

# Measurements of the Thermal Conductivity and Thermal Diffusivity of Polymer Melts with the Short-Hot-Wire Method<sup>1</sup>

X. Zhang<sup>2,4</sup>, W. Hendro<sup>3</sup>, M. Fujii<sup>2</sup>, T. Tomimura<sup>2</sup>, and N. Imaishi<sup>2</sup>

---

<sup>1</sup> Paper presented at the Fourteenth Symposium on Thermophysical Properties,  
June 25-30, 2000, Boulder, Colorado, U.S.A.

<sup>2</sup> Institute of Advanced Material Study, Kyushu University,  
Kasuga 816-8580, Japan.

<sup>3</sup> Interdisciplinary Graduate School of Engineering Sciences,  
Kyushu University, Kasuga 816-8580, Japan.

<sup>4</sup> To whom correspondence should be addressed.

## **ABSTRACT**

In this paper, the thermal conductivity and thermal diffusivity of four kinds of polymer melts are measured by using the transient short-hot-wire method. This method was developed from the hot-wire technique and is based on two-dimensional numerical solutions of unsteady heat conduction from a wire with the same length-to-diameter ratio and boundary conditions as those in the actual experiments. The present method is particularly suitable for the measurements of molten polymers where natural convection effect can be ignored due to their high viscosities. The measured results have shown that the present method can measure the thermal conductivity and thermal diffusivity of molten polymers within errors of 3 and 6 %, respectively. Further, the thermal conductivity and thermal diffusivity of solidified samples are also measured and discussed.

**KEY WORDS:** molten polymers; solidified polymers; thermal conductivity; thermal diffusivity; transient short-hot-wire method.

## **1. INTRODUCTION**

The measurements of thermal conductivity and thermal diffusivity of polymer materials in molten state have always been difficult problems. These are mainly because of factors like thermal contact resistance, inhomogenities in the sample, different measurement methods [1] and etc. Due to the lack of experimental data and difficulties involved in accurate measurements, approximations were often used in the early times. However, even a number of correlations associating such structural variables as molecular weight of the polymer, crystallinity, orientation etc. with the thermal conductivity were proposed [2-3], accurate measurements of thermal properties are still important. Since Ross et al. [4] (1984) reviewed the transient or steady-state methods used to measure the thermal properties of polymers, some researchers [5-6] have continuously made great efforts to improve their measurement accuracy and/or to develop new effective measurement methods. The present authors [7] (1993) had proposed an effective method so called 'Transient Short-Hot-Wire Method' which can measure the thermal conductivity and thermal diffusivity of liquids simultaneously. By using this method, the thermal conductivity and thermal diffusivity of water and organic liquids [8], alternative refrigerants in liquid phase [9], and molten carbonates [10] had been measured successfully. In this paper, the thermal conductivity and thermal diffusivity of four kinds of commercial polymers are measured in the temperature range from 20 to 250 °C and atmospheric pressure. Because the present method uses a short hot wire (about 10 mm long) as the probe, only a small amount of test sample is needed. This makes it easy to solve the problem of inhomogenities in the sample. Uncertainty analysis shows that the present method can measure the thermal conductivity and thermal diffusivity of polymers within errors of 3 and 6 %, respectively.

## **2. PRINCIPLE OF MEASUREMENT**

As described in our previous papers [7-10], the present method was developed from the conventional hot-wire technique and is based on two-dimensional numerical

solutions of unsteady heat conduction from a short wire with the same length-to-diameter ratio and boundary conditions as those used in the actual experiments. The following procedure was proposed to determine simultaneously the thermal conductivity and thermal diffusivity of a liquid. The numerical results for the dimensionless temperature  $\theta_v$  ( $= (T - T_i) / (q_v r^2 / \lambda)$ ) are approximated by a linear equation with respect to the logarithm of Fourier number  $Fo$  ( $= (\alpha t) / r^2$ ), and the coefficients  $A$  and  $B$  are determined by the least-squares method.

$$\theta_v = A \ln Fo + B \quad (1)$$

The measured temperature rise of a wire can also be approximated by a linear equation with coefficients  $a$  and  $b$  in the above time range as

$$T_v = a \ln t + b \quad (2)$$

where  $T_v$  is the wire temperature rise based on the initial temperature  $T_i$ . Equation (1) is dimensionalized as

$$T_v = \frac{q_v r^2}{\lambda} A \ln t + \frac{q_v r^2}{\lambda} (A \ln \frac{\alpha}{r^2} + B) \quad (3)$$

Comparing the corresponding coefficients of Eqs. (2) and (3), the thermal conductivity and thermal diffusivity of a liquid are expressed by

$$\lambda = \frac{VI A}{\pi l a} \quad (4)$$

$$\alpha = r^2 \exp\left(\frac{b}{a} - \frac{B}{A}\right) \quad (5)$$

where  $r$  and  $l$  are the radius and length of the hot wire,  $V$  and  $I$  are the voltage and current supplied to the wire, respectively. Equations (4) and (5) are similar to those obtained for the conventional transient hot-wire method [11], except that the  $A$  and  $B$  are changed somewhat with the aspect ratio  $L$ , parameters  $R_{c1}$  and  $R_{d1}$ , etc. so that an iterative process is required to evaluate thermal properties accurately.

From Eqs. (4) and (5) the relative errors of the thermal conductivity and thermal diffusivity are estimated as

$$\frac{\delta\lambda}{\lambda} = \left\{ \left( \frac{\delta V}{V} \right)^2 + \left( \frac{\delta I}{I} \right)^2 + \left( \frac{\delta l}{l} \right)^2 + \left( \frac{\delta A}{A} \right)^2 + \left( \frac{\delta a}{a} \right)^2 \right\}^{\frac{1}{2}} \quad (6)$$

$$\frac{\delta\alpha}{\alpha} = \left\{ \left( \frac{2\delta r}{r} \right)^2 + \left[ \delta \left( \frac{B}{A} \right) \right]^2 + \left[ \delta \left( \frac{b}{a} \right) \right]^2 \right\}^{\frac{1}{2}} \quad (7)$$

In the present measurements, the total errors of this method are estimated to be 3 and 6 % for the thermal conductivity and thermal diffusivity, respectively.

