

Biomimetic polymeric membrane for proton transport channeled by self-columnar assembly and sandwiched with a sodium alginate hydrogel layer

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ABSTRACT Poly (epichlorohydrin-co-ethylene oxide) (PECH-co-EO), was modified with mesogenic potassium 3,4,5-tris[4-(n-dodecan-1-yloxy) benzyloxy] benzoate (TAPER group) units and characterized for the production of membranes for ionic transport. Different degrees of modifications were achieved: 68% and 100% in regard to the epichlorohydrin units. The monomers involved in the TAPER's group synthesis, the TAPER group and the obtained modified polymer were characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR). This last one product was also characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Finally, material based on un-crosslinked virgin sodium alginate was synthesized and different conditions were used for their crosslinking. The crosslinking degree of sodium alginate films was approach by FTIR and water uptake experiments were made.

INTRODUCTION

Nowadays, the most commonly used power-generation and storage technologies are the fossil fuels in one hand and the metal-batteries as lead-based, lithium-based, nickel-based or sodium-based batteries in the other hand ^[1]. However, all these current energy sources have got some limitations such as their low energy conversion efficiency and their associated costs. In addition, their biggest drawback is the pollution caused during their use with an extremely high carbon print. These facts have pushed research towards focusing on alternative ways for energy production and storage: an example of these alternative energies lies in the use of fuel cells.

Fuel cells possess higher efficiency than the fossil fuels, their carbon emission is much lower and, for example, even nonexistent in the case of the hydrogen fuel cells, where the formed by-product is water. For their choice, their silent way of operation during energy producing, their low heat transmission, their longer operation time and their non-existent memory effect when there are getting refueled

in comparison with the conventional batteries, are also taken into account. Furthermore, the fuel cells are promising energy sources because they do not need to be recharged with an external power source since they produce energy from electrochemical reactions using most of the time hydrogen from sources as methanol and oxygen from the air ^[2]. The products of this electrochemical reaction are carbon dioxide and water, as shown in Figure 1.

In this work, we focused in Direct Methanol Fuel Cells (DMFCs) for several reasons. The first one is that methanol is the alcohol with more power of energy generation, since it can produce 4 protons atoms per 1 carbon atom. It is also more readily available from both renewable and non-renewable sources; it is easy to transport. Also, methanol does not exhibit such storage problems as hydrogen for instance, because it can be stored at room conditions. Due to its hydrogen bonding, is a dense liquid containing far more energy than even highly compressed hydrogen in the same volume. Its polar nature creates a better binding with active sites on the fuel cell and fuel cell catalyst bed ^[3].

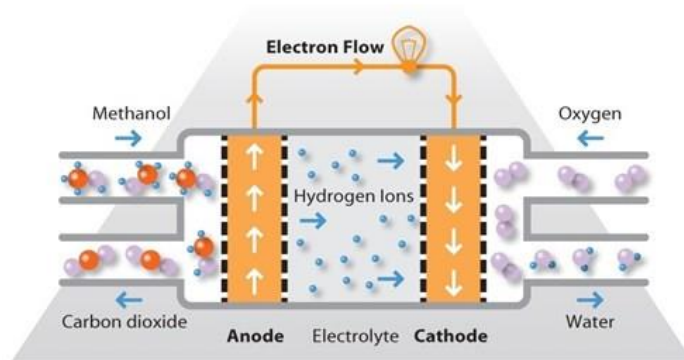
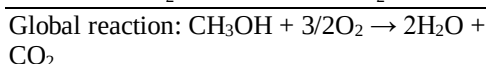
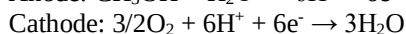


Figure 1. Schematization of a methanol fuel cell.

Methanol provides the cell's protons as a result of methanol's oxidation in presence of water and also forming carbon dioxide and electrons, which in the end are responsible of power generation. The generated protons cross the electrolyte from the anode to the cathode and it recombines with the oxygen in the cathode producing water.



In-between the electrodes, there is a proton exchange membrane which forms an assembly with the electrodes (called the membrane electrode assembly, MEA) and allows the transport of the protons from the anode to the cathode. Currently Nafion is used for the proton-exchange membrane but its main drawback is that it does not have proton selectivity. In the case of the Nafion, the transport mechanism is vehicular and it is based on the motion of the protons through the membrane thanks the flow of the water [4] as shown in the Figure 2. The protons are bound with water $\text{H}^+(\text{H}_2\text{O})_x$ and are dragged by one or more molecules of water. In this case the protons concentration increases with the increasing content of water, ionic groups inside the membrane and also with the temperature's rise. However, the increase of the water content also reduces the mechanical stability by the swelling of the Nafion's membrane. The flow of the water also promotes the methanol crossover through the membrane's channels; fact that reduces the cell efficiency due to several reasons:

- The methanol that crosses is oxidized in the cathode and it consumes extra energy.

- Methanol fuel that can be involved in the anode process increasing the reductions yield is wasted.

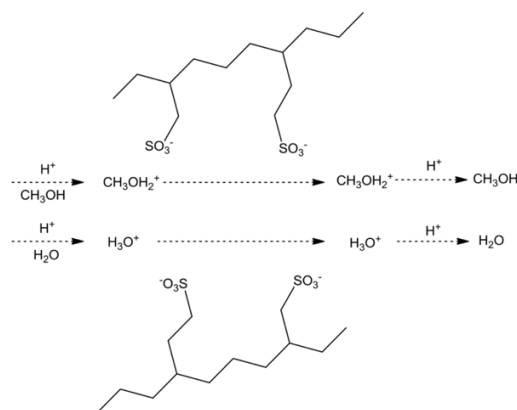


Figure 2. Vehicular mechanism of proton transport in Nafion.

So, the transport mechanism in the case of the commercial Nafion is not proton selective and this fact decreases the efficiency of the cell and the motion of the electrons and, consequently, the generated power is much lower.

To solve the methanol crossover problem and the low proton selectivity, we design a polymeric membrane with specific characteristics in order to optimize the transport process of the protons and to make the hole design more efficient. To do so, we pose a new mechanism of proton transport and another chemical interaction between the protons and the membrane. The mechanism of transport is based on proton's motion by hopping from one active site to another; the protons form and destruct hydrogen bonds with active functional selective groups inside the membrane's channels. The following specifications are in mind when the MEA is designed:

- High proton conductivity, in order to allow the transport of the ions and having, at the same time, a low methanol permeability.
- Good thermal and hydrophilic stability.

