Gyroid-Nanostructured All-Solid Polymer Films Combining High H⁺ Conductivity with Low H₂ Permeability

Tsubasa Kobayashi, Ya-xin Li, Yuichiro Hirota, Asako Maekawa, Norikazu Nishiyama, Xiang-bing Zeng,* and Takahiro Ichikawa*

Gyroid-nanostructured all-solid polymer films with exceedingly high proton conductivity and low H₂ gas permeability have been created via crosslinking polymerization of mixtures of a zwitterionic amphiphilic monomer and a polymerizable imide-type acid that co-organize into bicontinuous cubic liquid-crystalline phases. The gyroid nanostructures are visualized by reconstructing a 3D electron map from the synchrotron X-ray diffraction patterns. These films exhibit high proton conductivity of the order of 10⁻¹⁵ S cm⁻¹ and extremely low H₂ gas permeability of the order of 10⁻¹⁵ mol m⁻² s⁻¹ Pa⁻¹. These properties can be ascribed to the presence of the ionic liquid-like layer along the gyroid minimal surface. Since these two characteristics are required for improving the performance of proton-exchange membrane fuel cells, the present membrane design represents a promising strategy for the development of advanced devices, pertinent to establishing sustainable energy sources.

1. Introduction

Polymer electrolytes are attracting increasing attention for the development of safe and efficient batteries[1] and fuel cells.[2] Depending on their application, the required properties of polymer electrolytes vary significantly. When intended for use in fuel cells, electrolytes should exhibit several important properties, including high proton conductivity, which decreases the power loss responsible for internal resistance, as well as low H₂/O₂ permeability to prevent cross-leakage of gas substrates, and high mechanical and long-term use stability.

To achieve high proton conductivity of the order of 10⁻¹⁵ S cm⁻¹, the construction of hydrogen-bonding networks between water molecules in polymer electrolytes is essential for enabling proton relay conduction based on the Grothuss mechanism.[3] On the other hand, to create polymer membranes with extremely low gas permeability, polymer design must encompass the following two crucial aspects:[4] the suppression of gas solubility into polymer membranes, and the minimization of free volume in polymer membranes to inhibit physical diffusion of gas molecules. To date, numerous approaches have been adopted for creating gas barrier materials.[5] Among them, the use of ionic liquids has emerged as one of the most promising strategies because ionic liquids show extremely low gas solubility of non-polar gases, such as H₂, O₂, and N₂.[6] This property results from their high viscosity, high material density, and high polarity. Exploiting these advantageous properties, ionic liquids have been utilized as gas barriers in several ionic-liquid-derived materials, such as polymerized ionic liquids,[7] ionic-liquid-gels,[8] and ionic liquid/inorganic hybrid materials.[9]

Over the past decade, we have developed an original material design strategy for creating proton-conductive materials based on the combination of amphiphilic zwitterions and acids.[10–13] An advantage of this system is the co-organization of two-component mixtures into liquid-crystalline (LC) nanosegregated structures, such as bicontinuous cubic (Cub̅₆) phases, depending on the molecular design and component ratios. Cub̅₆ phases are representative materials capable of spontaneous formation of nano-sized gyroid structures.[10,12–14] Recently, we succeeded in the development of a polymerizable zwitterionic amphiphilic molecule, Diene-GZI (Figure 1a), and a polymer membrane, Film-A, having a gyroid nanostructure,
via in-situ polymerization of a mixture of **Diene-GZI** and bis(trifluoromethanesulfonyl)imide (**HTf₂N**) (Figure 1b).[^13] Upon the uptake of ≈16 wt% of water, **Film-A** exhibits extremely high ionic conductivity of the order of 10⁻¹ Sc m⁻¹ with a low activation energy.[^13] We revealed that the gyroid-structured ionic layer acts as a platform that induces efficient proton conduction via the Grotthuss mechanism, by collecting absorbed water molecules exclusively onto its gyroid minimal surface.[^13] The gyroid-structured ionic layer exhibits 3D continuous cubic periodicity and ionic-liquid-like characteristics. Here, we envisage that the gyroid-structured ionic layer should also act as a multilayered gas barrier, especially for H₂ and O₂ gases. Assuming that a gas molecule penetrates the gyroid-nanostructured polymer film with a thickness of 100 µm, it is roughly calculated that it would cross the ionic layers ≈20,000 times. This is expected to force the gas molecules to travel longer distances to pass through the membrane. In the present study, we modified **HTf₂N** to a polymerizable acid, 4-styrenesulfonyl (trifluoromethylsulfonyl)imide (**HStyTf**) (Figure 1c),[^15] with the aim of avoiding acid leakage during gas permeability measurements and prepared an all-solid polymer film (**Film-B**) (Figure 1d). A schematic representation of the concept in this study is shown in Figure 1e.

