High Temperatures – High Pressures, 2002, volume 34, pages 127 – 134
15 ECTP Proceedings pages 1355 – 1362

DOI:10.1068/htwu457

A new apparatus for thermal diffusivity and specific heat measurements of films and liquids by means of Fourier transform thermal analysis

Akikazu Maesono, Youichi Takasaki, Yukio Maeda
Ulvac, Sinku-Riko, Inc., 1-9-19 Hakusan, Midori-ku, Yokohama 226-0006, Japan;
fax: +81 45 934 0448; email: maesono@ulvac-riko.co.jp

Ronald P Tye
Ulvac Sinku-Riko Consultant, Hunters Lodge, Wells Road, Draycott, Somerset BS27 3ST, UK;
fax: +44 1934 744 007

Junko Morikawa, Toshimasa Hashimoto
Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan;
fax: +81 3 5734 2435; email: toshimas@o.cc.titech.ac.jp, jmorikaw@o.cc.titech.ac.jp

Presented at the 15th European Conference on Thermophysical Properties, Würzburg, Germany, 5 – 9 September 1999

Abstract. A new apparatus based on the technique of Fourier transform thermal analysis for the measurement of thermal diffusivity, specific heat per unit volume, thermal effusivity, and thermal conductivity of thin solid and liquids films (of the order of micrometres) has been developed. The apparatus consists of the following components: specimen assembly; function synthesiser; DC potentiometer circuit; lock-in amplifier; DC microvoltmeter; temperature controller; computer; and special attachments. An electrically insulating specimen, 5×10 mm^2 and $1 \sim 100$ μm in thickness, is sandwiched between two gold layer resistors sputtered on two Pyrex glass plates, one being the heat generator and the other the sensor. For an electrically conductive specimen, a three-layered specimen stack, insulating film/conductive specimen/insulating film, can be used. By means of the Fourier transform technique, the thermal diffusivity across the specimen thickness can be obtained under heating or cooling at a constant rate of $0.2 \sim 10$ K min^{-1} from -50 °C to 300 °C. By prior calibration measurements with a reference material of known properties, the specific heat per unit volume of the specimen film can be obtained simultaneously, so that the thermal conductivity and thermal effusivity can be derived. In addition, simultaneous measurement of thermal diffusivity, specific heat per unit volume, and thermal conductivity can be obtained during the melting process. Experiments illustrating various applications and measurements are described and discussed.

1 Introduction

While there are standard techniques for measuring the dielectric, magnetic, and mechanical susceptibilities of condensed matter systems over a wide range of frequency or time, few examples of simultaneous measurements of the frequency-dependent thermal properties exist to date. This is because the thermal properties are considered as a static quantity and because heat flow obeys a diffusion equation, so that it is difficult to apply a uniform temperature field instantaneously to a specimen of finite thickness.

Polymer materials have wide application in many fields of industry and there is a continuing need in particular now to obtain relevant thermal properties data in the solid and molten states. Polymer processing, which is based on the physical property, requires detailed data to assist in the development of the appropriate models that are required. However, as mentioned, data accumulation and analysis is still inadequate not only because of the difficulty in the measurement of heat conduction but also because the thermal property normally measured in the static condition may not be directly appropriate for the analysis of the thermal properties of practical polymer materials during rapid cooling.

To obtain the accurate thermal property as a function of temperature, the specimen needs to be small and thin in order to diminish the temperature distribution in the specimen and to allow it to respond quickly to the stimulation. Thermal properties such as specific heat and thermal diffusivity have been measured as a response function to AC stimulation in the same way as dielectric, magnetic, or mechanical susceptibilities and can be described as complex quantities. Measurement techniques (Parker et al 1961; Sullivan and Seidel 1968; Rosencwaig and Gersho 1976; Adams and Kirkbright 1977; Birge and Nagel 1985; Hatta et al 1988; Reading et al 1992, 1993; Kato et al 1993) have varied in the means of stimulation, the position of detection of the response, and the frequency range, but few examples have been observed for the frequency dependence of thermal properties.

