



## Short Communication

# On the development of electrochemical sensors coated with polycaprolactone

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## ABSTRACT

The main aim of this study was to test the biopolymer polycaprolactone (PCL) as an electrode modifier for the electrochemical detection of dopamine (DA). PCL was chosen following a search for polymers with the appropriate geometry and functional groups for dopamine detection. The chemical structure and the average molecular weight of the synthesized PCL were determined by <sup>1</sup>H NMR, while DSC measurements showed a decrease in the crystallinity of a star-shaped polymer compared to a linear polymer. Atomic force microscopy and wettability tests performed on PCL-coated ITO electrodes demonstrated the influence of polymer architecture and functional groups on hydrophilicity and film morphology. Electrochemical studies revealed that electrodes coated with star polymers ending with carboxyl groups show good activity and selectivity, thus demonstrating the effectiveness and applicability of the developed sensors for the electrochemical detection of DA.

## 1. Introduction

Dopamine (DA), a catecholamine neurotransmitter, plays a very important role in the human body as it participates in hormone regulation and in the renal, cardiovascular, and central nervous systems [1,2]. Moreover, it is essential in regulating attention, memory, cognition, movement and the operation of hormones [1,2]. Indeed, Parkinson's disease, attention deficit disorder, schizophrenia, and hyperactivity disorder are associated with low levels of dopamine [3]. It is therefore very important to be able to detect low concentrations of dopamine with high levels of specificity and selectivity. Among the different approaches available for DA recognition, electrochemical detection is a good choice for this redox-active analyte [4–6]. However, there is a poor response to DA on conventional electrodes owing to slow interfacial electron transfer and to the fact that other species present in blood, such as uric acid (UA) and ascorbic acid (AA), may interfere by producing overlapping signals [4]. Indeed, the presence of these molecules, which have similar electrochemical properties to dopamine, can make electrochemical identification difficult and many studies have demonstrated that bare carbon electrodes may not clearly separate the signals of these compounds. In order to address these issues, various materials have been used to improve electrode performance, including

carbon-based materials [7], metal nanoparticles [8], oxides [9] and composites [10]. Another promising strategy is based on coating electrodes with anionic compounds, which increase selectivity to DA detection due to discrimination towards negatively charged species, such as the anionic forms of AA and UA [11,12]. Nafion-modified electrodes, in particular, have been found to improve selectivity for dopamine by stopping ascorbic acid from reaching the electrode surface as well as producing an enhancement of the dopamine electrochemical signal. This peculiar phenomenon is related to the accumulation of DA in the Nafion membrane. More recently, Fabregat et al. [13] reported on the use of cold plasma to functionalize the surfaces of polymer-based electrochemical sensors. Although this technique can be quite effective, uniform and reproducible modification of the surface can be difficult.

Therefore, in this work, we have developed PCL-based polymers characterized by functional groups capable of interacting with DA to explore the advantages of modifying electrodes by controlled polymer deposition. This approach is used for this particular application for the first time. The choice of the PCL polymer is related to: (i) the possibility of using simple, low impact and easily scalable synthesis and modification methods [14,15]; (ii) the fact that it can be easily structured, a property important in controlling mediator diffusion [16]; and (iii) it is

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**Table 1**

Thermal properties of the synthesized polymers and water contact angle of the bare ITO and PCL-coated ITO electrodes.

| Sample code        | $T_m^a$<br>[°C] | $T_c^a$<br>[°C] | $\Delta H_m^a$<br>[J·g <sup>-1</sup> ] | $X_c^a$<br>[%] | $\theta$<br>[°] |
|--------------------|-----------------|-----------------|--|----------------|-----------------|
| ITO electrode      |                 |                 |  |                | 114 ± 0.5       |
| Dod-PCL-2k-OH      | 59              | 33              | 95                                     | 70             | 73 ± 0.8        |
| PCL-star-4-2k-OH   | 51              | 28              | 80                                     | 57             | 57 ± 1.9        |
| PCL-star-6-2k-OH   | 52              | 28              | 70                                     | 50             | 57 ± 1.8        |
| Dod-PCL-2k-COOH    | 55              | 31              | 102                                    | 74             | 69 ± 0.5        |
| PCL-star-4-2k-COOH | 54              | 28              | 72                                     | 52             | 55 ± 1.2        |
| PCL-star-6-2k-COOH | 52              | 24              | 71                                     | 51             | 53 ± 1.4        |

