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Description	

Synthesis of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] and anomalous proton conductivities of the thin films

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Abstract

New proton-conductive polyamide oligomers, oligomeric poly[(1,2-propanediamine)-*alt*-(oxalic acid)], were synthesized to investigate the proton transport properties of bulk and thin films. The obtained oligomers were characterized by the X-ray diffraction, FT-IR spectra, ^{1}H NMR, Matrix Assisted Laser Desorption / Ionization Time of Flight (MALDI-TOF) mass spectrum, and electrical conductivity measurements. The bulk proton conductivity is 3.0×10^{-4} S cm^{-1} at the relative humidity (RH) of 80 %. The proton conductivity of thin film is relatively higher than that of bulk sample. Thickness dependence of the proton conductivity was observed in these thin films. The maximum proton conductivity of the thin film is 4.0×10^{-3} S cm^{-1} at the relative humidity (RH) of 80 %, which is higher one order magnitude than that of the bulk sample. The activation energies of bulk and 200 nm thick film are 1.0 and 0.69 eV at the RH of 60 %, respectively.

Keywords: proton conduction, thin films, thickness dependence

1. Introduction

Since Liang had reported approximately 50 times enhancement in Li^+ ion conduction at room temperature simply by dispersing ultrafine particles of inert Al_2O_3 in LiI [1], a large number of two-phase composite systems have been investigated with the conductivity enhancement of one to three orders of magnitude [2, 3]. This high ionic conductivity makes these materials good candidates for solid-state electrolytes in the devices such as fuel cell, solid-state battery, sensor, etc. In the most cases, the second phase consists of a nonconducting material such as SiO_2 or Al_2O_3 which is nearly insoluble in the host material. The conductivity enhancement in the 2-D system has been also reported [4-15]. These anomalies are supposed to be attributed to interfacial effects like structural effects and/or effects of a space charge region. The interfacial effects for the proton conduction in the 2-D system also attract considerable attention. But the enhancement of the proton conductivity has not been clearly reported in the thin films of the organic proton conductors. We have investigated a series of the proton-conductive oligomers containing amide groups. In this paper, we synthesized new proton-conductive polyamide oligomers, oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)], and investigated the proton transport properties of the bulk and thin films to study the enhancement of the proton conductivities.

2. Experimental

Oxalic acid dihydrate and 1, 2-propanediamine (Wako Pure Chemical Industries, Ltd.) of reagent grade were used as received. A solution of 1, 2-propanediamine in methanol was added to a solution of oxalic acid dihydrate in methanol with stirring at 30 ^{o}C. The obtained ammonium salt was dissolved with water, and oxalic acid dihydrate was added for the preparation of the oligomeric polyamides with the carboxyl end groups. An adhesive sample was obtained after heating for ~6 hours.

The quality of the sample was checked by the X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectrum, ^{1}H NMR, and Matrix Assisted Laser Desorption / Ionization Time of Flight (MALDI-TOF) mass spectrum measurements. X-ray diffraction analysis was performed with CuKα radiation using a PANalytical X'Pert PRO MPD. For the FT-IR absorption measurement, the sample was diluted with KBr and the mixture was pressed into a pellet. The FT-IR spectrum was measured with a PerkinElmer Spectrum GX in the frequency range of 400 – 4000 cm^{-1}. The ^{1}H NMR spectrum in DMSO-*d*6, using TMS as internal reference, was obtained on a ECA-600 (JEOL) operated at 14 T. The MALDI-TOF mass spectrum was recorded in linear mode, using a SHIMADZU AXIMA-CFR Plus mass spectrometer, equipped with a nitrogen laser (λ = 337 nm), working in a positive ion mode. The average degree of polymerization was determined by a Kratos Analytical Ltd. Kompact program.

The thin films were synthesized by using a Active ACT-200 Spincoater on SiO_2 glass substrates. The thickness of the thin films was determined by using a KLA-Tencor P-10 contact stylus profiler. The obtained thin films are flat, and their thicknesses are 60, 80, 200, and 400 nm, respectively.