### 3. EXPERIMENTS

Figure 1 shows the transient short-hot-wire cell used in the present study. A short platinum wire 8.70 mm in length and 51.0  $\mu\text{m}$  in diameter (1) is welded at both ends to platinum lead wires of 1.5 mm in diameter (3) which are supported with a ceramic slat (2) and connected with voltage (5) and current (6) platinum lead wires 0.5 mm in diameter. The ceramic slat is fixed with a stainless-steel rod which can move up and down. A glass crucible (4) 50 mm in inner diameter and 100  $\text{cm}^3$  in volume is heated with an electric furnace (8) which is covered with a thermal insulator (9). The temperatures at the outside of the crucible wall are measured with thermocouples (7) to provide a feedback signal for the temperature controller.

The platinum hot wire is annealed at 800  $^{\circ}\text{C}$  for a few hours, and the temperature coefficient of its electric resistance  $\beta$  is determined through a calibration for the temperature range from 20 to 400  $^{\circ}\text{C}$ . The calibrated probe was carefully cleaned with an ultrasonic cleaner, and then slowly inserted into the solid pellet samples before heating. At the beginning of molten state, lots of air bubbles are dispersed uniformly inside the polymer melt. The air bubbles go up slowly due to the effect of buoyancy force. About 3 hours later, the molten polymer becomes transparent and all of the bubbles disappear. After the temperature of polymer melt becomes uniform and constant, the initial temperature of polymer melt is measured with the hot-wire by

$$T_i = \frac{1}{\beta} \left( \frac{Ri}{Rt_o} - 1 \right) \quad (8)$$

where  $Rt_o$ ,  $Ri$  are the electrical resistance of the probe at 0 °C and the initial temperature, respectively. On the other hand, when the probe is heated, the wire temperature rises but the lead terminal temperature remains at the initial temperature because of its large heat capacity. Therefore, the hot-wire temperature rise is estimated as

$$T_v = \frac{1}{\beta} \left( \frac{Rt(t) - \epsilon Ri}{(1 - \epsilon)Rt_o} - 1 \right) T_i \quad (9)$$

where  $\epsilon$  is the electrical resistance ratio of the lead terminals and the entire probe and is about 0.03 for the present probes.

The measurement system is similar to that described in Ref. 10. It consists of a dc power supply and voltage and current measuring and control systems, that is, two digital multimeters, a personal computer, and a PI/O controller. The power supply (Advantest R6245) can generate a maximum constant current of 600 mA with 0.01-mA resolution. Two DMs (Keithley 2002) are the same type and have a 8.5-digit accuracy at a sampling rate of 18 per s. The PC controls both switching and logging of data.

#### 4. RESULTS AND DISCUSSION

At first, the characteristics of the short-hot-wire probe are examined by using pure water and toluene as standard liquids with known thermal conductivity and thermal diffusivity. The temperature evolutions for these liquids are compared with corresponding numerical results, and the evaluated thermal conductivity and thermal diffusivity are compared with reference values [12]. Then, the effective hot-wire length and diameter and the electrical resistance ratio are determined. The length differs by, at most, 3% from that measured with a microcathetometer. The reason for the difference is attributed mainly to an uncertainty of accurate welding positions on the lead terminals. The thermal conductivity and thermal diffusivity of these standard liquids have been measured under normal gravity conditions, because the effect of natural convection will not appear, at least in the range  $Fo < 200$  [13]. The reproducibility of the hot-wire temperature rise is examined for water, and it is confirmed that the differences among

the repeated data are within 0.01 °C, if we allow more than 60 min between successive measurements.

Four kinds of polymers, polycarbonate, polyethylene, polypropylene, and polystyrene are tested. These samples were supplied by Sumitomo Chemical Industries Ltd. The measured values of the thermal conductivity, thermal diffusivity and the product of specific heat and density with their dispersions are shown in Table I, respectively. These data are the average values of five measurements at the same temperature.

Figures 2 and 3 show the measured thermal conductivity and thermal diffusivity of polyethylene, respectively. In the following figures 2 to 9, the closed circles indicate the present results, and the open symbols indicate the various reference values. As shown in Fig. 2, the present results of the thermal conductivity agree well with the values obtained by Eiermann and Hellwege [14] for a low pressure polyethylene, and decrease monotonously with increasing temperature in the solid state and are almost a constant value in the molten state. Since the polyethylene is a semi-crystalline polymer, the value of the thermal conductivity in the solid state depends mainly on its degree of crystallinity. The present results differ from the values obtained by Kline [15]. The difference may be attributed to the degree of crystallinity. The measured thermal diffusivity shown in Fig. 3 also decreases with increasing temperature in the solid state, and is almost a constant value in the molten state.

Figures 4 and 5 show the measured results of polycarbonate. In contrast with polyethylene, the present thermal conductivity in Fig. 4 increases slightly with temperature in the solid state and is almost unchanged with temperature in the molten state. Further, the present data are about 30 % higher than those obtained by Choy *et al.* [16] with the flash radiometry method. As for the thermal diffusivity, the present results are about 30 % higher than those obtained by Morikawa *et al.* [17] for the amorphous state, and about 60 % higher than those obtained by Choy *et al.* [16]. Similar to the

results obtained by Morikawa *et al.* [17], the present results of the thermal diffusivity also show higher values in the solid state than those in molten state.

Figures 6 and 7 show the measured results of polypropylene. Because the polypropylene is a semi-crystalline polymer, both the thermal conductivity and thermal diffusivity are much higher in the solid state as compared to its molten state. The present values of the thermal conductivity agree with those of references [1] and [18], but show a big difference in the solid state. Figure 7 further shows a minimum value of the thermal diffusivity at the melt transition temperature.

Figures 8 and 9 show the measured results of polystyrene. Figure 8 shows almost no change of thermal conductivity with temperature. But big changes are observed for the thermal diffusivity (Fig. 9) near the glass transition temperature. The present values shown in Fig. 8 agree well with those obtained by Dashora and Gupta [19] for the rubber-modified polystyrene Monsanto HT 88-1000, the symbol x, but differ from those obtained by Dashora and Gupta [19] for the polystyrene Monsanto HT 99-L2020, the symbol +; Lobo and Cohen [1],  $\Delta$ ; and Underwood and McTaggart [20],  $\nabla$ . Figure 9 compares the present results with the values obtained by Morikawa *et al.* [17] for the thermal diffusivity. About 50 % differences are observed except for the data near the melt transition temperature.