To achieve the mentioned characteristics, the polymeric membrane should have an internal organized nano-channeled and proton-selective structure and being stable in the electrolyte's media. By creating such narrow channels, the water mobility will be reduced and, at the same time, the methanol permeability will be reduced. These channeled structures can be achieved by the use of a liquid crystalline (LC) columnar polyether or polyamine, and its subsequent proper orientation for efficient transport across the membrane as shown in the Figure 3^[5]. In previous studies ^{[6][7][8]}, we prepared columnar liquid crystalline polymers based, among others, on Poly (epichlorohydrin-co-ethylene oxide) (PECH-co-EO), chemically modified with the TAPER mesogenic group Potassium methyl 3,4,5-tris-[p-(n-dodecan-1-yloxy) benzyloxy] benzoate (TAPER). Due to a mechanism of exo-recognition of the TAPER group, this copolymer adopts a columnar structure where the polyether main chain lies in the central part of the column and it is responsible for cation transport through a proton "hopping mechanism".

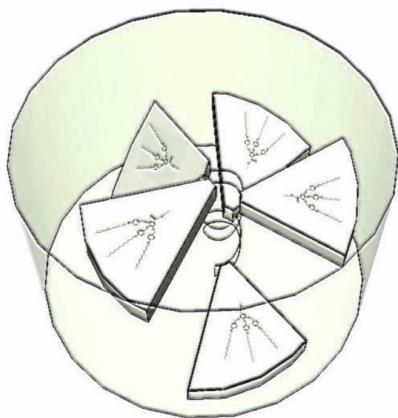


Figure 3. Scheme of the TAPER group forming a self-organized structure with a channeled shape.

In previous works from our group, during the evaluation of the conductivity and efficiency of the membrane based on our polymers, we have observed a drawback in MEA design: and it was that in the conventional design of MEA, we can find a free space between the proton exchange membrane, the catalyst and the electrodes due to their different material nature (Figure 4). This happens because of the difference of polarity between the polymeric membrane (non-polar) and the electrodes and

catalysts (metallic polar). Also, for this difference of behavior, the mobility of the protons is not high enough, the protons do not feel attracted to the membrane's ionic channels. To solve it, our approach consists of filling the gap of the MEA set with a gel as a contact material, thus forming a sandwich layer. In this way, we expect to decrease the difference of polarity between the protons and the membrane, thus increasing the affinity between them.

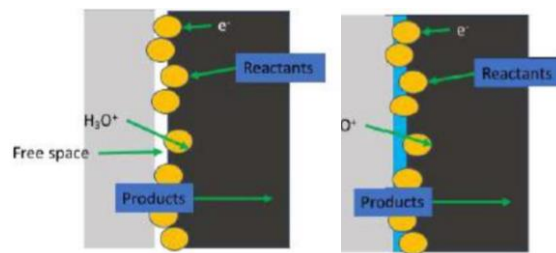


Figure 4. Representation of the interface between the polymeric membrane and the electrode in a conventional MEA design. A classical MEA architecture scheme on the right and on the left, a scheme of MEA with virgin contacting material (gel in this case).

In this paper we describe the synthesis and characterization of a gel-layer which was designed with the aim of improving proton-conductivity in a methanol fuel cell based on modified PECH-co-EO as a proton conducting membrane. With this purpose several options were suggested from the literature and checked in previous studies: for instance, common gelatin from animal skin, soaked in phosphoric acid solutions was used, but in this case a progressive deterioration of this layer was observed, due to gelatin solubilization in methanol solution; moreover, leakage of the phosphoric acid solution was also observed. This drawback could be overcome by using, as sandwich layers, a crosslinked polymer like poly (vinyl alcohol) (PVA), properly reacted with glutaraldehyde, so to make it methanol- and water-insoluble and partially phosphorylated, in order to prevent leakage^[9]. Another possible crosslinked polymer to be used as a conductor, could be also phosphorylated lignin-free cellulose (nata-de-coco), which has been recently proposed as bio-based, environmentally friendly and cheap conductive polymer hydrogel film^[10]. In this work, we explored the possibility to use cross-linked sodium alginate hydrogel due to its several advantages: it's a natural biopolymer, has a high electrical conductivity^{[11][12]}.

Summing up, the aim of this work was:

- The synthesis and characterization of Poly (epichlorohydrin-co-ethylene oxide) (PECH-co-EO) modified with Potassium methyl 3,4,5-tris-[p-(n-dodecan-1-yloxy) benzyloxy] benzoate to be used in the membrane's preparation.

- Tuning a procedure for crosslinking sodium alginate films, in order to get gels that can be used to improve the efficiency of the methanol fuel cell. A satisfactory balance between crosslinking degree and water uptake of the final crosslinked film should be achieved.

EXPERIMENTAL SECTION

Products used

For the preparation of 3, 4, 5-tris[4-(n-dodecan-1-yloxy) benzyloxy] benzoic acid, which is the first step of the synthesis of the TAPER group were used 1-bromododecane ($\geq 95\%$, *Sigma Aldrich*), anhydrous potassium carbonate (99.0% , *Panreac*), 18-crown-6 (99% , *Sigma Aldrich*). In the second step was synthesized the p-(n-dodecan-1-yloxy) benzyl chloride and the reagents used were the dichloromethane (*Scharlau*), thionyl chloride (99% , *Panreac*). In the third step, for the synthesis of the methyl 3, 4, 5- tris- [p-(n-dodecan- 1-yloxy) benzyloxy] benzoate, the reagents used were methyl 3, 4, 5 -trihydroxybenzoate (98% , *Sigma Aldrich*), previously dried dimethylformamide DMF (*VWR Chemicals*), argon gas. For the fourth and last step for the synthesis of potassium methyl 3, 4, 5- tris [p-(n- dodecan- 1-yloxy) benzyloxy] benzoate was needed potassium hydroxide (90% , *Scharlau*), tetrahydrofuran THF (*VWR Chemicals*), ethanol (*Scharlau*) and potassium hydroxide (90% , *Scharlau*).

For the PECH-co-EO synthesis also it is used bromate de tetra-n-butylammonium (*Sigma Aldrich*).

Finally, others reagents are used in the purification step and also for their follow up of all the intermediate products: acetone (*VWR Chemical*), diethyl ether (*Scharlau*), n-hexane (*Scharlau*), ethyl acetate (*Panreac*) and an 5% aqueous solution of sodium hydrogen carbonate ($>99\%$, *Acros Organics*), Toluene (*Scharlau*), isopropanol (*Quifransa*), methanol (*Carlo Erba*) and deuterated chloroform (*Sigma Aldrich*).

For the gel's crosslinking were needed sodium alginate and different solutions with different

concentration of ethanol, methanol and mixtures.

