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Synthesis and Characterization of the Monomer 2,2′ diallylbisphenol-A (ABFA) for obtaining Proton Exchange Membranes based on Crosslinked Sulphonated Poly(Arylene ether sulphone)s

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Summary: In the present work, a methodology of synthesis and characterization of the monomer 2,2′ diallylbisphenol-A (ABFA) was developed, aiming at getting a precursor, with adequate purity, for obtaining cross-linked membranes based on sulphonated poly(arylene ether sulphone)s. The monomer synthesis involved the synthesis of 2,2′ bis(4-allyloxiphenyl)propane (Bisphenol-A, diallyl ether - BFAAE), from Bisphenol-A (BFA), followed by Claisen rearrangement of BFAAE, for the production of the target compound 2,2′ diallylbisphenol-A (ABFA). All the compounds, reagent BFA and obtained products, intermediate product BFAAE and final product ABFA, were characterized by FTIR (Fourier Transform infrared spectroscopy), TGA (Thermo-gravimetric analysis) and HPLC (High-performance liquid chromatography). The compound BFAAE was obtained with a yield of 94.5% and a purity of 97.3%, the latter characterized by TGA and by HPLC. The structure of the product was confirmed by FTIR. The thermal Claisen rearrangement process was conducted by using Differential Scanning Calorimetry (DSC) technique, from a factorial experiment planning, with two factors and three levels, with temperature and time being the variables. The above cited techniques were used for monitoring the Claisen rearrangement and for the characterization of the final product. The best results yield ABFA purity between 85 and 90%, approximately, for 220 °C/60min, 230 °C/30min and 210 °C/90min conditions. The obtained results suggest that, in the studied range, polymerization and degradation of the monomer ABFA occur, simultaneously to its formation.

Keywords: crosslinked membrane; 2,2′diallylbisphenol-A; differential scanning calorimetry (DSC); PEMFC; Proton exchange membrane fuel cell

Introduction

The state of the art regarding polymeric membrane used in polymer electrolyte fuel cells (PEMFC) belongs to the family of the fully fluorinated materials, developed by DuPont in the late 1960s. Nafion® is a copolymer formed from tetrafluoroethylene (TFE), with a comonomer endowed with side chains based on perfluorinated vinyl ethers terminated with perfluorsulphonic acid groups.[1–3]

Nevertheless, one of the major constraints for the commercial application of PEMFC is the cost, since the high need for membrane humidification limits the operating temperature of the set and requires the reagent gases to be humidified and

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supplied under pressure. In addition, the low operating temperature makes the metallic catalyst susceptible to poisoning by carbon monoxide (CO), making it necessary to use reagent gases extremely pure and even the use of expensive alloys as catalysts.[4,5] A major challenge, then, is to produce cells which could be operated at higher temperatures without need of extensive moisture control. Under these conditions, the system would have the advantage of being less sensitive to the catalyst poisoning, reducing the construction and operation costs of the cell. Part of this challenge is, however, the development of a new polymeric electrolyte membrane (PEM), capable of operating at temperatures near 120 °C, with less humidity, but maintaining the same level of conductivity achieved by Nafion®, or higher.

Almost all polymers employed for PEM constructions depend on their acidic groups interaction with the water absorbed by it, to produce the desired proton conductivity. However, at higher temperatures, both the mechanical properties and proton conductivity of the membrane can be damaged, due to the great need of moisture absorbed by the material, requiring an accurate cell moisture control, especially in the membrane. The development of membranes that are capable of conducting protons with little or no moisture is one of the biggest challenges for researchers. Specifically for automotive applications, the Department of Energy of the U.S. government established, in 2004, a goal for delineating the development of a cell capable of operating at 120 °C with 50% relative humidity and producing a proton conductivity of $0.1\,S \cdot cm^{-1}$.[1]

In this context, different approaches have been used, such as the synthesis of new polymers, composites and polymer blends. The recent literature[6–19] shows that polymer crosslinking is a promising way to develop good protons conductor materials with lower need for humidification. An example of this potential is a crosslinked sulphonated poly(arylene ether sulphone), polymer known for its good chemical resistance, both in oxidizing or reducing environments and acidic or basic environments, as well as having good mechanical strength. Crosslinked sulphonated poly(arylene ether sulphone) has interesting results already published,[6,10,13,17] such as lower expansion and moisture absorption, decreased methanol permeability coefficient, but maintaining a proton conductivity comparable to Nafion® 117.