Figure 10 shows the products of specific heat and density of above four kinds of polymers. It is noted that the product values of polyethylene and polystyrene are almost unchanged with temperature in the molten state although they fluctuate near the melt transition temperatures. The value of polypropylene shows a maximum value at the melt transition temperature, and that of polycarbonate fluctuates sharply with temperature in the molten state.

## 5. CONCLUSIONS

The thermal conductivity and thermal diffusivity of four kinds of commercial polymers have been measured. The main conclusions are as follows.

- (1) The transient short-hot-wire method can be effectively used to measure simultaneously the thermal conductivity and thermal diffusivity of polymers in molten and solidified states, because of a small amount of test sample and negligible effect of natural convection.
- (2) The estimated errors of measurements for the thermal conductivity and thermal diffusivity are 3 and 6 %, respectively.
- (3) Because the thermal conductivity in the solidified state depends on the degree of crystallinity, systematical measurements should be done in the near future.

#### **ACKNOWLEDGMENTS**

This work is supported partly by Japan Space Environment Utilization Promotion Center and the Grant-in-Aid for Encouragement of Young Scientists No. 11750167 from the Ministry of Education, Science, Sports and Culture of Japan. The authors also want to express their thanks to Mr. K. Hamano at the Institute of Advanced Material Study, PhD student Mr. S. Fujiwara at the Interdisciplinary Graduate School of Engineering Sciences, Kyushu University for their assistance and useful discussion.

## REFERENCES

1. H. Lobo and C. Cohen, *Polymer Engineering and Science* **30/2**:65 (1990).
2. M. Luba, T. Pelt, and R. G. Griskey, *J. Appl. Polym. Sci.* **23**:55 (1979).
3. M. G. Kulkarni and R. A. Mashelkar, *Polymer* **22**:867 (1981).
4. R. G. Ross, P. Anderson, B. Sundqvist, and G. Backstrom, *Rep. Prog. Phys.* **47**:1347 (1984).
5. K. N. Madhusoodanan, Mini R. Thomas, and Jacob Philip, *J. Appl. Phys.* **62**:1162 (1987).
6. B. Dessain, O. Moolaert, R. Keunings, and A. R. Bunsell, *J. Mater. Sci.* **27**:4515(1992).
7. X. Zhang, T. Tomimura, and M. Fujii, *Proc. 14<sup>th</sup> Japan Symposium on Thermophysical Properties*, 23 (1993).
8. M. Fujii, X. Zhang, N. Imaishi, S. Fujiwara, and T. Sakamoto, *Int. J. Thermophysics* **18**:327 (1997).
9. T. Tomimura, X. Zhang, S. Maki, and M. Fujii, *Proc. 19<sup>th</sup> Japan Symposium on Thermophysical Properties*, 275 (1998).
10. X. Zhang and M. Fujii, *Int. J. Thermophysics* **21**:71(2000).
11. N. Nagasaka and A. Nagashima, *Rev. Sci. Instrum.* **52**:229 (1981).
12. C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, R. D. Trengove, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **15**:1073(1986).
13. X. Zhang, S. Fujiwara, Z. Qi, and M. Fujii, *J. Jpn. Soc. Microgravity Appl.* **16/2**:129(1999).
14. K. Eiermann and K.-H. Hellwege, *J. Polymer Sci.* **57**: 99(1962).
15. D. E. Kline, *J. Polymer Sci.* **L**: 441(1961).
16. C. L. Choy, W. P. Leung, and Y. K. NG, *J. Polymer Sci.: B: Polymer Physics* **25**: 1779(1987).
17. J. Morikawa, J. Tan, and T. Hashimoto, *Polymer* **36**: 4439(1995).

18. C. L. Yen, H. C. Tseng, Y. Z. Wang, and K. H. Hsieh, *J. Applied Polymer Sci.* **42**: 1179(1991).
19. P. Dashora and G. Gupta, *Polymer* **37**: 231(1996).
20. W. M. Underwood and R. B. McTaggart, *Heat Transfer (Storrs), Chem. Eng. Progr. Sym. Series* 56, No. 30, 261(1960).

Table I. Measured Thermal Conductivity, Thermal Diffusivity, and Product of Specific Heat and Density

Substance	Temperature (°C)	$\lambda$ (W· m <sup>-1</sup> · K <sup>-1</sup> )	$\alpha$ (m <sup>2</sup> · s <sup>-1</sup> )	$\rho C_p$ (J· m <sup>-3</sup> · K <sup>-1</sup> )	Dispersions of $\lambda$ , $\alpha$ , and $\rho C_p$ (±%)
Polycarbonate	30	0.261	2.13E-07	1.23E+06	0.78, 4.03, 3.43
	40	0.265	2.18E-07	1.22E+06	0.24, 3.73, 3.55
	60	0.274	2.14E-07	1.28E+06	0.17, 1.85, 1.69
	80	0.283	2.00E-07	1.41E+06	0.66, 4.31, 3.65
	100	0.290	2.00E-07	1.45E+06	2.11, 0.88, 1.05
	110	0.294	2.00E-07	1.47E+06	0.22, 3.00, 2.93
	120	0.296	2.03E-07	1.46E+06	0.39, 1.67, 1.28
	130	0.299	2.08E-07	1.44E+06	0.71, 5.20, 4.52
	140	0.284	1.38E-07	2.06E+06	0.22, 3.54, 3.36
	150	0.291	1.61E-07	1.81E+06	0.16, 3.22, 3.13
	160	0.290	1.50E-07	1.93E+06	0.48, 3.71, 3.25
	180	0.287	1.52E-07	1.89E+06	0.77, 5.68, 5.00
	190	0.287	1.72E-07	1.67E+06	0.44, 1.67, 1.84
	200	0.264	1.20E-07	2.21E+06	0.54, 1.97, 1.32
	210	0.271	1.51E-07	1.79E+06	0.22, 1.54, 1.77
220	0.269	1.47E-07	1.84E+06	0.20, 6.49, 6.16	
Polyethylene	27	0.371	2.64E-07	1.41E+06	0.50, 2.83, 2.86
	50	0.337	2.29E-07	1.47E+06	0.65, 3.94, 3.80
	100	0.264	2.22E-07	1.20E+06	0.25, 3.53, 3.43
	110	0.256	1.94E-07	1.32E+06	0.32, 3.77, 3.59
	120	0.254	1.98E-07	1.28E+06	0.61, 5.68, 5.00
	130	0.251	1.87E-07	1.34E+06	0.42, 4.25, 4.15

