Interfacial and Internal Proton Conduction of Weak-acid Functionalized Styrene-based Copolymer with Various Carboxylic Acid Concentrations

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ABSTRACT

Investigation of interfacial proton transport is necessary to elucidate biological systems. As commonly found in biomaterials, the carboxylic acid group was proven to act as a proton-conducting group. This study investigated the influence of carboxylic acid concentration on both interfacial and internal proton transport. Several styrene-based polymers containing the carboxylic acid group were synthesized. The amount of carboxylic acid group in the polymer chain was varied to explore the effects of weak acid concentration on polymer thin films’ electrical properties. The IR p-polarized multiple-angle incidence resolution spectroscopy (pPMAIRS) spectra show the higher ratio of the free carboxylic acid groups rather than cyclic dimers in polymers with a higher concentration of carboxylic acid group, facilitating the more hydrogen bonding networks in films. The water uptake results reveal the similar number of adsorbed water molecules per carboxylic acid group in all thin films. Remarkably, polymer thin films with high carboxylic acid concentration provide internal proton conduction because of the relative increase in the amount of the free carboxylic acid group. In contrast, interfacial proton conduction was found in low carboxylic acid concentration polymers because of the relatively large amount of cyclic dimer carboxylic acid group and poor amount of free carboxylic acid group. This study provides insight into interfacial proton transport behavior according to the weak acid concentration, which might explain proton transport in biological systems.

Keywords : Biological Proton Transport, Hydrogen Bonding Network, Interfacial Proton Transport, Internal Proton Transport

1. Introduction

Proton conductive polymers, which can conduct protons for long distances, mostly contain acids or proton-donating functional groups that release free protons as the charge carrier to enable proton conduction. Strong acids such as sulfonic acid derivatives, for example, commercial NafionTM, have been used widely because of their high deprotonation ability. As biopolymers, sugar and protein derivatives have gained much attention for proton conductive derivatives because they contain proton-donating functional groups. Selberg et al. reported the high proton conductivity of glycosaminoglycans. Wang et al. claimed that the incorporation of amino acid functionalize nanofibers enhanced the proton conductivity in sulfonated poly(ether sulfone) (SPES) membrane. Pena-Francesch et al. reported outstanding proton conductivity of stretchable and self-healing of synthetic tandem repeat polypeptides based on cephalopod proteins. Even though the reported biomaterials show impressive proton conduction performance, further investigation of the proton transportation mechanism is necessary.

Typically, protons can transport across hydrogen bonding networks. The hydrophilic functional groups reportedly induce proton-conducting pathways from interaction between hydrophilic residues of polymer and water molecules. Many studies have published proton transport improvement in an anhydrous state using acid–base combinations of proton conductors. In this system, proton donors are acid groups with low pKa values because protons are readily dissociated. By contrast, the basic groups act as proton acceptors, this proton reception and release continue the transport. The effects of acid and base functional group
concentration on the proton conductivity across protein biopolymers have been reported. Improvement of proton conductivity was found in bovine serum albumin (BSA)-mat with hydroxyl, amine, and carboxylic acid functionalized carbon-dots addition. Simultaneously, hydrophobic substitution on carboxylic acid or amine functional groups of BSA-mat hinders proton transport. This finding attests to the strong influence of acid–base functional groups’ concentration on the charge carrier density and proton conduction. The differences of polar functional groups affecting proton conductivity in the materials has been documented. Functional groups with high polarity or hydrophilic character allow better proton conduction than low hydrophilicity functional groups do. Superior proton conductivity of the materials with a carboxylic acid functional group to that of amine or other hydrophobic groups has also been reported. Collectively, these findings confirm the ability and importance of carboxylic acid as a proton-conducting group.

The study of proton transport is fundamentally important to elucidate the working mechanism in many biological systems because protons can flow through both the inside and on the surface of materials. Consideration of the biomaterial surface is crucially important because it can affect various properties, including cell interactions on biomaterials, polarity, and electrical properties. Many investigations of surface proton transport at the lipid monolayer have been reported. Proton translocation across the biomembrane surface has also been investigated in several studies. Carboxylic acid is commonly found in biomaterial surfaces. However, the effects of carboxylic acid concentration on surface or interfacial proton conductivity remain unclear.