In the approach adopted by the Research Group on Gels and Polymers of UFMG (GGP/DEQ/UFMG), it is intended to employ the monomer 2,2′ diallylbisphenol-A (ABFA) for the synthesis of polymeric membranes with a higher crosslinking degree, but with a greater capacity for accommodation of water molecules. It is expected that its use in the synthesis of a series of highly crosslinked sulphonated poly(arylene ether sulphone)s could decrease the moisture absorption without damaging the proton conductivity of the systems.

This paper reports the development of a methodology for the synthesis and characterization of the monomer 2,2′ diallylbisphenol-A, in order to obtain a precursor for the preparation of membranes based on crosslinked sulphonated poly(arylene ether sulphone)s. The monomer commercially available[20] is sold with 85% purity and its purification is difficult, moreover, the available literature on the monomer is limited and inconclusive. The synthesis of 2,2′ diallylbisphenol-A (ABFA) is described by two steps: (i) synthesis of 2,2′ bis(4-allyloxiphenyl) propane (Bisphenol-A, diallyl ether - BFAAE), and (ii) Claisen rearrangement of the BFAAE compound to produce the target compound ABFA.

Classically, the Claisen rearrangement can be defined as the thermal [3,3]-sigmatropic rearrangement of an allyl-vinyl ether into a carbonyl compound γ,δ-unsaturated by an intramolecular process.[21] The thermal rearrangement of allyl-phenyl ethers leads to the formation of a carbonyl intermediate, which rapidly tautomerizes forming an ortho-substituted phenol.[22]

The study of the ABFA synthesis was performed by using DSC (differential scanning calorimetry) technique and the structure of a factorial design with two factors, time and temperature, and three levels in order to determine what are the optimal conditions for the Claisen rearrangement execution, in order to obtain the monomer 2,2′ diallylbisphenol-A with good purity.

Experimental Part

To develop the process of synthesis and purification of the monomer 2,2′ diallylbisfenol-A (ABFA) the 4,4 isopropylidenediphenol (Bisphenol-A - BFA), Sigma-Aldrich®, was used as the precursor, without any treatment or further purification.

The other reagents: acetone, allyl bromide (3-bromo-1-propene), anhydrous potassium carbonate, methanol, n-hexane, N-methyl-2-pyrrolidinone (NMP), *N,N*′-dimethylacetamide (DMAC) and toluene, were purchased from commercial sources and used without further purification or treatment.

Synthesis of 2,2′ diallylbisfenol-A (ABFA)

The synthesis of 2,2′ diallylbisfenol-A (ABFA) is described by two quite distinct steps that will be treated independently: (i) synthesis of 2,2′ bis(4-allyloxiphenyl) propane (bisphenol A, diallyl ether - BFAAE), and (ii) Claisen rearrangement of the compound BFAAE to produce the target compound ABFA.

Synthesis of 2,2′ bis(4-allyloxiphenyl) propane (BFAAE)

The intermediate compound was synthesized by the reaction of bisphenol-A (BFA) with allyl bromide under reflux for 24 hours with acetone in the presence of potassium carbonate in the molar ratio of 1:2.2:3. After addition of excess water, the supernatant oily phase was separated and washed three times with deionized water in a separation funnel, to remove the acetone and residual salts. The viscous and yellowish liquid, rich in 2,2′ bis(4-allyloxiphenyl) propane (BFAAE), containing trace amounts of moisture, acetone and BFA, was dried on a hot plate for 60 minutes at 100 °C and then filtered through quantitative filter paper. The product was analyzed and characterized by Fourier Transform infrared spectroscopy (FTIR), thermogravimetry (TG) and high performance liquid chromatography (HPLC).

Claisen Rearrangement and Obtainment of ABFA

The compound previously synthesized, BFAAE, was subjected to various conditions of time and temperature, by using DSC technique, in order to obtain the final compound ABFA, via Claisen rearrangement.