Recently a new modified technique (Hashimoto et al 1990; Hashimoto and Tsuji 1992, 1993; Hashimoto 1993; Morikawa et al 1995; Morikawa and Hashimoto 1998) for measurements of thermal diffusivity of polymers, in which a solution to the heat diffusion equation is used for analysing the temperature wave diffusion in the specimen, has been developed. The thermal diffusivity is obtained from the relationship between the square root of frequency and the phase delay of the sinusoidal temperature wave at a constant temperature. A data base for polymers (Hashimoto 1993) indicates that this method is rapid enough and effective for providing reliable properties to be used for studying the melting process and glass transition of materials. This technique is also extremely useful because it can be applied to a continuous measurement of thermal diffusivity as a function of temperature under both heating or cooling at a constant rate.

The purpose of this work is to describe a new piece of apparatus that is based on the related theory of the technique which is described elsewhere (Morikawa et al 2001). This method now makes it possible to determine simultaneously the thermal diffusivity and heat capacity per unit volume at plural frequencies under temperature scanning by analysing the higher order harmonics of temperature waves. The major advantages and application are its uses to determine thermal properties of materials in the solid and liquid state during one run and to provide reliable quantitative and qualitative data on heating and cooling. Here, a detailed description of the measurement technique of Fourier transform thermal analysis is shown with the example of liquid n-alkane. The frequency dependence of the thermal property at the phase transition is discussed elsewhere (Morikawa and Hashimoto 1998; Morikawa and Hashimoto 2000; Morikawa et al 2001).

2 Theory

The technique exploits the fact that the solution to the heat diffusion equation is simple near a thin, flat plane heater of negligible heat capacity. The specimen with thickness d is sandwiched with substrates having a semi-infinite thickness and known thermal properties. On the assumption of only one-dimensional heat flux, generated in the heater on one surface of the specimen ($x = 0$), the temperature modulation with sinusoidal or square wave form generated on the front surface by AC Joule heating propagates in the specimen and reaches the rear surface ($x = d$). If the temperature wave decays to zero at infinite position in the plate, the temperature oscillation at the rear surface, $T(d,\ t)$, detected by the sensor is obtained by solving the one-dimensional thermal diffusion equation (Carslaw and Jaeger 1959) for each nth order harmonic:

$$T(d,\ t) = \frac{2c\alpha^{1/2}}{(c\alpha^{1/2} + c_s\alpha_s^{1/2})^2} j_0 \left[\!\!\left[\sum_{\substack{n=-\infty \\ (n\neq 0)}}^{\infty} \left| \frac{\sin(an\pi)}{n\pi} \right| \frac{1}{(|n|\omega)^{1/2}} \exp\left[-\left(\frac{|n|\omega}{2\alpha} \right)^{1/2} d \right] \exp\left\{ \mathrm{i} \left[n\omega t - \left(\frac{|n|\omega}{2\alpha} \right)^{1/2} d - \frac{\pi}{4} - an\pi \right] \right\} \right]\!\!\right] , \qquad (1)$$

if $kd \gg 1$ or $k\lambda - k_s\lambda_s \cong 0$.

The phase delay ($\Delta\theta_n$) and decaying amplitude (A_n) of each nth order harmonic is given as follows:

$$\Delta\theta_n = \left(\frac{|n|\omega}{2\alpha}\right)^{1/2} d - \frac{\pi}{4} - an\pi \ , \tag{2}$$

$$A_n = B\frac{2c\alpha^{1/2}}{(c\alpha^{1/2} + c_s\alpha_s^{1/2})^2}\, j_o \left|\frac{\sin(an\pi)}{n\pi}\right| \frac{1}{(|n|\omega)^{1/2}} \exp\left[-\left(\frac{|n|\omega}{2\alpha}\right)^{1/2} d\right] \ , \tag{3}$$

$$F(n) = \left|\frac{\sin(an\pi)}{n\pi}\right| \frac{1}{(|n|)^{1/2}} \ ,$$

$$E(n) = \exp[-(|n|)^{1/2}kd] \ .$$

In the above, α is the thermal diffusivity of the specimen, ω is the angular frequency of the temperature wave, a is the duty factor of the square wave, d is the thickness of the specimen, B is the constant of the apparatus, j_0 is the heat flux, and c is the specific heat of the specimen; the subscript s means plate substrate material.

