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Interfacial polycondensation of polyamides studied at the electrified liquid-liquid interface

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Abstract

In this work, we present the possibility to electrochemically assist and study the interfacial polycondensation derived from the reactions between 1,6-diaminohexane or *p*-phenylenediamine (used as the diamine initially present in the aqueous phase) and acyl chlorides in a form of 1,3,5-benzenetricarbonyl trichloride, terephthaloyl chloride or adipoyl chloride (present in the organic phase – 1,2-dichloroethane solution). Polyamides are synthesized at the polarized liquid – liquid interfaces (or the interface between two immiscible electrolyte solutions – ITIES) as a consequence of the transfer of partly protonated diamines from the aqueous to the organic phase. In this respect, we have defined the aqueous phase pH assuring the availability of amine groups (-NH₂) for the reaction with the acyl chloride and protonated amine groups (-NH₃⁺) defining the electrochemical interfacial activity of chosen compounds. The possibility to electrochemically assist the interfacial formation of polyamides was first tested using the macroscopic ITIES. Formed polyamides were collected and analysed using scanning electron microscopy, energy dispersive x-ray spectroscopy and Raman spectroscopy. Next, we have employed the microscopic ITIES (microITIES) based system formed using fused silica microcapillaries. Cyclic voltammetry was employed for the polyamide modified microITIES assessment (evolution of molecular sieving properties using a model ion - tetramethylammonium cation).

Keywords: polyamides, interfacial polycondensation, polarized liquid – liquid interface, Kevlar, Nylon, acyl chlorides, diamine.

1. Introduction

Polyamides belong to the large group of polymers having an amide bond present in their structure. Polyamides can be divided into aliphatic (straight-chain), aromatic (aramids) and semi-aromatic (polyphthalamides). Aliphatic polyamides form straight chain monomers. Whenever two monomers, each containing an aromatic ring in its structure, react, we obtain aramid. Polyphthalamides are formed as the result of the reaction between aromatic and aliphatic monomers. Polyamides hold valuable commercial importance. They have many industrial applications, primarily in the textile industry for the production of clothes, but are also a component of ropes, lines, toothbrushes or tights [1,2]. Polyamide based materials are also frequently applied in R&D laboratories due to the high resistivity to organic solvents. These class of materials is especially useful as membranes [3], but also find applications as adsorbents [4] or for labware fabrication [5]. One can obtain polyamides by interfacial polymerization derived from a reaction between compounds containing multiple amine and acid chloride groups [6]. The substrates are dissolved in the aqueous and the organic phases (based on their solubility) and react at the junction formed between two immiscible liquids to form a polyamide material. The interfacial deposit is formed until (i) one of the reactants is exhausted, or (ii) the compactness of the formed polymer inhibits the transfer of the reactants to the soft junction. The reaction can be also impeded by the proton formed upon amide bond formation. Very popular example of a polyamide derived from the interfacial polycondensation is Nylon-6.6 [7]. It can be obtained quickly, spontaneously and easily in a spectacular manner, known as the "nylon rope trick" [8]. Since the protons are formed as by-products of the reaction between amine and acyl chloride groups, the interfacial polycondensation can be electrochemically assisted at the polarized liquid – liquid interfaces (the presence of protons allows the protonation of the amine groups triggering the interfacial electrochemical activity of the concerned compounds) [9].

Electrochemistry at the Interface between Two Immiscible Electrolyte Solutions (ITIES) is a platform that when combined with electroanalytical techniques allows the study of interfacial phenomena under the influence of an applied potential difference [10]. ITIES-based

systems are defect-free and self-healing, take the shape of the container, and can be studied with all available electrochemical techniques. The intrinsic properties of the ITIES are frequently employed to study purely ion interfacial charge transfer, providing an alternative to solid electrodes [11]. Macroscopic ITIES can be studied in a classical electrochemical cell equipped with two Luggin capillaries. Usually, the volume of each phase (either aqueous or organic) equals to a few mL. In the vast majority of reports, the ITIES is formed between an aqueous phase (highly hydrophilic salt (e.g. NaCl, HCl, LiCl) dissolved in water) and an organic phase (hydrophobic salt (e.g. bistriphenylphosphoranylidene ammonium tetrakis(4-chlorophenyl)borate, BTPPA⁺TPBCl⁻) dissolved in a solvent like 1,2-dichloroethane, α,α,α -trifluorotoluene) [12–14]. A lot of attention is also given to miniaturize polarized liquid – liquid interfaces to ensure greater stability of the soft junction (aided by the employed supports with predesigned surface wettability/capillary forces) and allow the reduction in consumption of toxic chemicals (and chemicals in general) [15]. The liquid-liquid interface can be downscaled with supports made of polymer [16], silicon [17,18], or fiberglass membranes [19]. MicroITIES systems are also created by using glass tubes, or single/double barrel capillaries with a dimensionality ranging from few tens of nm to a few tens of microns [20,21]. In this work, the microITIES was formed by placing a short piece of silica microcapillary tubing having 25 μm in diameter into a micropipette tip, further secure via heat treatment [22]. Resulting platforms allowed for the rapid fabrication that was beneficial for the microITIES modification with the polyamide material.

New properties of polarized liquid – liquid interfaces can be obtained by means of different materials placement at the soft junction. *In situ*-based modification methodology can be followed by (i) interfacial ion transfer, (ii) interfacial electron transfer, (iii) spontaneous adsorption to the interfacial region or (iv) interfacial polycondensation. An example of the interfacial deposition assisted by the ion transfer reaction of a surfactant molecules initially dissolved in the organic phase to the aqueous phase containing silanol species may lead to the electrochemically controlled synthesis of silica [23,24]. Moreover, the polarized liquid – liquid interfaces can be modified with metallic nanoparticles, which are formed as a result of interfacial electron transfer (e.g. from electron donor dissolved in the organic phase, to the aqueous reservoir of metallic NPs precursors) [25–28]. Examples cover the electrochemically controlled synthesis of Pd nanoparticles using an alumina membrane as a support [29],

synthesis of gold nanofilm [27,30], or silver nanoparticles [31] at the ITIES. Several elegant papers by Cunnane's team describe the interfacial formation of methyl and phenyl – pyrrole oligomers [32] and electropolymerization of 2,2':5',2''-terthiophene [33], the polymeric materials was controlled by interfacial electron transfer. Recent works discuss the formation of electrosynthesized poly(2,5-dimercapto-1,3,4-thiadiazole) films [34] or poly(3,4-ethylenedioxythiophene) thin films (the latter displaying exceptional biocompatibility) [35] at the polarized water- α,α,α -trifluorotoluene. Interfacial polycondensation defines a vast amount of growth polymerization reactions originating from a reaction between two or more monomers separated based on their solubility in the immiscible phases in contact. Vast amount of reactions can be rediscovered at the ITIES, especially when charged/ionisable function groups can be found within the structure of involved monomers. Recently, we have shown that polyamide interfacial polycondensation can be studied and assisted at the ITIES by electrochemical control leading to a simple methodology allowing the LLI modification [9,25].