The experiments were performed using a DSC TA Instruments model 2920. For each analysis two identical hermetic aluminum crucibles were used, being one the empty reference and the other containing the sample. In order to maintain a similar amount of BFAAE in all crucibles, about 10mg of sample was added to each one using a 0–20 μL micro-pipette, air displacement type from Eppendorf. The experiments were performed under inert atmosphere of nitrogen at a flow rate of 75mL.min^{-1} and constant temperature (isothermal) for a set period of time, following a factorial design of experiments (DoE) with two factors, time and temperature, and three levels, as can be seen in Table 1.

The Differential Scanning Calorimetry (DSC) technique was chosen as a means for controlled heating of the experimental object, because it offers operational advantages such as: (i) the need for small amounts of sample, (ii) its ballistic heating capacity (iii) maintaining a stable temperature level, (iv) the possibility of performing experiments in a nitrogen atmosphere and (v) use of hermetically sealed crucible to avoid contact of material with oxygen of the air.

After each step of DoE, a representative sample was collected and analyzed by

Table 1.
Summarized results of analysis carried out.

Sample		FTIR	TG	HPLC	
		($3050 \div 3800 cm^{-1}$)	P_m (%)	BFAAE (% area)	ABFA (% area)
BFA	–	0.023	99.9	–	–
BFAAE	–	0.0003	97.3	90.6	–
210 °C/30 min.	(Smp. 1)	0.021	94.6	30.5	15.3
210 °C/60 min.	(Smp. 2)	0.034	92.5	4.2	55.7
210 °C/90 min.	(Smp. 3)	0.041	90.1	0.8	76.6
220 °C/30 min.	(Smp. 4)	0.033	90.5	5.5	54.4
220 °C/60 min.	(Smp. 5)	0.040	85.3	0.3	79.8
220 °C/90 min.	(Smp. 6)	0.041	83.9	0.5	74.2
230 °C/30 min.	(Smp. 7)	0.040	88.2	0.4	72.6
230 °C/60 min.	(Smp. 8)	0.039	80.5	0.6	67.6
230 °C/90 min.	(Smp. 9)	0.038	73.8	0.9	49.0

FTIR, TG and HPLC for characterization and monitoring the reaction.

Methods of Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

It was used a FTIR, supplied by Thermo Nicolet, model NEXUS 470 with DTGS detector (Deuterated triglycine sulfate) and KBr beam splitter. It was used the Attenuated Total Reflectance (ATR) technique on crystal germanium (Ge), with resolution equal to 4 cm^{-1} and 64 scans ranging from 4000 cm^{-1} to 675 cm^{-1}. The spectra obtained were treated by the Nicolet OMINC software v.7.0, with baseline correction.

Thermogravimetry (TG)

The equipment used was a Hi-Res TG 2950 supplied by TA Instruments, according to the following procedure: samples of about 4mg were placed in platinum crucibles and heated between room temperature and 800 °C with variable heating rate of 10 °C.min^{-1} and resolution factor of 3 (instrumental dimensionless parameter) under inert atmosphere of nitrogen at a flow rate of 80 ml.min^{-1} to the end of the experiment.

From the thermogravimetric curves obtained, the mass loss (Pm) was calculated, expressed as a percentage difference, between a point located at a stable level before the event and another stable point after the event of interest.

High Performance Liquid Chromatography (HPLC)

All synthesized materials from the BFA, including BFAAE and the results of intermediate steps of obtaining ABFA were analyzed by liquid chromatography with UV detection, to evaluate the rearrangement progress. The samples were prepared as a solution of 0.5 mg/mL in methanol. The analyses were performed by the automated injection of 1 μL sample into a HPLC Thermo Finnigan, Surveyor model, fitted with a C-18 reverse phase analytical column (250 mm x 4.6 mm ID), stabilized at 30 °C. As mobile phase, it was used a flow of 1 mL.min^{-1} between 0 and 10 minutes, with a linear gradient changing from 90%v/v methanol and water to 100%v/v methanol at the end. The peaks detection was performed with a UV-visible with a photodiode array detector (PDA) fixed at 275 nm.