**2. Results and Discussion**

**Diene-GZI** exhibits lyotropic LC behavior in the presence of water and acids, as previously reported by us.[^13] By adjusting the water content and selecting appropriate acid species, it is possible to induce **Diene-GZI** to form Cub₃ phases. For example, we reported that a mixture of **Diene-GZI**, **HTf₂N**, and water in a molar ratio of 1:0.5:14 forms a Cub₃ phase at room temperature.[^13] In addition to **HTf₂N**, it has been found that Cub₃ phases can be induced when using **HStyTf** (see the Supporting Information). As a representative polymerization experiment, a mixture of **Diene-GZI** and **HStyTf** in a molar ratio of 1:0.5, containing 1 wt% of 2,2-dimethoxy-2-phenylacetophenone (DMPA), was prepared by slow evaporation of a methanol/chloroform solution of the three components. After drying the mixture under vacuum, a requisite amount of water was added to the mixture to obtain a **Diene-GZI**:**HStyTf**:H₂O molar ratio of 1:0.5:14. The obtained mixture is henceforth referred to as **MX-B**. **MX-B** exhibited no birefringence under polarizing optical microscope (POM) observation, while two intense XRD peaks were observed for **MX-B** in the small-angle region (Figure S1, Supporting Information). The reciprocal d-spacing ratio of the two XRD peaks was $\sqrt{6} : \sqrt{8}$, which can be indexed as the (211) and (220) reflections of an Ia₃d-type Cub₃ phase with a cubic lattice length of 95.3 Å.

Polymerization of **MX-B** was performed under UV irradiation for 1 h at 30 °C, thereby converting the viscous LC material to an all-solid polymer material (**Film-B**) (Figure 2a). Polymerization progress was followed by IR measurements. A comparison of the IR spectra of the sample before and after UV irradiation indicated decreases in the peak intensities at 1597 and 1624 cm⁻¹ for the latter, corresponding to the vibrations of styrene and diene groups, respectively (Figure 2b). Preservation of the initial gyroid nanostructure was confirmed by POM observation and synchrotron XRD measurements (Figure 2c,d). It was found that **Film-B** maintained the gyroid nanostructure even at an elevated temperature of 150 °C. We reconstructed a 3D electron density map in **Film-B** by transforming the obtained XRD patterns to scattering electron density waves (Figure 2e). It can be seen that the high electron density region (purple) forms a 3D continuous layer along a gyroid minimal surface, while low electron density regions (green and red) form 3D interwoven nanochannels, which is similar to the result obtained for **Film-A**.[^13]

Considering the molecular structure of **Diene-GZI**, it is assumed that the high electron density layer is composed of the zwitterionic

[^13]: D. Y. S. and J. H., Macromol. Rapid Commun. 2021, 42, 2100115.
components, water and HStyTf, while the low electron density regions are composed of the long alkyl chains.

We then evaluated the characteristics and properties of Film-A and Film-B. Both films are self-standing polymer films with glass transition temperatures \( T_g \) of 25 and 27 °C, respectively, as determined by differential scanning calorimetry (DSC) measurements (Figure 3). The endothermic peaks at around \( T_g \) can be ascribed to enthalpy relaxation. The slight increase in \( T_g \) upon the substitution of HTf\(_2\)N by HStyTf can be explained by the polymerization progress of the StyTf anions. Both Film-A and Film-B maintained their film state morphology even after immersion in conventional organic solvents such as methanol and chloroform. Furthermore, extractions from Film-B were not detected by \(^1\)H NMR measurement even though we found that the monomer (HStyTf) and polymerized HStyTf (Poly-HStyTf) were soluble in these solvents (Figure S4, Supporting Information).\[^{15}\] There are two plausible explanations for this observation. The first is that co-polymerization of Diene-GZI and HStyTf proceeded upon UV irradiation. The other is that Poly-HStyTf is entangled with the polymerized Diene-GZI network, which prevents its release from the membrane. It should also be noted that both Film-A and Film-B were structurally stable against temperature changes and water uptake (Figures S2 and S3, Supporting Information).