This study specifically examined the influence of carboxylic acid concentrations of styrene (St)-based copolymers on the water uptake and proton conduction, including interfacial proton conduction. The St-based polymer was selected because of its stability and ease in functionalization. Polymers were synthesized systematically with different concentrations of carboxylic acid group. The ester derivative monomer was chosen for the polymerization reaction instead of the monomer in carboxylic acid form because of the marked difference of reactivity between St and carboxylic acid monomers. The polymers were functionalized with different numbers of carboxylic acid group to observe the carboxylic acid concentration effects on proton transport behavior. To investigate the interfacial proton transport properties, the polymers were prepared as thin films to increase the ratio of film interface area to bulk.

2. Materials and Methods

2.1 Materials

4-Vinylbenzoic acid (4VBA, >97.0%) was purchased from Fujifilm Wako Pure Chemical Corp., Japan, and was recrystallized from a mixture of ethanol and water before use. Styrene with TBC stabilizer (St, >99.0%) and 2,2’-azobis(isobutyronitrile) (AIBN, >98.0%) were purchased from Tokyo Chemical Industry Co. Ltd., Japan, and were then purified respectively using vacuum distillation and recrystallization from methanol. Other chemicals were purchased and used as received from Fujifilm Wako Pure Chemical Corp., Japan.

2.2 Synthesis of 4VBZA

After 4VBA was mixed with methanol and sulfuric acid, it was then refluxed for 3 h. The product, 4-vinylbenzoate (4VBZA), was extracted and washed with ethyl acetate and brine, then dried under vacuum to remove residual solvent.

2.3 Polymerization

Several styrene-based polymers containing the carboxylic acid groups were synthesized through free-radical polymerization. This polymer consists of two monomers, St monomer and 4VBA monomer, including St monomer with a carboxylic acid group located at the benzene ring. Table 1 shows that the ratio of 4VBZA and St monomers amount added for the reaction varied from 1 : 4 to 1 : 0. It is noteworthy that the monomer input ratio differed from the actual obtained monomer ratio. According to the monomer input ratio, the polymerization products were designated as P4VBZA100 (poly-4-vinylbenzoate100) and PS4VBZA75, 50, and 33 (polystyrone-co-4-vinylbenzoate75, 50, and 33).

2.3.1 P4VBZA100

After 18 mmol of 4VBA was dissolved in 4 mL toluene and 3 mL ethyl acetate, 0.2 mmol of AIBN was added. Then the mixture was degassed through three freeze–evacuate–thaw cycles. Polymerization was reacted at 80 °C for 24 h under an inert atmosphere. The P4VBZA100 polymer was precipitated from hot methanol and dried under a vacuum with a 82% yield.

2.3.2 PS4VBZA75

This study used 13.5 mmol of 4VBA and 4.5 mmol of St. Scheme 1 shows that the polymerization reaction was done using the same procedure as that used for polymerization of P4VBZA100. PS4VBZA75 polymers were obtained with a yield of 62%.

2.3.3 PS4VBZA50

For this polymer, we used 9 mmol of 4VBZA and 9 mmol of St. The polymerization reaction was done using the same procedure as that used for the polymerization of P4VBZA100. PS4VBZA50 polymer was obtained with 40% yield.

Table 1. Ratio of monomers amounts added for the polymerization reaction and the final ratio of obtained polymers.

| Polymers       | Molar ratio (4VBA : St) | Added | Obtained |
|----------------|------------------------|-------|----------|
| P4VBZA100      | 4 : 0                  | 4 : 0 |
| PS4VBZA75      | 3 : 1                  | 3 : 1 |
| PS4VBZA50      | 2 : 2                  | 2 : 2 |
| PS4VBZA33      | 1 : 3                  | 1 : 2 |

Scheme 1. Polymerization of PS4VBA.
2.3.4 PS4VBZA33
We mixed 4.5 mmol of 4VBZA and 13.5 mmol of St in the
toluene and ethyl acetate. The polymerization reaction was done
with the same procedure as the polymerization of P4VBZA100.
Then PS4VBZA33 polymer was obtained with a yield of 67%.

2.4 Hydrolysis
The solution of sodium hydroxide in methanol, water, and
THF was added to the polymer solution. The reaction was done
at 37 °C for 30 min before cooled. The polymer product in salt
form was precipitated in THF and dried under vacuum at room
temperature.