Results and Discussion

Synthesis of 2,2′ bis(4-allyloxiphenyl)propane (BFAAE)

The synthesis was conducted with the work of Feng and co-workers[13] as a reference, whose description of the synthesis of 3,3′-

diallyl-4,4′-dihidroxibisfenol was adapted. The pale yellow liquid, viscous, rich in BFAAE, was obtained with a molar yield of 94.5% and 97.3% purity, determined via thermogravimetric analysis. The structure of the product was confirmed by FTIR analysis, by means of observation of the BFAAE characteristic bands: 1608 cm^{-1} and 1509 cm^{-1} (characteristic vibrations of the aromatic ring), 1299 cm^{-1} (plane deformation of the allyl group), 1246 cm^{-1} (ν COC), 1182 cm^{-1} (skeleton deformation -C(CH$_3$)$_2$-), 1024 cm^{-1} (δ =CH out of the plane), 997 cm^{-1} (δ =CH$_2$ out of plan) and 828 cm^{-1} (−CH out of plane; disubstituted aromatic ring at the para position).[23,24] The BFAAE spectrum is shown in Figure 1.

Claisen Rearrangement and Obtainment of ABFA

In Figure 2 it's shown the sequence identified as the BFAAE thermally initiated Claisen rearrangement to produce the compound ABFA. The process occurs through the formation of a transition state with a cyclic geometry and has no intermediate structures, producing a carbonyl compound through a single step. The second step of the process occurs as a consequence of the previous rearrangement to form the desired phenolic from unstable carbonyl intermediate compound through tautomerization.

The Attenuated Total Reflectance (ATR) technique was used to obtain the infrared spectra due to its particularity to keep the optical path, traveled by the infrared beam through the sample, constant. This feature allowed the application of the Beer-Lambert Law principle, establishing the proportionality relationship between the absorbance and concentration of the species. Applying the Beer-Lambert Law principle, the absorbance between 3050 cm^{-1} and 3800 cm^{-1}, band characteristic of phenolic –OH group with inter and intramolecular interactions,[23,24] species present in the ABFA but absent in BFAAE, was measured to assess the BFAAE rearrangement progress into ABFA, as shown in Table 1. From these results, the absorbance response surface, related to time and temperature treatment, was built and is shown in Figure 3.

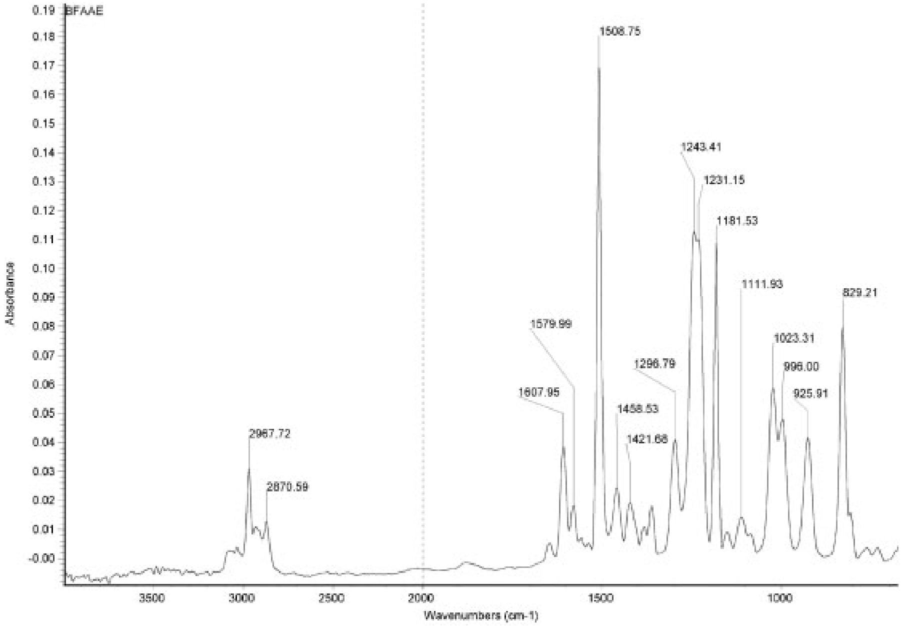

Figure 1.
BFAAE infrared spectrum.