<sup>a</sup> First heating scan of the solution-crystallized samples. The subscripts m and c indicate the values measured during melting and crystallization, respectively.  $X_c$  is the degree of crystallinity calculated by assuming the ideal enthalpy of fusion of PCL crystals as 139 J/g. Errors for  $T_m$  and  $T_c$  ± 0.1 °C, errors for  $\Delta H_m$  and  $X_c$  ± 5%.

biocompatible and biodegradable, features which could potentially allow PCL-based materials to be used in biosensor development [16]. In particular, the ability of the system to detect DA has been evaluated as a function of the type of architecture (linear or star shape), and the nature of the end groups (hydroxyl or carboxyl).

## 2. Materials and methods

### 2.1. Materials

$\epsilon$ -Caprolactone, 1-dodecanol, pentaerythritol, dipentaerythritol, indium tin oxide (ITO)-coated glass slides (25 × 25 × 1.1 mm, 8–12  $\Omega$ ), tin octanoate (Sn(Oct)<sub>2</sub>), toluene (anhydrous, purity 99.7%), dichloromethane, chloroform, methanol, maleic anhydride, dopamine (DA) and ascorbic acid (AA) were purchased from Sigma Aldrich®.  $\epsilon$ -caprolactone was purified prior to use by vacuum distillation over CaH<sub>2</sub>. All the other reagents were of analytical grade and used without further purification.

### 2.2. Synthesis of hydroxyl-terminated PCL polymers

Hydroxyl-terminated PCL was synthesized, as previously reported [17], by the ring-opening polymerization reaction (ROP) of  $\epsilon$ -caprolactone in bulk using Sn(Oct)<sub>2</sub> as a catalyst. The initiator, which was 1-dodecanol for the linear polymer (referred to as Dod-PCL-2k-OH), pentaerythritol for a star polymer with four arms (referred to as PCL-star-4-2k-OH) and dipentaerythritol for a star polymer with six arms (referred to as PCL-star-6-2k-OH), was adjusted in order to obtain star polymers with the same molecular mass as the linear structures, i.e. 2000 g·mol<sup>-1</sup>.

<sup>1</sup>H NMR,  $\delta$  (300 MHz, CDCl<sub>3</sub>, ppm). Dod-PCL-2k-OH: 4.06 (–CH<sub>2</sub>–, t); 3.65 (–CH<sub>2</sub>–OH PCL chain terminal, t); 2.30 (–CH<sub>2</sub>–, t); 1.66 (–CH<sub>2</sub>–, m); 1.40 (–CH<sub>2</sub>–, m); 1.31 (–CH<sub>2</sub>– dodecanol chain, m); 0.88 (–CH<sub>3</sub> terminal dodecanol, t). PCL-star-4-2k-OH: 4.09 (–CH<sub>2</sub>– pentaerythritol, s); 4.05 (–CH<sub>2</sub>–, t); 3.63 (–CH<sub>2</sub>–OH PCL chain terminal, t); 2.29 (–CH<sub>2</sub>–, t); 1.64 (–CH<sub>2</sub>–, m); 1.38 (–CH<sub>2</sub>–, m). PCL-star-6-2k-OH: 4.09 (–CH<sub>2</sub>–

dipentaerythritol, s); 4.06 (–CH<sub>2</sub>–, t); 3.65 (–CH<sub>2</sub>–OH PCL chain terminal, t); 3.38 (–CH<sub>2</sub>–O–CH<sub>2</sub>– dipentaerythritol, s); 2.30 (–CH<sub>2</sub>–, t); 1.65 (–CH<sub>2</sub>–, m), 1.39 (–CH<sub>2</sub>–, m).