	150	0.250	1.85E-07	1.35E+06	0.36, 4.27, 4.15
	200	0.244	1.77E-07	1.38E+06	0.08, 2.15, 2.06
	250	0.240	1.90E-07	1.26E+06	0.09, 2.20, 2.14
Polypropylene	70	0.287	2.00E-07	1.44E+06	0.18, 0.58, 0.57
	80	0.284	1.94E-07	1.46E+06	0.35, 1.42, 1.31
	90	0.280	1.86E-07	1.51E+06	0.55, 4.20, 3.59
	100	0.274	1.67E-07	1.64E+06	0.17, 3.09, 2.99
	110	0.267	1.63E-07	1.64E+06	0.33, 2.89, 2.52
	120	0.259	1.57E-07	1.65E+06	0.33, 2.73, 2.43
	130	0.231	9.68E-08	2.40E+06	1.52, 8.68, 7.54
	140	0.184	5.06E-08	3.65E+06	0.91, 4.96, 4.06
	150	0.157	1.01E-07	1.55E+06	0.25, 0.95, 0.84
	160	0.157	1.07E-07	1.48E+06	0.66, 5.84, 5.84
	170	0.157	1.05E-07	1.49E+06	0.53, 3.57, 3.22
	180	0.156	1.01E-07	1.55E+06	0.50, 3.94, 3.42
	200	0.156	1.07E-07	1.46E+06	0.50, 3.54, 3.14
	210	0.155	1.02E-07	1.51E+06	1.13, 4.28, 3.60
	220	0.155	1.01E-07	1.54E+06	0.36, 4.30, 3.95
230	0.149	8.38E-08	1.78E+06	1.22, 3.41, 2.68	
Polystyrene	30	0.187	1.99E-07	9.41E+05	0.41, 2.45, 3.56
	40	0.189	2.00E-07	9.46E+05	0.61, 3.96, 3.56
	50	0.190	1.87E-07	1.02E+06	0.32, 1.21, 1.18
	60	0.192	1.78E-07	1.08E+06	0.45, 2.53, 2.08
	70	0.194	1.78E-07	1.09E+06	0.09, 4.76, 4.68
	80	0.195	1.80E-07	1.09E+06	0.13, 3.80, 3.60
	90	0.194	1.62E-07	1.20E+06	1.38, 8.67, 7.26
	93	0.199	1.98E-07	1.01E+06	0.09, 3.41, 3.43

	96	0.201	2.08E-07	9.67E+05	0.56, 2.38, 1.80
	99	0.203	1.95E-07	1.04E+06	0.40, 1.79, 1.40
	100	0.202	1.82E-07	1.11E+06	0.19, 1.27, 1.18
	102	0.195	1.45E-07	1.35E+06	0.48, 2.76, 2.24
	105	0.193	1.36E-07	1.42E+06	0.50, 3.25, 2.72
	120	0.194	1.39E-07	1.40E+06	0.18, 1.76, 1.59
	140	0.196	1.39E-07	1.41E+06	0.43, 2.40, 1.97
	150	0.195	1.39E-07	1.41E+06	0.16, 1.92, 2.03
	170	0.196	1.37E-07	1.43E+06	0.24, 3.44, 3.22
	180	0.197	1.36E-07	1.44E+06	0.28, 0.86, 0.66
	200	0.197	1.40E-07	1.40E+06	0.37, 3.28, 2.82
	210	0.197	1.49E-07	1.33E+06	0.35, 0.70, 0.25
	220	0.198	1.51E-07	1.32E+06	0.54, 5.81, 5.31

## **Figure Captions**

Fig. 1. Schematic of experimental setup.

Fig. 2. Measured thermal conductivity of polyethylene.

Fig. 3. Measured thermal diffusivity of polyethylene.

Fig. 4. Measured thermal conductivity of polycarbonate.

Fig. 5. Measured thermal diffusivity of polycarbonate.

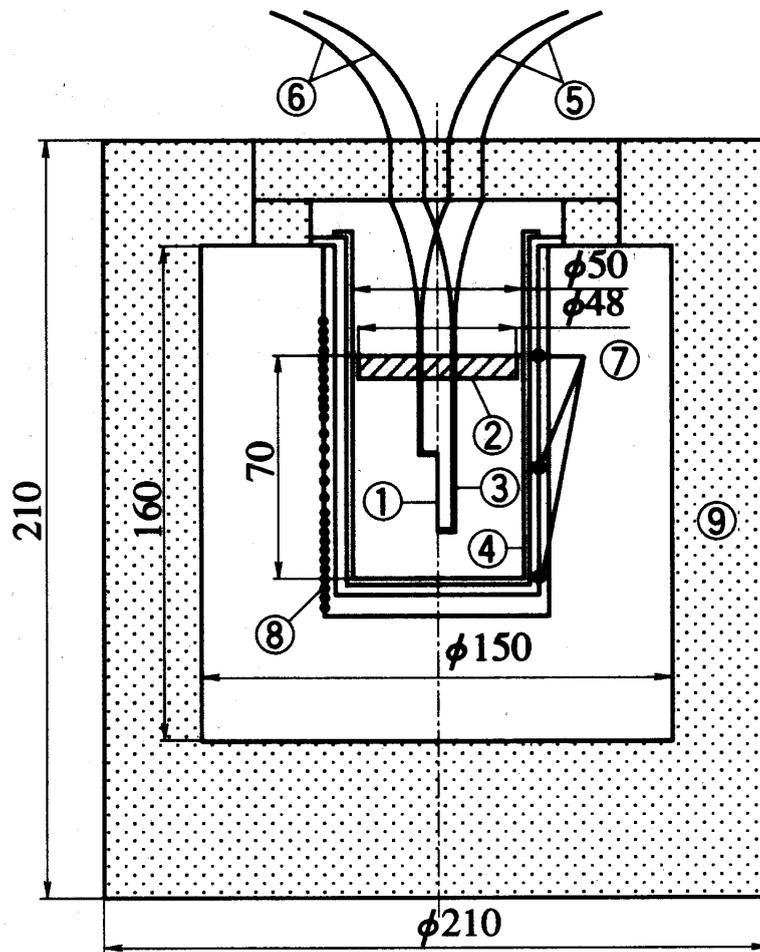
Fig. 6. Measured thermal conductivity of polypropylene.