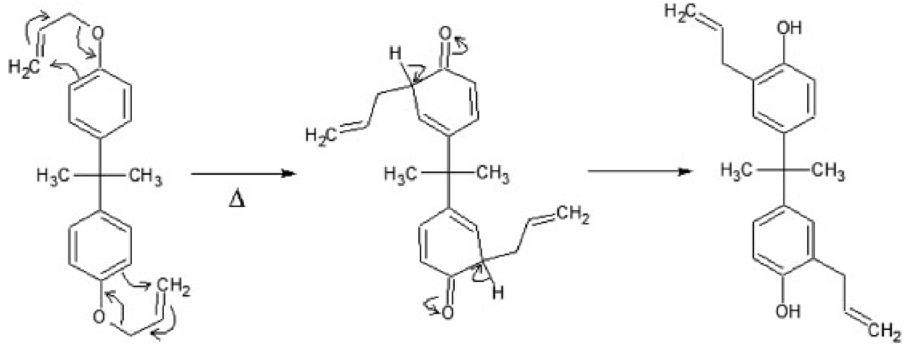

Figure 2.
Transfer mechanism of the Claisen rearrangement to obtain the ABFA. From left to right: BFAAE → Intermediate → ABFA.

Figure 3 suggests the existence of a direct dependence of the OH species "concentration" in relation to time and temperature factors. This is called the main effect, given as the variation at the response due to the change in the factor level. However, one can observe that the difference in response between the levels of a factor is not the same at all levels of the other factor, these interaction effects in practice lead to a twisted plan formation.

The comparison of the nine spectral samples allows their grouping by similarity. Thus, five groups of samples were formed: G1, containing only the sample 1; G2, containing the samples 2 and 4; G3, containing the samples 3, 5 and 7; G4, containing the samples 6 and 8; and, finally, G5, with only the sample 9. The correlative assignment of the FTIR spectra can be seen below, at Table 2.

The spectral analysis of these groups relating to the BFAAE compound reveals that, among all the samples, the G1 is the one least rearranged to produce the ABFA. This evaluation is based on the G1 and BFAAE's spectrum similarity and on its difference compared to the other samples observed evolution. Moreover, the phenolic -OH group absorbance was the lowest among all samples, and corroborates the first affirmative. Based on these arguments,

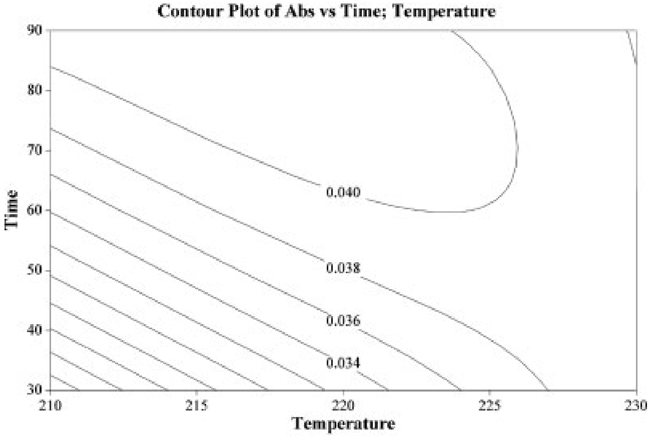

Figure 3.
Surface response for the variable absorbance of the connection (-OH) as a function of time and temperature of treatment.

Table 2.
Correlative assignment of the FTIR spectra.

Sample		G1	G2	G3	G4	G5
210 °C/30 min.	(Smp. 1)	X				
210 °C/60 min.	(Smp. 2)		X			
210 °C/90 min.	(Smp. 3)			X		
220 °C/30 min.	(Smp. 4)		X			
220 °C/60 min.	(Smp. 5)			X		
220 °C/90 min.	(Smp. 6)				X	
230 °C/30 min.	(Smp. 7)			X		
230 °C/60 min.	(Smp. 8)				X	
230 °C/90 min.	(Smp. 9)					X

the G2 has a more evolved spectrum related to the rearrangement process, which is clear from the -OH groups absorbance, higher than the G1, but still lower compared to G3. The spectral analysis suggests that the G3 samples reached a maximum of rearrangement, which is notorious by the absorbance data analysis, the greatest of all samples. Samples of the G4, especially the sample 230 °C/60 min began to display a decrease on their -OH groups absorbance. In addition, the samples spectral analysis denotes the emergence of bands at 1237 cm^{-1} and 1032 cm^{-1}. This becomes even clearer by the analysis of G5 sample, whose absorbance reading decreases further and these bands are highlighted, as shown in Figure 4.