The thermal diffusivity and heat capacity per unit volume are obtained as a function of temperature or as a function of frequency to a limit determined by kd, where k is $(\omega/2\alpha)^{1/2}$, by the detection of phase delay and amplitude decay under the temperature scanning at a constant rate. This can be accomplished by the use of a thin sputtered metal film element as both the heater and temperature sensor. It is not necessary to make an extremely thin sample cell or make the range of frequency high, because the high frequency limit is determined by kd.

3 Apparatus requirements and constituents

The essential requirements for the design and use of the apparatus were: (i) to measure thermal properties such as α, c, and λ across thin films as a function of temperature and/or as a function of frequency; (ii) to obtain static values and the continuous changes of thermal properties under a temperature scanning rate range of $\pm 0.2-10$ K min^{-1} including melting, crystallisation, or glass transition regions; (iii) to be useful for a wide range of materials including plastics, ceramics, and metals; (iv) to provide in situ observation of the specimen with a microscope and also simultaneous measurement of differential thermal analysis (DTA) for the same specimen during the measurement of thermophysical properties; (v) to cover the approximate temperature range between -50 °C and 300 °C.

A schematic diagram of the measurement system is shown in figure 1. In the measurement system, the DC temperature difference between the specimen and a reference material film, such as silica glass, located near the specimen film, can be continuously detected with the duplicate heaters and sensors and input to a computer as a DTA signal through a DC microvoltmeter.

A thermocouple is buried in the substrate plate near the sensor cell to detect the absolute temperature of the specimen. The sandwich cell is surrounded by a copper jacket, which can be controlled at a constant temperature or heating or cooling at a selected constant rate between 0.2 K min^{-1} and 10 K min^{-1} in the temperature range -50 °C to 300 °C. The function synthesiser, lock-in amplifier, and temperature controller are all automatically controlled by a computer with GPIB interface cable and RS232C.

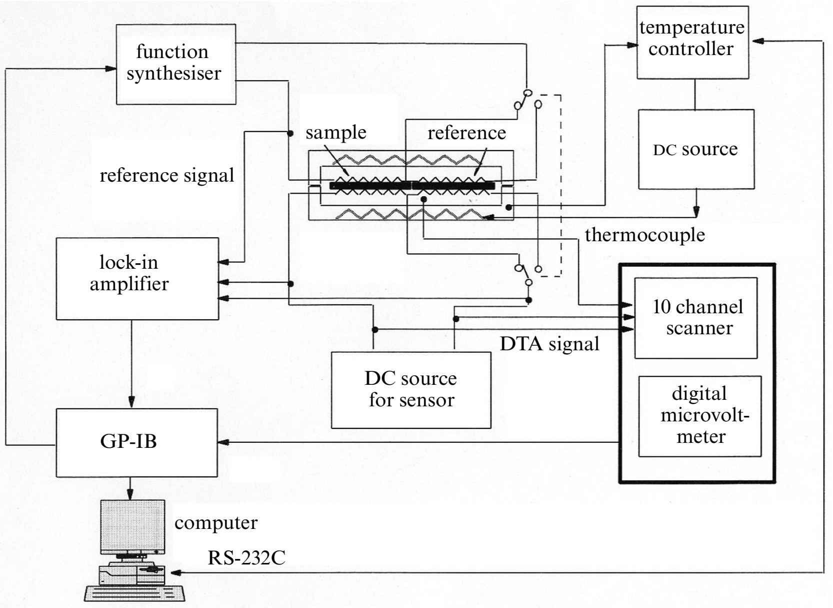

Figure 1. Schematic diagram of measurement system (both specimen film and reference film are sandwiched symmetrically for simultaneous DTA).