Impedance measurements of the bulk and thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] were carried out in the relative humidity (RH) range of 50 – 80 % at 298 K with a Solartron 1260 Impedance/Gain-Phase analyzer and a 1296 Dielectric Interface system. The RH and temperature were controlled with an Espec Corp. SH-221 humidity- and temperature-controlled chamber. In the case of the impedance measurements of the bulk sample, the sample was processed into pellets of 2.5 mmϕ under pressure of ~1GPa and porous gold paint (Tokuriki Chemical Research, SILBEST No. 8560) was used as electrodes. The activation energy was studied in the temperature range of 298 -323 K. In the case of the impedance measurements of the thin films, the electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. The conductivity of the SiO_2 substrate is negligible because its resistance is at least two orders of magnitude higher than that of the film over the film thickness range of 60 – 400 nm.

3. Results and Discussion

3.1 CHARACTERIZATION

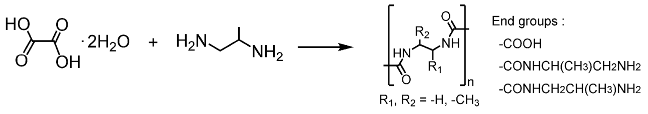
Figure 1 shows the X-ray diffraction patterns of the ammonium salt (before heating) and synthesized sample (after heating). The diffraction pattern derived from the crystal structure of the ammonium salt was disappeared after heating. The synthesized sample was found to be amorphous.

Figure 2 shows the FT-IR spectra of the ammonium salt (before heating) and synthesized sample (after heating). The intense and broad bands at 1680 and 1525 cm^{-1} in the spectrum of the synthesized sample can be assigned as the CO and NH bonds of the amide groups. The synthesized amides was found to be polymerized by the reaction of oxalic acid and 1, 2-propanediamine.

Figure 3 shows the ^1H NMR spectrum of the synthesized amides in DMSO-*d*6. According to the spectrum, it is suggested that the degree of polymerization is low because the width of the peaks is narrow. The spectrum of the oligomeric amides shows peaks at δ 2.87 – 4.03 ppm corresponding to the methylene and methine protons ($-CH_2-CH-$) and shows peaks at δ 1.05 –

1.26 ppm corresponding to the methyl protons (-CH_3). The peaks at δ 8.31 – 8.97 ppm are due to the amide protons and amine protons at the end groups. Since many peaks derived from the methyl, methylene, methine, amide, or amine protons were observed, the synthesized amides were found to be mixture of the amides with the different end groups and molecular weights.

From the MALDI-TOF mass spectrum, the peak ($m / z = 391.3$ (H^+) and 413.3 (Na^+)) due to the low-molecular-weight amides (n = 1) with the carboxyl end groups were observed. It is also suggested that the end groups of some amides are –NH_2 and –COOH, and the average degree of the polymerization is ~5. The peak ($m / z = 151.1$ (Na^+) and 279.3 (Na^+)) due to the macrocyclic amides (n = 1, 2) were also observed. So the synthesized amides are found to be the mixture of the oligomers with the different end groups and low-molecular-weights including the macrocyclic amides as shown in below.



3.2 PROTON TRANSPORT PROPERTIES OF THE BULK AND THIN FILMS

In general, the amide groups exhibit the proton exchange property because of the amide/imidic acid tautomerism. Since the obtained oligomers was found to be acidic, the oligomers could exhibit the proton transport properties. The typical complex impedance plots of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] at the RHs of 60 and 70 % are shown in Figure 4. A resistance is directly given by the intersection of a depressed semicircle with the real axis. The obtained electrical conductivities at the RHs of 60 and 70 % are found to be 1.4×10^{-6} and 5.2×10^{-5} S cm^{-1}, respectively. The electrical conductivities of the polyamide oligomers strongly depend on the RH. Such a large dependence of the electrical conductivity on the RH could arise from the proton conduction paths developed by the water uptake. The activation energy for the proton conduction of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] is 1.0 eV at the RH of 60 % in the temperature range of 298 – 323 K. This value is high because the oligomeric polyamides do not contain enough water molecules for the proton conduction at the RH of 60 %.