The samples analysis by groups allowed one to state that the treatments performed are more severe in ascending order from G1 to G5. Moreover, knowing that the modeled response surface is a distorted plan, as shown in Figure 3, and bearing in mind that the Claisen rearrangement process is followed by a polymerization/decomposition process, it is assumed that on the upper end of this sequence the decomposition effect can already be observed. According to this statement, the G1 is inefficient to the rearrangement; the G2, despite being better in relation to the G1, is still insufficient; G3 is located in the region of optimal performance in relation to thermal rearrangement process; apparently, in the G4 a product decomposition process began, which is aggravated in the G5.

The ABFA structure was confirmed by its characteristic bands, through the sample treated at 220 °C for 60 minutes: 3447 cm^{-1}

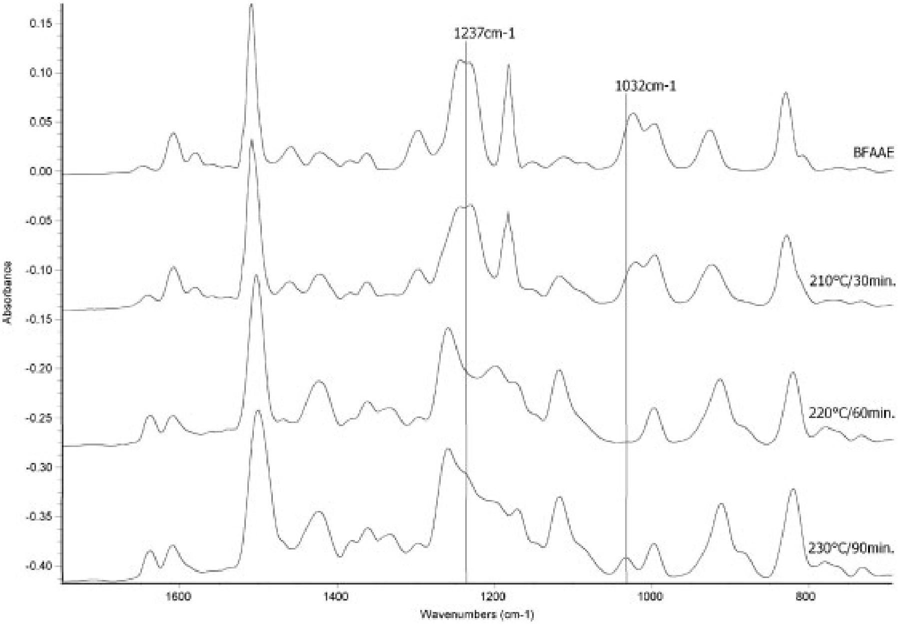

Figure 4.
Spectrum comparison between the BFAAE and samples extracted from G1, G3 and G5, showing the bands emergence at the wavenumbers equal to 1237 cm^{-1} and 1032 cm^{-1}.

(ν -OH with hydrogen bonds), 1608 cm^{-1} and 1502 cm^{-1} (aromatic ring characteristic vibrations), 1260 cm^{-1} (ν CO), 1198 cm^{-1} and 1117 cm^{-1} (skeleton deformation -C(CH$_3$)$_2$-), 996 cm^{-1} (δ =CH$_2$ out of plane), 912 cm^{-1} and 818 cm^{-1} (−CH out of plane, aromatic ring trisubstituted at positions meta and para).[23,24] The ABFA's spectrum is presented in Figure 5.

For each heat treatment carried out by DSC, the weight loss (Pm) was calculated for the first observed event, given as the mass loss of rearrangement's reactants and products, which are volatile at the same temperature range. The results, also presented at Table 1, are consistent with the FTIR results and fit into the same categorization as described. The results allowed one to say that heat treatments performed are more severe in ascending order from G1 to G5. Furthermore, the results analysis shows a trend in favor of Pm's reduction of the samples in ascending order of groups, in other words, as a function of the treatment severity.

The influence of time and temperature on the polymerization degree for the treated samples was studied using statistical analysis of data variance. Two null hypotheses were tested, $H_{0,1} = 0$ to test the absence of main effects for time and $H_{0,2} = 0$ to verify the absence of main effects for temperature. Figure 6 shows the output of the computational V.14 Minitab statistical software for analysis of variance of the hypotheses, with a significance level of 0.05.