Equipment used

The equipment involved in the NMR characterization work was Bruker model AvanceNeo NMR 400Mhz, Probe: 5mm Smart PI HR-400-S1-BBF/H/D-5.0-Z SP N with a sequence of zg30, el D1=1s and 16 scans to screen the carbon and proton spectra. To do the Fourier-Transform Infrared characterization (FTIR) spectra was used JascoFT/IR 4000 with 18 scans. To do all the DSC analysis we used the Mettler-Toledo mod. 822 in dynamic mode at a heating or cooling rate of $10^\circ\text{C}/\text{min}$. Nitrogen was used as the purge gas. The calorimeter was calibrated with an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration). The POM was made with the following equipment Axiolab Zeiss optical microscope equipped with a Linkam TP92 hot stage.

Synthesis of the TAPER mesogenic group

To synthesize the TAPER group, we were following the description of an already mentioned published article ^[7] by our group. The synthesis is divided in four steps and each one depends on the previous step's product and a purification step was required in all cases. All the reactions involved can be schematized in the Scheme 1.

First step: 3, 4, 5-tris[4-(n-dodecan-1-yloxy) benzyloxy] benzoic acid (Melting point: $65 - 66.5^\circ\text{C}$)

A solution of 4-hydroxybenzyl alcohol (20.0892 g, 0.1608 mol), 1-bromododecane (40.0894 g, 0.1608 mol), anhydrous potassium carbonate (22.2305 g, 0.1608 mol), 18-crown-6 (2.1345 g, 8.1648 mmol) and 500 ml of acetone was refluxed (at 67°C) under stirring for 90 hours in a double necks 1000 ml round bottom flask. The reaction was monitored by thin-layer chromatography (TLC) with n-hexane/ethyl acetate (2:1) mixture as an eluent. If it is necessary, more acetone can be added during the reaction time if part of the volume is evaporated. Once the reaction was completed, the brownish transparent mixture was filtered over 1611L Fisher brand filter (diam. 190 mm) and the solvent was evaporated in a rotavapor. The remained weak white yellowish solid is dissolved in diethyl ether, washed two times with 30% aqueous NaHCO_3 and one time with deionized water. The concentration of the NaHCO_3 was modified from the original

procedure because it was observed that with lower percentage of salt, a dense interphase is created and it remains for days. After the washes the mixture was dried over MgSO_4 and the solvent is evaporated. The white solid formed is recrystallized once from n-hexane and dried under vacuum at room temperature. 43,5852 g of a pure white solid product was obtained with a yield of reaction of 92%. The results of the product's characterization are exposed later on.

Second step: p-(n-dodecan-1-yloxy) benzyl chloride (Melting point: 35 – 36°C)

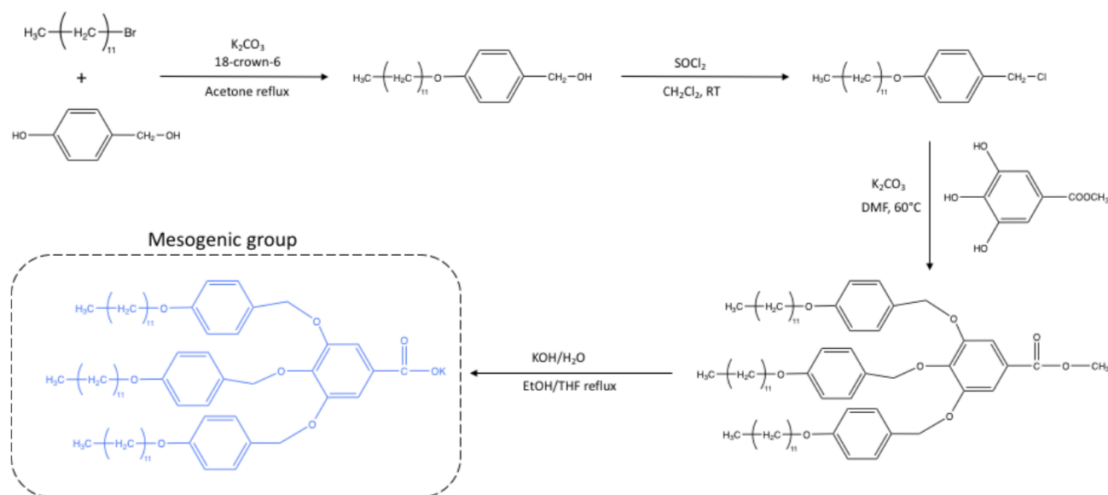
A solution of p-(n-dodecan-1-yloxy) benzyl alcohol (43,5852 g, 0.128 mol) and CH_2Cl_2 (305 ml) was prepared; a couple of hours are needed in order to wait the alcohol solid to dissolve completely under stirring at room temperature in a 500 ml round bottom flask. To that solution, SOCl_2 (17.76 g, 0.128 mol) was added dropwise under stirring. The mixture is stirred at room temperature during 3 hours. The reaction is monitored by TLC with h-hexane/ethyl acetate (15:1) mixture as an eluent. If after 3 hours the reaction is not completed yet, more SOCl_2 can be added to the mixture dropwise until the reactions was completed being able to reach an excess of 25% of this acid. Then, the granate transparent mixture was washed two times with deionized water, two times with 2% of aqueous NaHCO_3 and two times more with deionized water. The weakly yellowish organic phase was dries with MgSO_4 , filtered and the solvent was evaporated in rotavapor. The white solid was dried under vacuum at room temperature to obtain 42.1517 g of with 91% of yield. The results of the product's characterization are exposed later on.

Third step: methyl 3, 4, 5- tris- [p-(n-dodecan-1-yloxy) benzyloxy] benzoate (Melting point: 63 – 65°C)

p-(n-dodecan-1-yloxy) benzyl chloride (42.1517 g, 0.116 mol), methyl 3,4,5-trihydroxybenzoate (8.3994 g, 0.039 mol) and powdered K_2CO_3 (56.4545 g, 0.349 mol) and dry DMF (470 mL) are added into a 1000 ml twin-neck round bottom flask. The mixture was stirred and heated at 60 °C during 4 h under argon atmosphere. The reaction was monitored by TLC using toluene as an eluent. After 4 h, the dark brown solution was poured to 1.5 L of ice water, filtered and recrystallized twice in acetone. Finally, the product was filtered and dried under vacuum at room temperature to yield 31.1666 g, 69% of a white solid. The results of the product's characterization are exposed later on.

Forth step: potassium methyl 3, 4, 5- tris [p-(n- dodecan- 1-yloxy) benzyloxy] benzoate (Melting point: 132 – 134°C)

First, a solution of KOH (4.8252 g, 28.04 mmol) in 40 mL of deionized water is made. Then, the basic solution was added to a solution in a 1000 ml round bottom flask with methyl 3,4,5-tris[p-(n-dodecan-1-yloxy) benzyloxy] benzoate (31.1666g, 10.01 mmol) in a mixture of 62 mL of THF and 250 mL of ethanol. The reaction mixture was refluxed and monitored by TLC with toluene as an eluent and stopped after 30 min by pouring it into 2 L of ice water. The precipitate was filtered and the resulting solid was re-dissolved in chloroform. The yellowish transparent organic layer was separated and washed several times with deionized water, dried over anhydrous MgSO_4 and filtered. The solvent was vacuum distilled and the obtained solid was recrystallized from isopropanol to yield 29.3573 g (92%) of the white product. The results of the product's characterization are exposed later on.



