

Synthesis and Characterization of Stable Anion Exchange Membranes: The Addition of Electron-withdrawing Group

Gülşen ALBAYRAK ARI*¹, Cristina IOJOIU², Jean-Yves SANCHEZ²

¹İstanbul Üniversitesi, Mühendislik Fakültesi, Kimya Mühendisliği Bölümü, 34320, İstanbul

²LEPMI, Institut Polytechnique de Grenoble, Saint Martin d'Herès Cedex, France

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Abstract: Anion exchange membranes (AEM) based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were used as polymer electrolyte membrane for fuel cell applications. The membranes were prepared via bromination, quaternization and nitration reactions and their fuel cell-related properties (water uptake, ion exchange capacity, ionic conductivity) were determined. Also, the structures and thermal properties were studied with Fourier transform infrared spectroscopy (FTIR), Size exclusion chromatography (SEC) and Differential scanning calorimetry (DSC). Nitration of quaternized PPO (Q-PPO) led to a decrease in water uptake and ion exchange capacity of the AEM. However, Q-PPO membrane treated with nitration reaction (NO₂-Q-PPO) exhibited a significant alkaline stability compared to quaternized PPO (Q-PPO). The results indicated that the addition of electron-withdrawing group, such as nitro, into the structure in order to improve in alkaline stability is a promising new route for preparation alkaline stable AEM membranes.

Kararlı Anyon Değişim Membranların Hazırlanması ve Karakterizasyonu: Elektron Çekici Grup Katkılması

Anahtar Kelimeler

Polifenilen oksit,
Yakıt hücresi,
Anyon değişim
membran

Özet: Yakıt Hücresi uygulamaları için polimer elektrolit membran olarak Poli(2,6-dimetil-fenilen oksit) (PPO) esaslı anyon değiştirici membranlar (ADM) hazırlanmıştır. Membranlar, brominasyon, kuaternizasyon ve nitrasyon reaksiyonları üzerinden hazırlanarak, yakıt hücresi ile ilgili özellikleri (su tutma, iyon değişim, iyonik iletkenlik) belirlenmiştir. Ayrıca, yapı ve ısıl özellikleri Fourier dönüşümlü infrared spektroskopisi, Büyüklükçe ayırma kromatografisi ve Diferansiyel taramalı kalorimetri ile belirlenmiştir. Kuaternize-PPO (Q-PPO)'nun nitrasyonu, ADM'nin su tutma ve iyon değişim kapasitesinde düşüşe neden olmuştur. Ayrıca, nitrasyon reaksiyonu ile muamele edilmiş Q-PPO membranı (NO₂-Q-PPO), kuaternize-PPO membrana (Q-PPO) göre daha yüksek alkali ortam kararlılığı göstermiştir. Sonuçlar, alkali ortam kararlılığını arttırmak için yapıya nitro gibi elektron çekici grupların ilave edilmesinin, alkali ortam kararlılığına sahip ADM'lerin hazırlanması için umut veren yeni bir yöntem olduğunu göstermiştir.

1. Introduction

In today's world, increasing energy needs and declining fossil fuel reserves reveal the need to replace older energy production technologies with new ones. Fuel cell technologies have become the most attractive technology among the alternative energy system for portable power sources and stationary applications due to their high efficiency and high energy density. Proton exchange membrane fuel cell technologies (PEMFC) have actively

investigated over the last few decades. Although there are numerous successful study and significant technical development about the PEMFC technology, they still have several challenges (cost, lifespan and operating temperature) against their commercialization worldwide. Nowadays, anion exchange membrane fuel cell (AEMFC) has received an increasing interest among the fuel cell technologies. In AEMFC, alkaline medium allows the use of non-precious metal catalysts (such as Ag, Ni, Co) because of the faster oxygen reduction reaction in

alkali media than acidic one. Also, the lower amount fuel crosses into cathode due to hydroxyl ion (OH^-) transfer from cathode to anode [1]. These advantages of AEMFC over PEMFC and PEMFC's disadvantages set off an upsurge in AEMFC research. The key challenge in the development of AEMFCs is that there is no available AEM having high conductivity and chemical stability simultaneously.