Figure 5 shows the RH dependence of the proton conductivity (σ) for oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] and their thin films. In the proton conduction of the bulk sample, the proton conductivity increases by four orders of magnitude with increasing the RH from 50 to 80 %. The proton conductivity of the bulk sample is 3.0×10^{-4} S cm^{-1} at the RH of 80 %. However the proton conductivity of the thin film also depends on the RH, the proton conductivity of the thin film exhibits different value from that of the bulk sample. The proton conductivity of the 200 nm thick film is found to be 4.0×10^{-3} S cm^{-1} at the RH of 80 %. This value is found to be one order of magnitude higher than that of the bulk sample of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)], however this value is one order of magnitude lower than that of Nafion 117 membrane at the RH of 80 % [16]. The proton conductivity of the 400 nm thick film exhibits relatively higher value than that of the bulk sample. Its conductivity is not the same value of the 200 nm thick film at the same RH. However the proton conductivities of the 60 and 80 nm thick films are lower than those of the 200 and 400 nm thick films, their conductivities are about three times higher than that of the bulk sample. In many kinds of the inorganic ionic conductors, some theoretical models including the space charge models for understanding the enhancement phenomena of the ionic conductivities have been discussed [3]. But the study on the proton conductivity enhancement of the organic thin films is still unexplored. Comparing the activation energy between bulk sample and thin film, the activation energies of bulk and 200 nm thick film are 1.0 and 0.69 eV at the RH of 60 %, respectively. The activation energy of 200 nm thick film exhibits lower value than that of bulk sample. These results could be originated from the structural effects like a molecular orientation by the synthesis of the thin film on the substrate rather than the interface effects like the space charge models in this system. We have not yet estimated the quantitative contribution of space charge region at the interface. Further investigation is required to understand this phenomenon.

4. Conclusions

New proton-conductive polyamide oligomers, poly[(1,2-propanediamine)-*alt*-(oxalic acid)], were synthesized to investigate the proton transport properties of bulk and thin films. The proton conductivity of the bulk sample is 3.0×10^{-4} S cm^{-1} under the RH of 80 % and 298 K. The maximum proton conductivity of the thin film is 4.0×10^{-3} S cm^{-1} at the RH of 80 %, which is higher one order magnitude than that of the bulk sample. Thickness dependence of the proton conductivity was observed in these thin films. The activation energies of bulk and 200 nm thick film are 1.0 and 0.69 eV at the RH of 60 %, respectively. These results could be originated from the structural effects like a molecular orientation by the synthesis of the thin film on the substrate rather than the interface effects like the space charge models in this system. Further investigation is needed to understand this phenomenon.

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Figure Captions

Fig. 1: X-day diffraction patterns of the ammonium salt (Before heating) and oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] (After heating).

Fig. 2: IR spectra of the ammonium salt and oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)].

Fig. 3: ^{1}H NMR spectrum of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] in DMSO-*d*6.

Fig. 4: Impedance plots of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] at the RHs of 60 and 70 %.

Fig. 5: RH dependence of the proton conductivity with bulk and thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)].

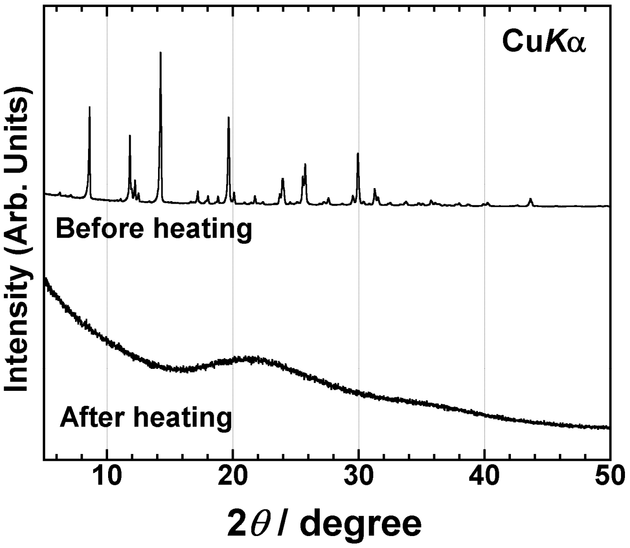
CuKα
Before heating
After heating
Intensity (Arb. Units)
10
20
30
40
50
2θ / degree