In this work, the electrochemically controlled synthesis of different polyamide materials was carried out. We modified ITIES with the polyamide films derived from the reaction between 1,6-diaminohexane or *p*-phenylenediamine used as the diamine (always initially present in the aqueous phase) and acyl chlorides, either 1,3,5-benzenetricarbonyl trichloride, terephthaloyl chloride or adipoyl chloride (present in the organic phase – 1,2-dichloroethane solution). The chemical species selected are popular monomers used for different polyamides formation, and hence, were studied at the ITIES. Polymers were formed at the macroscopic and miniaturized ITIES. The latter brought the stability to the interfacially formed deposit that could easily be collected, characterized and applied for further electrochemical studies. Cyclic voltammetry was employed to assist the deposition process and to characterize modified ITIES permeability to ionic species. The materials extracted from ITIES were characterized using Raman spectroscopy and SEM – EDX.

2. Methods and materials

2.1. Chemicals

Sodium chloride (NaCl, $\geq 99,5\%$, Fisher Chemicals), acetic acid (CH_3COOH , 99.5 – 99.9%, POCh), phosphoric acid (H_3PO_4 , 80%, for analysis, ChemPur), boric acid (H_3BO_3 , for analysis, ChemPur) were used to prepare the Britton – Robinson buffer. Sodium hydroxide (NaOH, for analysis, POCH) were used to prepare 1M solution that were further employed for pH adjustment.

Demineralized water (Hydrolab®) was used in all cases to prepare the aqueous solutions. The organic phase was hydrophobic salt (BTPPA⁺TPBCl⁻) dissolved in 1,2 – dichloroethane (1,2-DCE, for analysis, POCH). The organic phase electrolyte BTPPA⁺TPBCl⁻ was synthesized using bis(triphenylphosphoranylidene)ammonium chloride (BTPPA⁺Cl⁻, 97%, Sigma-Aldrich) and potassium tetrakis(4-chlorophenyl)borate (KTPB⁺Cl⁻, ≥98%, Sigma-Aldrich) salt via mixing equimolar amounts of both reagents in methanol:water mixture (2:1). Resulting precipitate was then filtrated and recrystallized from acetone. The following compounds of diamines and di- or tri-acid chlorides were used for the synthesis of polyamide materials: p-phenylenediamine (PPD, 98%, Sigma – Aldrich), 1,6 – diaminohexane (1,6-DAH, ≥99,5%, Acros Organics), 1,3,5-benzenetricarbonyl trichloride (1,3,5-BTCTCl, for analysis, Apollo Scientific), terephthaloyl chloride (TCl, ≥99%, Sigma – Aldrich), and adipoyl chloride (AC, 98%, Alfa Aesar). A quaternary amine - tetramethylammonium chloride (TMACl, >98%, Acros Organics) was used to test molecular sieving properties of polyamide modified microITIES. The fused silica capillary tubing having the internal diameter equal to 25 μm (value indicated by the manufacturer) was purchased from VWR.

2.2. Electrochemical experiments

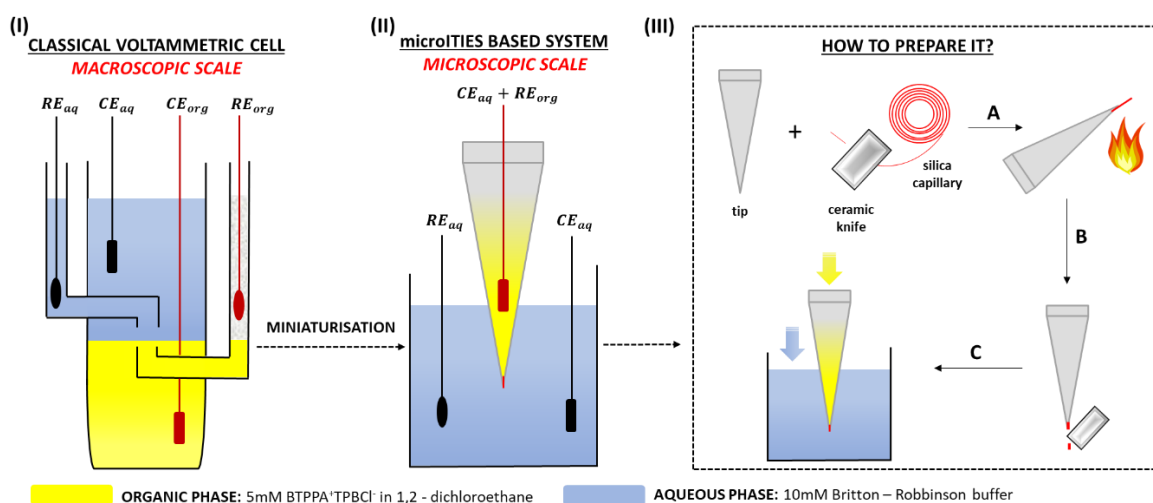


Figure 1. Scheme showing classical voltammetric cell (I) used for macroITIES polarization and modification, (II) used for microITIES modification and electroanalytical characterization. The organic phase is marked in yellow, whereas the aqueous phase is marked in blue. Set of electrodes being in contact with the organic phase are marked in red, and for the water phase in black. $RE_{aq/org} = \text{Ag/AgCl}$ wire, $CE_{aq/org} = \text{platinum electrode (Pt)}$. The third part of figure

(III) shows the preparation protocol of the microITIES based system by embedding (A) a silica capillary in a micropipette tip, (B) removing excess capillary using a ceramic knife, and (C) filling the created system with the organic phase followed by a set of electrodes placement.

Electrochemical studies were carried out on macroscopic and microscopic scale. In macroscopic scale (see Fig.1-(I)) a classical voltammetric glass cell (interface radius equal to 0.7 cm) equipped with a set of four electrodes was used. Two Ag/AgCl reference electrodes and two Pt counter electrodes were involved. In microscopic scale (Fig. 1-(II)), the ITIES was supported with a micropipette tip finished with the silica capillary tubing having a diameter equal to around 25 μm . The created microtip was filled with the organic phase and immersed in the aqueous phase. Here, the platinum, and the Ag/AgCl electrodes were used as the aqueous phase counter and reference electrodes, respectively. The platinum wire electrode contacted with the organic phase served as both: the organic phase counter and reference electrode. MicroITIES support was fabricated following procedure reported elsewhere.[22] All experiments were conducted using Autolab 108 (Metrohm®) with Nova 1.11 software.

All experiments involving the microITIES modification with polyamide materials were performed with a single use, disposable fused silica capillary based tips. This means, that data shown in Fig. 5 and Fig 6 (also, Fig. S5 – S8), were performed in the following manner: (i) first the microITIES tip was fabricated; (ii) unmodified microITIES was tested using cyclic voltammetry in the presence of fixed concentration of TMACl dissolved in the aqueous phase; (iii) microITIES was modified with a chosen polyamide using a fixed number of voltametric scans (each condition requires the utilization of a separate tip); (iv) tip was removed from the aqueous phase containing diamines and was placed in the cell filled with the aqueous phase ($[\text{TMA}^+] = 60 \mu\text{M}$); (v) tip was removed and placed in the cell containing $[\text{TMA}^+] = 180 \mu\text{M}$.

During the electrochemical experiments the concentration of monomers dissolved in the aqueous and the organic phase were set to either 5 or 10 mM. These values are based on the finding that are published in our previous work (see [9]).

2.3.SEM - EDX

The scanning electron microscopy (SEM, a Phenom G2 Pure, FEI Company, the Netherlands) was used to examine the morphology of polyamide material formed at the macroscopic and

microscopic LLI. SEM images were acquired using a high sensitivity backscatter electron detector (BSD) with an accelerating voltage of 5 kV.