AEMs as solid polymer electrolyte should conduct hydroxyl ions from cathode to anode. AEM must consist of a polymer bearing cationic group, e.g. quaternary ammonium/phosphonium or containing a hydroxide salt, e.g. potassium hydroxide (KOH) to conduct the OH^- ions through the membrane. AEMFCs suffer from performance issues related to sustainability of AEM's conductivity properties in the cell medium. For AEMs doped KOH, the main challenge is to prevent the leakage of KOH [2]. In the case of quaternary ammonium-functionalized AEMs, the main concern is the degradation of the cationic groups because of OH^- nucleophilic attack at high pH. Nowadays, there is intensive effort to enhance the alkaline stability of functionalized polymeric membrane. Solerno and Elabd synthesized Nafion-based AEMs with variety of covalently attached cations to understand the effect of cation type on the chemical stability of AEMs (ammonium, phosphonium, piperazinium, pyrrolidinium, pyridinium and quaternized DABCO)[3]. All of the studied cations apart from pyridinium and phosphonium exhibited high chemical and thermal stability. Park et al. reported the effect of the length of alkyl chain on the OH^- conductivity and thermal stability of AEMs aminated by a diamine or a mixture of monoamine and diamine [4]. The AEMs prepared with the mixture of trimethylamine and N,N,N',N'-tetramethyl-1,6-hexanediamine exhibited higher hydroxyl ion conductivity and thermal stability than those aminated by pure diamine. In another study, the effect of tertiary amines having different alkyl chain on the alkaline stability of polysulfone-based AEMs was investigated. They reported that the smaller methyl group, e.g. TMA, had the highest conductivity. In addition to the stability of cationic group in the polymer structure, the stability of the polymer backbone is also important and taken into account while the alkaline stability of AEM is evaluated [5]. Zhang et al. showed that the presence of fluorine atoms in the aromatic ring caused a decrease in alkaline stability of AEM [6].

For AEMFCs applications, PPO as a membrane material offers several advantages over other aromatic polymers. PPO has strong hydrophobicity, high strength and modulus and high hydrolytic stability [7,8]. PPO can be readily modified in both aryl- and benzyl-position by electrophilic or radical substitution reactions [7]. Bromomethylated PPO allows the introduction of quaternary ammonium groups on the aromatic ring by reacting with different amines for AEMFCs applications [9-13].

In this study, we try to introduce an electron-withdrawing group, e.g. nitro group, into the membrane structure in order to prevent the degradation of quaternary ammonium group on PPO at high pH. The electron-withdrawing nature of nitro group will lead to weaken the interaction between OH^- ions and quaternary ammonium groups in structure. So, the quaternized group will be less prone to chemical degradation through nucleophilic substitution ($\text{S}_{\text{N}}2$). Here, AEMs based on PPO were prepared through nitration, bromination and quaternization reactions. The effect of nitration reaction on membrane's properties was studied. Especially, the alkaline stability test results show that our approach is promising to obtain a more alkaline stable structure for AEMFC applications.

2. Material and Method

PPO and Bromine (99 wt %) were purchased from Acros Organics, Belgium. Sulphuric acid (95-98 wt %) and nitric acid (65 wt %) were obtained from Panreac Quimica, Spain and Carlo Erba, Italy, respectively. Trimethylamine (in gas form) (TMA) was purchased from Aldrich, Germany. All organic solvents were of analytical grade.

2.1. Nitration of PPO or Br-PPO (NO_2 -PPO, NO_2 -Br-PPO)

PPO was nitrated as reported by Pan et al. and Bhole et al. [8, 14]. 5 g of pure PPO or Br-PPO was dissolved in 125 ml of chloroform (CHCl_3) under argon (Ar) flow. The nitration reaction was carried out by drop wise addition of the mixture of nitric acid and sulphuric acid (3:1 v/v, 25 ml) into the solution at 25°C. The reaction mixture was stirred for 30 min, then, precipitated into methanol. It was purified and washed with methanol until a neutral pH was obtained. It was dried at 60°C for 1 day.

2.2. Bromination of PPO or NO_2 -PPO (Br-PPO, Br- NO_2 -PPO)

0.5 g pure PPO or NO_2 -PPO was dissolved in 15 ml of chlorobenzene and heated to the boiling point of chlorobenzene under reflux conditions and Ar flow. 0.2 ml of bromine was slowly carefully added into solution. The reaction temperature was fixed at 135°C and stirred for 3,5 h. The brominated polymers were slowly precipitated into stirred methanol, filtrated and dried at 60°C. The degree of bromination was determined by ^1H NMR analysis.

2.3. Quaternization of Br-PPO, NO_2 -Br-PPO or Br- NO_2 -PPO (Q-PPO, NO_2 -Q-PPO, Q- NO_2 -PPO)

Brominated polymers were dissolved in N-methylpyrrolidone (NMP) to obtain homogeneous solution. Then, these solutions were bubbled with TMA in gas form for 2 h at room temperature.