Fig. 7. Measured thermal diffusivity of polypropylene.

Fig. 8. Measured thermal conductivity of polystyrene.

Fig. 9. Measured thermal diffusivity of polystyrene.

Fig. 10. Products of specific heat and density of four kinds of polymers.



- |  |   |
|--|---|
| (1) Pt hot wire ( $d = 51.0 \mu\text{m}$ , $l = 8.70 \text{ mm}$ ) | (2) Ceramic slat                              |
| (3) Pt lead terminal ( $d = 1.5 \text{ mm}$ )                      | (4) Glass crucible ( $\phi = 50 \text{ mm}$ ) |
| (5) Voltage lead wire  | (6) Current lead wire                         |
| (7) Thermocouples  | (8) Electric furnace                          |
| (9) Insulating material  |   |

Fig. 1.

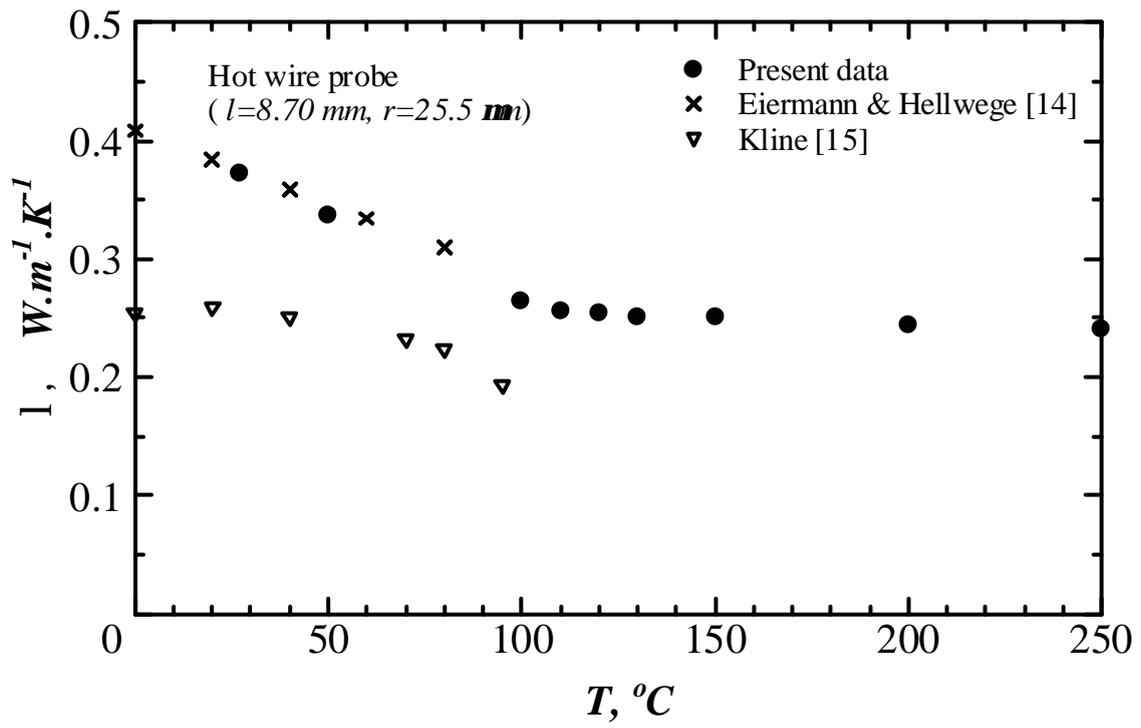


Fig. 2

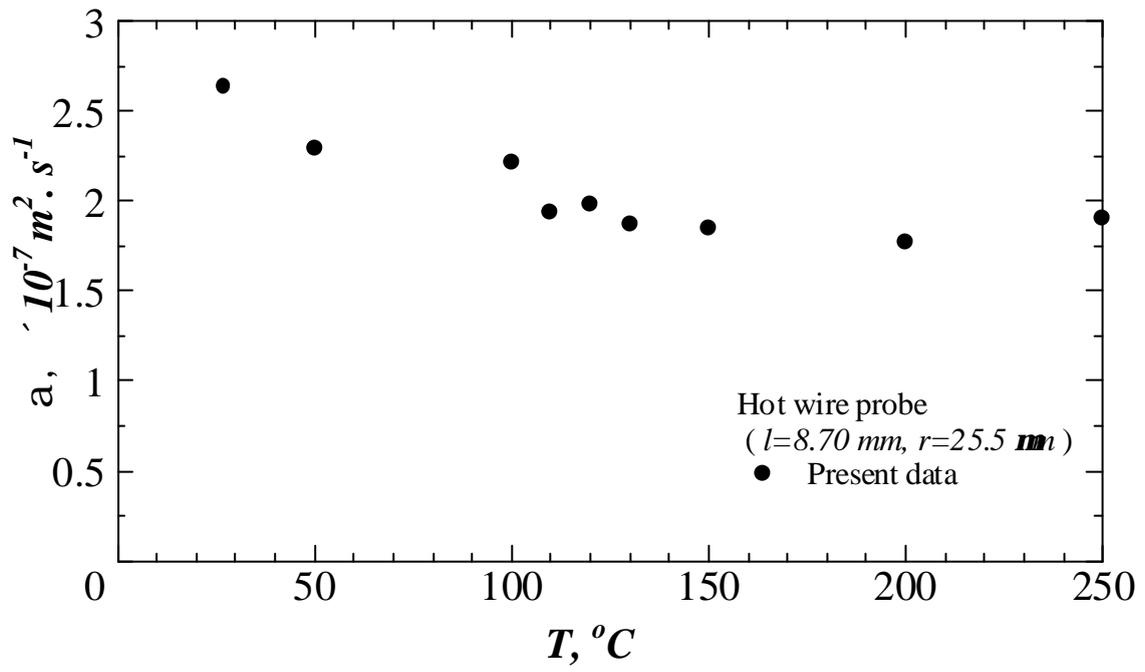


Fig. 3

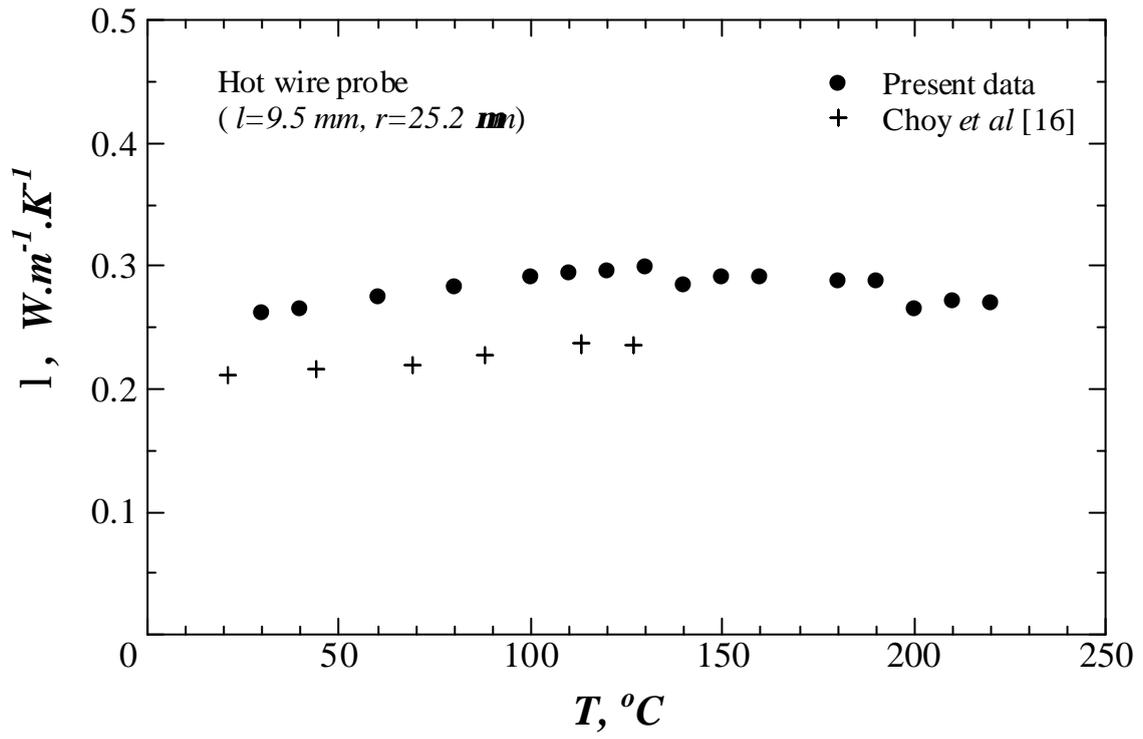


Fig. 4