### 2.3. Synthesis of the carboxyl-terminated polymers

The carboxyl-terminated polymers were synthesized from the hydroxyl-terminated PCL by applying an esterification reaction. In detail, four equivalents with respect to the hydroxyl end groups were used and the reaction was carried out at 80 °C for 24 h in anhydrous toluene under an argon flow. The crude product was precipitated in cold methanol and subsequently filtered, washed with cold methanol and finally dried at 40 °C for 72 h.

<sup>1</sup>H NMR,  $\delta$  (300 MHz, CDCl<sub>3</sub>, ppm). Dod-PCL-2k-COOH, PCL-star-4-2k-COOH, PCL-star-6-2k-COOH: along with characteristic chain signals of PCL, two additional signals were observed in the vinylic proton zone, at 6.42 ppm (R–OOC–CH=CH–COOH, d) and 6.31 ppm (R–OOC–CH=CH–COOH, d), generated by the proton of the maleic moiety. In addition, the signal of the PCL terminal (–CH<sub>2</sub>–OOC–, t) was shifted to a value of 4.28 ppm, typical of maleic esters [3].

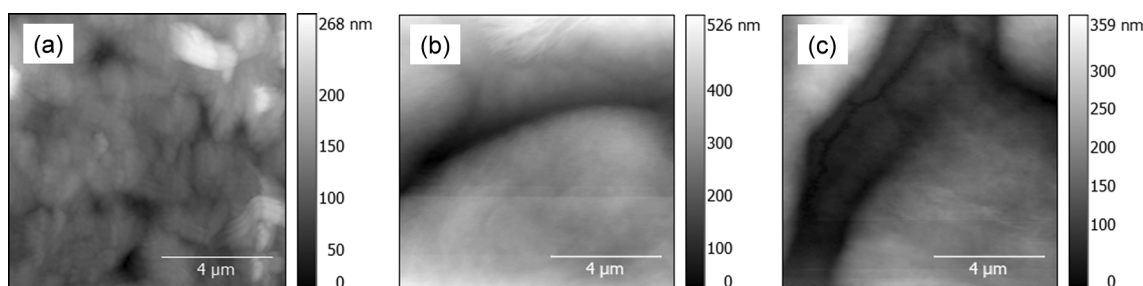
### 2.4. Preparation of coated ITO electrodes

Coated electrodes were prepared by a simple spin coating method. 200  $\mu$ L of a polymer solution in anhydrous toluene (60 mg/mL) was dropped on the surface of the ITO electrode, which was then rotated for 2 min at 25 rps.