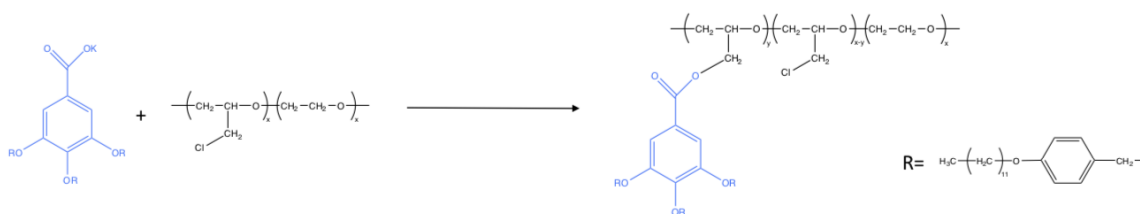
Scheme 1. Synthetic route of the mesogenic units (TAPER group).

Synthesis of PECH-co-EO modified with TAPER group units

Two identical compound batches of modified copolymer were synthesized with the same route of reaction, as shown in the Scheme 2, with different reaction time.

reaction, the copolymer achieved a 62% of degree of modification and in the case of the reaction with a duration of 8 days, the degree of modification was apparently of 100%.

In both cases, was characterized by proton and carbon NMR, POM and DSC. The results are shown later on. The degree of modifications



Scheme 2. Synthetic route of PECH-co-EO modified with TAPER group

Synthesis of PECH-co-EO modified with TAPER 1:1 was obtained by dissolving 0.0448 g of PECH-co-EO in 13 ml of THF (which is the minimum amount of volume to dissolve the copolymer with an excess of 20%) overnight under stirring at room temperature and under reflux in order to avoid the solvent's evaporation. Once the polymer is dissolved, 0.1126 g of TAPER salt and 0.1148 g of TBAB were added. The first mixture reaction batch was left stirring for 5 days at 60°C and the second one, was left stirring for 8 days at 60°C and both under reflux. Once the reactions were over, the mixtures were poured dropwise in 1L of ice water under stirring. The obtained yellowish solids were filtered, re-dissolved in room temperature THF under stirring overnight and precipitated twice from warm ethanol under stirring.

Both obtained white solids achieved different degrees of modifications. From the 5 days

obtained were calculated using the intensity of the peaks by $^1\text{H-NMR}$.

Synthesis of the non-crosslinked Sodium Alginate gel

Non-crosslinked films were prepared by adding 2.0 g of sodium alginate in a 250 ml round bottom flask with 10 ml of ethanol. Once the sodium Alginate is well dispersed, 100 ml of deionized water were added under vigorous stirring at 60°C until the solution gets transparent, it tooked approximately an hour. Once no air bubble is left in the solution, it was poured in glass petri dishes of 5cm diameter (8 petri dishes per polymer batch with 11 ml of the mixture in each). Then the resulting solution was left evaporating at room temperature until a transparent and dry films were obtained. The obtained films were characterized by FTIR and cut in 4 pieces each one (32 samples in total) in order to have

enough samples for tasting. So, by the FTIR technique, was done the monitoring of the crosslinking reaction evolution of the samples exposed later.

Synthesis of the crosslinked Sodium Alginate gel

Several identical samples of non-crosslinked sodium alginate (30 samples in total) were crosslinked in different conditions in order to compare the degree on crosslinking, the water uptake of the gels and the evolution of the reaction.

For the reactions we used both methanol (MeOH) and ethanol (EtOH) and a mix of them (50% of methanol and 50% of ethanol) for the media of reaction. As a crosslinker agent we used the HCl in different concentrations (0.2 M and 0.3 M) and reaction time of the gel membranes were different. We used different membranes for different time of reaction and we checked their characteristics instead of measure the characteristics of the same samples in different time of reactions in order to make the method more reproducible. In the following table (Table 1) are shown the first samples' batch different conditions of crosslinking 1 hour-reaction. There were made also crosslinking reactions in four more batches of 4, 6, 9 and 25 hours with the same conditions shown in the Table 1 with the same number of samples per batch.

Table 1. Crosslinking reaction conditions for the one hour-batch of samples.

Sample	Reaction time (h)	Media	[HCl] (M)
S1	1	MeOH	0.3
S2	1	MeOH	0.2
S3	1	EtOH	0.3
S4	1	EtOH	0.2
S5	1	EtOH/MeOH	0.3
S6	1	EtOH/MeOH	0.2

The 4 hours-reaction samples batch has got the name from S7 to S12, the 6 hours-reaction samples batch, from S13 to S18, the 9 hours-reaction, from S19 to S24 and the 25 hours-reaction, from S24 so S30.

After the crosslinking reactions, we let the samples to dry completely at room temperature for 4 days and FTIR characterization of the samples was done. Since the evolution of the

reaction consists in the transformation of the non-crosslinked sodium alginate's acid functional group in a crosslinked sodium alginate's ester group, during the IR characterization, we used the area of those two peaks in order to monitor the crosslinking reaction of the different samples. The water uptake measurements were made to the sample after having them at 35°C in the vacuum with phosphorus pentoxide as a desiccator during 48 hours. The obtained results are shown later on.

RESULTS AND DISCUSSIONS

NMR results

The NMR results for the 3, 4, 5-tris[4-(n-dodecan-1-yloxy) benzyloxy] benzoic acid from the first step of the TAPER group synthesis are the following one:

- $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 0.88 (3H, $-\text{CH}_3$), 1.26 (18H, $-(\text{CH}_2)_9-$), 1.46 (2H, $-\text{CH}_2-(\text{CH}_2)_2-\text{O-Ar}$), 1.77 (2H, $-\text{CH}_2-\text{CH}_2-\text{O-Ar}$), 1.84 (1H, $-\text{OH}$), 3.94 (2H, $-\text{CH}_2-\text{O-Ar}$), 4.58 (2H, $\text{Ar-CH}_2-\text{OH}$), 6.87 (2H, meta $\text{HO-CH}_2-\text{Ar-H}$), 7.25 (2H, ortho $\text{HO-CH}_2-\text{Ar-H}$).
- $^{13}\text{C-NMR}$ (CDCl_3 , TMS, δ , ppm): 14.3 ($-\text{CH}_3$), 22.9 ($-\text{CH}_2-\text{CH}_3$), 26.2 ($-(\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3)$), 29.4-29.8 ($-(\text{CH}_2)_{7-}$), 32.1 ($-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 65.2 ($-\text{Ar-CH}_2-\text{OH}$), 68.2 ($-(\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3)$), 114.7 (ArC meta to CH_2-OH), 128.8 (ArC ortho to $-\text{CH}_2-\text{OH}$), 133.0 ($\text{ArC-CH}_2-\text{OH}$), 158.9 ($\text{ArC}-\text{O}-(\text{CH}_2)_{11}-\text{CH}_3$)

For the second step's product p-(n-dodecan-1-yloxy) benzyl chloride, the NMR data was similar to p-(n-dodecan-1-yloxy) benzyl alcohol except the signal of $\text{Ar-CH}_2-\text{Cl}$ which was found at 4.57ppm in ^1H NMR.