2.5 Ion exchange
The ion exchange was done by immerse polymer salt in 1 M HCl
solution, then shaken for 1 min or until the color of a polymer
change from pale yellow to white and insoluble in acid solution.
Then we separated the polymer using a centrifuge and replaced it
with the new acid solution. The ion exchange process was repeated
three times. The final polymer, polystyrene-co-4-vinylbenzoic acid
(PS4VBA) or poly-4-vinylbenzoic acid 100 (P4VBA100), was
washed with water until it became neutral. Then it was dried under
vacuum at room temperature and 35 °C.

2.6 Characterization
The polymer structures were characterized using nuclear
magnetic resonance (NMR), infrared (IR) spectroscopy, gel
permeation chromatography (GPC), thermogravimetric analyzer
(TGA), X-ray photoelectron spectroscopy (XPS), and IR p-polarized
multiple-angle incidence resolution spectrometry (pMAIRS). Details of measurements are included in Supporting Information.

2.7 Preparation of polymer thin films
The polymer was dissolved in the solvent of dimethylformamide
(DMF) and tetrahydrofuran (THF) (2 : 3) before spin-coating (ACT-
200 spin-coater; Active) on the cleaned quartz substrate. Then the
films were dried under vacuum at 60 °C overnight to remove the
residual solvent. The film thickness was examined using a white
light interferometric microscope (BW-S506; Nikon Corp.). IR
spectroscopy confirmed that no DMF remained in the thin films.

2.8 Water uptake measurement
The water uptake of polymer thin films was measured using a
relative humidity (RH)-controlled in-situ quartz crystal micro
balance (QCM) system. A QCM substrate (QA-A9M-SiO2-
Si(5M SEP); Seiko EG&G Co. Ltd.) was connected to a frequency
counter (53131A; Agilent Technologies, Inc.). The change of
frequencies between bare and film-coated substrate was recorded.

2.9 Proton conductivity measurements
The thin film’s proton conductivity was investigated in the RH-
controlled and temperature-controlled chamber (SH-221; Espec
Corp.) using impendence spectroscopy measurements obtained with a
frequency response analyzer equipped with a high-frequency
dielectric interface (SI1260 and SI1293; Solartron Analytical). The
in-plane conductivity was examined using the two-probe method
with porous gold paste (SILBEST No. 8560; Tokuriki Chemical
Research Co. Ltd.) as electrodes. The conductivity (σ) was
calculated using the following equation.

\[ \sigma = \frac{d}{Rlt} \]  

Where, \( \sigma \) is the conductivity, \( d \) is the thickness, and \( Rlt \) is the resistance at each RH.

The interfacial proton conduction using the following equation.

\[ R' = \frac{R}{d} \]  

The interfacial proton conduction can occur at both the air-film
interface and substrate-film interface since water can be adsorbed
on both interfaces. If the interfacial proton conduction mainly
takes place, then the normalized resistance is independent of the film
thickness. However, if the internal proton conduction occurs in the
thin film, then the normalized resistance depends on the film
thickness.

3. Results and Discussion

3.1 Establishment of polymerization route and character-
ization
Obtaining a copolymer by direct mixing of St and 4VBA
monomers in the reaction solution was challenging because of their
considerable polymerization reactivity differences. The carboxylic
acid can interact with other carboxylic groups through the strong
hydrogen bonding interaction. This intermolecular interaction
might cause the accumulation of 4VBA monomer in the solution,
resulting in the higher reactivity of 4VBA monomer than St
monomer during free-radical polymerization.

To avoid this situation, the influence of hydrogen bonding
intermolecular interaction among 4VBA monomers should be
reduced. The conversion of a carboxylic acid group to an ester
monomer is one method to minimize the hydrogen bonding effect
because of weaker interaction among the ester groups. Therefore,
a series of styrene polymers with different amounts of the
vinylbenzoic group was synthesized through free-radical polymerization
of St monomer and St-based monomer containing ester groups.
First, the carboxylic acid group of 4VBA monomer was converted
to the methyl ester, 4VBAZ, by an esterification reaction. Scheme 1
shows that this lowered reactivity monomer was then mixed directly
with St monomer and other solvents for the polymerization reaction.

