

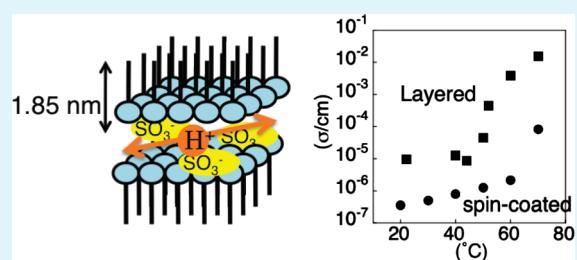
# Layered Ultrathin Proton Conductive Film Based on Polymer Nanosheet Assembly

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 Supporting Information

**ABSTRACT:** As described in this paper, a layered ultrathin proton conductive film was prepared using a poly(*N*-dodecylacrylamide-*co*-2-acrylamido-2-methylpropanesulfonic acid) (p(DDA/AMPS)) polymer nanosheet. The surface pressure–area isotherm revealed that p(DDA/AMPS) formed a stable monolayer at the air–water interface. The polymer monolayer was transferred onto a solid substrate using the Langmuir–Blodgett technique. X-ray diffraction measurements of a 30-layer film of p(DDA/AMPS) showed clear Kiessig fringes and one Bragg peak, which indicate that the multilayer film took a uniform layered structure. The monolayer thickness was determined as 1.85 nm from the Bragg peak. The proton conductivity of p(DDA/AMPS) polymer nanosheet through the layer plane direction was studied with changing temperature and relative humidity. The proton conductivity of the multilayer film was on the order of  $1 \times 10^{-5}$  S/cm at 100% RH with 20 °C and increased to  $1 \times 10^{-2}$  S/cm at 70 °C. The proton conductivity of the multilayer film showed a more than 10 times higher value than that of the spin-coated film because of the formation of a uniform and consecutive hydrophilic nanochannel through the hydrophilic region in the multilayer film.



**KEYWORDS:** proton conductive membrane, polymer nanosheet, Langmuir–Blodgett technique, ultrathin film, nanoionics, multilayer film

## ■ INTRODUCTION

Recently, fuel cells have attracted much attention for future energy devices because of their high conversion efficiency and environmental friendliness.<sup>1–3</sup> Among the fuel cells of several kinds, polymer electrolyte fuel cells (PEFCs), which use proton conductive polymer electrolyte membranes (PEMs) as electrolytes, have been an active area of research because of their wide application in vehicles, portable electric devices, and others using its lightweight and thin structure.<sup>4,5</sup> Present PEFCs typically use perfluorosulfonated polymers such as Nafion, Flemion, Aciplex, and Dow membranes as PEMs. Recently, several groups have reported ultrathin PEMs produced by layer-by-layer (LbL) deposition of a polyanion/polycation couple.<sup>6–9</sup> Application of such ultrathin films for PEMs is interesting not only for technological applications but also for studying proton conductivity in a nanoscale-confined area, which is called “nanoionics”.<sup>10–13</sup> Protons are well known to move through hydrophilic nanochannels in PEMs.<sup>14</sup> Therefore, for proton nanoionics research, a uniform and consecutive hydrophilic nanochannel is necessary.

We have reported that *N*-dodecylacrylamide (DDA) polymer forms a highly oriented polymer monolayer at the air–water interface. The polymer forms a densely packed and stable polymer monolayer (polymer nanosheet) because of the two-dimensional hydrogen-bonding network that exists between amide groups. The polymer monolayer can be deposited onto a solid substrate using the Langmuir–Blodgett (LB) technique to produce a polymer nanosheet multilayer film. The polymer

nanosheet multilayer film forms a layered structure with 1.74 nm periodicity composed of hydrophilic amide and hydrophobic alkyl side chain regions in each layer.<sup>15</sup> The structure is suitable for studying proton nanoionics using the hydrophilic region as a proton conductive nanochannel. In this report, a proton conductive molecule, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was copolymerized with DDA to prepare a proton conductive polymer nanosheet. The monolayer property of the polymer was studied using a surface pressure ( $\pi$ )–area (A) isotherm. The polymer monolayer was transferred onto a solid substrate and characterized with UV–vis absorption spectroscopy and X-ray diffraction (XRD) measurements. The proton conductivity of the transferred film was studied using impedance spectroscopy.