To obtain further information regarding the molecular structure organization in the films, we investigated the differences in the electron density (ED) map of Film-A and Film-B. The high ED regions of Film-A and Film-B, which occupy 30% of the total unit cell volume enclosed by isoelectronic surfaces, are visualized in Figure 4a,b. The high ED region in Film-A appears as a 3D continuous layer that continues along a gyroid minimal surface (Figure 4a), as reported in our previous paper.\[^{13}\] As ED maps generally reflect material density, this 3D layer was identified as the ionic layer composed of the zwitterion components of Diene-GZI and HTf\(_2\)N. An important characteristic is that the thickness

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**Figure 2.** a) An image of Film-B. b) IR spectra of MX-B and Film-B at 30 °C. c) A POM texture of Film-B at 30 °C. d) X-ray diffraction patterns of Film-B at various temperatures. e) Reconstructed electron density maps of Film-B.

**Figure 3.** DSC thermograms of Film-A and Film-B upon heating at a rate of 10 K min\(^{-1}\).

**Figure 4.** High density regions (30% of total volume) of the reconstructed electron density maps of: a) Film-A and b) Film-B. Low density region (5% of total volume) of: c) Film-A and d) Film-B. Enlarged images of the three-way junctions are shown.
presence of suitable acids,[10,12] the present results suggest that considering the general fact that amphiphilic zwitterions prefer to do nothing in the layer is virtually uniform, which indicates that the Tf₂N anions are homogeneously dispersed in the 3D ionic layer because they can diffuse freely along the gyroid minimal surface with strong interactions with the pyridinium cation of the zwitterion components in the layer. On the other hand, the high ED region in Film-B is less uniform with an uneven thickness, which leads to the appearance of “holes” in the 3D continuous layer. Here, we should note that the holes would possibly not be observed if the visualized volume occupancy is set at higher values, such as 40% and 50%. That is, the 3D image shown in Figure 4b does not indicate the presence of holes in the 3D ionic layer, but rather the unevenness in the thickness of the ionic layer. This unevenness can be ascribed to the following two factors. The first is the slow diffusion of Poly-StyTf anions in the ionic layer. The other is the preferential positioning of the Poly-StyTf anions in the gyroid-structured ionic layer. Considering the result that the holes appear in the areas of the gyroid minimum surfaces closest to the junctions of the 3D networks, it is assumed that the Poly-StyTf anions prefer to be positioned furthest away from the junctions in the 3D ionic layer.

In order to further confirm our assumption, we also visualized the low ED regions occupying 5% of the total unit cell volume enclosed by isoelectronic surfaces (Figure 4c,d). The low ED regions appear as 3D branched nanochannels. It is assumed that these nanochannels indicate the locations of Diene-GZI alkyl chain termini. Comparing the 3D branched nanochannels of Film-A and Film-B, it was found that the nanochannels of Film-A presented relatively uniform diameters, while uneven diameters were observed for the nanochannels of Film-B. Consequently, the nanochannels of Film-A are sharply branched at the junctions, while those of Film-B presented webbed junctions. The presence of webs indicates that the interfacial curvature in the vertical regions of the junctions is smaller than in the other regions. Considering the general fact that amphiphilic zwitterions prefer to form a flat interface while they form a curved interface in the presence of suitable acids,[10,12] the present results suggest that the probability of finding Poly-StyTf anions is lower in the vertical regions of the junctions than in the other regions. This is consistent with the conclusion in the above paragraph.

Previously, it was reported that the creation of differential ED maps for ionic liquid crystals is a powerful strategy for obtaining insights regarding the positioning of ionic species in dynamic molecular assemblies.[16] In order to derive insights into the molecular arrangement in the gyroid nanostructures of Film-A and Film-B, we focused on the construction of a differential ED map of the two films (for details, see the Supporting Information). The generated 3D differential ED maps are shown in Figure 5a,b. Figure 5a depicts the high ED region of the differential ED map occupying 30% of the total unit cell volume, while Figure 5b shows the high-density region occupying 15% volume, as well as the differential low ED regions as red surfaces. Considering the fact that the only difference between Film-A and Film-B is the anion species, the high and low ED regions in the differential map can result either from the difference in the electron density of the two anions, or from the difference in the distribution of the two anions. This figure further supports our conclusion that the Poly-StyTf anions are inhomogeneously distributed in the gyroid-structured ionic layer.