The chemical structure of synthesized polymers and the ester
group’s ratio was confirmed from 1H-NMR spectra, shown in Fig. 1.
Peak of an ester group was found clearly in all spectra at around
3.8 ppm. According to the ratio of the 4VBAZ monomer consisted
in the polymer chain, the various ester peak intensity ratio refers to
the difference of ester group concentration in each synthesized
polymer. P4VBA100, for which all units contain an ester group,
shows the highest peak intensity ratio followed by PS4VBA75, 50,
and 33. These were consistent with the intensity ratio of peak b,
which decreased with the increasing ester group on the polymer
chain and wholly vanished in the P4VBAZ100 spectrum. However,
the polymer with the ester group ratio of 33 % or PS4VBA33 was
obtained from the initial ratio of 1 : 3 or 25 % 4VBAZ monomer.
Table S1 shows that GPC was performed to investigate the molecular weight ($M_w$) of the polymer in an ester form. The polymer with an ester group was then reacted with a strong base through the hydrolysis reaction followed by the ion exchange in an acidic solution to recover the carboxylic acid group to the polymer chain (Scheme 1). The absence of the ester group (3.8 ppm) and the presence of the carboxylic acid group (12.7 ppm) of all polymers was clearly apparent in 1H-NMR spectra, as shown in Fig. 2. The peak intensity ratio of all spectra for carboxylic acid is conformable with the amount of an ester group before the hydrolysis reaction, confirming that the hydrolysis and ion exchange reactions were 100% successful. Moreover, these 1H-NMR spectra were also verifying the different carboxylic acid concentrations for each fabricated polymer.

The 13C-NMR spectra show a sharp peak of carbon from carboxylic acid at 167.5 ppm, attesting to the existence of a carboxylic acid group. Then ATR-FTIR spectroscopy was applied to investigate the synthesized polymer powder. The bands of $\text{C}=\text{O}$ (1690 cm$^{-1}$) and C-O (1250 cm$^{-1}$) were observed in IR spectra, which also confirmed the presence of the carboxylic acid group in the polymer chain (Fig. S6).$^{37,38}$ The thermal stability of the fabricated polymer was examined through TGA (Fig. S7). The TGA analysis of all polymers shows two steps weight loss. First, the weight loss can be attributable to water evaporation starting from 50 °C. The second weight loss, which started from 350 °C, is attributable to polymer backbone degradation, which is similar for all polymers. The degradation of polymers was completed after 500 °C, the remaining weight of char obtained by chemical reactions of organic substance was also consistent with the carboxylic acid concentration in the polymer chain. The carboxylic acid group might cause dehydration, carbonization, and oxidation, resulting in more char remaining in the polymer with the higher carboxylic acid group concentration.

C 1s XPS spectra (Fig. S8) of polymer thin films confirm the varying carboxylic acid concentration at the films’ surface. The polymer with the highest percentage of carboxylic acid concentration, P4VBA100, shows the most significant amount of C=O (289 ± 0.1 eV)$^{39-41}$ relative intensity, following by PS4VBA75, 50, and 33. All results confirm the different carboxylic acid concentrations for each polymer, which tends to depend on the 4VBZA monomer’s ratio before polymerization. We conclude that the free-radical polymerization of styrene-based monomer in ester form, instead of carboxyl form, can control the carboxylic acid concentration in the styrene-based copolymer.

Moreover, the polymers’ thin-film structure was investigated using an IR pMAIRS technique, as shown in Fig. 3 and S9. The different shapes of the carbonyl (C=O) bands from 1670 to 1690 cm$^{-1}$ were observed in IR spectra, which also confirmed the presence of the carboxylic acid group in the polymer chain (Fig. S6).$^{37,38}$ The thermal stability of the fabricated polymer was examined through TGA (Fig. S7). The TGA analysis of all polymers shows two steps weight loss. First, the weight loss can be attributable to water evaporation starting from 50 °C. The second weight loss, which started from 350 °C, is attributable to polymer backbone degradation, which is similar for all polymers. The degradation of polymers was completed after 500 °C, the remaining weight of char obtained by chemical reactions of organic substance was also consistent with the carboxylic acid concentration in the polymer chain. The carboxylic acid group might cause dehydration, carbonization, and oxidation, resulting in more char remaining in the polymer with the higher carboxylic acid group concentration.