SEM - EDX was also used for local analysis and mapping of manufactured polyamide materials using the JEOL JMS-IT500HR microscope (JEOL, Japan) equipped with the Ultim Max 170 EDS detector (Oxford Instruments, UK).

2.4. Raman Spectroscopy

Raman spectra have been taken with a Renishaw Qontor set-up equipped with a Peltier-cooled CCD camera, a laser of 785 nm wavelength working at 50 mW and an edge filter to separate the Rayleigh from the Raman scattered light. A grating with 1200 grooves/mm was used, leading to a spectral resolution of 1 cm^{-1} . The laser light was focused on the microscope stage using a X50 objective with long working distance (11 mm) and a numerical aperture of 0.75. Typical experiments required an average of 4 acquisitions with 5 s of integration time on the detector.

3. Result and discussion

3.1 Polyamides synthesis at macroscopic polarized liquid-liquid interface

We have studied the possibility to assist electrochemically the synthesis of polyamides at the macroscopic ITIES. As the interfacial polycondensation reaction product is not removed from the LLI during electrochemically assisted synthesis, the reaction is catalysed by the electrochemically controlled delivery of the diamine substrate (partly protonated diamine is transferred to the LLI and to the organic phase upon application of the positive potential) and removal of the formed protons (during negative polarization direction the protons are transferred to the organic phase, and are used to further protonate diamine). The possible reaction routes between the various monomers dissolved in either aqueous or the organic phase that we have studied are shown in Fig. 2. The polyamides synthesised are derived from the reaction between one out of two employed diamines and one out of three selected di- or tri-acyl chlorides. As shown in Fig. 2, the investigated pair of monomers are (aq stands for the aqueous phase; org stands for the organic phase): I - *p*-phenylenediamine (aq) and 1,3,5-benzenetricarbonyl trichloride (org), II - *p*-phenylenediamine (aq) and terephthaloyl chloride (org), III - *p*-phenylenediamine (aq) and adipoyl chloride (org), IV - 1,6-diaminohexane (aq) and

1,3,5-benzenetricarbonyl trichloride (org), **V** - 1,6-diaminohexane (aq) and terephthaloyl chloride (org). The numbering **I-V** is adopted and refer to resulting polyamides in all section of this manuscript. The interfacial polycondensation of nylon-6,6 (**VI**; reaction between 1,6-diaminohexane and adipoyl chloride) is purposely not marked as it was investigated previously by our group (see [9]). The interfacial polycondensation reaction can be controlled and monitored with electrochemical techniques due to two crucial molecules being involved in the polymerization process, this is an aqueous phase monomer (diamines) which exist in the aqueous phase as monocations (A^+) or dications (A^{2+}) and protons, that are released upon dissociation of the chloric acid formed as the byproduct of the polycondensation reaction. We have found that the electrochemically controlled transfer of these molecules accelerate the interfacial polycondensation reaction. Monoprotonated amines can be transferred to the organic phase where these react with the acid chloride functionality of the organic phase monomer whereas protons, increase the apparent concentration of protonated (and hence electrochemically active) amines in the aqueous phase.

For *p*-phenylenediamine and 1,6-diaminohexane we have plotted concentration fraction diagrams (Fig. S1). *p*-phenylenediamine pK_a values are $pK_{a1} = 2.8$ and $pK_{a2} = 6.2$ [36]. For 1,6-diaminohexane, these values are $pK_{a1} = 10.8$ and $pK_{a2} = 11.9$ [9]. Both monomers soluble in the aqueous phase, have two amine groups located at the periphery of the aromatic ring or alkyl chain. As such, for each diamine, we can distinguish three possible species that may exist in the aqueous phase depending on its pH: this is neutral diamine (A^0); monoprotonated diamine (A^+) or diprotonated diamine (A^{2+}). To form an amide bond, a fraction of compounds providing amine groups with a lone pair of electrons need to be available to attack carbon atom (with a net positive charge). A fraction of protonated amine groups, which are deprived from a lone electron pair, will provide the interfacial electrochemical activity of the amine monomers. In other words, we need charged species that may undergo electrochemically controlled ion transfer from the aqueous to the organic phase being reservoir of the monomers equipped with acyl chloride functionalities. The inspection of the concentration fraction diagrams revealed that the optimal aqueous phase pH for the electrochemically assisted interfacial polycondensation reaction is pH = 6.2 for the *p*-phenylenediamine pH = 11.3 for the 1,6-diaminohexane. Further information taken from the concentration fraction diagrams indicates that at pH = 6.2 (*p*-phenylenediamine; Fig. S1A) the aqueous phase contains 50% of A^0 ; 50% of A^+ ; and 0% of A^{2+} . For 1,6-diaminohexane we have selected the aqueous phase pH = 11.3 (see

Fig. S1B) that fixed its composition to 64% of A^+ ; 18% of A^{2+} , and 18% of A^0 . The reason why the pH of the aqueous phase solution of the 1,6-diaminohexane was not high (lowered fraction of the doubly protonated species – A^{2+}) is related to the occasional appearance of additional fraction of current (charge transfer processes with unknown origin) within the more negative side of the potential window.

With the pH of the aqueous phase fixed, we have designed the experiment to study the effect of the diamines concentration added to the aqueous phase (in the absence of the acyl chloride in the organic phase) to study their interfacial activity. Fig. S2A and Fig. S2B show the resulting current-potential dependencies for *p*-phenylenediamine and 1,6-diaminohexane in the concentration range from 20 μ M to 3 mM, respectively. Studied molecules were found to be active as both exist in the aqueous phase in a cationic form. In both cases, we have observed that starting from 20 μ M, we can distinguish a pair of signals (positive and negative currents) located on the positive potential difference side of the available potential window. As the concentration of diamine increases ($> 500 \mu$ M) the current intensity at $E > 0.6$ V grows (as expected) and overlaps with the current linked to the transfer of the background electrolyte, which limits the potential window on more positive side (Na^+ transfer from the aqueous to the organic phase). Our understanding is that, for *p*-phenylenediamine at pH = 6.2, the positive currents are due to A^+ transfer from the aqueous to the organic phase, whereas for 1,6-diaminohexane at pH = 11.3, the positive current is a mixture of the A^+ and A^{2+} transfer from the aqueous to the organic phase. By analogy, the negative currents are due to A^+ or A^+/A^{2+} back transfer to the aqueous phase. We also found, that all employed acyl chlorides soluble only in the organic phase, this is 1,3,5-benzenetricarbonyl trichloride (Fig. S2C), terephthaloyl chloride (Fig. S2D) and adipoyl chloride (Fig. S2E), at 5 mM each, do not provide significant current variation within the available potential window (only for adipoyl chloride extra signals were recorded at around 0.5V). Acyl chloride functional group may react with water to form carboxylic acid groups and hydrochloric acid as a side product. This means that small fraction of monoanionic or dianionic species with hydrolysed carboxylic groups (high pH) may exist within the interfacial region. At this point we can only speculate, that additional set of signals with very low intensity at around 0.5V in Fig. S2E may originate from the dissociated carboxylic acid transfer.