## ■ EXPERIMENTAL SECTION

Poly(*N*-dodecylacrylamido-*co*-2-acrylamido-2-methylpropanesulfonic acid), p(DDA/AMPS) (Figure 1), was prepared through free radical copolymerization of DDA with AMPS in THF/H<sub>2</sub>O mixture solvent at 60 °C using 2,2'-azobis(isobutyronitrile) (AIBN) as a thermal initiator. The mole fraction of AMPS in the copolymer was determined through elemental analysis using the atomic content of sulfur (2.06%). The AMPS content was

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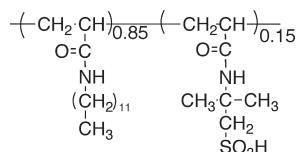


Figure 1. Chemical structure of p(DDA/AMPS).

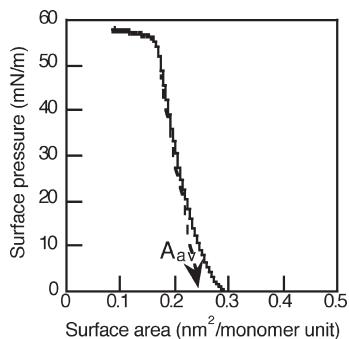


Figure 2.  $\pi$ –A isotherm of p(DDA/AMPS) at 15 °C. The straight arrow indicates the line extrapolated to determine the limiting surface area.

determined as 15 mol %.  $\pi$ –A isotherm measurement and the deposition of p(DDA/AMPS) monolayer were conducted using a computer-controlled Langmuir trough (FSD-50 and 51; USI Systems Inc.). Hydrophobic silicon, quartz, and glass substrates were used as a deposition substrate. Interdigitated array (IDA) electrodes were fabricated using thermal deposition of Au (50 nm) with a metal mask onto the glass substrate. The IDA electrode has two sets of comb-type Au arrays. Each array has eight electrode elements that are 0.5 mm wide and 8.0 mm long and separated by 0.2 mm from adjacent elements. The polymer monolayer was transferred onto substrates using a vertical deposition method at a dipping speed of 10 mm/min under surface pressure of 45 mN/m at 15 °C. Impedance measurements of the polymer were conducted using impedance analyzers (LCR HiTESTER 3522; Hioki E.E. Corp., or 1260 Impedance/Gain-Phase Analyzer with a 1296 Dielectric Interface system; Solartron Analytical). An atmosphere of saturated humidity was generated using a closed glass vessel containing water at the bottom that was not in contact with the sample (see Figure S1 in the Supporting Information for details of the measurement apparatus). Humidity between 70% and 95% at 25 °C was created with a temperature-controlled climate chamber (LHU-113; Espec Corp.). The surface morphology of the polymer film was measured using atomic force microscopy (AFM) (SPA-400; SII NanoTechnology Inc.). XRD measurements were conducted (D8 Advance; Bruker AXS K.K.) with CuKa (0.154 nm) as a target.

## RESULTS AND DISCUSSION

The FT–IR spectrum of p(DDA/AMPS) shows peaks related to AMPS groups at  $1042\text{ cm}^{-1}$  and around  $1200\text{ cm}^{-1}$  (broad), which is assigned to  $\text{S}=\text{O}$  and hydrated sulfonic acid and DDA at  $1642\text{ cm}^{-1}$  (Amide I),  $1550\text{ cm}^{-1}$  (Amide II), and at the region of  $2800\text{--}3500\text{ cm}^{-1}$  (C–H and N–H) (see Figure S2 in the Supporting Information).<sup>16</sup> The number average molecular weight ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) of p(DDA/AMPS) were determined respectively as 4000 and 1.5 using a polystyrene standard. It should be mentioned that accurate measurements of