H₂ gas permeabilities of Film-A and Film-B were examined by the sweep gas method. Polymer samples for the gas permeance experiments were prepared by generating composite plates consisting of a square-shaped porous alumina plate (1 cm × 1 cm, NGK Insulators, Ltd.) with an average pore size of 100 nm as a support and a thin film of the polymer sample deposited on the plate (Figure 6a). The thickness of each polymer sample was evaluated by cross-sectional observation with a scanning electron microscope (SEM) for the composite plates after Pt sputtering (Figure 6b). The experiments were also performed for an amorphous film (Film-AAn) control sample. The preparation method for Film-AAn is described in the Supporting Information. It should be noted that the composition of Film-AAn is the same as that of Film-A, while the presence/absence of nanostructures renders them distinct from one another.

A schematic representation of the gas permeance test apparatus is shown in Figure S10, Supporting Information. The permeated stream was analyzed by gas chromatography with a thermal conductivity detector (Shimadzu GC-8A). In the initial trial, we found that the thin films readily cracked as water evaporated from them during the experiments. To avoid cracking, we used a binary H₂/H₂O mixture. Consequently, we succeeded in obtaining the permeabilities of two types of gases, namely nonpolar (H₂) and polar (H₂O) gases.

Before discussing the gas permeabilities of H₂ and H₂O, we should note that, contrary to our concern that HTf₂N may leak...
cross-sectional SEM image of the composite plate. c) Time course of H2 permeability \([\text{mol m m}^{-2} \text{s}^{-1} \text{Pa}^{-1}]\) and H2O permeation performance of the membrane was evaluated based on the hard-soft acid-base principle. The permeation performance of the membrane was evaluated based on permeability \([\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}]\). Figures 6c and 6d illustrate the time course of H2 permeability of Film-A, Film-B, and Film-AAm. As different trends were found for the two gases, we will discuss each gas individually.

The H2 permeabilities of Film-A and Film-B were extremely low and time-independent (Figure 6c). For example, the average H2 permeability of Film-A was \(1.5 \times 10^{-15} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}\) and that of Film-B was \(2.1 \times 10^{-15} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}\). These values are comparable to those of Nafion and ionic liquids.[6,17] In general, when discussing the mechanism of gas permeation through polymer membranes, three possibilities should be considered, namely, Knudsen diffusion, molecular sieving, and solution-diffusion. Considering the extremely low H2 gas permeabilities of Film-A and Film-B, it is assumed that Knudsen diffusion can be ignored. Our rationale for this result is that there is a single large pore for H2 molecules to permeate through in the present polymer films. This feature may result from the dense packing of ionic LC monomers in LC states after cross-linking polymerization, which appreciably suppresses molecular diffusion. Therefore, it is expected that gas permeation through the films follows molecular sieving and solution-diffusion mechanisms. As Film-A and Film-B are composed of two continuous domains, namely a highly polar 3D gyroid-structured ionic layer and 3D interconnected hydrophobic nanochannels with low polarity, the following two possibilities could explain the low H2 gas permeabilities of these films. The first is that the gyroid-structured ionic layers may act as barriers that disturb H2 gas dissolution into the films, as expected. This idea is supported by the fact that polymerized ionic liquids exhibit negligible solubility of H2 gas.[18] Another explanation is based on the assumption that the pathway for H2 molecules is limited to the 3D interconnected hydrophobic nanochannels; in this case, H2 gas molecules would be forced to travel a considerably longer distance than the film thickness. These hypotheses can be appraised by comparing the H2 permeabilities of Film-A and Film-AAm. Film-A exhibited 1.7-fold lower H2 permeability than Film-AAm. Considering that the chemical composition of Film-AAm is identical to that of Film-A, the lower H2 permeability of Film-A is presumably attributed to the presence of the gyroid nanostructures. To date, gas permeation through LC polymers has been intensively investigated by Gin and co-workers.[19] They evaluated the gas permeabilities of polymer membranes obtained from lyotropic columnar and Cubic LC monomers, and the potential utilities of these nanostructured membranes for gas separation membranes have been explored.[19] Here we note that the conclusions in the present study are consistent with those obtained by Gin’s group.