The spontaneous interfacial polycondensation reaction may occur only when sufficient concentration of monomer in both phases is used (usually \gg mM) and when the pH of the

aqueous phase assures that only when the fraction of A^0 is equal to unity (>14). In our case, the chosen experimental conditions do not lead to the rapid and spontaneous polyamide film formation. Although the reaction can occur at open circuit potential, we have performed an experiment further confirming that the interfacial polycondensation may be controlled electrochemically. The electrochemical cell was filled with the aqueous and the organic phase being a solution of electrolytes and 1,6-diaminohexane and adipoyl chloride, respectively. Next, we have applied negative potential difference to the ITIES and have found that no film was formed within 30 minutes (time of the experiment).

Fig. 2 further depicts the ion transfer voltammograms recorded in the presence of different pair of diamines and di- or tri-acyl chlorides dissolved in the aqueous and the organic phase, respectively. For all cases I-V (for the numbering refer to Fig. 2A) the concentration of acyl chloride dissolved in the organic phase was fixed and equal to 5 mM, whereas the concentration of diamine was an experimental variable progressively increasing from 100 μM to 5 mM.

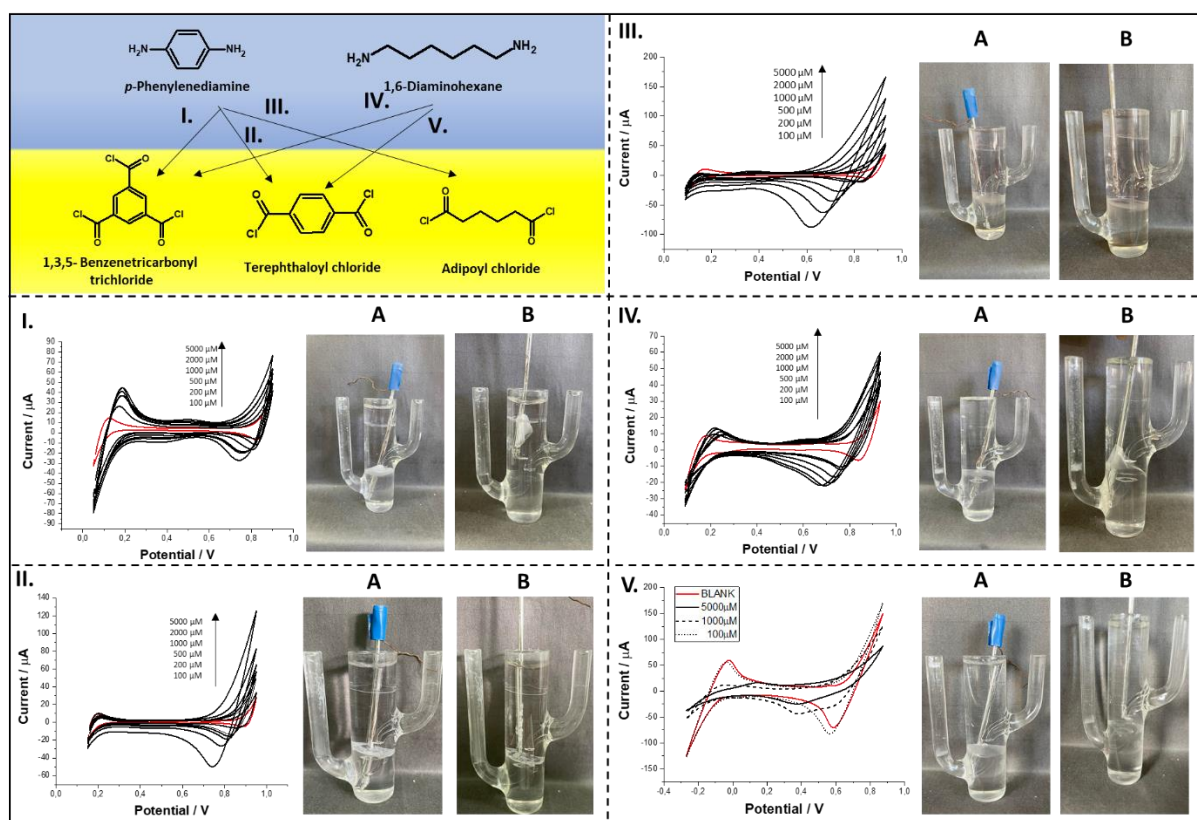


Figure 2. Left upper corner: Scheme displaying all possible reactions between acyl chlorides and di-amines studied at the ITIES. The numbers of reaction routes from I to V refer to the corresponding cyclic voltammograms recorded during the electrochemically assisted

polyamides deposition at the macroscopic ITIES. Concentration of acyl chloride was fixed (5 mM), whereas the concentration of di-amine dissolved in the aqueous phase was increased from 100 to 5000 μM . The photos on the right from cyclic voltammograms are recorded after the interfacial polycondensation reaction occurred. The image **(A)** shows the polyamide material formed at the ITIES. In the second picture **(B)**, the material is pulled from the interface using a counter electrode from the organic phase.

From Fig. 2, we notice that reactions I, II, III and IV provide similar features. As the concentration of *p*-phenylenediamine (I, II and III) and 1,6-diaminohexane (IV) increases, we observe the increase in the positive current limiting the potential window on the more positive potential difference side of the cyclic voltammogram. Also, we have noticed an additional pair of peaks located between +0.2 V and +0.5 V (especially visible in Fig. 2-I, $E_{1/2} = 0.41\text{V}$) for *p*-phenylenediamine and between +0.5V and +0.8V (see Fig. 2-IV, $E_{1/2} = 0.58\text{V}$) for 1,6-diaminohexane. Similar set of additional signals was also recorded in Fig. 2-III. In the presence of the aqueous and the organic phase monomers, a number of electrochemical and chemical reactions can occur: (i) the electrochemically controlled transfer of either A^+ or A^{2+} from the aqueous to the organic phase giving positive current; (ii) reaction of the nitrogen atom having a lone pair of electrons with the carbon atom of the acyl chloride functionality occurring either at the ITIES or on the organic phase side of the ITIES after A^+ transfer or A^0 partitioning to the interfacial region; (iii) the A^+ or A^{2+} dissociation in the organic phase followed by the ion transfer reaction providing new amine groups for the reaction with acyl chloride; (iv) acidification of the aqueous phase side of the ITIES as the interfacial polycondensation proceeds (release of protons) that may affect the distribution of $\text{A}^0/\text{A}^+/\text{A}^{2+}$ further affecting the shape of the cyclic voltammograms; and finally, (v) the formation of charged dimers/trimers that may transfer back from the organic phase to the aqueous phase. As a matter of fact, for the latter, we believe that the extra pair of signals recorded before the prominent limiting current obtained for the higher diamine concentration may originate from these complex species transfer. This hypothesis assumes that formed amides (dimers, trimers) should be more hydrophobic as compared with the charged diamine species shifting their ion transfer potentials to less positive potential difference values. Reaction between 1,6-diaminohexane and terephthaloyl chloride (V) gave rise to initially increasing signals attributed to the amine transfer from the aqueous to the organic phase (up to 100 μM), followed by a visible current drop, even these attributed to

