Synthesis of the polythiophene series and evaluation of the thermoelectric properties

Kazuki Ohara, Kento Ishii, Yoshikazu Shinohara and Hachirou Nakanishi

Institute of Multidisciplinary Research for Advanced Materials,Tohoku University,
Katahira 2-1-1,Aobaku,Sendai 980-8577,Japan

We have examined the measuring method of thermoelectric properties and evaluated the relation between Seebeck coefficient and electrical conductivity of polythiophene. Important for measuring method are 1) Stable temperature is important for Seebeck coefficient measurement., 2) Contact resistance should be eliminated to obtain reproducible data, and 3) Thin probes and a metal cover are useful to quantitative data. Thermoelectric properties of polythiophene changed by the synthesis method molecular weight of side chains; 1)Poly(3-alkylthiophene) showed low electrical conductivity but high Seebeck coefficient. 2) Polythiophene synthesized by electric polymerization showed high electrical conductivity but low Seebeck coefficient, and 3) Electrical conductivity of poly(3-dodecylthiophene) was lower than that of poly(3-hexylthiophene).

Key words: Electrical conductivity, Seebeck coefficient, Polythiophene, Thermoelectric material

1. INTRODUCTION

Thermoelectric materials, which convert directly from heat to electricity as shown in Fig.1, can generate power from waste heat. Polymer materials are considered not to be suitable for thermoelectric energy conversion, because Seebeck coefficient and electrical conductivity are low. High thermoelectric properties of Seebeck coefficient and electrical conductivity are necessary to develop a new field of polymer thermoelectric materials. Measuring method of quantitative and reproducible data on thermoelectric properties are not established for polymers. In this work, we have first examined the measuring method to obtain quantitative and reproducibility data, and secondly evaluated the relationship between Seebeck coefficient and conductivity of polythiophene series.
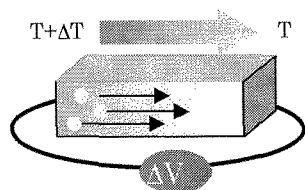

Fig. 1 Thermoelectric conversion

2. MEASURING METHOD OF THERMOELECTRIC PROPERTIES

Thermoelectric figure of merit (Z) and power factor (TPF) can be calculated according to following equations:

$$Z = \alpha^2 \sigma / \kappa \qquad (\, i \,)$$
$$TPF = \alpha^2 \sigma \qquad (\, ii \,)$$

α, σ and κ are Seebeck coefficient, electrical conductivity and thermal conductivity. Thermoelectric figure of merit presents energy conversion efficiency. High α and σ, and low κ are necessary to high efficiency. TPF which is a numerator of Z is especially important for power generation. In this study, the measuring methods of α and σ were examined.

2.1 ELECTRICAL CONDUCTIVITY

To solve the problem of low reproducibility and quantity of measured data, the material of the probe was first examined. Four-probe method was used for the measurement (Fig. 2). When indium was used as the probe, the contact resistance was generated between the probe and sample. On the other hand, when platinum was used, there was no contact resistance and reproducibility was obtained. Figure 3 shows the measured I-V curve of polyaniline. The current and potential difference are in proportion, which indicated that there is no contact resistance between the platinum probe and sample.
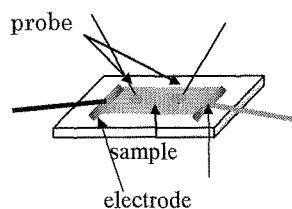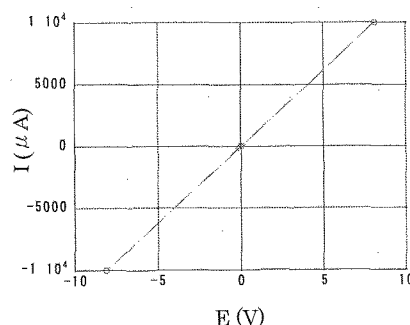

Fig.2 Four-probe method

E (V)

Fig. 3 I-V curve of polyaniline

2.2 SEEBECK COEFFICIENT

Bi-Te Peltier module was used in order to give a stable temperature difference to the sample. Figure 4 and 5 shows the schematic view and photograph of Seebeck coefficient measurement of thin film. To prevent the inflow and outflow of heat to the sample, the thin R-type thermocouples of 50μmφ were used, and the equipment

was covered with the metal box. As a result, reproducibility of the measured values was obtained. Figure 6 shows the result of measuring the Seebeck coefficient of the platinum film. The same value as a reference value was measured.