Next, we focused on the H2O permeability of these films. It was found that H2O permeabilities were \(\approx 100\)-fold higher than those of H2 gas (Figure 6d). For example, the average H2O and H2 permeabilities of Film-A were \(1.1 \times 10^{-13}\) and \(1.5 \times 10^{-15}\) mol m m2 s−1 Pa−1, respectively. This difference between H2 and H2O permeabilities can be explained as follows. As the zwitterionic moieties in the films have the ability to strongly attract and bind water molecules, the permeation of H2O in the films is assumed to be governed primarily by the solution-diffusion mechanism. We will discuss the results of H2O permeability based on this assumption. Generally, gas permeability \((P)\) based on the solution-diffusion mechanism is proportional to the product of solubility \((S)\) and diffusivity \((D)\), as described by the following equation:

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P = S \times D
\]  

Film-B displayed a significantly lower H2O permeability than Film-A, being of the order of \(10^{-14}\) mol m m2 s−1 Pa−1. The difference in their H2O permeability can be rationalized by the difference in the \(D\) values between the films. It is expected that the molecular diffusion in Film-B is suppressed to a higher degree compared to that in Film-A because the StyTf anions are also polymerized. This expectation can be confirmed by the difference in \(T_{gs}\) for the two films obtained from the DSC results. In general, the polymerization of component ions in ionic liquids increases...
the $T_a$.\textsuperscript{[20]} Next, we compared the $\text{H}_2\text{O}$ permeabilities of Film-A and Film-$\text{AAm}$. Film-$\text{AAm}$ displayed an average $\text{H}_2\text{O}$ permeability of $1.3 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, which was comparable to, or slightly higher than that of Film-A. We attributed this to the difference in $\text{H}_2\text{O}$ solubility into the films. The higher $\text{H}_2\text{O}$ solubility of Film-$\text{AAm}$ can be confirmed by comparing the relationships between the water content and RH for the two films (see the Supporting Information). The presence/absence of nanostructures in the films is expected to influence the diffusivity of $\text{H}_2\text{O}$ in the films. However, as we have no means of directly evaluating the molecular alignment in Film-$\text{AAm}$, we currently cannot evaluate the effects thereof on diffusivity.

The relationship between the ionic conductivity ($\sigma$) and water content ($X$) for Film-A was reported in our previous study.\textsuperscript{[13]} An important finding was that the $\sigma$ values of Film-A drastically increase as the $X$ values increase, which can be explained by the shift in the dominant proton conduction mechanism from the vehicle to the Grotthuss mechanism, upon water uptake.\textsuperscript{[14]} In the present study, the $\sigma$-$X$ relationship for Film-B was examined. The $X$ values for Film-B were regulated by placing the film under controlled RH conditions for 24 h until equilibrium was reached. The $X$ values in the humidified films were estimated from the change in the weight of the film sample. Film-A and Film-B containing $X$ wt% of water are denoted as Film-A($X$) and Film-B($X$). The $X$ values under various RH conditions are summarized in Table S3, Supporting Information. Evidently for Film-B, the $X$ values increase as the RH values increase (Figure S14, Supporting Information), analogous to that observed for Film-A.\textsuperscript{[13]} By plotting the $\sigma$ values with respect to the RH values, we found that the $\sigma$ value of Film-B increases in proportion to the RH values (Figure 7a). For example, the $\sigma$ of Film-B is $6.2 \times 10^{-14}$ S cm$^{-1}$ at $X = 6.6$, reaching $6.5 \times 10^{-12}$ S cm$^{-1}$ at $X = 18.7$. Comparing the $\sigma$ values of Film-A($X$) and Film-B($X$), it can be seen that the maximum $\sigma$ value for Film-B is slightly lower than that of Film-A. This is due to the difference in acidity between H$\text{StyTf}$ ($pK_a = -7.49$) and H$\text{TF$_2$N}$ ($pK_a = -10.42$),\textsuperscript{[21]} and the distinction in the ion carrier species between the two films. In other words, while both the protons and TF$_2$N anions act as ion carriers in Film-A, protons are the sole active carriers in Film-B because the StyTf anions are strongly immobilized in the polymerized matrix. In addition to these two reasons, we will discuss another important reason in the last paragraph.