the transfer of the aqueous phase background electrolyte ions. This is especially visible on the cyclic voltammogram from Fig. 2-V, marked with a black solid line and attributed to the 5 mM 1,6-diaminohexane and 5 mM terephthaloyl chloride. The intensity of the peak current located at $E = +0.05$ V is nearly unaffected after addition of 100 μ M of 1,6-diaminohexane and drops by around 85% when final concentration of diamine equal to 5 mM is present in the aqueous phase. This demonstrates that the permeability of the formed polyphthalamide terephthaloyl/1,6-diaminohexane film is low, and hence, should display efficient ionic sieving properties. Each pair of monomers, after excessive cycling (> 20 cycles) resulted in the formation of the deposit at the ITIES. Visual inspection of the formed polymeric films is additionally depicted on the photos taken for the cell after cyclic voltammetry (see Fig. 2, photos on the right from the cyclic voltammograms). First photo was taken for the cell with the intact ITIES whereas the second shows the film after lifting the organic phase counter electrode. By doing this, we observed that compact and relatively thick films were obtained via reaction route I and IV (reaction between 1,3,5-benzenetricarbonyl trichloride and *p*-phenylenediamine or 1,6-diaminohexane, respectively). In both cases, the film could be lifted from the ITIES after the voltammetric deposition. Most probably, formed polyamide films hold a relatively open and cross-linked structure originating from the existence of three acyl chloride substituents in 1,3,5-benzenetricarbonyl trichloride monomer, which do not inhibit the mass transfer of diamine from the aqueous to the organic phase. This is in line with the increasing ionic currents growing along with the increasing aqueous phase monomer concentration. For the reaction routes II and III, we have obtained films that were breaking easily once the organic phase counter electrode was moved. Similar features were attributed to the reaction route V, which displayed significant blocking effect on the transfer of all ions present in the cell (see Fig. 2-V). The fragile polyamide film could be easily disrupted, most probably meaning that this thin film is not permeable to either of the monomers already at the initial deposition time.

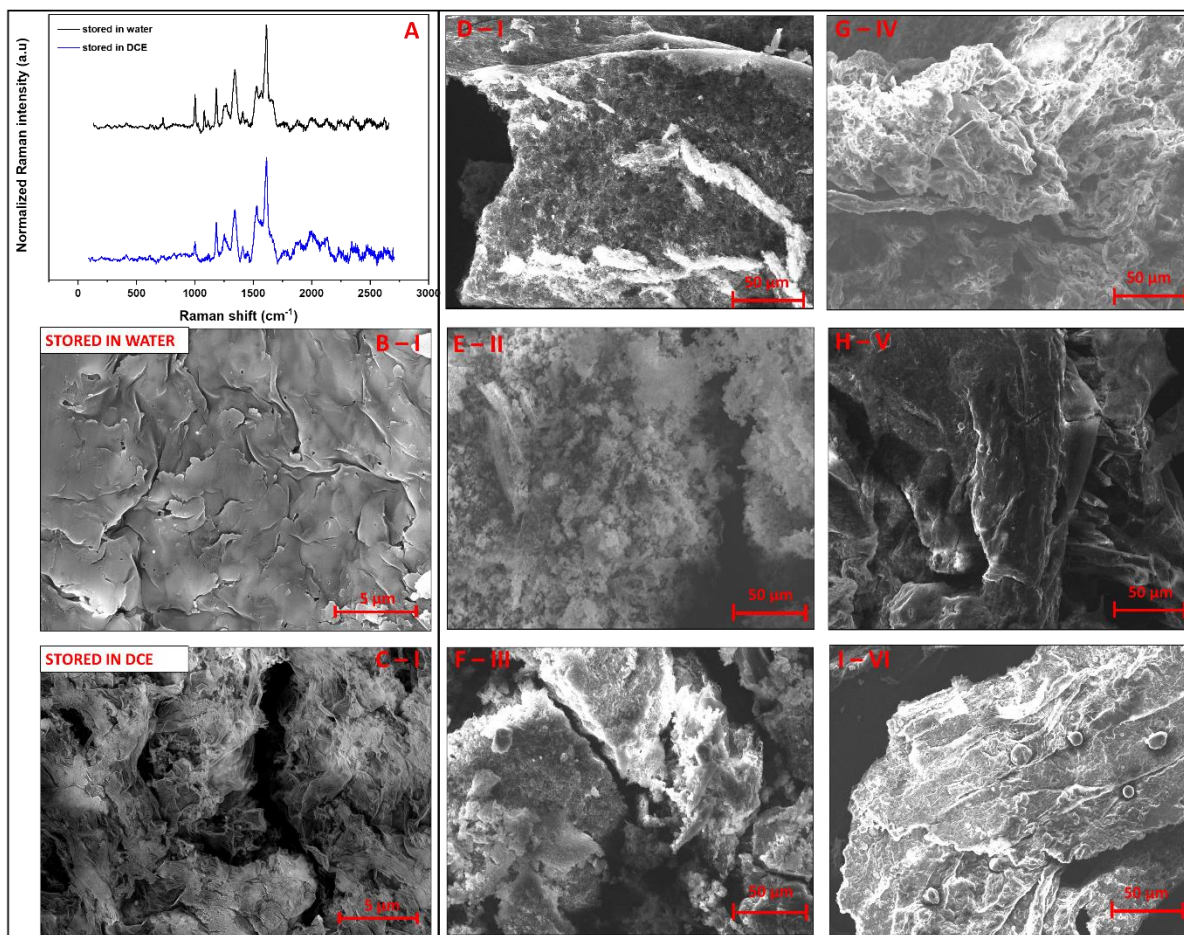


Figure 3. Raman spectra (A) recorded for polyamides derived from a reaction between *p*-phenylenediamine and 1,3,5-benzenetricarbonyl trichloride stored in different solutions – water or 1,2-DCE and corresponding SEM images (B-I, C-I). Other SEM images recorded for polyamide films synthesized and collected from the ITIES after measurement. D-I – *p*-phenylenediamine and 1,3,5-benzenetricarbonyl trichloride, E-II – *p*-phenylenediamine and terephthaloyl chloride, F-III – *p*-phenylenediamine and adipoyl chloride, G-IV – 1,6-diaminohexane and 1,3,5-benzenetricarbonyl trichloride, H-V – 1,6-diaminohexane and terephthaloyl chloride, I-VI – 1,6-diaminohexane and adipoyl chloride.

Fig. 3 shows the data obtained for the polyamide materials extracted from the macroscopic ITIES after electrochemically assisted deposition process. With scanning electron microscopy, we have noticed that different polyamides, as expected, exhibit different surface morphologies. The inspection of the SEM images (Fig 3B – F) reveals that polyamides formed via routes I, II and III are rather spongy with the debris existing at the material surface whereas the remaining polymers obtained in reaction IV, V and VI (Fig. 3G – I) display significantly less