We established the reproducibility and quantitative measuring method of thermoelectric of polymers.
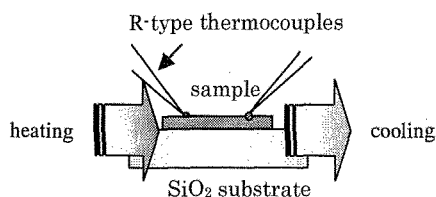

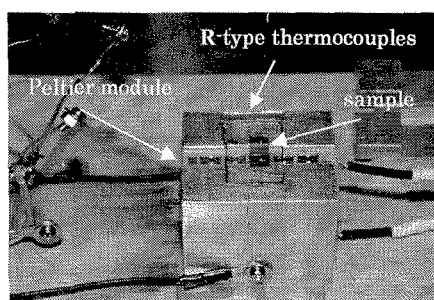Fig. 4 Measurement of Seebeck coefficient of thin film

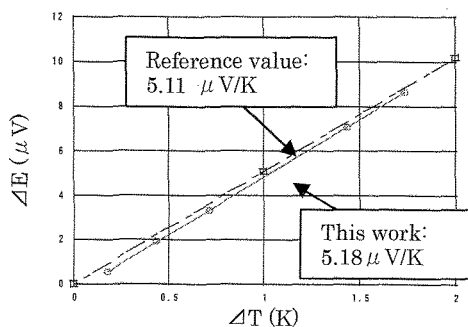Fig. 5 Experimental arrangement for measurement of Seebeck coefficient

Fig. 6 Seebeck coefficient of platinum

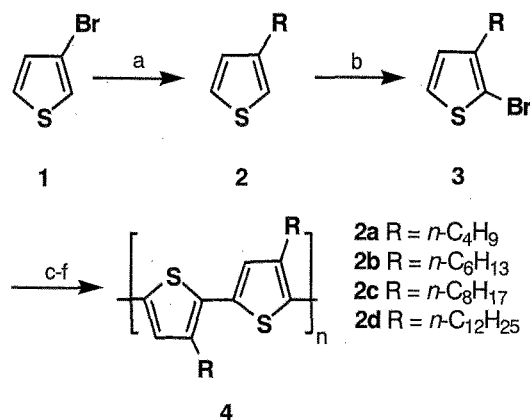# 3 EVALUATION OF THERMOELECTRIC PROPERTIES OF POLYTHIOPHENE

3.1 SYNTHESIS OF CONDUCTIVE POLYMER

Polythiophene which was typical conductive polymer was synthesized with various alkyl group side chains. Almost completely regioregular head-to-tail poly(3-alkylthiophenes) was obtained by using Ni(DPPE)Cl$_2$ ([1,2-bis-(diphenylphoshino)ethane]nickel(II)chloride). Using the method of McCullougu and co-workers (Scheme 1). The yield of poly(3-alkylthiophene) was 43%(R=butyl), 32%(R=hexyl), 25%(R=octyl), 31%(R=dodecyl). The poly(3-alkylthiophene) was doped with perchloric acid and iron chloride.

Polythiophene film was also synthesized by electritic polymerization. Thiophene was mixed with an electrolyte solution of tetra-n-butyl ammonium and nitrobenzene. ITO was used as an anode and Ni was as a cathode. The applied voltage between the electrodes was 12V. The synthesized film was about 15μm thick.

2a R = n-C$_4$H$_9$
2b R = n-C$_6$H$_{13}$
2c R = n-C$_8$H$_{17}$
2d R = n-C$_{12}$H$_{25}$

[a] (a) RMgBr, Ni(dppp)Br$_2$, Et$_2$O, 0°C. (b) Br$_2$, AcOH, 10°C. (c) i-Pr$_2$NH, n-BuLi, THF, -40°C, (d) MgBr$_2$ · OEt. (e) -40°C to -5°C. (f) Ni(dppp)Br$_2$, rt.