As a control sample, a mixture of unpolymerized Diene-G21-HT$_2$N in a molar ratio of 1:0.5 (MX-A) was also prepared to further examine the effects of polymerization on ionic conductivity. The water content $X$ in MX-A was controlled as before. Comparing the $\sigma$ values of Film-A($X$) and MX-A($X$), it can be seen that the polymerized sample displayed significantly higher $\sigma$ values than its unpolymerized counterpart. Numerous studies have reported that $\sigma$ values of ionic monomers decrease after polymerization,\textsuperscript{[20,22]} due to a decrease in molecular diffusion.\textsuperscript{[21]} The present result is distinct from the previous examples, suggesting that ion conduction in the present films is not dependent on molecular diffusion but rather on the Grotthuss mechanism. The reason for the increase in $\sigma$ values upon polymerization may be attributed to the average distance between neighboring sulfonic acid groups in the two materials. In Film-A, this distance remains largely unchanged after water absorption because of polymerization. Consequently, the situation whereby the sulfonic acid groups are densely aligned is maintained even with high water content. On the other hand, this distance in MX-A expands with an increase in the water content. Recently, Yamaguchi et al. reported the dense packing of acidic groups enhances proton conduction, and termed this the “packed acid mechanism”.\textsuperscript{[24]} This observation led us to conclude that the same or similar mechanism was operational in our materials.

In our previous study, the temperature dependence of $\sigma$ for humidified Film-A was measured under conditions where RH was not controlled. In the present study, we have revised the apparatus set-up by combining an RH/ temperature controller and impedance analyzer to measure the in-situ ionic conductivity under RH- and temperature-controlled conditions (Figure S13, Supporting Information). The temperature dependence of $\sigma$ under RH = 90% was investigated for Film-A and Film-B upon heating at a heating rate of 1 °C min$^{-1}$. The obtained results are illustrated as Arrhenius plots in Figure 7b. The $\sigma$ values of Film-A linearly increase with increasing temperature in the temperature range from ≈30–70 °C. On the other hand, those of Film-B increase up to ≈50 °C and then gradually decrease in the higher temperature range. For example, the $\sigma$ of Film-B at 50 °C was $1.1 \times 10^{-11}$ S cm$^{-1}$, decreasing to $8.5 \times 10^{-12}$ S cm$^{-1}$

![Figure 7](image-url)
at 70 °C. The decrease in \(\sigma\) results from the evaporation of water from Film-B upon heating. A decreasing trend was not found for Film-A in the current temperature range. A plausible explanation is that Film-A has a stronger hydration ability than Film-B, which prevents the absorbed water from evaporating even at high temperatures. We then examined the slopes of the Arrhenius plots to determine the proton conduction activation energies \(E_a\) of these films. Based on the slopes of the Arrhenius plots from 30 to 50 °C, the \(E_a\) values for Film-A and Film-B were calculated to be 12.4 and 20.3 kJ mol\(^{-1}\), respectively. These values are comparable to those of Nafion under conditions wherein the water content of Nafion is sufficient to induce the Grotthuss mechanism of proton conduction.\(^{[25]}\) These results indicate that the water molecules in Film-A and Film-B are placed in a suitable arrangement for inducing Grotthuss-mechanism-dominant proton conduction. It is noteworthy that the \(E_a\) for Film-A is distinctly lower than that of Film-B. A plausible explanation for this difference is that Film-A provides a proton conduction pathway with a highly homogeneous proton potential, while Film-B presents a slightly uneven potential. This idea is supported by the differences in the ED maps of the two films (Figures 4 and 5). This significant finding suggests that the construction of a well-designed situation wherein the potential for protons is highly homogeneous is an effective approach for realizing highly proton-conductive membranes.

In the present study, we have succeeded in evaluating the gyroid nanostructured polymer films from the viewpoints of proton conductivity and gas permeability. In order to evaluate the potential utility of these films as polymer electrolytes for fuel cells, examinations of their physicochemical properties, such as electrochemical stability, mechanical stability, and thermal stability, are required although these examinations have not been achieved due to the limitation of the amount of samples. We are now exploring ways for performing these examinations with a small amount of samples.

3. Conclusion
We have successfully created a gyroid-nanostructured all-solid polymer film with exceedingly high proton conductivity and low \(\text{H}_2\) gas permeability via crosslinking polymerization of a zwitterionic amphiphilic monomer and a polymerizable imide-type acid. It was revealed that the proton conductivity and \(\text{H}_2\) gas barrier ability were enhanced by the presence of the gyroid nanostructure in the membrane. By comparing the structure and properties of two types of gyroid-nanostructured films, we concluded that homogeneity in the proton conduction pathway is crucial for creating advanced proton-conductive materials. This conclusion was made possible by the unique technique of creating a 3D differential electron density map from synchrotron XRD results. The material design presented herein exemplifies the importance of controlling the molecular orientation in polymer materials for achieving advanced functions and properties.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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bicontinuous cubic phases, gyroids, liquid crystals, polymer electrolytes, proton conduction

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.
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