fine features. Fig. S3 available in the electronic supporting information provide more SEM images recorded at three different magnifications. We have also found, that all polymeric materials directly collected from the ITIES were decorated with debris and features that disappeared after storing the films collected from the ITIES in water and DCE for a few days. This step was performed to remove the electrolytes from the film framework that severely interfered during Raman analysis. For the polyamide derived from the reaction I, the surface of the material stored in water (Fig. 3B) is rather smooth (cracks and wrinkles are most probably the artefacts of the drying and film processing process), and distinctly different from the same material having a number of fibrous features at its surface before washing as shown in Fig. 3D. Storing the material in 1,2-DCE also affected the analysed polyamide I surface as shown in Fig. 3C giving the impression of an open polyamide structure. EDX analysis done on the polymeric samples analysed directly after collecting these from the ITIES has shown that in addition to carbon, nitrogen, and oxygen polymeric films contain other elements at non-negligible contribution. We have found sodium, phosphate, and chloride indicating that the background electrolyte salts (from both phases) may be entrapped within the polyamide material during the interfacial polycondensation process. We have found that on average, more background electrolyte ions are present in the polyamides derived from reactions IV, V and VI (e.g. up to 11.20% of Na^+ found in film IV) (see Table S1 for details). Raman spectra recorded for the polymeric films before removal of the background electrolyte salts did not reveal any vibrational bands that could be attributed to the presence of amide bonds. As a matter of fact, only through rinsing of the films allowed the observation of the contribution from the polyamide structure which are shown in Fig. 3A. For the polyamide (I) stored either with water or 1,2-DCE we have found a characteristic band at around 1600 cm^{-1} that is attributed to the phenyl ring C-C stretching [37]. Other contribution that were found include 1550 cm^{-1} (in-plane bending of NH from the amide bond); $1410 - 1440\text{ cm}^{-1}$ (CH bonds bending from the aromatic rings); 1349 cm^{-1} (CH in-plane deformation) or the band at 1000 cm^{-1} (trigonal ring breathing vibration and CH ring deformation). These findings confirm that the interfacial deposition of the polyamide materials obtained via route I at the electrified liquid-liquid interface do occur. For all films, we have obtained a number of Raman signals that were attributed to the organic phase electrolyte which suggest its encapsulation into the film framework [38].

3.2. Microscopic liquid-liquid interface modified with different polyamides

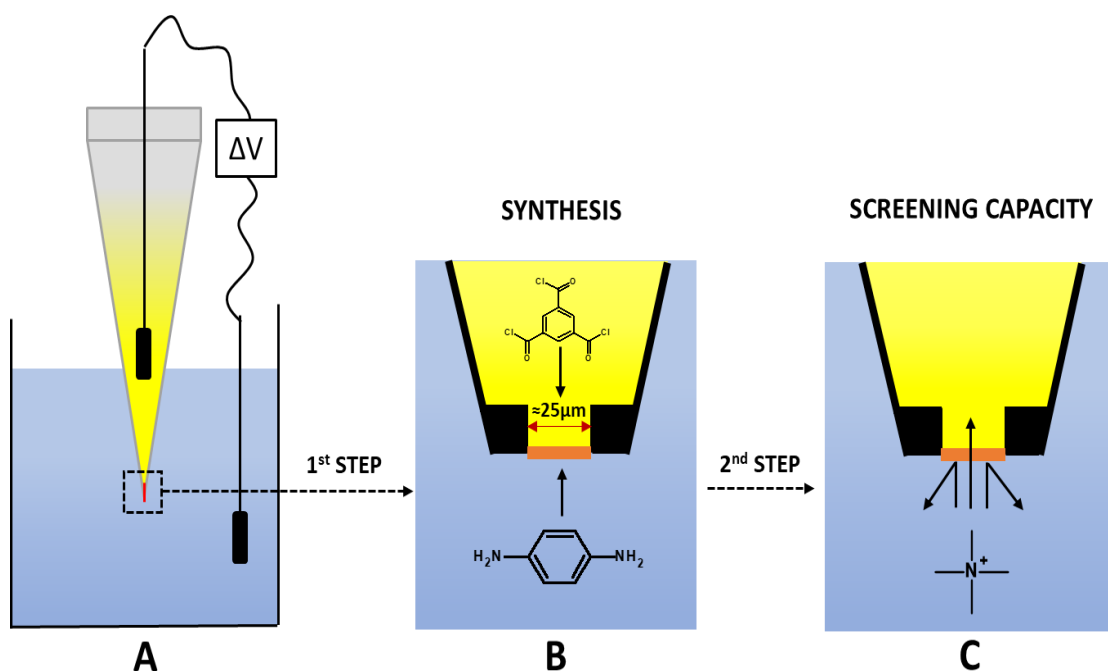


Figure 4. Experimental sequence aiming at (A) bare microITIES characterization; (B) microITIES modification with the chosen polyamide (example shows the reaction between *p*-phenylenediamine (aq) and 1,3,5-benzenetricarbonyl trichloride (org) and (C) modified microITIES characterization with quaternary ammonium cations.

In order to test polyamides compactness formed at the ITIES, the entire system was miniaturized using fused silica capillaries serving as the soft junctions supports. Each number of cycles used to modify the electrified LLI supported with the fused silica capillary required the utilization of the separate support (microplatform). All supports, before being modified with the polyamide film were characterized with the ion transfer voltammetry in the presence of the fixed concentration of the TMAcI dissolved in the aqueous phase. Only the tips, for which the calculated ITIES diameter were found in the range from 24.0 to 25.5 μm were used for interfacial modification. Experiments for each studied pair of monomers were performed three times when the polyamide materials were formed after applying 20 voltametric cycles. For other conditions, each material was formed after a single experiment. As such, we decided to focus on the obtained tendencies to inspect how the synthesis conditions affects the modified ITIES permeability. The exception was the polyamide formed between *p*-phenylenediamine and adipoyl chloride. Already during the modification of the macroITIES we have found that this material form brittle films that can easily break when the electrochemical cell is perturbed. During microITIES modification we have found, that occasionally, for the fixed experimental

conditions, the resulting material was either permeable or its was blocking the LLI. We believe that this observation is related with the material fragility, meaning that special modified ITIES handling had to be applied not to affect the formed film.

Fig. 4 shows the typical processing route applied for all studied polyamides. The **1st step (Fig. 4A)** accounts for the microITIES preparation (see procedure reported elsewhere [22]) and the resulting supports electroanalytical evaluation with the cyclic voltammetry in the presence of the model ion. The currents originating from the tetramethylammonium (TMA^+) cation transfer from the aqueous to the organic phase were used to calculate the diameter of the supported ITIES [39]. As it will be shown for all voltammograms displayed below, the mass transfer of TMA^+ from the aqueous to the organic phase follows the hemispherical diffusion layer profile providing sigmoidal current response. The back transfer happening inside the capillary is limited by the linear diffusion, and hence, the negative, peak like signal is recorded. Only the tips having $24.5 \pm 1.0 \mu\text{m}$ were used for further processing. **Fig. 4B** shows the electrochemically assisted microITIES modification step. The concentration of monomers was set to 10 mM and 5 mM for diamine and di-/tri-acyl chloride dissolved in the aqueous and the organic phase, respectively. For given concentrations we were obtaining enough material for further analysis, and we also found that these concentrations provided films affecting the interfacial charge transfer reactions. The interfacial polycondensation was assisted by cyclic voltammetry with the experiential variable being the number of recorded cycles: 5, 10, 15 or 20. In the last step (**Fig. 4C**), the microITIES modified with polyamide film, with the predefined number of cycles, was removed from the aqueous phase containing diamine. The tip was rinsed with demineralized H_2O and was further inserted into a fresh cell to which the quaternary ammonium model ion (TMA^+) was added. The outcome of the molecular sieving properties for each formed polyamide film was analysed and is discussed below.