The NMR spectra signals corresponding to the third product of the TAPER synthesis, methyl 3, 4, 5- tris- [p-(n-dodecan- 1-yloxy) benzyloxy] benzoate, are the following one:

- $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 0.78 (9H, CH_3), 1.16 (48H, $-(\text{CH}_2)_8-$), 1.36 (6H, $-\text{CH}_2-(\text{CH}_2)_2-\text{O-Ar}$), 1.68 (6H, $-\text{CH}_2-\text{CH}_2-\text{OAr}$), 3.94 (overlapped 6H, $-\text{CH}_2-\text{O-Ar}$), 3.78 (3H, $-\text{COOCH}_3$), 4.90 (2H, $\text{Ar-CH}_2-\text{O}$ in central benzylic group), 4.94 (4H, $\text{Ph-CH}_2-\text{O}$ in external benzylic groups), 6.65(2H, $-\text{O-Ar-H-CH}_2-\text{O-}$, 3and 5 positions of group), 6.79 (4H, $-\text{O-Ar-H-CH}_2-\text{O-}$, 3and 5 positions of external groups), 7.15(2H, $-\text{O-Ar-H-CH}_2-\text{O-}$, 2 and 6 position of group), 7.23 (4H, $-\text{O-Ar-H-CH}_2-\text{O-}$, 2 and 6 position of external groups), 7.26 (2H, Ar-H-COOCH_3).
- $^{13}\text{C-NMR}$ (CDCl_3 , TMS, δ , ppm): 14.3 ($-\text{CH}_3$), 22.9 ($-\text{CH}_2\text{CH}_3$), 26.2 ($-(\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3)$), 29.4-29.8 ($-(\text{CH}_2)_6-$), 32.1 ($-\text{CH}_2-\text{CH}_2-$

CH₃), 52.4, (-COOCH₃), 68.1 (-CH₂-(CH₂)₁₀-CH₃ due to group), 68.2 (-CH₂-(CH₂)₁₀-CH₃ due to external groups), 71.2(-CH₂-O-Ar-COOCH₃ group), 74.8(-CH₂-O-Ar-COOCH₃ external groups), 109.2 (ArC ortho to COOCH₃), 11.4 (ArC ortho to -O-(CH₂)₁₁-CH₃ due to group), 114.6 (ArC ortho to -O-(CH₂)₁₁-CH₃ due to external groups), 125.1 (ArC-COOCH₃), 128.7 (ArC-CH₂-O-Ar-COOCH₃), 129.4 (ArC meta to -O-(CH₂)₁₁-CH₃ group), 130.4 (ArC meta to -O-(CH₂)₁₁-CH₃ external group), 142.5 (ArC para to -COOCH₃), 152.8 (ArC meta to COOCH₃), 159.1 (ArC-O-(CH₂)₁₀-CH₃ group), 159.2 (ArC-O-(CH₂)₁₀-CH₃ external groups), 166.8 (-COOCH₃).

The NMR spectra signals corresponding to the fourth product of the TAPER synthesis, potassium methyl 3, 4, 5- tris [p-(n- dodecan-1-yloxy) benzyloxy] benzoate, are the following one:

- ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.88 (9H, CH₃), 1.27 (48H, -(CH₂)₈-), 1.40 (6H, -CH₂(CH₂)₂-O-Ar), 1.71 (6H, -CH₂-CH₂-OAr), 3.74 (6H, -CH₂-O-Ar), 4.50 (2H, Ar-CH₂-O benzylic group), 4.60 (4H, Ar-CH₂-O external benzylic group), 6.47 (6H, ArH ortho to -CH₂-O-), 6.88 (2H, ArH meta to -CH₂-O- benzylic group), 6.97 (4H, ArH meta to -CH₂-O- external benzylic group), 7.20 (2H, ArH-COOK).

- ¹³C-NMR (CDCl₃, TMS, δ, ppm): 14.3(-CH₂CH₃), 22.9 (-CH₂CH₃), 26.4 (Ar-O-CH₂CH₂CH₂), 30.1–29.5 (C2 and C4 to C9 in aliphatic chains), 32.2 (-CH₂CH₂CH₃), 67.9 (R-CH₂-O-Ar), 70.4 (Ar-CH₂-O-Ar external benzylic groups), 74.7 (Ar-CH₂-O-Ar in benzylic group), 108.1(ArC ortho to COOK), 113.8 (ArC meta to CH₂-O-Ar benzylic

group), 113.9 (ArC meta to -CH₂-O-Ar in external groups), 129.2 (ArC ipso to OCH₂-O-Ar), 129.6 (ArC ortho to -CH₂-O-Ph in external benzylic groups), 130.2 (ArC ortho to CH₂-O-Ar benzylic group), 133.4 (ArC ipso to COOK), 139.7 (ArC para to COOK), 152.0 (ArC meta to COOK), 158.6 (ArC para to -CH₂-O-Ph), 173.2(COOK).

The synthesized copolymers had got two different degrees of modifications depending on the time spent in the reaction. The first one (CP1), with 5 days of reaction, had got a 62% degree of modification, and the second one (CP2), had been reacting for 8 days and the degree of modifications achieved was 100% in principle, as will be explain later on. In the Figure A from the Annex can be seen the ¹H-NMR spectrum of copolymer PECH-co-EO modified with TAPER group 1:1 with 100% of degree of modification.

By diluting the PECH-co-EO NMR sample 10 times, as it is observed in the Figure B from Annex, appeared sharps peaks on top of the width peaks so, we cannot totally confirm that the polymer conversion was 100%. Checking the shims of the spectra we can be safer about the polymeric nature of the sample, but anyway, a Gel permeation chromatography (GPC) should be done in order to confirm the degree of modification.