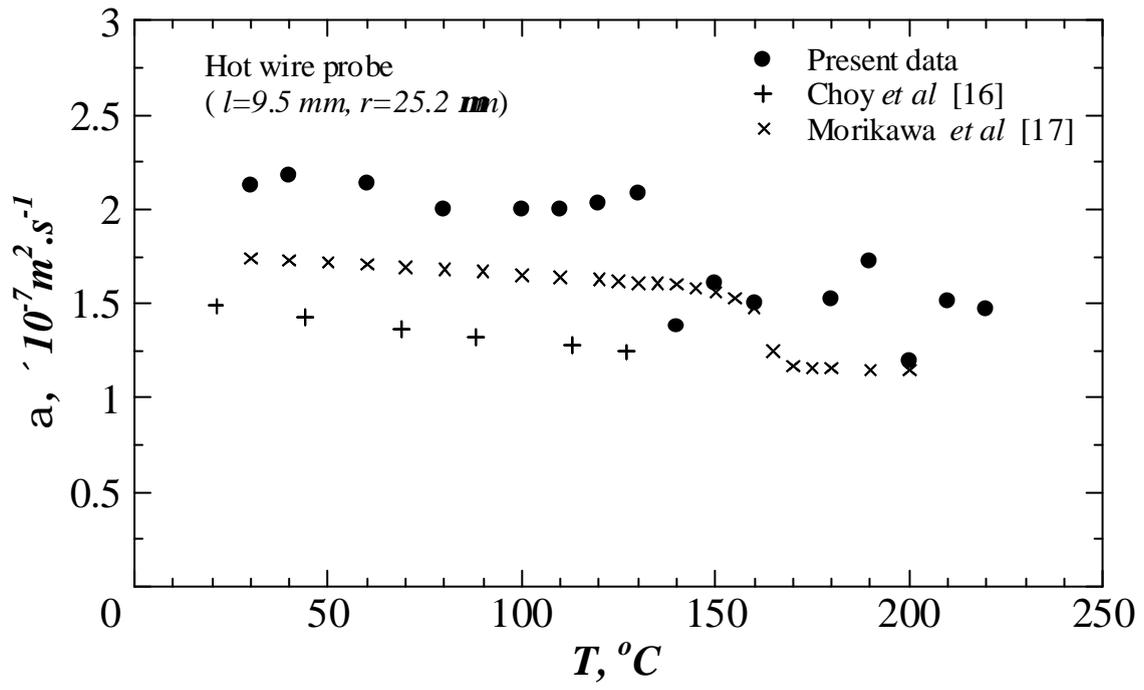


Fig. 5

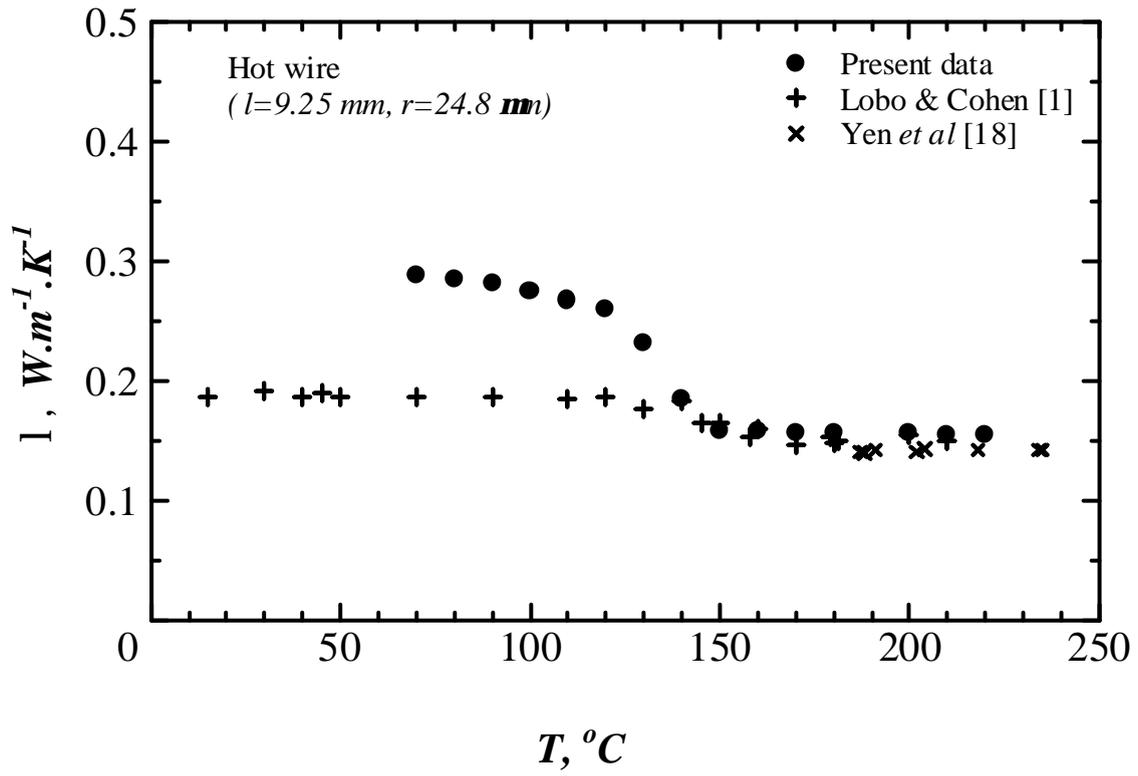


Fig. 6

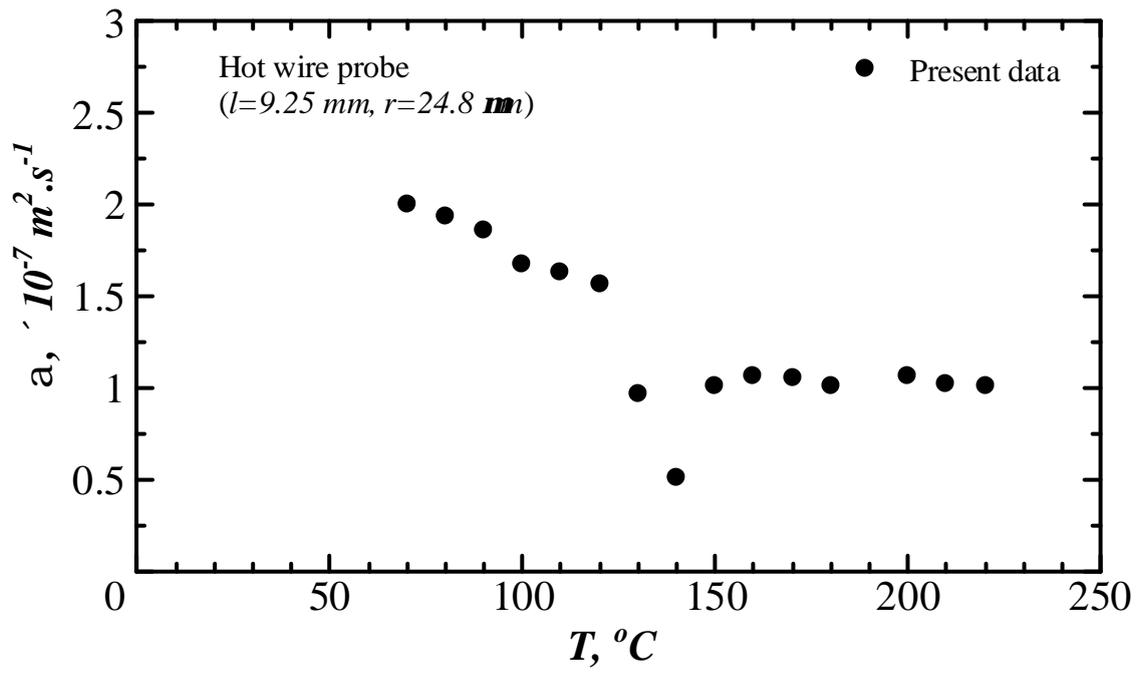


Fig. 7

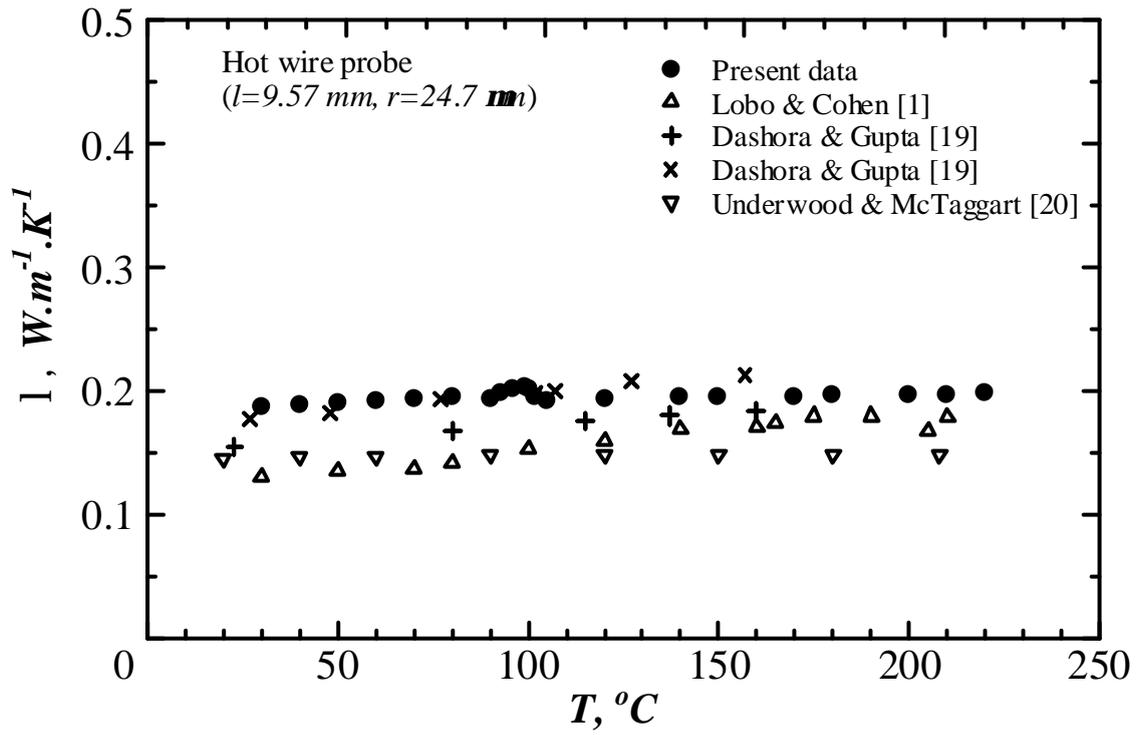


Fig. 8

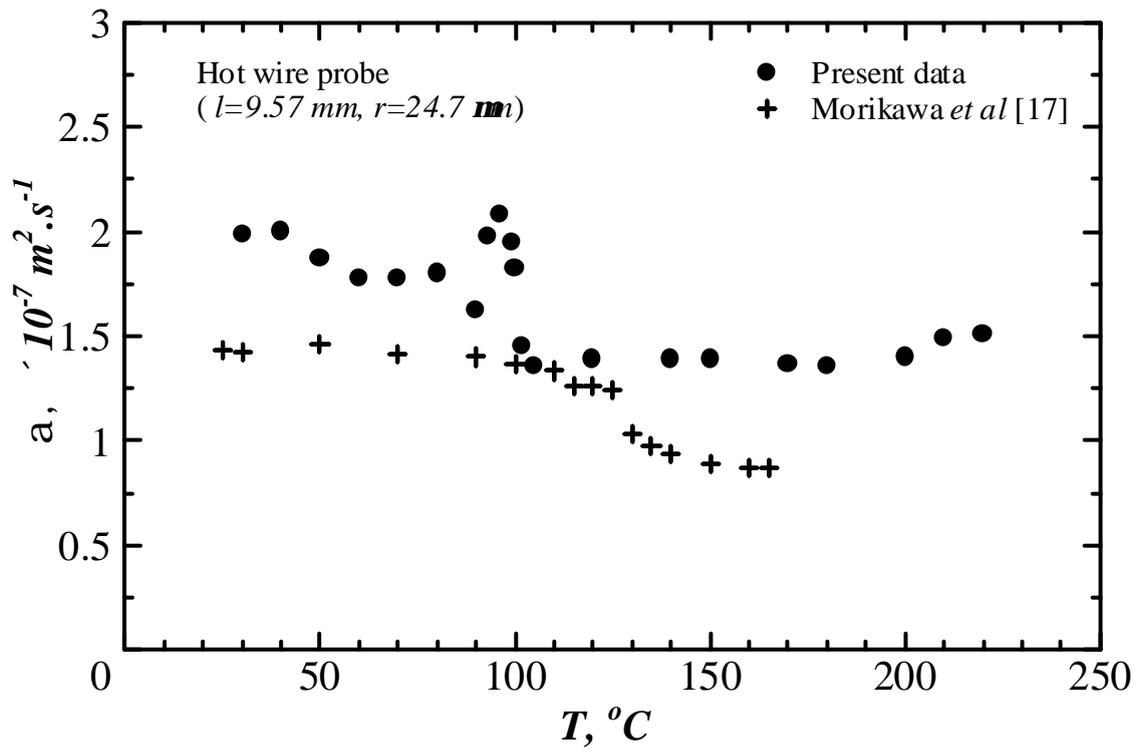


Fig. 9

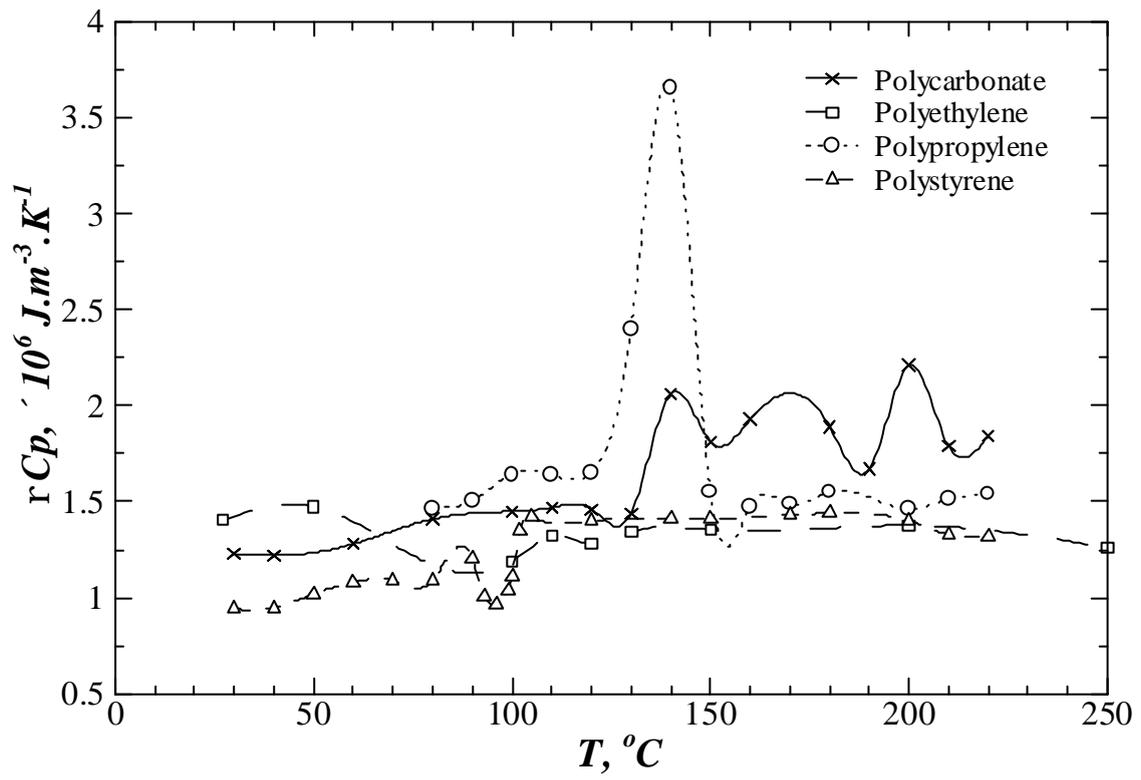


Fig. 10