First, we have investigated the polyamide (I) created using *p*-phenylenediamine and 1,3,5-benzenetricarbonyl trichloride. **Fig. 5A and 5B** shows the monomer structures used during electrochemically assisted interfacial polycondensation. Before ITIES modification the composition of both phases was set to: the aqueous phase - 10 mM *p*-phenylenediamine dissolved in a 10 mM BRB at pH = 6.2; the organic phase – 5 mM 1,3,5-benzenetricarbonyl trichloride dissolved in a 5 mM $\text{BTPPA}^+\text{TPBCl}^-$ in 1,2-DCE. As shown in Fig. 5C, the material formed covers a surface slightly greater than the surface of the pore (around 25 μm in

diameter) indicating that: (i) the material grows towards the aqueous phase side of the ITIES as the reaction time pass by; or (ii) the drop in the ITIES interfacial tension caused by the adsorbing dimers/trimers/oligomers affects the position of the soft junction going into the aqueous phase during the electrochemically assisted modification. In Fig. 5D or Fig. S9 one can notice that the film obtained is not homogenous. Analysis of the image suggests that the surface of the polyamide formed is heterogeneous, which is difficult to assess with SEM analysis. **Fig. 5E – 5H** are the cyclic voltammograms recorded in the absence and in the presence of TMA⁺ (in the aqueous phase) at the ITIES modified with polyamide (I) after indicated number of cycles. We have observed that in the absence of the TMA⁺ in the aqueous phase, the positive and the negative limiting currents are becoming more resistive for the longer deposition process, although still being permeable to Na⁺ ions (limiting currents of the more positive potential difference side of the potential window) and the aqueous phase background electrolyte anions (Cl⁻, phosphate, borate or CH₃COO⁻; more negative side of the potential window). The inspection of the positive currents (sigmoidal wave corresponding to the transfer of the TMA⁺ from the aqueous to the organic phase) reveals that up to 10 cycles the signal intensity for 180 μM TMA⁺ remains rather unaffected, after 15 cycles it drops by around 93%, whereas after 20 cycles the signal is missing. This suggests that the film compactness do not allow for the TMA⁺ transfer or its thickness affects the TMA⁺ diffusivity across the modified ITIES.

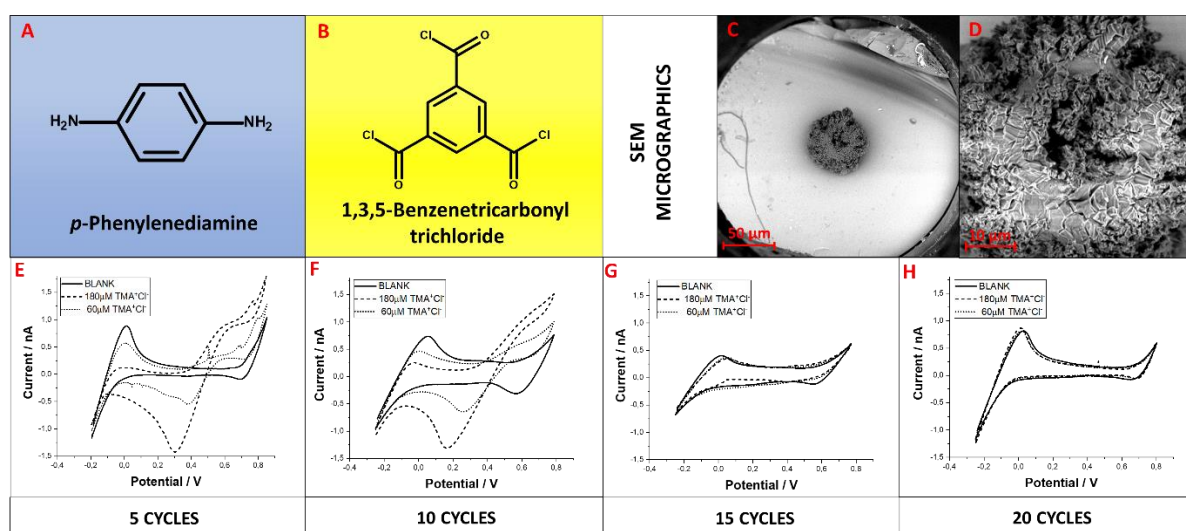


Figure 5. The figure shows structural formulas of *p*-phenylenediamine and 1,3,5-benzenetricarbonyl trichloride dissolved in the aqueous (A) and the organic (B) phase, respectively. C and D shows SEM micrographics taken for the polyamide modified microITIES

formed after 20 consecutively recorded voltammetric scans. E, F, G and H are the voltammograms recorded at modified microITIES in the presence of $[TMA^+] = 60$ or $180 \mu\text{M}$ after different amounts of voltammetric cycle recorded during polyamide film formation at the ITIES. The recorded blank reading corresponds to the bold cyclic voltammogram recorded at modified microITIES in the absence of TMA^+ .

The same characterization procedure was applied to all studied pairs of monomers. Analogical set of data for polyamide (II) is depicted in Fig. S5 and Fig. S9-II. SEM micrographies indicate that the formed film entirely covers the pore. The morphology of the interfacially formed material is distinct from the polyamide (I) as not clear pinholes and holes are visible at its surface. Also, from Fig. S9-II (the SEM image recorded at the highest magnification) one can notice a clear boundary between the film and the edge of the micropore, which indicates that the film formation occurs within the capillary ingress. With the exception of the sigmoidal wave intensity attributed to $180 \mu\text{M}$ TMA^+ for the film formed with 5 voltammetric scans, we have observed that the polyamide (II) affected the sigmoidal positive signal intensity from 0.90 nA recorded for 10 modification cycles, to 0.56 nA for 15 cycles, and 0.16 nA for 20 cycles.

The polyamide (III) (derived from the *p*-phenylenediamine and adipoyl chloride) gave a material with very interesting surface properties. SEM images from Fig. S6C and S6D clearly indicate that the film surface is packed with a number of black spots which we have attributed to the film intrinsic porosity. Similar to other capillaries the film was formed within the pore slightly covering its edges. The biggest holes of the polyamide (III) are having up to a few hundred of nanometres (see Fig. S9-III; SEM image recorded at highest magnification), and hence, our expectation was that the film will be permeable to TMA^+ . Our prediction was confirmed with the voltammetric data shown in Fig. S6E – S6H. As a material with apertures having size being a few orders of magnitude larger than the hydrodynamic radius of the TMA^+ , the drop of the positive ionic current attributed to the studied model ion was equal to around 20% when comparing the film formed after recording 5 and 20 voltammetric cycles.

The 4th pair of tested monomers (1,6-diaminohexane and 1,3,5-benzenetricarbonyl trichloride) gave a set of data depicted in **Fig. S7**. SEM images from Fig. S7C and S7D (also **Fig. S9-IV**) indicate that: (i) the film is compact; (ii) wrinkles exist at the surface and may be attributed to the artefacts formed during the drying process, and (iii) the surrounding of the

capillary pore is decorated with a fibrous features which suggests that some polymeric fibres may grow on the aqueous phase side during interfacial polycondensation, and further collapse and remain at the surface of the capillary as the polyamide is dried. Interestingly, polyamide (IV) started to become an obstacle for the TMA⁺ transfer either from the aqueous to the organic or from the organic to the aqueous phase already after five deposition cycles (see Fig. S7E). MicroITIES modified with polyamide (IV) with five deposition cycles gave additional voltammetric features located within less positive potential difference side (see positive peak signal at around +0.2V), that we think can be attributed to the anionic species (anions of the aqueous phase background electrolyte) transfer from the organic (inside of the capillary, where the mass transfer is governed by the linear diffusion) to the aqueous phase. Further increase in the number of deposition cycles blocked the interface, and even triggered the electrochemical instability manifested by the irregular current patterns as shown in Fig. S7F and Fig. S7G. The film formed after 20 modification cycles was entirely impermeable for the TMA⁺ transfer.