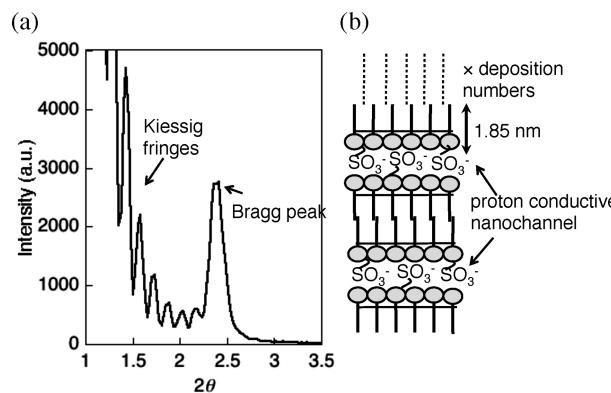
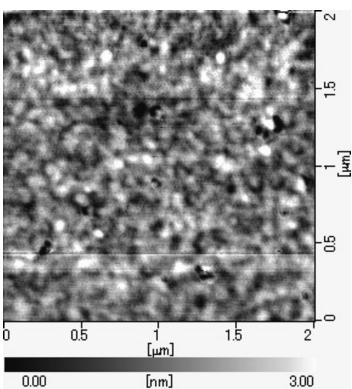


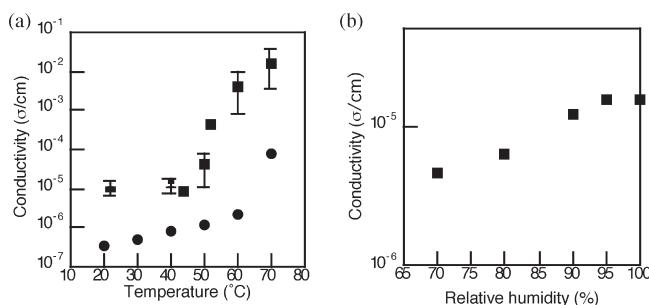
Figure 3. (a) XRD pattern for 30-layer p(DDA/AMPS) polymer nanosheet multilayer film on a silicon substrate. (b) Schematic illustration of the film structure.

$M_n$  is difficult because of the polyelectrolyte effect.<sup>17</sup> The onset temperature of decomposition was about 270 °C in the  $\text{N}_2$  atmosphere (see Figure S3 in the Supporting Information). p(DDA/AMPS) was spread on a water surface from a chloroform solution to measure the  $\pi$ –A isotherm at 15 °C. The isotherm showed a steep rise in surface pressure with decreasing surface area, which indicates a stable and highly oriented monolayer formation at the air–water interface (Figure 2). The average limiting surface area ( $A_{av}$ ) is estimated by extrapolating the linear portion of the condensed state in the  $\pi$ –A isotherm to 0 surface pressure. From the average limiting surface area, the surface occupied by the AMPS unit is calculated as  $0\text{ nm}^2/\text{molecule}$ ,<sup>18</sup> which indicates that the AMPS unit located below the water surface.

The copolymer monolayer can be transferred onto a solid substrate using the LB technique, yielding a stable polymer nanosheet. The transfer ratios were  $1.0 \pm 0.1$  in both the downward and upward strokes, creating a Y-type LB film layer structure. Deposition of the monolayer was monitored by an optical absorption spectrum of the deposited film (see Figure S3 in the Supporting Information). The copolymer monolayer showed a broad absorption around 192 nm related to amide bond in the side chains of the polymer. The absorbance increased linearly with an increasing number of deposition layers, indicating that regular deposition of the monolayer was conducted. The XRD pattern of a 30-layer p(DDA/AMPS) film has Kiessig fringes caused by interface reflection and one Bragg peak caused by periodic bilayers, as shown in Figure 3a. The monolayer thickness, as determined from the Bragg peak, is 1.85 nm, which is slightly larger than that of the monolayer thickness of p(DDA) nanosheet (1.74 nm).<sup>15</sup> The XRD spectrum of the multilayer film showed no peak at higher angle ( $5\text{--}20^\circ$ ), which indicates that the p(DDA/AMPS) has no regularity in the layer plane (see Figure S5 in the Supporting Information). The  $\pi$ –A isotherm, UV–vis spectra, and XRD results indicate that p(DDA/AMPS) forms a uniform and highly oriented structure. The observation of Kiessig fringes in the XRD spectrum also supports the uniform and flat film formation.<sup>19,20</sup> The dodecyl side chains orient almost perpendicularly to the layer plane similar to p(DDA) polymer nanosheet.<sup>15</sup> The AMPS units located in the hydrophilic head-to-head region in the layer plane caused by the fact of the increase of the monolayer thickness (Figure 3b). The two-layer p(DDA/AMPS) nanosheet surface morphology was observed using AFM. The AFM image showed a uniform surface with  $\text{RMS} = 0.65\text{ nm}$  (Figure 4, Figure S6 in the Supporting Information).