Also, the ¹H-NMR was made of the PECH-co-EO polymer modified with TAPER group and a degree of modification of 62%. In the Figure 5 is shown a comparison between the proton spectra of the different degree of modification polymers. Sharper peaks can be seen in the less modified polymer due to shorter relaxation

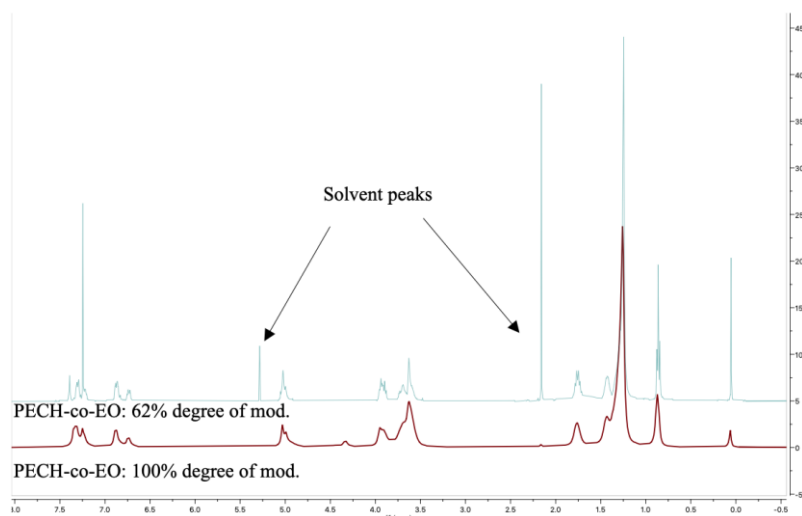


Figure 5. ¹H-NMR spectra of PECH-co-EO with different degree of modification with TAPER group.

time of the sample's units.

DSC results of the PECH-co-EO modified with TAPER group polymer

The PECH-co-EO modified with the TAPER group 1:1 with a 62% degree of modification sample was submitted to two different DSC cycles. From the sample with a modification degree of 100% we could not get conclusive results, so we did not expose them in this work report. In both cases, the temperature modification rate was of 10°C/min and the nitrogen was used as an inner gas. The first running cycle was performed in the following conditions: heating process from -80°C to 160°C then, from 160°C to -80°C and finally, again from -80°C to 160°C. The second cycle at first, was start heating from 20°C to 54°C, the temperature was hold for 2 hours at 54°C then, the temperature was cooled from 54°C to -80°C and a second heating was done rising the temperature from -80°C to 160°C.

The second cycle shown in the Figure C from Annex from the annex allowed us to visualize the melting point of the sample. The polymeric sample had got glass transition temperature (T_g) around 0°C, a melting temperature (T_m) around 55°C and a clearing temperature (T_c) around 115°C. The low clearing temperature indicates that the modification degree is low, as the NMR spectra as indicated previously.

POM images obtained

The PECH-co-EO modified with the TAPER group 1:1 with a 62% degree of modification sample was submitted to heat and sample observation with POM in order to estimate and verify the clearing temperature (T_c) result obtained from the DSC results.

First, the polymer was submitted to a heating process and all the temperature changes were made with a rate of 10°C/min. The temperature was heated first from 30 °C to 60°C and hold at 60°C for 3 minutes for observations. Then, from 60°C to 120°C and hold at 120°C for 3 minutes for observation. Finally, from 120°C to 160° and hold at that temperature again, for 3 minutes for observation. To cool the polymeric sample, we applied the following conditions: from 160°C to 120°C with a cooling rate of 0.1°C/min, then hold at that temperature overnight under observation, then, from 120°C to 60°C with a cooling rate of 0.1°C/min, hold at 60°C again overnight for observation, then from 60°C to 30°C with a cooling rate of 10°C/min and then, hold at 30°C overnight for

more observation. In the Figure D and Figure E from the Annex is shown the POM results for the sample's heating process and in the Figure F can be observed an image of the sample during the cooling process respectively for the polymeric sample. The polymer was expected to be more colorful near its clearing point and black outside of this temperature range. So, we were able to see a change on the sample's texture near the 120°C, which was the temperature expected from the results from the DSC characterization.

FTIR Sodium alginate gels crosslinking reaction following

As the Figure 6 shows, the most influential factor in the crosslinking reaction is its media. The fastest crosslinking reactions are those which were made in a methanol media due to its hydrophobic character, which favors the reaction. Those reaction made in ethanol media are the slowest and those which were made in a media with a mix of methanol and ethanol, have got a surprising slow rate of reaction, even if the proportion was of 50% of each. That indicates us that the reaction is quite sensitive to water, which decreases the crosslinking ration significantly. Also, highest is the concentration of the hydrochloric acid, higher is the crosslinking ratio in the sample, fact that can be deducted since the acid in the crosslinker agent which catalyze the reaction. Observing all the graph's lines, we can also observe al phenomenon which is repeated in all the samples and it is the fact that all the all of them suffer an unexpected change of the slop's tendency after 6 hours of reaction more or less, after this time, the crosslinking reaction is slowed and the tendency of the slop turns less abrupt. This can happen because of a hydrolysis reaction which is going against the crosslinking reaction. This water sensitivity also is remarked when the reaction's data is exposed in graphs (Figure G a to f, Annex) which compare the progress of the acid versus the ester group of each sample in time. In all the cases, an anomalous tendency of the functional groups is seen when the trend of the specie's lines is not met. The concentration of the acid group should be reducing while the ester group's concentration should increase until both curves intersect and remain constant. But in this case only the samples from the methanol media reactions have an intersection point and after it, the tendency of both functional groups is increasing. Those facts, indicate that a hydrolysis process could.

Water uptake of the crosslinked sodium alginate gel samples

All the samples were weight before the water uptake measurement and after and the results obtained are that in all the cases the samples showed an obvious structural decomposition before 1 hour of being immersed in deionized water. There were two samples that had a slower decomposition and they were these ones that had been crosslinked in MeOH with 0.3M of HCl during 4 and 6 hours. These samples started losing weight from the first moment of being in the water bath and the structural decomposition started to be visible after 3 hours of bath. These results show us that the hydrolysis occurred in all the samples.

The crosslinked reaction of the sodium alginate used as contacting material between the proton exchange membrane and the electrodes showed a better tendency in hydrophobic median and high concentration of acid, but the behavior of the final gels tend to suffer hydrolysis easily and having high water sensitivity.