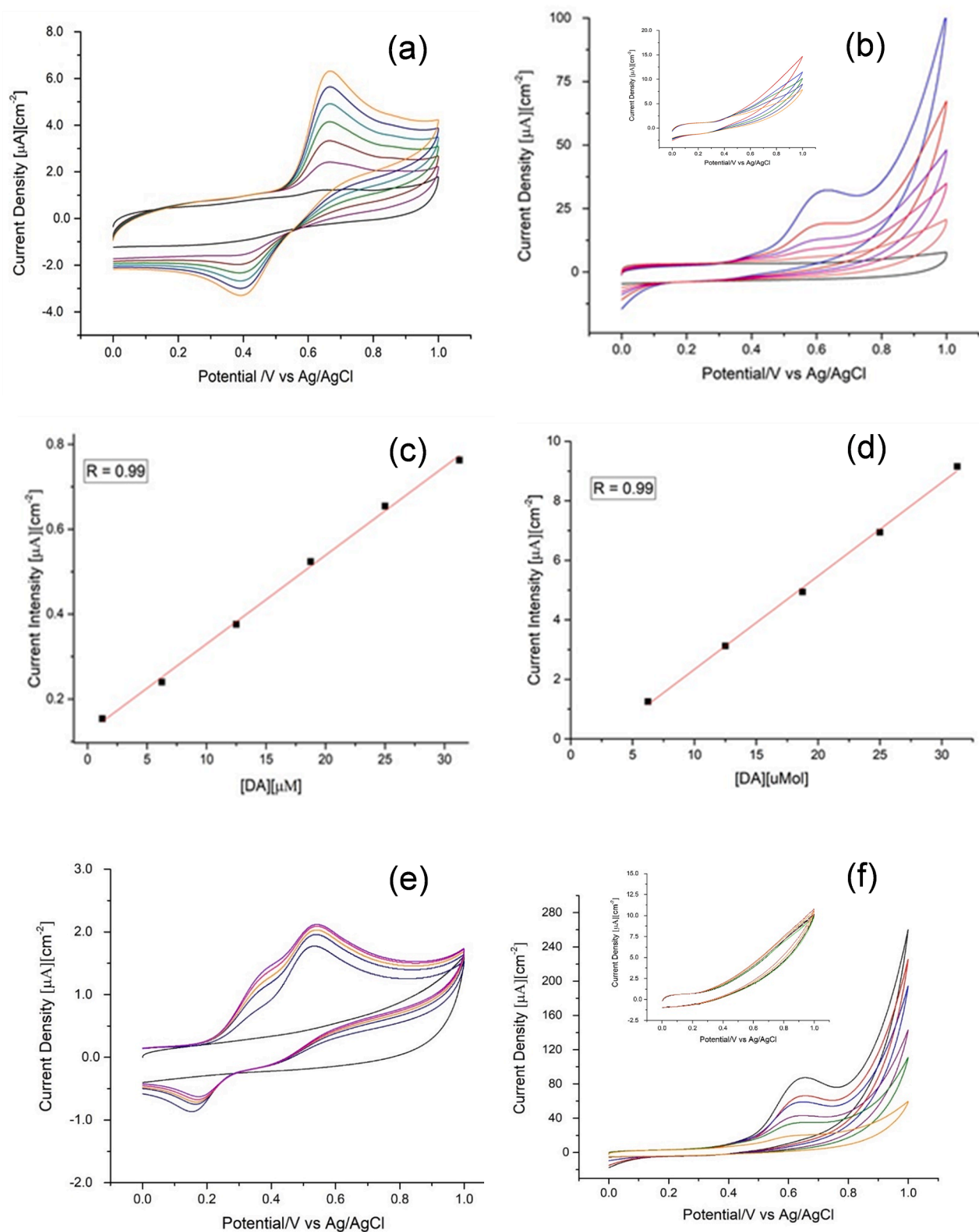
### 2.5. Characterization

<sup>1</sup>H NMR spectra were collected using a Varian NMR Mercury Plus instrument at a frequency of 300 MHz in CDCl<sub>3</sub> solutions containing tetramethylsilane as internal standard. Thermal properties were studied using a Mettler Toledo “DSC1 STARE System®” differential scanning calorimeter (DSC), in the temperature range from –100 to 150 °C at a heating rate of ±10 °C/min, under a nitrogen flow (20 mL/min). Contact angle experiments were carried out at room temperature by means of an Attension contact angle meter, using pure water as probe liquid. The surface topography of the coated films was examined by Atomic Force Microscopy (AFM) using a CoreAFM Nanosurf instrument on an area 10 × 10  $\mu$ m in tapping mode with a sampling rate of 512 points/line. Images were processed with the open-source Gwyddion software to determine the surface root mean square roughness ( $R_{sm}$ ).

Electrochemical detection was carried out by cyclic voltammetry using an electrochemical analyzer (CH Instruments, model CHI705E). The electrochemical experiments were performed in a glass cell with saturated Ag|AgCl as the reference electrode and platinum (Pt) wire as the counter electrode, and containing 10 mL of NaCl 0.1 M (pH = 7.4) at 20 °C. Voltammograms were recorded in the potential range from 0 to 1 V at a scan rate of 50 mV s<sup>-1</sup>. All the electrodes, both bare and modified, were left in contact with the electrolyte solution for 3 min prior to CV measurements.