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1750 cm\(^{-1}\) between in-plane (IP) \(\times 2\) and out-of-plane (OP) direction were observed. The strong absorption band at 1691 cm\(^{-1}\) assigned as the carbonyl groups of carboxylic acids in a cyclic dimer form. Another band at 1729 cm\(^{-1}\) attributed to the carbonyl groups of the free carboxylic acid groups.\(^{42,43}\)

The C=O group’s absorbance ratios of free carboxylic acid groups to cyclic dimer carboxylic acid groups in different carboxylic acid concentrations polymers were investigated (Table 2). The ratio values increasing with carboxylic acid concentration of polymers thin films, refers to the higher amount of free carboxylic acid groups. This higher amount of free carboxylic acid groups might provide the internal proton conduction since free carboxylic acid concentration can interact with water molecules and improve the hydrogen bonding network formation. The lower ratio values in lower carboxylic acid concentration polymers refer to the relatively higher amount of dimer carboxylic groups in the thin films. The relatively higher amount of dimer carboxylic acid groups might inhibit the internal proton conductivity in lower carboxylic acid concentration polymers. Because the carboxylic acid in dimer form cannot provide a free proton carrier for long-range transportation, and fewer water molecules can interact with carboxylic acid groups to extend the hydrogen bonding network.

The distribution of carboxylic acid groups in thin films were investigated by comparing the absorbance ratios of free carboxylic acid groups to dimer carboxylic acid groups with decreasing thicknesses in PS4VBA50 and 33 thin films. The more influence of the interface was expected to be observed when the film became thinner. Figure 3 and Table 2 show that the absorbance ratios in both IP and OP directions increase with decreasing thickness. This film thickness dependence behavior suggests that the free carboxylic acid groups are more located at the film interface.

### 3.2 Influence of carboxylic acid concentration on water uptake

It is necessary to consider the water adsorption ability of materials because the water molecules can form a hydrogen bonding network. These networks can act as a proton pathway that promotes the proton transport properties. The carboxylic acid functional group can interact with water molecules in the hydrogen bonding network formation.\(^{4,7,44}\) Therefore, the existence of carboxylic acid group is expected to affect the water uptake properties of materials. The water uptake ability of synthesized polymers was investigated using a QCM system under varied RH. Figure 4 demonstrates that all thin films show similar water adsorption capability because of the low water molecules in the environment at low RH. Then the enhancement of water uptake was observed when increasing the RH. The high carboxylic acid concentration might improve thin-film hydrophilicity and provide more extensive hydrogen-bonding networks, raising the water uptake of P4VBA100. However, the water uptake of P4VBA100 is not markedly different, in fact it is almost comparable to that of all PS4VBA polymers. At least half of the carboxylic acid group adsorb one water molecule at 60 % RH for all polymers. And it should be noted that the total number of water molecules in polymer thin film increases as the carboxylic acid concentration increases. The information above can be summarized to state that the carboxylic acid groups of all fabricated polymers can adsorb water molecules and might provide protons as a carrier.

### 3.3 Influence of carboxylic acid concentration on in-plane proton transport properties of polymer thin films

The in-plane proton conductivity of synthesized polymers thin films was measured to assess the influence of carboxylic acid concentrations on proton transport properties. According to the water uptake values at 60 % RH, half of the carboxylic acid group might adsorb the water molecules. Therefore, some probability exists that half of the proton from the carboxylic acid group will dissociate and be able to transport. In the case of a weak carboxylic acid with high \(pK_a\), the interfacial proton conduction might occur, depending on the number of adsorbed water molecules and the concentration of the acid group. Earlier, surface proton transport was reported in fully protonated poly(aspartic acid) thin films.\(^{31}\) Consequently, the possibility exists that interfacial conductivity, instead of internal conductivity, occurs in fabricated thin films. We found that the number of adsorbed water molecules in four polymers thin films was almost the same. Therefore, the proton conduction pathway was discussed along with the role of carboxylic acid concentrations. All polymer thin films were prepared using the same procedure and the interfacial proton conductivity were investigated. Then the conductivities of polymer thin films with different thicknesses were measured and compared. Figure 5 shows the RH dependence of proton conductivity for polymer thin films. Only P4VBA100 shows the film thickness independence of conductivity, whereas all PS4VBA thin films exhibit the film thickness dependence, by which the lower conductivity was found in a thicker film. Usually, the internal conductivity is expected to be equivalent irrespective of the film thickness.\(^{31}\) Therefore, interfacial proton transport, which might occur in this case, must be considered.\(^{5,46}\)