2.4. Membrane preparation

The modified polymers (Br-PPO, Br-NO₂-PPO and NO₂-Br-PPO) were dissolved in NMP, filtrated and degassed to obtain a homogeneous solution of about 10 wt.%. Then, they were cast onto petri dishes and dried at 60°C for 5 days. To remove the membranes from petri dishes, the petri dishes with dried membranes were immersed in hot water.

2.5. Nitration of quaternized-PPO membrane (NO₂-Q-PPO)

The prepared Q-PPO membrane was nitrated by stirring with a mixture of nitric acid and sulphuric acid (3:1 v/v, 25 ml) at room temperature for 1 day. After nitration, the membrane was washed with water until neutral waste water was obtained.

2.6. Characterization

The chemical structure of membranes was probed using FT-IR analysis, Perkin Elmer Spectrum One FT-IR with attenuated total reflectance (ATR) unit, and ¹H NMR Spectra, Bruker spectrometer cryospec WM 250.

SEC analyses were performed by using a Waters 515 HPLC equipped with a Waters 2414 refractometer. THF was used as the solvent. The calibration was performed using polystyrene standards.

For water uptake measurements, membranes previously dried in vacuum and weighed (for 24 h and 60°C) were immersed into deionized water at room temperature for 4 days, then, taken out and quickly weighted. The water uptake values were calculated from the ratio of the amount of water absorbed by the membrane versus the dried membrane weight.

The ion exchange capacity (IEC) of the membrane was determined by using the Mohr method. Firstly, the membrane in the chloride form was converted to the sulfate form by immersing in a Na₂SO₄ aqueous solution for 8 h. Then, the chloride ions released from the membrane were titrated with a 0.1 M AgNO₃ solution using K₂CrO₄ as an indicator. The IEC values were calculated from the released Cl⁻ ions and given as meg/g dry membrane (in Cl⁻ form).

Thermal properties of the samples were investigated by using TA Instruments DSC 2920 modulated DSC from 30 to 350°C at a heating rate of 10°C/min.

The ionic conductivity of the AEMs was measured using a Hewlett-Packard 4192A LF frequency response analyzer in water at room temperature.

To investigate the long term stability of the membranes, the prepared AEMs were immersed in

de-ionized water at room temperature and their conductivity changes were followed by repeating the conductivity measurements during 10 days. Also, membranes were immersed in 2 mol/l NaOH to determine the alkaline stability and the change in conductivity was followed as a function of the contact time.

3. Results

3.1. FTIR Spectra

A series of samples were prepared by nitration and bromination reaction of PPO. To confirm these reactions, FTIR and ¹H NMR analysis were carried out. Figure 1 shows FTIR spectra of pure PPO, NO₂-PPO and Br-NO₂-PPO. The characteristic absorption peaks of the symmetrical and asymmetrical stretching vibrations of C-O-C (aromatic ether) at 1180 and 1305 cm⁻¹ and those of phenyl group at 1470 and 1602 cm⁻¹ can be observed in spectra of pure PPO. Two new absorption peaks in spectra of NO₂-PPO appeared at 1365 and 1530 cm⁻¹ due to nitration [14]. After bromination reaction of NO₂-PPO (Br-NO₂-PPO), there are no new peaks for the benzyl bromide (C-Br) stretches, which is expected at 1080 and 740 cm⁻¹[10]. This suggests that the methyl groups of NO₂-PPO cannot react with bromine due to the fact that the nitro group deactivates the aromatic ring towards further electrophilic substitution, strongly inhibiting the introduction of a second electrophilic species like bromine [15].