Finally, testing the performance of the obtained alginate gel in the MEA containing the proton transport membrane is a future experiment work to do in order to observe the behavior of the final assembly as power and current density

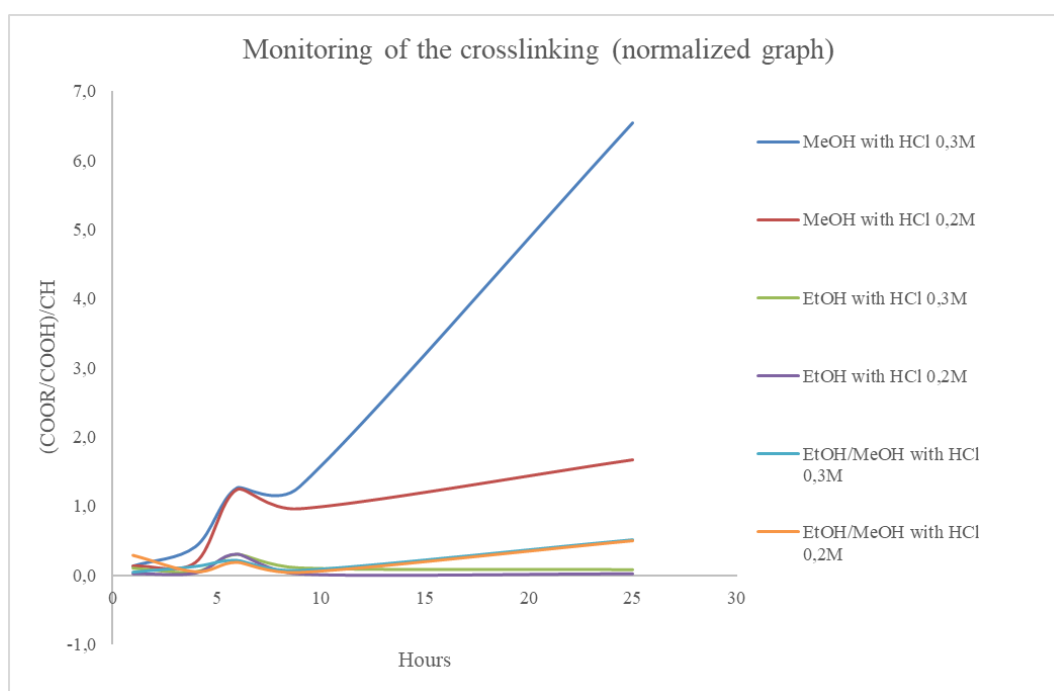


Figure 6. Monitoring of the crosslinking reaction of the sodium alginate.

CONCLUSIONS

The synthesis of the TAPER group and the posterior modification of the PECH-co-EO polymer sowed an excellent and predictable results. Now, the preparation of an oriented membrane based on this copolymer, to be used as proton-transport layer, remains to do in order to make shore about the capacity of the channel's orientation and transport, and x-ray experiments should be done in order to test that orientation and current-voltage experiments in order to reveal the preferential transport of the protons.

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ANNEX

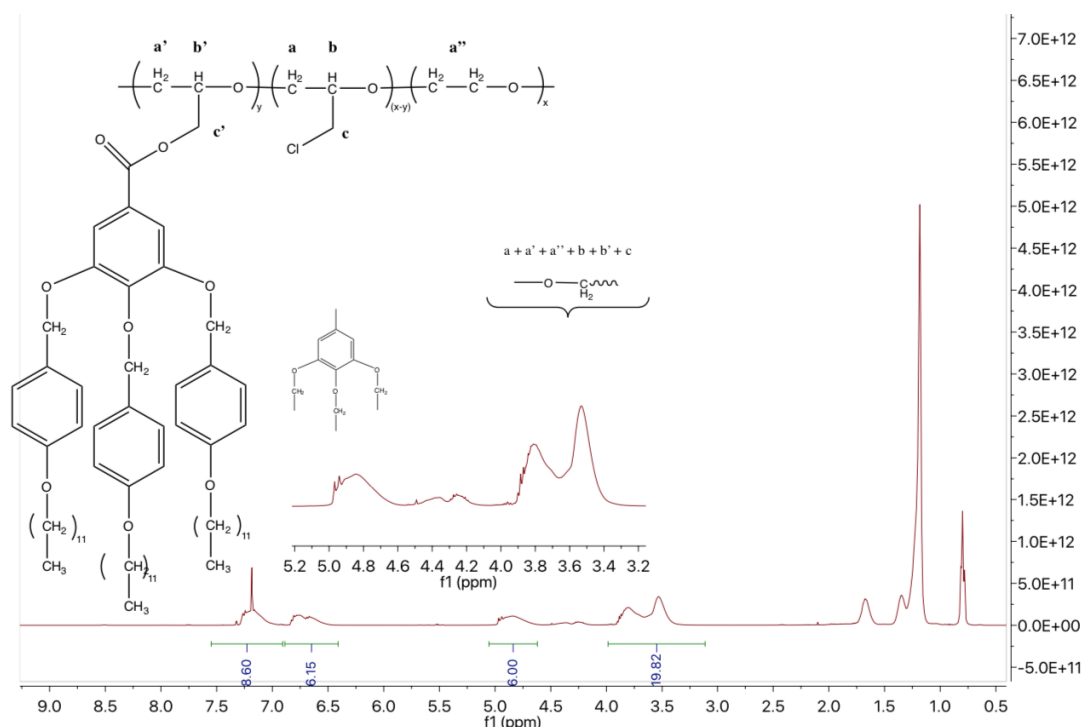


Figure A. ^1H -NMR spectrum of copolymer PECH-co-EO modified with TAPER group 1:1 with 100% of degree of modification

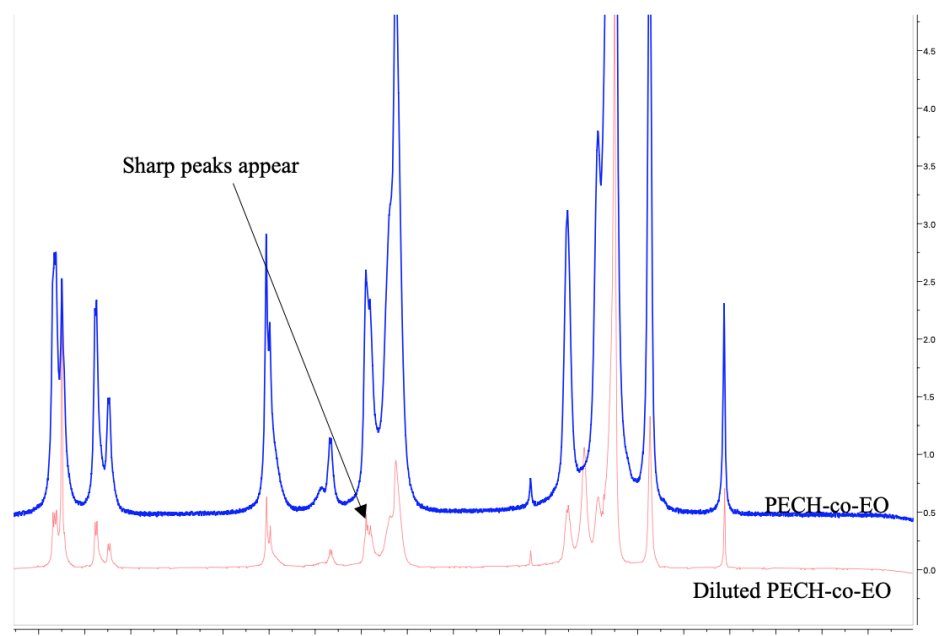


Figure B. Comparative spectra between the ^1H -NMR of a sample of PECH-co-EO with a degree of modification of 100% with TAPER group above and the same sample diluted 10 times below.