According to the Fischer distribution, to the point with a significance level of 0.05 and 2 degrees of freedom for both factors and 8 for the error, the percentage point $f_{0.05;2;8}$ equals 4.46.[25] Since the F values, calculated for the time and temperature, are higher than the $f_{0.05;2;8}$ value, one can reject both null hypotheses in favor of alternative hypotheses. With this we conclude that both factors, time and temperature, have major effects on the response variable Pm. That is, a change in the level of a single factor affects the variable's response under study. This analysis was only possible because the interaction effects between time and temperature are negligible. Since there is only one replica

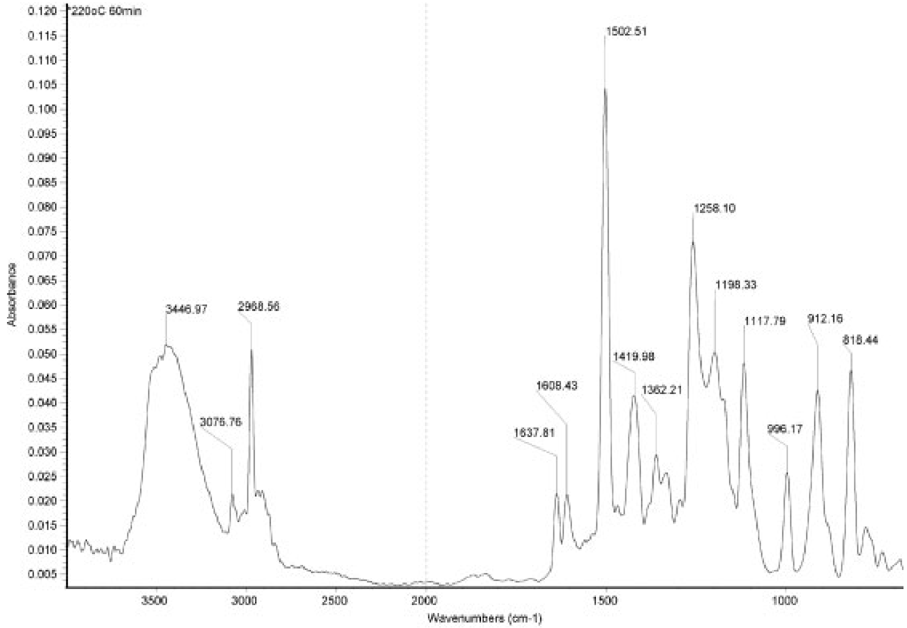

Figure 5.
ABFA infrared spectrum.

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General Linear Model: Pm versus Temperatura; Tempo

Factor       Type   Levels  Values
Temperatura  fixed       3  -1; 0; 1
Tempo        fixed       3  -1; 0; 1

Analysis of Variance for Pm, using Adjusted SS for Tests

Source       DF   Seq SS   Adj SS   Adj MS      F      P
Temperatura   2  200.689  200.689  100.344  14.06  0.016
Tempo         2  109.554  109.554   54.777   7.67  0.043
Error         4   28.556   28.556    7.139
Total         8  338.799


S = 2.67190   R-Sq = 91.57%   R-Sq(adj) = 83.14%
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Figure 6.
Output for the computational analysis of variance of the variable Pm with respect to time and temperature.

for each experiment and the number of degrees of freedom for the error is zero, the variance analysis is conditioned on the assumption that the interaction effects are negligible.

The use of a UV detector, at a wavelength of 275 nm, referring to aromatic compound substituted with electroreceptors, was preferred to perform the chromatographic analysis. Under these conditions, it allows direct integration of the obtained chromatograms, normalizing the results relating to the total area and considering the obtained area for each peak as a proportional response to the amount of aromatic rings present in each eluted substance. From the first step of this study, every involved species had a constant number of aromatic rings: two, so, one can assume that the absorbance response would be proportional to the molar concentration of these substances. It is known that the answer is certainly not quantitative, but it is expected that the involved error meets the needs of the proposed analysis.