**Fig. 1.** AFM micrographs of: (a) Dod-PCL-2k-COOH, (b) PCL-star-4-2k-COOH and (c) PCL-star-6-2k-COOH.



**Fig. 2.** Cyclic voltammograms of (a) bare ITO and (b) coated electrode with PCL-star-6-2k-COOH (inset: electrode coated with Dod-PCL-2k-OH) at different concentrations of DA (from 1.245  $\mu\text{M}$  to 31.25  $\mu\text{M}$ ). Plots of the oxidation peak current vs. the concentration of dopamine for: (c) bare ITO and (d) electrode coated with PCL-star-6-2k-COOH. Cyclic voltammograms of (e) bare ITO and (f) electrode coated with PCL-star-6-2k-COOH (inset: electrode coated with Dod-PCL-2k-OH) in the presence of [0.015  $\mu\text{M}$ –0.15  $\mu\text{M}$ ] AA and of [0.65  $\mu\text{M}$ –3.12  $\mu\text{M}$ ] DA. Measurements were performed in NaCl (0.1 M, pH 7.4) and cyclic voltammograms recorded at a scan rate of 50  $\text{mV s}^{-1}$ .

### 3. Results and discussion

The first part of this work focused on the synthesis of PCL-based polymers characterized by linear or star-shaped architecture and ending with hydroxyl or carboxyl groups. A study of these systems highlights the effects of the structure and the type of end group on sensor performance, in terms of selectivity and activity towards DA detection.  $^1\text{H}$  NMR was used for chemical structure validation and in particular corroborated the effectiveness of the functionalization reaction as well as the molecular mass, which was  $2000\text{ g}\cdot\text{mol}^{-1}$ . The thermal properties of the synthesized polymers were evaluated by DSC measurements – the results are summarized in Table 1. The linear polymers were characterized by high crystallinity ( $X_c$ ), ca. 70%, as expected for low molecular mass PCL [14]. Moreover, the values of both the crystallinity and the crystallization temperature ( $T_c$ ) turned out to be lower for the star polymers, a phenomenon which can be explained by considering that the structures in these systems are more hindered than in linear polymers [15].

The contact angle of the ITO electrodes was significantly modified by polymer deposition, changing from  $114^\circ$  to about  $70^\circ$  in the case of linear PCL (Dod-PCL-2k-OH and Dod-PCL-2k-COOH) deposition, in agreement with the values found in the literature for PCL films [17]. Moreover, a considerable reduction in the contact angle was observed for systems coated with star-shaped PCL terminated with both hydroxyl and carboxyl groups. This phenomenon may be related to the increase in film hydrophilicity caused by the larger number of polar end groups in the star-shaped systems, functional groups which promote dipole–dipole interactions [17]. The polymer architecture was also found to influence the morphology of the film, as shown by the AFM measurements (Fig. 1). Indeed, while the Dod-PCL-2k-COOH coating (Fig. 1a) had a mean square roughness ( $R_{sm}$ ) of ca. 30 nm, the corresponding figure for the star polymers was ca. 150 nm (Fig. 1b and c). The roughness values suggest that the star-shaped architectures do not allow chain entanglement, thus promoting the formation of less homogeneous surfaces.