4 Detail

4.1 *Heater and sensor*

A sputtered thin gold layer of resistance R_h (approximately 50 Ω) is used as a temperature wave generator (heater) and another similar layer as a temperature sensor with resistance R_s. Gold is used because of its high temperature coefficient of resistance and its stability under repeated heating and cooling runs. The thickness of the sputtered gold layer ($\sim$ 100 Å) is much lower than the specimen thickness. The specimen film of the order of 5×10 mm^2 in area and 1 to 100 μm in thickness is inserted between two glass plates on which the thin gold layers are sputtered as sensor, generator, and leads. The thickness is maintained by the insertion of spacers, or it is entirely enclosed by epoxy resin in order to avoid specimen deformation during measurement. This type of sandwich cell is also applicable for liquids or for measurements during melting and solidification. Alternatively, for polymers or other insulators, a direct sputtering method is used. In this case the thermal contact between specimen and sensor or heater is improved, and the specimen is entirely enclosed in epoxy resin or inorganic adhesives to avoid deformation due to shrinkage or melting of specimen.

A square wave current supplied from a function synthesiser (NF1940) through the heater layer generates a temperature wave at the front surface of the specimen, which propagates through the film to the rear surface. The frequency or the amplitude of the temperature wave is chosen by considering the relationships between the thermal diffusion length (μ) and the specimen details (for example, $kd > 1$). When constant current I is applied to the resistor R_s, the resistance is obtained as follows:

$$R_s(t) = R_{so}[1 + \gamma T(d, t)] \ , \tag{4}$$

and the signal voltage is

$$V_{sig} = IR_{so}\gamma T(d, t) \ , \tag{5}$$

where γ is a temperature coefficient of the resistor and R_{so} is the intitial resistance value. Thus, the signal voltage is proportional to the temperature oscillation at $x = d$. The AC temperature oscillations at the rear surface are detected by the signal voltage V_{sig}, which is analysed with a digital lock-in amplifier (SR 830) with the *nf* (frequency of the *n*th harmonic) mode of each harmonic.

The heat flux at the heater is controlled at 50 mW, or at least less than 100 mW. From the measured relationships between the heat flux and the phase delay, $\Delta\theta$, and between the heat flux and amplitude it has been found that the heat flux of 50 mW has little or no effect on the phase delay in the temperature diffusion. The AC temperature at the heater is estimated to be approximately less than 0.1 K. The exothermic heat at the sensor is also controlled to be less than 100 mW. It has been found that the use of a higher resistance than 500 Ω causes a breakage during repeated runs, while a resistance lower than 50 Ω produces a higher generating heat.

When the specimen thickness is 50 μm, the ratio of the heater width to specimen thickness is approximately 20. Thus, the heat flow in the in-plane direction can be neglected. In addition, the ratio of length and width of the rectangle of the resistance has no influence on the measurement providing the generated heat flow is maintained at a constant level.

4.2 *Heater/thermometer temperature calibration*

This method is based on the measurement of AC temperature diffusion in a material at a selected frequency with a lock-in technique, such that the DC temperature has an influence only on the temperature of the system but not on the AC temperature diffusion. Thus, the amount of exothermic heat at the heater or at the sensor is kept as small as possible in order to detect the temperature wave, which can have an amplitude of 0.1 μV at the sensor.

If V_{sig} (at sensor) is assumed to be 1 μV and the temperature coefficient, γ, of gold is $4 \times 10^{-4}\ \mathrm{K}^{-1}$, the AC temperature at the sensor, T_{ac}, is $6.7 \times 10^{-4}\ \mathrm{K}^{-1}$. Thus if $kd = 1$ is satisfied, the AC temperature at the heater is 1.8 mK. Experimentally, the time constant of the gold sensor is small enough up to 50 kHz.