**Figure 4.** AFM image of two-layer p(DDA/AMPS) polymer nanosheet on a silicon substrate.



**Figure 5.** (a) Proton conductivity of p(DDA/AMPS) polymer nanosheet multilayer film (square) and spin-coated film (circle) measured at different temperatures. (b) Proton conductivity of p(DDA/AMPS) polymer nanosheet multilayer film with different RH at 25 °C. The error limit in each measurement was 10%.

The proton conductivity of p(DDA/AMPS) polymer nanosheet through the layer plane direction was measured using IDA gold electrodes. Thirty layers of p(DDA/AMPS) were deposited onto the electrode for a polymer nanosheet multilayer film sample. Spin-coated film of p(DDA/AMPS) was prepared onto the electrode using 1 wt % toluene solution at a spin speed of 500 rpm. The spin-coated film thickness was determined to be  $130 \text{ nm} \pm 10 \text{ nm}$  using surface profiler (decktack 3ST). The film resistance was given directly by the intersection of a semicircle with the real axis in the complex plane of impedance plots (Cole–Cole plots). The proton conductivity ( $\sigma$ ) of the samples was calculated as

$$\sigma = \text{const}/(Rd)$$

where  $\text{const} = 1.47 \times 10^{-3}$ , which is related to the shape of the IDA electrode,  $R$  represents the resistance, and  $d$  denotes the film thickness ( $55.5 \times 10^{-7} \text{ cm}$  for polymer nanosheet multilayer and  $120 \times 10^{-7} \text{ cm}$  for spin-coated film). Figure 5a shows the proton conductivities of p(DDA/AMPS) polymer nanosheet multilayer film and spin-coated film at 100% RH with different temperature. The p(DDA/AMPS) polymer nanosheet multilayer showed conductivity of  $10^{-5} \text{ S/cm}$  at room temperature and increased to  $1 \times 10^{-2} \text{ S/cm}$  at 70 °C. A dramatic increase of the conductivity around 55–70 °C might result from the increase of microscale movement of the polymer side chains. The glass transition temperature of p(DDA/AMPS) was measured as ca. 63 °C. We have reported that local movement of side chains in polymer nanosheets starts at a temperature lower than the  $T_g$ .<sup>21</sup> It should be described

that the layer structure of the p(DDA/AMPS) polymer nanosheet multilayer film was retained, even when the temperature was increased to 70 °C and set in this condition about 2 h, although the monolayer thickness was decreased to 1.55 nm/monolayer (see Figure S7 in the Supporting Information). The slight decrease in the monolayer film thickness shows that the side chains were tilted because of the microscale movement. The proton conductivity of the polymer nanosheet multilayer film shows a more than 10 times higher value than that of the spin-coated film in the measurement temperature condition. The higher proton conductivity in the polymer nanosheet is explainable by the difference in a proton conductive channel structure. In the polymer nanosheet multilayer film, the AMPS units locate at the layered hydrophilic region, which acts as a uniform proton conductive nanochannel. However, the AMPS units were distributed randomly in the spin-coated film, which results in a discontinuous proton conductive channel. The uniform and continuous nanochannel in the polymer nanosheet assembly is the reason for the high proton conductivity. The activation energy of p(DDA/AMPS) nanosheet assembly below the transition was estimated as 29 kJ/mol, which is smaller than that of the spin-coated film (36 kJ/mol). Figure 5b shows the effects of humidity to the proton conductivity of the polymer nanosheet multilayer film. The conductivity of 100% RH is three times higher than that in 70% RH, which indicates that water molecules adsorbed in the hydrophilic region to support the proton conduction in the nanochannel.