The normalized resistance or \(R'\) was then calculated for all fabricated thin films to elucidate the interfacial proton conduction. Figure 6 portrays the influence of film thickness on \(R'\). As presented
Figure 7 shows that all polymers were expected to display superior proton transport properties.\(^4\) Therefore, an extensive hydrogen-bonding network and dissociation of proton carriers.\(^4\) Nonetheless, PS4VBA100 (red), PS4VBA75 (blue), PS4VBA50 (black), and PS4VBA33 (green). It is important to note that the conductivity derives from different proton transport behaviors. Details are discussed in the next paragraph.

Typically, the high concentration of carboxylic acid group promotes the proton carrier density, which benefits the proton transport properties.\(^4\) Moreover, the water molecules induce the extensive hydrogen-bonding network and dissociation of proton carriers.\(^4\) Therefore, films with high carboxylic acid concentration were expected to display superior proton transport properties. Figure 7 shows that all polymers’ conductivity at a similar film thickness of 70–80 nm were compared. The dependence of proton conductivity on the RH was observed for all polymers which the conductivity increased with RH. The improvement of the water network can explain this RH-dependent proton conductivity. A better extension of the hydrogen bonding network can occur under high RH conditions when the number of water molecules in the thin film increases, facilitates proton transport, and enhances proton conductivity. However, all polymers’ conductivity is almost comparable, even though the proton carrier density was expected to be different. It is important to note that the conductivity shown in Fig. 7 derives from different proton transport behaviors. The conductivities of PS4VBA50 and 33 were derived from the interfacial proton conduction. At low RH, the hydrogen bonding network inside the polymers’ film was not connected due to the lack of water molecules and relatively large amount of cyclic dimer carboxylic acid group. Moreover, free carboxylic acid groups are more located at the thin film interface. While at higher RH, with a higher number of adsorbed water molecules in the polymers’ film, the continuous hydrogen bonding network was not improved much because of the low carboxylic acid group density. Therefore, the interfacial transport was dominant for all RH in low carboxylic acid concentrations polymers thin films as PS4VBA50 and 33. The conductivity of P4VBA100 dominantly originated from internal proton transport. The efficient hydrogen bonding network can form inside the film, resulting in internal proton conduction and increasing conductivity with RH. Differently, both internal and interfacial proton conduction occurred in PS4VBA75 thin film. The interfacial conductivity tends to be preferred at low RH because the lower carboxylic acid concentration might engender a less-efficient hydrogen bonding network inside the film than the P4VBA100 thin film. Then, the internal conduction occurred because of the hydrogen bonding network extension inside the film at high RH (Fig. 6b). Moreover, proton carrier density tends to affect the internal proton conductivity. As shown in Fig. 7, at 95% RH, the internal proton conductivity of P4VBA100 was higher than that of PS4VBA75. This different in internal proton conductivity might be affected by the higher proton carrier density of P4VBA100 than PS4VBA75, providing a better internal proton conductivity.

It is particularly interesting that the information above engenders the assumption of a relation between carboxylic acid concentration and the main proton transport properties. Table 3 displays the
summarized main proton transport path of fabricated thin films. The films of high carboxylic acid concentration polymers, P4VBA100 and PS4VBA75, tend to provide internal proton transport. In contrast, the films of lower carboxylic acid concentration polymers as PS4VBA50 and 33 prefer interfacial proton transport instead of internal proton transport. This difference in the main proton transport behavior is attributable to the carboxylic acid concentration, which influences the water channel or the proton transport pathway. The high amount of free carboxylic acid groups in high carboxylic acid concentration polymers (Fig. 3) improve the hydrogen bonding network between water molecules and free carboxylic acid groups in the polymer thin films, thereby facilitating internal proton transport.

In comparison, low carboxylic acid concentration films with relatively large amount of dimer carboxylic acid groups led to inefficient proton transport pathway inside the films. Therefore, the internal proton transport is not preferred for PS4VBA50 and 33 thin films. The proton transport then shifts to interfacial proton transport because of the free carboxylic acid groups located on the film’s interfaces. However, PS4VBA75 favors both internal and interfacial proton transport. Because of rather high carboxylic acid concentration, the water channel can be improved under high RH. Internal proton transport can also occur alongside the interfacial proton transport. The relative increase of free carboxylic acid groups also supports this discussion.