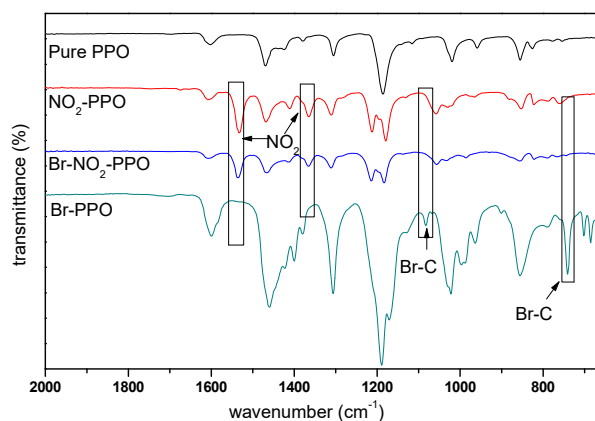


Figure 1. FTIR spectra of PPO, NO₂-PPO and Br-NO₂-PPO

In Figure 2, the FTIR spectra of Br-PPO exhibits two new peaks at 740 and 1080 cm⁻¹ corresponding to the C-Br stretches. Those peaks disappeared in the FTIR spectra of NO₂-Br-PPO. This can be ascribed as the benzyl bromide of PPO is indurable towards aggressive medium of nitration reaction. In Figure 3, after quaternization reaction of PPO (Q-PPO), the benzyl bromide stretches band vanished due to substitution reaction between bromide and quaternization agent and a new absorption peak at 970 cm⁻¹ appeared due to C-N stretching. This is indicating that quaternization was successfully completed [16]. Comparing Q-PPO spectra with NO₂-

Q-PPO, no new characteristic peak was observed. This result showed that the NO_2^+ group couldn't attach to aromatic ring of PPO during nitration reaction, only embed in the membrane structure.

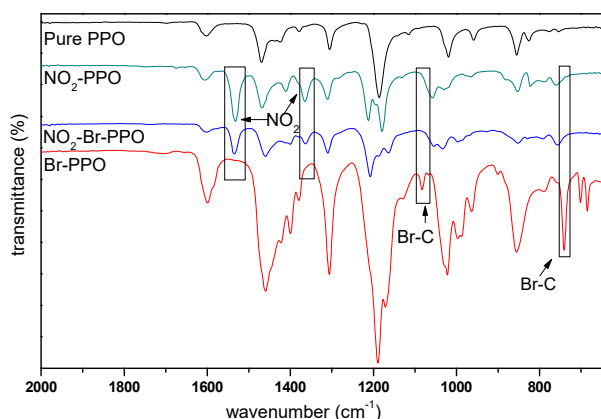


Figure 2. FTIR spectra of Br-PPO ve NO_2 -Br-PPO

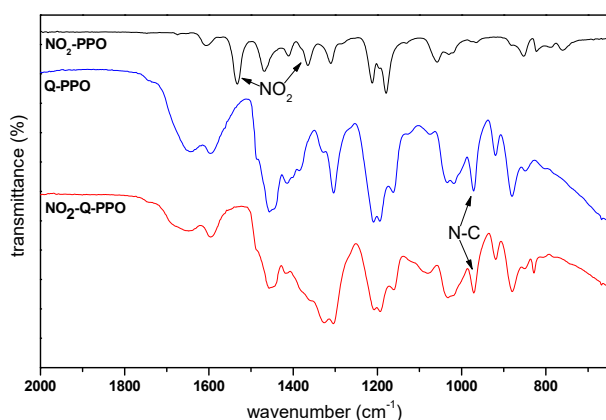


Figure 3. FTIR spectra of Q-PPO, NO_2 -PPO and NO_2 -Q-PPO

3.2. ^1H NMR Spectra

The chemical structure of the synthesized PPO samples was also characterized by the ^1H NMR. The characteristic proton resonance signals of PPO were observed at 6.4 ppm (Aryl-H) and 2.1 ppm (Aryl- CH_3). After nitration reaction, the NMR spectrum showed a new peak at 6.1-6.2 ppm due to the protons belonged to substituted PPO repeat unit (Figure 4) [14]. In the spectra of Br-PPO, there was a new peak at 4.2-4.3 ppm, which was due to the CH_2 -Br groups [11]. For Br- NO_2 -PPO and NO_2 -Br-PPO, the broad peak between 4.0 and 4.6 ppm showed the existence of CH_2 -Br group in PPO repeat unit. For quaternized membranes (Q-PPO and NO_2 -Q-PPO), ^1H NMR Spectra were not recorded because of their insolubility in CDCl_3 .