The standard deviation of the average value of thermal diffusivity is less than 2%, but the average value deviates in the range of ±3%. A change of the sample thickness due to thermal expansion on heating or cooling is less than 1% for a temperature change of 100 K. Therefore, the effect of thermal expansion is negligible and can be included in the experimental error.

5 Measurement data

The harmonics of a temperature wave propagating in liquid n-alkane ($C_{12}H_{26}$) was examined. Figure 2a shows some examples of the phase delay ($\Delta\theta + an\pi$) and the amplitude decay (A_n) of each harmonic of the temperature wave detected in the $C_{12}H_{26}$ liquid. The fundamental frequencies, f, are 18 Hz and 30 Hz, the duty factors, a, are 0.2 and 0.125, and the order, n, is 1st ~ 4th or 1st ~ 7th. The detected signal is analysed with the mathematical rule described in equations (1)–(3), and compared with the result of the sinusoidal temperature wave. Each data point can be plotted on the master line both for the phase delay and the amplitude, in which the slope leads to the thermal diffusivity, and the intercept of amplitude leads to the specific heat per unit volume. The good linearity in figure 2a means that the harmonics can be analysed by equations (1) to (3) successfully. It was also confirmed that there is a linear relationship between the amplitude of each harmonic and the Fourier coefficient corrected value, $F(n)E(n)/\omega^{1/2}$, in figure 2b. The amplitude of each harmonic is well described by equation (3).

The fast Fourier transform signals of the harmonics of the temperature wave in $C_{12}H_{26}$ detected on the sensor are shown in figure 3. The prohibition rule in equation (3); which states that the harmonics of the fifth multiple cannot be observed when $a = 0.2$, is clearly confirmed.

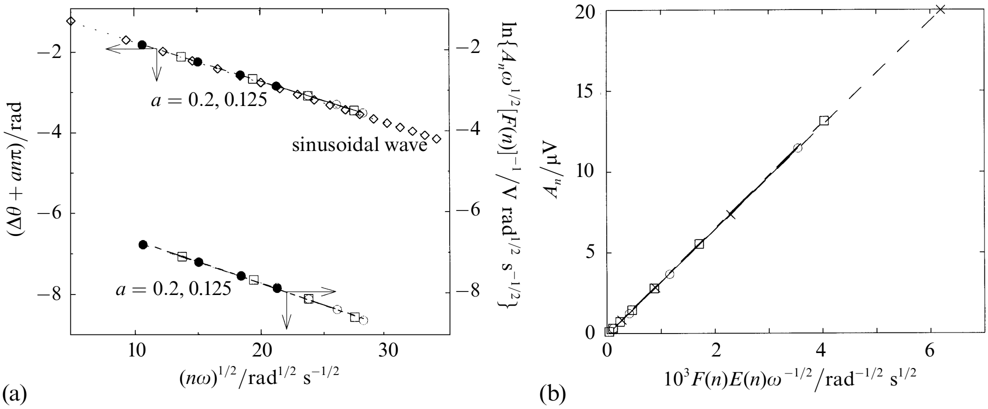

Figure 2. (a) The phase delay ($\Delta\theta + an\pi$) and the amplitude decay (A_n) of each harmonic corrected by Fourier coefficient defined as $F(n)$. The fundamental frequency f and the duty factor a are as follows: ●, $f = 18$ Hz, $a = 0.2$, $n = 1 \sim 4$; □, $f = 30$ Hz, $a = 0.2$, $n = 1 \sim 4$; ○, $f = 18$ Hz, $a = 0.125$, $n = 1 \sim 7$; ◇, frequency scan of sinusoidal wave. (b) The relationship between the amplitude A_n of each harmonic and the corrected Fourier coefficient $F(n)E(n)/\omega^{-1/2}$: □, $f = 18$ Hz, $a = 0.2$, $n = 1 \sim 4$; ×, $f = 30$ Hz, $a = 0.2$, $n = 1 \sim 4$; ○, $f = 18$ Hz, $a = 0.125$, $n = 1 \sim 7$.