4. Conclusions

After several St-based copolymers were synthesized through free-radical polymerization of ester derivative monomers, we applied 1H-NMR, TGA, and XPS techniques to confirm the synthesized polymers’ various carboxylic acid concentrations. The IR pMAIR spectra show both free carboxylic acid groups and cyclic dimer carboxylic acid groups. The higher ratio of the free carboxylic acid groups to the dimers in polymers with higher concentration of carboxylic acid groups, which facilitates the more hydrogen bonding networks in films. The water uptake results indicate that a similar
number of water molecules was adsorbed per carboxylic acid group in all thin films. The in-plane proton transport was examined by an impedance spectroscopy. The normalized interfacial resistance ($R'$) was also calculated to explore the possibility of the interfacial proton transport. The internal proton transport was found in thin films with higher carboxylic acid concentration, whereas the interfacial proton transport was observed in lower carboxylic acid concentration films. Differences in proton conduction paths were discussed in relation to the two types of carboxylic acids, free and cyclic dimer carboxylic acid groups. Polymers with high carboxylic acid concentrations contain suitable free carboxylic acid groups inside, which causes internal proton conduction. Polymers with low carboxylic acid concentration contain relatively large amount of cyclic dimer carboxylic acid groups. In addition, the presence of more free carboxylic acid groups on the interface causes interfacial proton conduction. The results presented above demonstrate that polymers’ carboxylic acid concentration influences films’ proton transport behavior.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.21-00042.