3.3. Membrane Preparation and Size Exclusion Chromatography

Figure 5 represents photographs of Br- NO_2 -PPO and NO_2 -Q-PPO membranes. Among the all prepared samples, Br- NO_2 -PPO and NO_2 -Br-PPO samples couldn't form a membrane and broken into small pieces during drying process (Figure 5) while NO_2 -Q-

PPO could form a membrane. The number average molecular weight's (M_n) of Br- NO_2 -PPO and NO_2 -Br-PPO from SEC measurements were 12,300 and 15,850, respectively, while pure PPO's M_n was 20,350. As seen from SEC results (Table 1.), the nitration reaction leads the polymer chain degradation, therefore, a membrane couldn't be obtained from these samples. The molecular weight loss in Br- NO_2 -PPO is more than that of NO_2 -Br-PPO. It is understood that the nitration reaction damaged further for pure PPO than for Br-PPO. The molecular weight of NO_2 -Q-PPO membrane couldn't determine with SEC analysis because of its insolubility in THF. As seen from Figure 5, this membrane didn't loss its appearance and integrity during drying process. This may be explained as follow; nitration reaction of quaternized PPO (Q-PPO) was carried out after membrane preparation and Q-PPO membrane has the stable structure towards aggressive medium of nitration reaction. Based on these observations, NO_2 -Q-PPO and Q-PPO membranes were used for the other characterization tests.

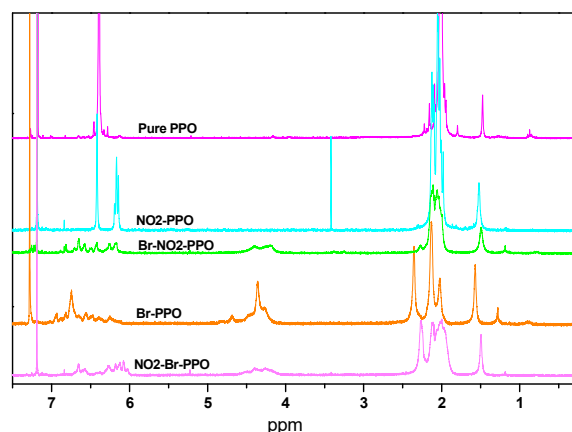


Figure 4. ^1H NMR spectra of the products

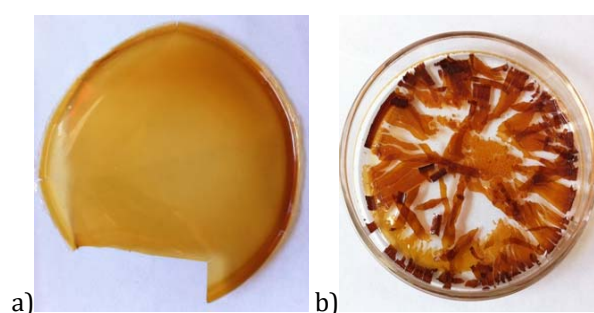


Figure 5. Appearance of NO_2 -Q-PPO(a) and Br- NO_2 -PPO(b)

Table 1. Average molecular weights and polydispersity index of products

Product	M_n (g/mol)	M_w (g/mol)	PDI
Pure PPO	20350	40100	2.0
NO_2 -PPO	15750	24900	1.6
Br- NO_2 -PPO	12300	29200	2.4
Br-PPO	22100	48300	2.2
NO_2 -Br-PPO	15850	43700	2.7

3.4. Ion exchange capacity, Water uptake and DSC analysis

The amount of ion exchangeable groups existing in the membrane directly affects its conductivity, therefore, determination of IEC is important to forecast the performance of polymer electrolyte membranes. The IEC value of Q-PPO decreased from 0.92 to 0.82 meq/g after nitration reaction. The decrease in IEC can be attributed that aggressive medium of nitration reaction causes a bit loss of the quaternary ammonium groups which are responsible for ion exchange. The IEC and water uptake capacity are interrelated properties. As expected, water uptake value decreased a bit depending on the loss of IEC value after nitration reaction (Table 2). Also, polar groups, such NO_2^+ , lead to an increment in packing density and a decrement in chain mobility. This restricts the sorption of water into the membrane and contributes to the reduction in water uptake. These results of water uptake tests of membranes complied with DSC results. After nitration reaction, glass transition temperature (T_g) value of Q-PPO membrane increased from 207°C to 221°C , which was seen from Table 2. The increase in T_g demonstrated that the NO_2 -Q-PPO membrane had the decreased chain mobility and the higher degree of crystallinity as compared with Q-PPO due to the addition of polar groups into the structure. Bhole et al. [14] showed that the nitration led to higher chain packing density and lower chain mobility in PPO matrix than that of unmodified PPO through polar interactions caused by NO_2^+ groups.