The last deposit studied was derived from a reaction between 1,6-diaminohexane and terephthaloyl chloride. SEM images from Fig. S8C, S8D and Fig. S9-V are in line with the observations we have made when performing the experiments at the macroscopic ITIES. The formed film covers only part of the micropore, which further confirms its high fragility (brittleness). The film formed at the macroscopic ITIES could not be lifted with the organic phase counter electrode as it was breaking and remaining as a broken flake suspended at ITIES. Fig. S8D shows that film covers only part of the pore ingress and probably has broken when both phases were removed from the film neighbourhood. The very high compactness of the film was already visible during the macroITIES modification process as the ionic currents originating from the 1,6-diaminohexane transfer were dropping as the film thickness was increasing. MicroITIES modified with polyamide (V) with 5 cycles gave a curve with potential window elongated at the more negative potential difference side (anionic species transfer blocking effect) and blocked transfer of the TMA⁺ from the aqueous to the organic phase (significantly reduced positive current signals). Also, the signal of the TMA⁺ back transfer was shifted towards negative potential difference values indicating that additional portion of the Gibbs free energy must be supplied to the system to cross the ITIES modified with polyamide (V). Fig. S8F, S8G and S8H shows that the microITIES is not permeable to any ions present in both phases indicating that the ITIES is entirely blocked by the interfacially formed material.

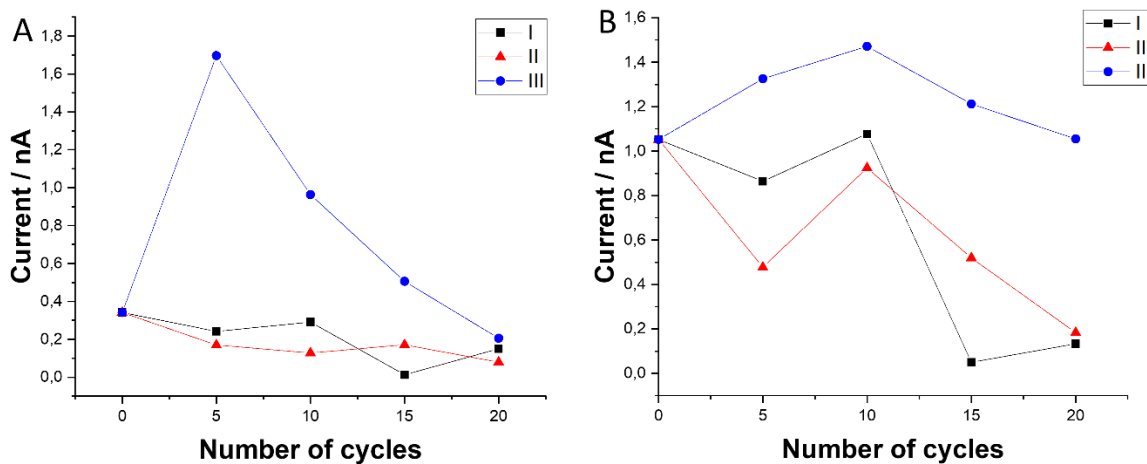


Figure 6. Positive current intensity attributed to the TMA⁺ transfer from the aqueous to the organic phase at the microITIES modified with three different polyamides (I; II and III) plotted in function of the number of cycles recorded during electrochemically assisted interfacial polymerization reaction. A and B correspond to 60 μM and 180 μM TMA⁺ initially present in the aqueous phase, respectively. Each data point represents individual capillary modified (Number of cycles: 5; 10; 15 and 20) with polyamide.

Based on our screening study, we have concluded that in all cases the polyamide deposits were formed within the capillary ingress. For most deposits (I – IV) it was obvious that the reaction proceeds over time as the formed polymeric material could be found at the pore surroundings. In case of reaction (V) the film was found to be thin and located only within the pore, which further suggests that the compactness of the deposited polymer self-inhibited its further growth. To further support the claim that the interfacial polycondensation reaction is electrochemically assisted we have left the microITIES at OCP with both monomers being present in the aqueous and the organic phase. Further electrochemical characterization revealed no blocking effect, which means that the presumably formed films exhibit high permeability. **Fig. 6A** and **6B** summarize the values of the positive currents that were attributed to the transfer of TMA⁺ from the aqueous to the organic phase. The overall dependency suggests that with the increasing number of cycles recorded during electrochemically assisted interfacial polycondensation reaction, the permeability of the modified ITIES decreases. Concerned dependency could only be proposed for polyamides derived from reactions I, II and III. For reaction IV and V, resulting materials entirely blocked the interface. Also, for the polyamide III we have observed the increase in the ionic current attributed to the TMA⁺ transfer

after initial modification step followed by successive drop. Such behaviour can be explained as either: (i) formed film holds open structure and needed higher number of cycles to impact its compactness, or/and (ii) during polyamide III formation the ITIES surface area is changes (grows) which may originate from the affected wettability of the capillary walls by the used solvent. Based on the analysis of SEM images, and voltammograms recorded at the modified ITIES in the presence of the TMA⁺ dissolved in the aqueous phase the interfacially formed polyamides can be attributed to three classes of materials: (i) deposits displaying high porosity that are permeable to the employed model ion – reaction - III; (ii) deposits with the compactness increasing with the applied number of cycles during the ITITES modification process – reaction I, II and IV; and (iii) deposit that entirely block the liquid-liquid interface – reaction V.

4. Conclusions

In this work, we have used cyclic voltammetry to study and assist the interfacial polycondensation of a number of polyamides formed at the electrified liquid-liquid interface. Optimized soft junction modification conditions were chosen to form polymeric materials derived from reactions between aqueous phase soluble 1,6-diaminohexane or *p*-phenylenediamine and acyl chlorides dissolved in the organic phase, this is 1,3,5-benzenetricarbonyl trichloride, terephthaloyl chloride or adipoyl chloride. Formed materials were characterized using SEM, EDX and Raman Spectroscopy. Next, the microscopic liquid-liquid interface supported with a fused silica capillary was modified with all studied polyamide materials and the resulting platforms were characterized in terms of their permeability properties. The effect of the deposition conditions on the ionic currents being attributed to the tetramethylammonium cation interfacial transfer were investigated. We have found that the polyamide formed as a result of the reaction between *p*-phenylenediamine and adipoyl chloride gave a porous deposit being permeable even when longer deposition times (number of applied voltammetric deposition cycles) were applied. The film formed using 1,6-diaminohexane and terephthaloyl chloride entirely blocked the interface, whereas for the other pairs the model ion (tetramethylammonium cation) transfer was inhibited only for thicker films, still being permeable to the background electrolyte ions. We believe, that proposed platform can be used as the model system for the evolution of the polymeric films permeability derived from the interfacial polycondensation reactions.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgements

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