, hybridization offers a means to synthesize heterogeneous POM-based catalysts with useful properties such as enhanced processability, recoverability, and reusability [15]. As the charges and structure of both POM and weak polyelectrolytes are highly dependent on the pH conditions [19], a fundamental understanding of the POM-polymer association under different pH conditions is necessary to optimize their properties for practical applications e.g. heterogeneous catalysis.

Quartz Crystal Microbalance (QCM) has emerged as a powerful technique to study the dynamics of adsorption processes on soft and solvated interfaces between solid surfaces and bulk liquids, with mass resolution of a few  $\text{ng}/\text{cm}^2$  [20,21]. The technique is operational under liquid media, and is highly useful to quantitatively monitor the growth of soft layers of e.g. adsorbed proteins on solid substrates [22]. In another application of the technique, QCM was recently used to monitor the growth of organic–inorganic hybrid films. The high sensitivity of QCM allows the growth process of the hybrid material to be monitored either in situ, by the sequential deposition of molecular layers of the organic and inorganic species [23–26], or ex situ, after deposition of organic–inorganic hybrid directly on a substrate e.g. silica or alumina [27]. In all cases, the film growth was monitored by recording the frequency decrease of the quartz crystal during each adsorption cycle. With the advent of additional modules, such as flow- and temperature-controlled cells, QCM allows the temperature-dependent growth of hybrid films to be examined. For example, hybrid materials based on trimethylaluminum and ethylene glycol showed lower growth rates at higher temperatures [23,24]. Polyoxometalates, however, exhibit a structural stability largely dependent on the pH conditions. Flow cells equipping QCM offer means to investigate the POMs-polymer electrostatic association under liquid medium and in dynamic conditions. In such a way, it is thus possible to mimic with much realism the working environments used in applications involving POMs as heterogeneous catalysts.

The aim of this paper is to systematically investigate the adsorption of Keggin phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) POM on a polyampholyte copolymer (poly *N,N*-diallyl-*N*-hexylamine-*alt*-maleic acid) as a function of pH. The copolymer was coated on a QCM sensor and POM adsorption was then monitored as a function of time and in different pH conditions. The morphology of the sensor surface was also analysed using Atomic Force Microscopy (AFM) before and after POM adsorption.

## 2. Materials and methods

### 2.1. Polyampholyte polymer

The polyampholyte polymer used in this study is an alternating copolymer, poly(*N,N*-diallyl-*N*-hexylamine-*alt*-maleic acid) (from

now on called “copolymer C6”), having repeating units consisting of a diallylhexylamine group linked to a maleic acid group. The structure of the copolymer C6 is shown in Scheme 1. Copolymer C6 was synthesized according to a procedure reported elsewhere [28]. Depending on pH, the amine ( $\text{p}K_{\text{a}} = 8\text{--}9$ ) and carboxylic acid groups ( $\text{p}K_{\text{a}1} = 2\text{--}3$ ;  $\text{p}K_{\text{a}2} = 4\text{--}5$ ) may be positively and negatively charged, respectively.

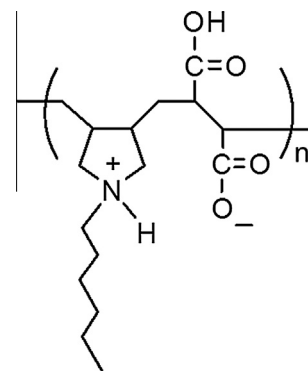
### 2.2. Preparation of copolymer C6-coated QCM crystals

Standard  $\text{SiO}_2$ -coated crystals (QX 303 from Q-sense, coating thickness  $\sim 50$  nm) were used for QCM experiments. The crystals were initially rinsed with ultrapure water (Elgastat Maxima system, resistance:  $18.2\text{ M}\Omega$ ) and subsequently immersed in absolute ethanol under ultrasonic bath for 20 min. The crystals were then dried under dry  $\text{N}_2$  and treated in an UV- $\text{O}_3$  chamber (Jelight USA) for 20 min. A drop (10  $\mu\text{L}$ ) of copolymer C6 solution (0.2 g/L in water) stabilized at pH 7 was deposited on the freshly cleaned crystals. The crystals were allowed to dry under ambient conditions for at least 48 h.

### 2.3. QCM measurements

The adsorption of phosphotungstic acid POM ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , purchased from Sigma Aldrich) under different pH conditions on the copolymer C6 coating was monitored in situ using QCM. The system used was a Q-Sense E4 (Biolin Scientific, Sweden) equipped with four QFM 401 flow modules. The flow was maintained at 50  $\mu\text{L}/\text{min}$  using a peristaltic pump (Ismatec, Germany) at constant temperature of 22  $^\circ\text{C}$ . The pH value of POM solutions (0.1 g/L in water, initial pH 3.5) was set at 2, 3, 4, and 5.6 using 0.1 N HCl and 0.1 N aq. ammonia to reach more acidic and more basic pH, respectively. In order to check the reproducibility of the measurements, each experiment was repeated on two independent flow cells. The frequency and dissipation shifts ( $\Delta f$  and  $\Delta D$ , respectively) were monitored as a function of time. Different experiments were designed as described in Table 1, with the aim to (i) study the effect of pH on POM adsorbed amount (program 1), (ii) investigate the sequential adsorption of POM at different pH values (programs 2 and 3), (iii) address the question of the saturation of the interface by POM at a given pH (program 3), and (iv) show the reversibility of POM adsorption/desorption processes depending on pH (program 3).

The mass adsorbed on the copolymer C6-coated crystal surface after the POM deposition step was calculated based on the shift of frequency ( $\Delta f$ ) recorded between the baselines established during



**Scheme 1.** Molecular structure of the zwitterionic polyampholyte polymer, poly(*N,N*-diallyl-*N*-hexylamine-*alt*-maleic acid). The amine and the two carboxylic functions may be charged or not depending on the pH conditions. For example, the scheme here (with the protonated amine and one of the carboxylic moiety deprotonated) corresponds to the situation likely obtained at pH 5.

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