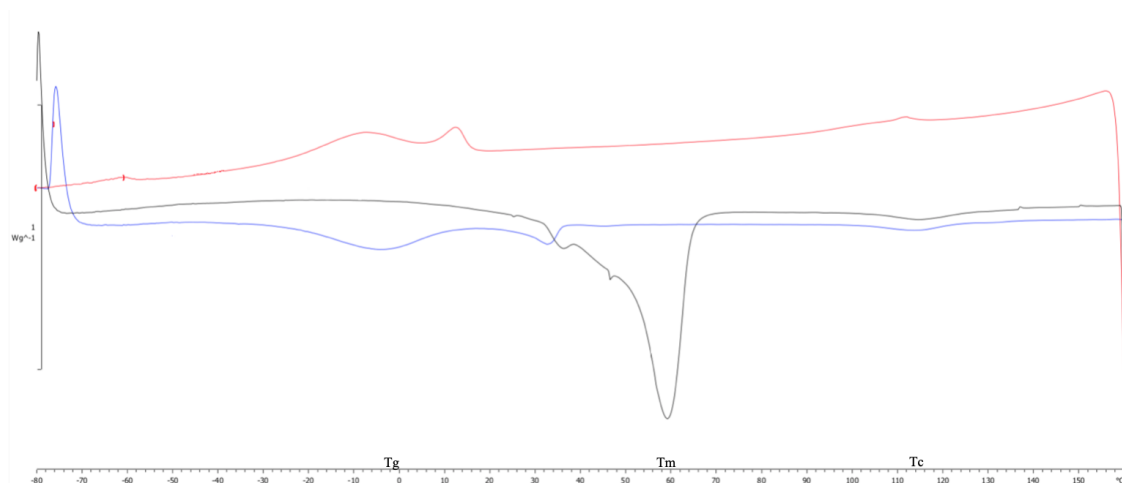


Figure C. Second cycle of DSC characterization of PECH-co-EO modified with TAPER group with a degree of modification of 62%. In black colour is represented the first heating, in red, the cooling process and in blue, the second heating process.



Figure D. POM image from the heating process of the polymeric sample at 60°C.



Figure E. POM image from the heating process of the polymeric sample at 120°C.



Figure F. POM image from the cooling process of the polymeric sample at 120°C.

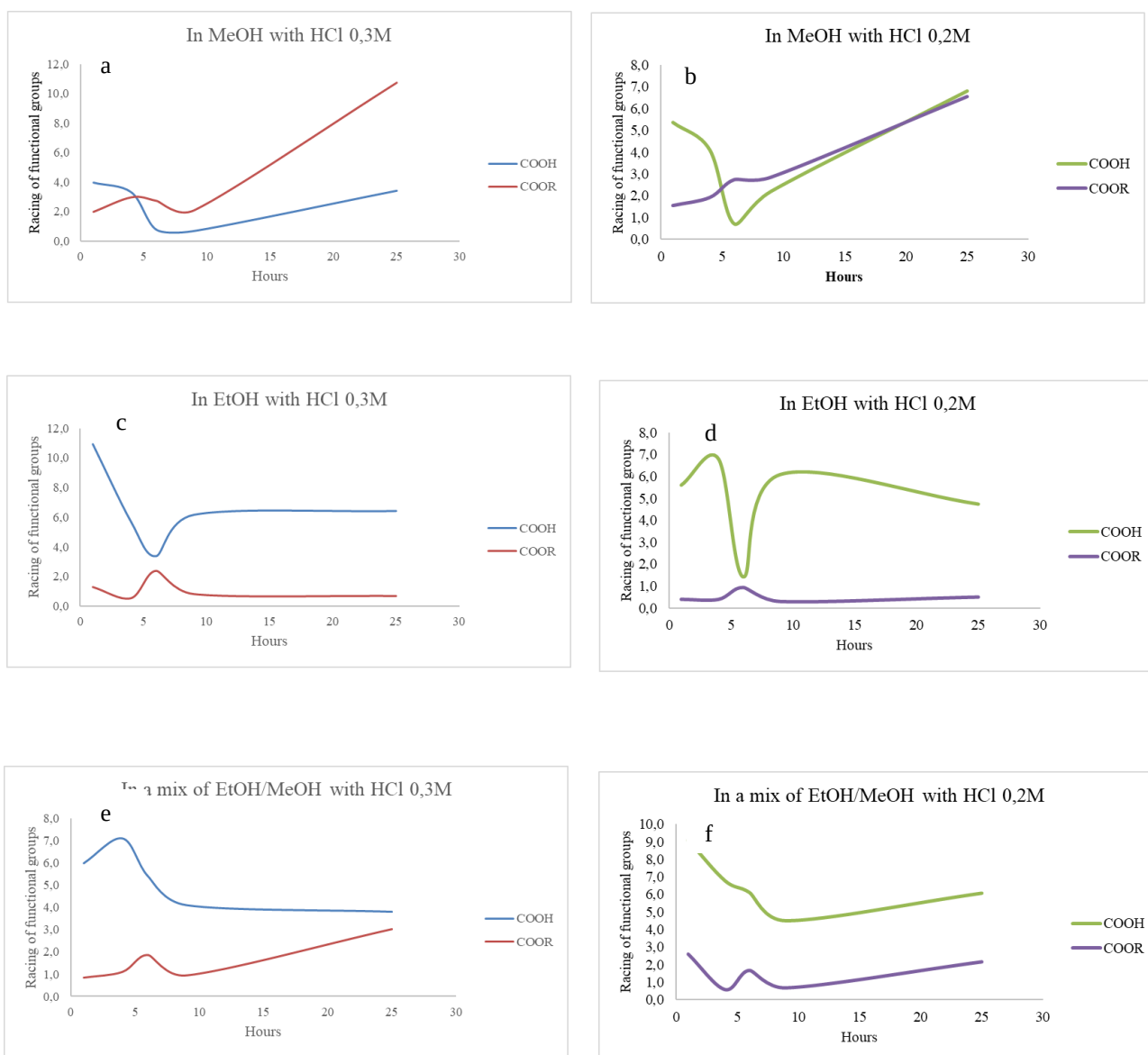


Figure G. Comparison between the progress of the acid versus the ester group. In the graphs a and b the media of the reaction is methanol, in the graphs c and d, the media is ethanol and in the graphs e and f, the media is a mix of 50% of methanol and 50% of ethanol. The left graphs represent the monitoring of the reaction with an acid concentration of 0.3M and the right graphs, with an acid concentration of 0.2M.