In conclusion, an ultrathin-layered proton conductive membrane was prepared using a p(DDA/AMPS) polymer nanosheet. The p(DDA/AMPS) forms a stable polymer nanosheet at the air–water interface. The polymer nanosheet can be transferred onto a solid substrate to form a multilayer film with thickness of 1.85 nm/monolayer. The polymer nanosheet multilayer film shows more than 10 times higher proton conductivity than that of the spin-coated film because of a uniform proton conduction nanochannel at the hydrophilic region. Because the  $T_g$  of p(DDA/AMPS) was ca. 63 °C, the uniform conduction channel will be disrupted in the prolonged time setting in the sample above the  $T_g$ . The stability will be increased by cross-linking each layer with a photochemical or thermal reaction.<sup>22</sup> Combination of p(DDA/AMPS) with a cationic polymer nanosheet<sup>23</sup> is in progress to prepare a heterogeneous nanointerface. Measurement of the proton conductivity of the polymer nanosheet multilayer film through the deposition direction is also in progress.

## ASSOCIATED CONTENT

**S Supporting Information.** FT–IR spectrum of p(DDA/AMPS), UV–vis spectra of the polymer nanosheet with different numbers of layers, AFM images of two polymer nanosheet layers, and XRD spectra of the polymer nanosheet multilayer film after conductivity measurements (PDF). This material is available free of charge via the internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) O'Hayre, R.; Cha, S.-K.; Colella, W.; Prinz, B. F. *Fuel Cell Fundamentals*; John Wiley & Sons: New York, 2009.
- (2) Norby, T. *Nature* **2001**, *410*, 877–878.
- (3) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345–352.
- (4) Larminie, J.; Dicks, A. In *Fuel Cell Systems Explained*; Larminie, J., Dicks, A., Eds.; John Wiley & Sons: West Sussex, U.K., 2003; pp 67–120.
- (5) Barbir, F. *PEM Fuel Cells: Theory and Practice*; Academic Press: New York, 2005.
- (6) Deligoz, H.; Yilmazturk, S.; Yilmazoglu, M.; Damyan, H. *J. Membr. Sci.* **2010**, *351*, 131–140.
- (7) Tago, T.; Shibata, H.; Nishide, H. *Chem. Commun.* **2007**, 2989–2991.
- (8) Ashcraft, J. N.; Argun, A. A.; Hammond, P. T. *J. Mater. Chem.* **2010**, *20*, 6250–6257.
- (9) Daiko, Y.; Katagiri, K.; Yazawa, T.; Matsuda, A. *Solid State Ionics* **2010**, *181*, 197–200.
- (10) Daiko, Y.; Katagiri, K.; Matsuda, A. *Chem. Mater.* **2008**, *20*, 6405–6409.
- (11) Maier, J. *Nat. Mater.* **2005**, *4*, 805–815.
- (12) Kim, S.; Yamaguchi, S.; Elliott, J. A. *MRS Bull.* **2009**, *34*, 900–906.
- (13) Maier, J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3011–3022.
- (14) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535–4586.
- (15) Mitsuishi, M.; Matsui, J.; Miyashita, T. *Polym. J.* **2006**, *38*, 877–896.
- (16) Sliverstein, R. M.; Webster, X. F.; Kiemle, D. *Spectrometric Identification of Organic Compounds*; 7th ed.; John Wiley & Sons: New York, 2005.
- (17) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587–4612.
- (18) The limiting area for AMPS ( $A_{\text{AMPS}}$ ) in the copolymer monolayer was calculated using the limiting area of the copolymer ( $A_{\text{av}}$ ) and DDA homopolymer ( $A_{\text{DDA}} = 0.28 \text{ nm}^2/\text{molecule}$ ) and also using the mole fractions of DDA (0.85) and AMPS (0.15) in the copolymers under the assumption of the additivity of molecules according to the equation presented below.

$$A_{\text{av}} = 0.85A_{\text{DDA}} + 0.15A_{\text{AMPS}}.$$

- (19) Decher, G.; Lvov, Y.; Schmitt, J. *Thin Solid Films* **1994**, *244*, 772–777.
- (20) Linford, M. R.; Auch, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 178–182.
- (21) Matsui, J.; Mitsuishi, M.; Miyashita, T. *Colloids Surf, A* **2002**, 703–707.
- (22) Matsui, J.; Kubota, K.; Kado, Y.; Miyashita, T. *Polym. J.* **2007**, *39*, 41–47.
- (23) Tanaka, H.; Mitsuishi, M.; Miyashita, T. *Langmuir* **2003**, *19*, 3103–3105.