Table 2. Water uptake, IEC and T_g values of prepared membranes

	WU (%)	IEC (mmol g ⁻¹)	T_g ($^\circ\text{C}$)
Q-PPO	323	0.92	207
NO_2 -Q-PPO	238	0.82	221
PPO	-	-	215

3.5. Ionic Conductivity and Alkaline stability

The important criteria of the polymeric membranes for fuel cell applications are their conductivity and stability in conductivity. Hence, the behavior of AEMs under strong alkaline conditions should be determined to estimate the performance and operation life of fuel cell. The stability of the AEMs was evaluated by determining the conductivity after the membranes were exposed to different environments such as hydration and high pH. Table 3 presents the results of all conductivity measurements. The conductivities of Q-PPO and NO_2 -Q-PPO were found to be 17 and 21 $\text{mS}\cdot\text{cm}^{-1}$ in water, respectively. This improvement may be attributed to incorporation of HNO_3 into the structure like a dopant.

During the long term stability of NO_2 -Q-PPO membrane in deionized water, the membrane exhibited remarkably decline in conductivity over a period of 2 days, then, not change notably. This initial decrease in conductivity for NO_2 -Q-PPO sample can arise from the leakage of HNO_3 which embedded in membrane. As to the conductivity of Q-PPO, no decrease was observed during the test period. At the end of long term stability test, Q-PPO exhibited higher ionic conductivity than NO_2 -Q-PPO (17 and 11 $\text{mS}\cdot\text{cm}^{-1}$, respectively). The decrease in ionic conductivity of NO_2 -Q-PPO may be caused from the membrane having the lower water uptake, ion exchange capacity and chain mobility and leakage of HNO_3 . Also, the ion conductivity is related to the crystallinity and increases with decreasing the crystallinity. Since the crystallinity of NO_2 -Q-PPO membrane is higher than that of Q-PPO membranes due to T_g values, the transport of the ions is more difficult in NO_2 -Q-PPO membrane. Xiong et al. [17] showed that ion transport through the membrane was impressed by membrane structure. Their composite membrane having fewer crystalline region exhibited higher conductivity than the other one having higher crystalline region.

The results of long term alkaline stability test differed from the results of the long term stability test in water. The alkaline stability test of NO_2 -Q-PPO membrane was applied to the sample used for long term test in water in order to eliminate the dopant effect of HNO_3 . Both Q-PPO and NO_2 -Q-PPO membranes initially showed an increase in their ionic conductivities from 17 and 11 $\text{mS}\cdot\text{cm}^{-1}$ to 43 and 23 $\text{mS}\cdot\text{cm}^{-1}$, respectively, due to dopant effect of NaOH . From Table 3, it can be seen that the ionic conductivity of Q-PPO greatly decreased with the immersion time. The total conductivity loss at the end of 10 days was about 50%. The reduction in ionic conductivity with time is explained by (i) leakage of NaOH and (ii) the degradation of quaternary ammonium by nucleophilic substitution inducing to the formation of non-conductive species such as an alcohol and an amine. In the case of NO_2 -Q-PPO, the membrane did not exhibit any change in ionic conductivity during the test. It is concluded that the electron-withdrawing groups (NO_2^+) embedded in structure lead to decrease in the tendency to degrade of quaternized polymer against OH^- nucleophilic attack.

Table 3. Stability results of prepared membranes

Sample Time	Ionic Conductivity (mS/cm)			
	Long term stability (in water)		Alkaline stability (in 2M NaOH)	
	Q-PPO	NO_2 -Q-PPO	Q-PPO	NO_2 -Q-PPO
0 h	17	21	17	11
48 h	16	10	43	23
96 h	-	-	33	25
144 h	17	11	-	-
240 h	17	11	21	23

4. Discussion and Conclusion

Anion exchange membranes based on PPO were synthesized via nitration, bromination and quaternization reactions. The effect of NO₂⁺ group on membrane's properties was studied. The water uptake and IEC values declined with the addition of nitration reaction step into membrane preparation step. The ionic conductivity initially increased with the addition of NO₂⁺ group into the structure. Then, the ionic conductivity decreased as a result of leakage of HNO₃/ NO₂⁺ group into water during long term stability. Also, the DSC results showed that the addition of polar groups (NO₂⁺) into the structure (NO₂-Q-PPO membrane) lead higher chain packing density and crystalline domain and lower chain mobility, which directly affected the water uptake. The NO₂-Q-PPO membrane exhibited a high alkaline stability due to the electron-withdrawing nature of nitro group towards OH⁻ nucleophilic attack. These initial results point up the potential benefits of the addition of electron-withdrawing group into the structure and are promising for further investigations of similar structures so as to enhance the alkaline stability of the quaternized polymeric membrane for AEMFC applications.

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