3.2 PREPARATION OF POLYTHIOPHENE FILMS

Poly(3-alkylthiophene) (R=hexyl, dodecyl) films were prepared by casting chloroform solutions. The thickness was 2-5μm.

3.3 RELATIONSHIP BETWEEN ELECTRICAL CONDUCTIVITY AND SEEBECK COEFFICIENT OF POLYTHIOPHENE

Electrical conductivity and Seebeck coefficient of polythiophene films were measured The result are summarized in Table I and Fig. 7. Measurement was performed near room temperature. The amount of dope was changed for poly(3-alkylthiophenes) (R=hexyl, dodecyl) films. Poly(3-alkylthiophene) indicates the tendency that Seebeck coefficient decreases with an increasing electrical conductivities.

Electrical conductivity of electrically polymered polythiophene was high, whereas Seebeck coefficient was low. On the other hand, poly(3-alkylthiophene) presents low electrical conductivity, but higher Seebeck coefficient than polyacetylene and polyaniline. When poly(3-hexylthiophene) is compared with poly(3-dodecylthiophene), electrical conductivity of poly(3-dodecylthiophene) is lower. The molecular weight of dodecyl is larger than that of hexyl. It is considered that the large molecular weight of substituent causes reduction of volume fraction of main chains, resulting in reduced electrical conductivity.

Table I Electrical conductivity and Seebeck coefficient of poly(3-alkylthiophenes)

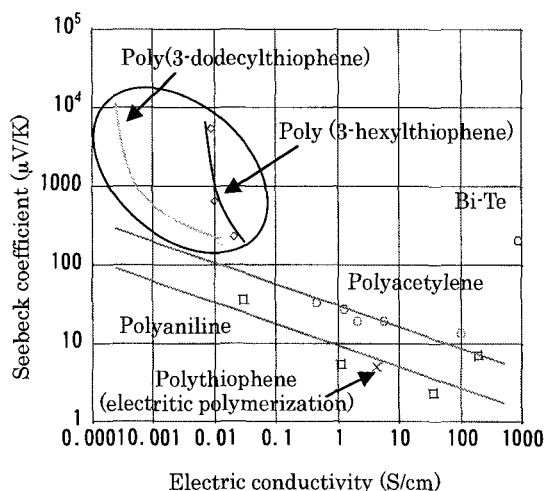| R(dopant)	conductivity (S/cm)	Seebeck coefficient (μV/K)
Hexyl(FeCl$_3$)	8.9x10^{-3}	5400
Hexyl(CHClO$_4$)	1.0x10^{-2}	650
Hexyl(CHClO$_4$)	2.1x10^{-2}	233
Dodecyl(FeCl$_3$)	2.9x10^{-4}	11000
Dodecyl(CHClO$_4$)	1.3x10^{-2}	206

Fig. 7 Relationship between Seebeck coefficient and electrical conductivity of p-type materials

4.CONCLUSIONS

We have examined the measuring method of thermoelectric properties and evaluated the relation between Seebeck coefficient and electrical conductivity of polythiophene. Conclusions are as follows:

①.Measuring method

• Stable temperature is important for Seebeck coefficient measurement.

• Contact resistance should be eliminated to obtain reproducible data.

• Thin probes and a metal cover are useful to quantitative data.

② Evaluation of thermoelectric properties of polythiophene

• Poly(3-alkylthiophene) showed low electrical conductivity but high Seebeck coefficient.

• Polythiophene synthesized by electric polymerization showed high electrical conductivity but low Seebeck coefficient.

• Electrical conductivity of poly(3-dodecylthiophene) was lower than that of poly(3-hexylthiophene).

REFERENCES

[1] T. C. Harman, *Semiconductor Products*, SEPTEMBER, 13(1963).

[2] D. Moses, A. Denestein, J. Chen and A. J. Heeger, *Phys. Rev. B*, 25, 7652 (1982).

[3] R. D. McCullough, S. Tristran-Nagle, S. P. Williams, R. D. Lowe and M. Jayaraman, *J. Am. Chem. Soc.*, 115, 4910 (1993).

[4] R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 58, 904 (1993).