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References

1. J. Selberg, M. Jia, and M. Rolandi, PLoS One, 14, e0202713 (2019).
2. H. Wang, Y. Ma, B. Cheng, W. Kang, X. Li, L. Shi, Z. Cai, and X. Zhang, Electrochim. Acta, 258, 24 (2017).
3. A. Pena-Francesc, H. Jung, M. A. Hickner, M. Tyagi, B. D. Allen, and M. C. Demirel, Chem. Mater., 30, 898 (2018).
4. S. Mondal, Y. Agam, and N. Amudursky, Small, 16, 2000526 (2020).
5. S. Mondal, Y. Agam, R. Nandi, and N. Amudursky, Chem. Sci. (Camb.), 11, 3547 (2020).
6. Y. Deng, E. Josberger, J. Jin, A. F. Rousdari, B. A. Helms, C. Zhong, M. P. Anantram, and M. Rolandi, Sci. Rep., 3, 2481 (2013).
7. D. D. Ordinario, L. Phan, Y. Van Dyke, T. Nguyen, A. G. Smith, M. Nguyen, N. M. Motif, M. K. Dao, and A. A. Gorodetsky, Chem. Mater., 28, 3703 (2016).
8. T. Sato, M. Tsukamoto, S. Yamamoto, M. Mitsuishi, T. Miyashita, S. Nagano, and J. Matsui, Langmuir, 33, 12897 (2017).
9. M. Tsukamoto, K. Ebata, H. Sakiyama, S. Yamamoto, M. Mitsuishi, T. Miyashita, and J. Matsui, Langmuir, 35, 3302 (2019).
10. R. Kautz, D. D. Ordinario, V. Tyagi, P. Patel, T. N. Nguyen, and A. A. Gorodetsky, Adv. Mater., 30, 1704917 (2018).
11. Y. Nagao, N. Naito, F. Iguchi, N. Sata, and H. Yugami, Solid State Ionics, 180, 589 (2009).
12. Q. Li, J. O. Jensen, R. F. Savinell, and N. J. Bjerrum, Prog. Polym. Sci., 34, 449 (2009).
13. C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, and A. B. Bocarsly, J. Power Sources, 103, 1 (2001).
14. T. L. Greaves and C. J. Drummond, Chem. Rev., 108, 206 (2008).
15. Y. Nagao, A. Haneda, N. Naito, F. Iguchi, N. Sata, and H. Yugami, Solid State Ionics, 179, 1142 (2008).
16. H. Huang, L. Nia, S. Xu, F. Luo, J. Fan, H. Li, and H. Wang, ACS Sustain. Chem. Eng., 9, 3963 (2021).
17. H. Wang, X. Li, X. Zhuang, B. Cheng, W. Wang, W. Kang, L. Shi, and H. Li, J. Power Sources, 340, 201 (2017).
18. S. C. Mehta, P. Somasundaran, C. Maldarelli, and R. Kulkarni, Langmuir, 22, 9566 (2006).
19. J. M. Pelto, S. P. Haimi, A. S. Sijilander, S. S. Miettinen, K. M. Tappura, M. J. Higgins, and G. G. Wallace, Langmuir, 29, 6099 (2013).
20. I. Sakurai and Y. Kawamara, Biochim. Biophys. Acta - Bioememb., 904, 405 (1987).
21. H. Morgan, D. Martin Taylor, and O. N. Oliveira, Biochim. Biophys. Acta - Biomembr., 1062, 149 (1991).
22. A. Polle and W. Junge, Biophys. J., 56, 27 (1989).
23. J. Teissier, M. Prat, P. Soucaille, and J. F. Tocanne, Proc. Natl. Acad. Sci. U.S.A., 82, 3217 (1985).
24. K. Leberle, I. Kempf, and G. Zundel, Biophys. J., 55, 637 (1989).
25. M. R. A. Blomberg and P. E. M. Siegbahn, Biochim. Biophys. Acta - Bioenerg., 1577, 969 (2006).
26. Y. Georgievski, E. S. Medvedev, and A. A. Stuchebrukhov, Biophys. J., 82, 2833 (2002).
27. N. Amudursky, Y. Lin, N. Aho, and G. Gruenhof, Proc. Natl. Acad. Sci. U.S.A., 116, 2443 (2019).
28. Y. Agam, R. Nandi, T. Bulava, and N. Amudursky, Mater. Adv., 2, 1739 (2021).
29. T. Hasegawa, Anal. Chem., 79, 4385 (2007).
30. T. Hasegawa, J. Phys. Chem. B, 106, 4112 (2002).
31. Y. Nagao and T. Kubo, Appl. Surf. Sci., 323, 19 (2014).
32. K. M. Hutchins, B. Soc. Open Sci., 5, 180564 (2018).
33. I. A. Heisler, K. Mazur, S. Yamaguchi, K. Tominaaga, and S. R. Meech, Phys. Chem. Chem. Phys., 13, 15573 (2011).
34. B. R. Francis, K. Watkins, and J. Kubekla, Life, 7, 35 (2017).
35. J. P. M. Lommerse, S. L. Price, and R. Taylor, J. Comput. Chem., 18, 757 (1997).
36. F. Bescuau, C. Laurence, and M. Bertholet, J. Chem. Soc., Perkin Trans. 2, 485 (1994).
37. A. S. Abreu, M. Oliveira, P. V. Rodrigues, I. Moura, G. Botelho, and A. V. Machado, J. Mater. Sci., 50, 2788 (2015).
38. Y. Yang, H. Li, Y. Zhang, H. Wang, L. Xu, and H. Zhao, Chem. Asian J., 12, 753 (2017).
39. S. Xiao, P. Xu, Q. Peng, J. Chen, J. Huang, F. Wang, and N. Noor, Polymers (Basel), 9, 735 (2017).
40. R. F. Hamilton, N. Wu, C. Xiang, M. Li, F. Yang, M. Wolfarth, D. W. Porter, and A. Holian, Part. Fibre Toxicol., 11, 43 (2014).
41. S. Yu, J. Liu, W. Zhu, Z. T. Hu, T. T. Lim, and X. Yan, Sci. Rep., 5, 16369 (2015).
42. K. Matsunaga, K. Tanaka, and J. Matsui, Chem. Lett., 47, 500 (2018).
43. S. Ouardani and F. Amrani, Macromol. Chem. Phys., 201, 2458 (2000).
44. C. Zhong, Y. Deng, A. F. Rousdari, A. Kapetanovic, M. P. Anantram, and M. Rolandi, Nat. Commun., 2, 476 (2011).
45. J. Schoonman, Solid State Ionics, 157, 319 (2003).
46. J. Maier, Solid State Ionics, 23, 59 (1987).
47. G. D. Wu, H. L. Zhou, Z. H. Fu, W. H. Li, J. W. Xiu, M. S. Yao, Q. H. Li, and G. Xu, Angew. Chem., Int. Ed., 60, 9931 (2021).