Table 1 shows the BFAAE and ABFA content in each sample analyzed via liquid chromatography (HPLC). They were obtained by direct integration of the chromatograms and the area normalization of each compound eluted from the analyzed samples. Regarding the conversion degree

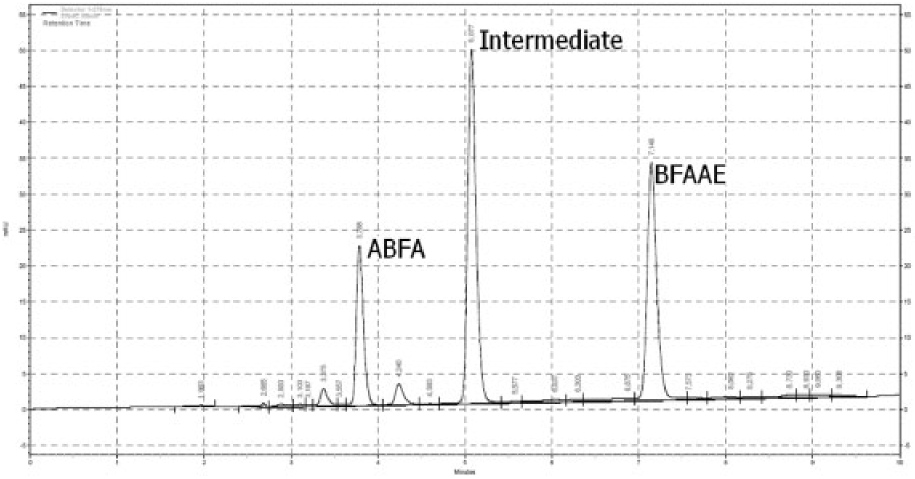

Figure 7.
HPLC chromatogram illustrating the composition of the sample treated at 210 °C for 30 minutes, evidencing the "intermediate" compound presence.

of BFAAE in ABFA, the analysis confirms the previously obtained conclusions, where the rearrangement process of BFAAE in ABFA appears as a direct function of time and temperature. In addition, the samples' grouping from G1 to G5, again, shows consistency. The analysis of sample 1 shows that BFAAE was not fully converted, having been observed about 30% of residual BFAAE, only 15% of ABFA and about 55% of intermediate compounds, including the 2,2′ (4-allyloxiphenyl, 3-allyl-4-phenyl) propane, given as an intermediate product of the rearrangement process, in which only one of the allyloxi groups is rearranged. Figure 7 illustrates the G1 sample composition and shows the presence of the intermediate compound. Samples of G2 were similar in terms of composition, with only 5% of unconverted BFAAE and 55% of ABFA. The samples in G3 presented between 75% and 80% of converted ABFA and 0.5% of residual BFAAE. The samples from group G4 presented 75% and 65% of ABFA and only traces of not rearranged BFAAE were observed. The G5 sample showed about 50% of converted ABFA.

Conclusion

The BFAAE compound was synthesized with good molar yield (94.5%) and purity (97.3%), as demonstrated by thermogravimetric, chromatographic and spectroscopic analysis, through which the structure of the intermediate compound was confirmed.

The Claisen rearrangement study allowed the following conclusions. Through FTIR technique, ABFA chemical structure was confirmed by analyzing the characteristic bands of the compound treated at 220 °C for 60 minutes. The results, according to the three characterization techniques used, provided evidence of the occurrence of a thermal decomposition process, which, apparently, produces a mixture of phenols, which reduce the converted ABFA content of the samples of groups G4 and G5 and the infrared radiation absorption in the region characteristic of -OH groups. The obtained results suggest that, in the studied range, polymerization and degradation of the monomer ABFA occur, simultaneously to its formation.

Finally, we conclude that the thermally initiated Claisen rearrangement process reaches an optimum, in terms of conversion of BFAAE in ABFA, at group G3, that means, at samples treated at 210 °C/90 min., 220 °C/60 min. and 230 °C/30 min., where the obtained ABFA content is as high as 85%–90%, given as Pm obtained by TG, similar and slightly higher than the commercially found product.

Due to the fact that the Claisen rearrangement is very sensitive to the time/temperature treatment, we believe that the obtained results can be improved, obtaining the desired monomer ABFA with higher purity, adequate for its use as a precursor for the obtainment of proton exhange membranes based on crosslinked sulphonated poly(arylene ether sulphone)s.

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