The performance of the developed systems was investigated through cyclic voltammetry (CV), comparing bare ITO electrodes with those coated with the synthesized PCL. A cyclic voltammogram (CV) of dopamine on an untreated electrode is shown in Fig. 2(a), together with CVs on two electrodes coated with Dod-PCL-2k-OH (inset of Fig. 2b) and PCL-star-6-2k-COOH (Fig. 2b). It is worth underlining that the traces obtained using linear PCL ending with carboxyl groups (Dod-PCL-2k-COOH) and those of the ITO electrodes coated with star-shaped PCL ending with hydroxyl groups (PCL-star-4-2k-OH and PCL-star-6-2k-OH) were similar to that obtained with Dod-PCL-2k-OH. In these systems, the anodic current traces do not show the peak related to DA oxidation. In the case of the linear polymers, this finding can be ascribed to the high polymer crystallinity, which may limit the diffusion of the analyte into the coated layer, while for the hydroxyl PCL the effect of the functional groups must be taken into account. Indeed, it is of particular interest that modification of the electrodes with both PCL-star-6-2k-COOH (Fig. 2b) and PCL-star-4-2k-COOH (results not shown) leads to completely different behaviour, as the DA peak is clearly visible with a 10-fold enhancement of the current with respect to the bare ITO electrode (Fig. 2c and d), as well as the current scaling linearly with the concentration of DA. This result can be ascribed to the accumulation of DA on the surface, a phenomenon which occurs before the oxidation process, and which may be explained by considering the specific electrostatic interactions between the amino groups of the analyte and the numerous carboxyl groups of the star-shaped polymers. It is possible to hypothesize that, as a result of such interactions, the concentration of DA on the coated film is higher than that of DA present in the solution, leading to an increase in the anodic peak current in systems based on carboxyl-terminated PCL. Moreover, in the case of the star-shaped polymers, the effective diffusion of DA towards the electrode surface is promoted by the non-homogeneous coating and the limited crystallinity of the polymers, a phenomenon which may contribute to signal enhancement.

It is worth noting the irreversibility of the DA oxidation, i.e. the absence of the corresponding reduction peak of the analyte that would be expected in the case of species accumulated on the electrode surface. This irreversible oxidation of DA is in agreement with recent work by Compton et al. [18], which reports irreversible cyclisation of this molecule at neutral pH and at low scan rates ( $<100\text{ mV}\cdot\text{s}^{-1}$ ).

It is even more interesting to consider the simultaneous detection of DA and AA. In the case of the bare ITO electrode, the oxidation peaks of the two analytes overlap, as has been widely reported [8–13] (Fig. 2e). In the case of electrodes coated with linear PCL (inset of Fig. 2f) or the star-shaped hydroxyl-terminated polymers, no peak is visible in the voltammograms obtained in the presence of both DA and AA. Conversely, the oxidation peak of DA is clearly resolved when using electrodes modified with the star polymers ending in carboxyl groups (Fig. 2f). This phenomenon, as already reported for Nafion-coated electrodes [11,12], may be related to the effect of electrostatic repulsion between the carboxyl groups and AA, thus limiting the diffusion of this analyte towards the electrode surface.

### 4. Conclusions

Sensitive and selective sensors for the electrochemical detection of dopamine were successfully obtained by coating ITO electrodes with PCL-based polymers. Indeed, star-shaped PCL ending in carboxyl groups produced coatings characterized by: (i) an elevated number of functional groups capable of interacting with DA and limiting the accumulation of acid species; (ii) higher wettability compared to the bare electrodes; and (iii) lower crystallinity and higher roughness compared to the linear polymers, thus favouring DA diffusion towards the electrode surface. The above features, together with the biocompatibility and biodegradability of the synthesized polymers, suggest that the developed systems are promising for applications in the sensor/biosensor field. Indeed, taking into account the results reported in the present communication, we have already started a study on the development of novel biosensors based on PCL, in which the mechanism of DA and AA detection will be studied in detail.

### CRediT authorship contribution statement

**Eva Raccosta Leone:** Investigation, Visualization. **Lucia Simona Ferraraccio:** Investigation, Visualization. **Giacomo Damonte:** Investigation, Visualization. **Paola Lova:** Investigation, Data curation. **Paolo Bertoncillo:** Methodology, Writing - review editing. **Orietta Monticelli:** Conceptualization, Supervision, Writing - review editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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