Fig. 1

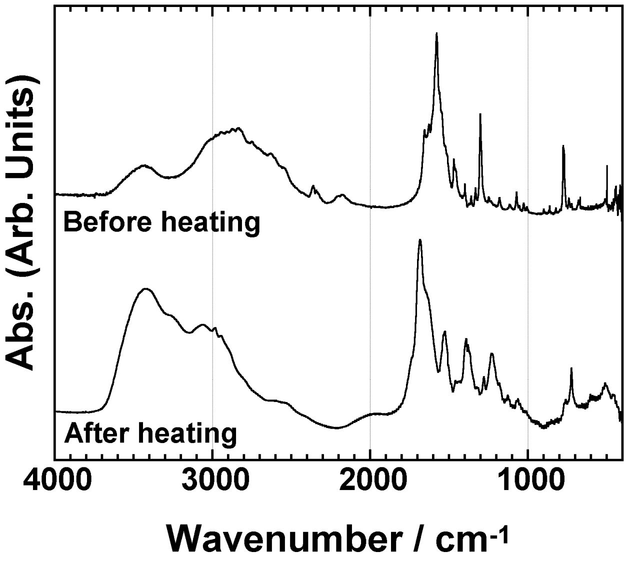
Abs. (Arb. Units)
Before heating
After heating
4000
3000
2000
1000
Wavenumber / cm-1

Fig. 2

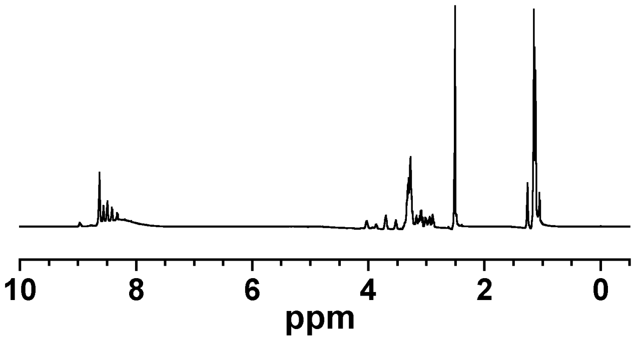

Fig. 3

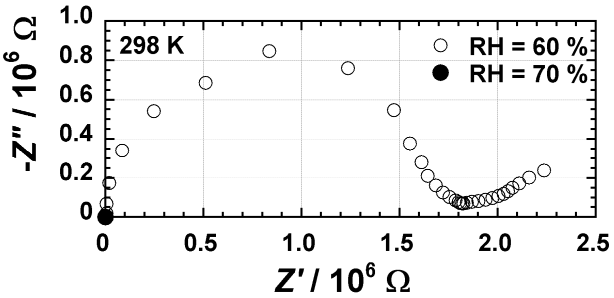

Fig. 4

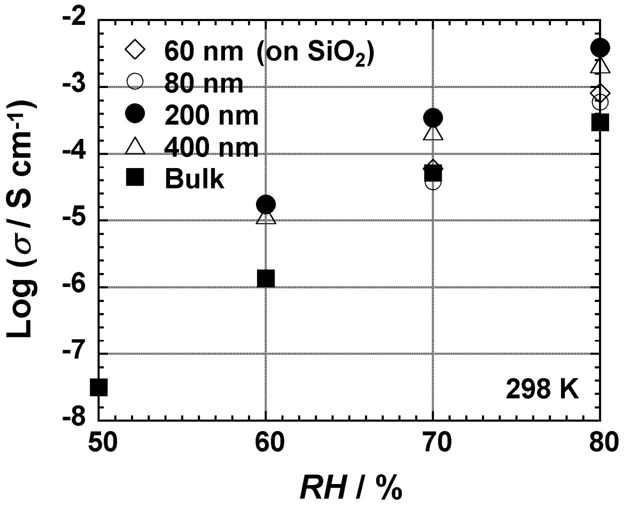
60 nm (on SiO2)
80 nm
200 nm
400 nm
Bulk
298 K
Log (σ / S cm-1)
-2
-3
-4
-5
-6
-7
-8
50
60
70
80
RH / %

Fig. 5