In the above figures 2a and 2b, the thermal effusivity, $c\alpha^{1/2}$, and then c can be calculated from the intercept in figure 2a or the slope in figure 2b when compared with the reference material with known thermal properties. Here, for the purpose of high accuracy, the third method is introduced. The signal amplitude increases with increasing amount of heat flux in response to the function of specific heat or thermal effusivity of the system according to equation (3).

Figure 4 shows the corrected amplitude, $A_n\omega^{1/2}/F(n)E(n)$, of each harmonic plotted against the wattage of heat flux on the heater for the liquid specimen (toluene, $C_{12}H_{26}$, $C_{17}H_{36}$) and solids ($C_{33}H_{68}$) at room temperature. The slope is a function of thermal effusivity, $c\alpha^{1/2}$, in equation (3). So the specific heat c can be obtained when α is obtained from the $\Delta\theta$ measurement with the reference data for estimating the heat flux amount. The results on thermal properties, α, c, and λ, are shown in table 1, in which toluene

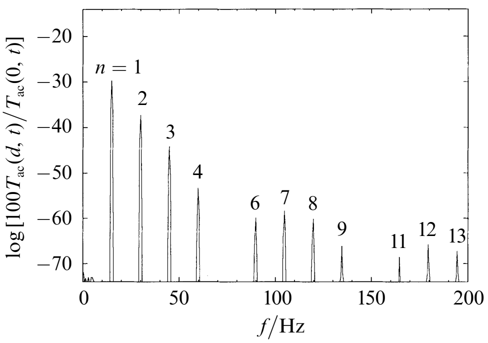

Figure 3. Fourier spectrum of the temperature wave in $C_{12}H_{26}$: $f = 15$ Hz, $a = 0.2$, $n = 1 \sim 13$, and $d = 38$ μm.

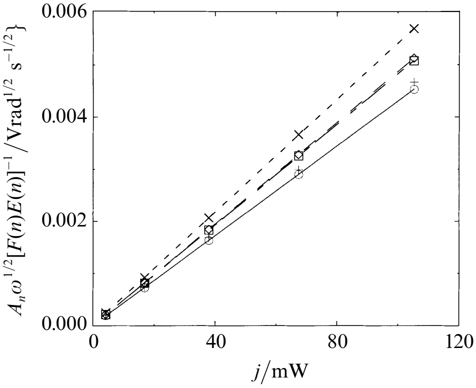

Figure 4. Plots of the corrected amplitude $A_n\omega^{1/2}/F(n)E(n)$ of each harmonic against the wattage of heat flux on the heater: ○, toluene, $f = 18$ Hz, $a = 0.2$, $n = 1$; ◇, $C_{12}H_{26}$, $f = 18$ Hz, $a = 0.2$, $n = 1$; □, $C_{17}H_{36}$, $f = 15$ Hz, $a = 0.2$, $n = 1$; ×, $C_{33}H_{68}$, $f = 15$ Hz, $a = 0.2$, $n = 1$.

Table 1. Comparison of measured thermal properties at room temperature by the Fourier transform thermal analysis technique with published values: (l), liquid; (s), solid.

Sample	$10^7\alpha/\mathrm{m^2\,s^{-1}}$	$c\alpha^{1/2}/\mathrm{J\,m^{-2}\,K^{-1}\,s^{-1/2}}$	$10^6 c/\mathrm{J\,m^{-3}\,K^{-1}}$	$\lambda/\mathrm{W\,m^{-1}\,K^{-1}}$	$\lambda/\mathrm{W\,m^{-1}\,K^{-1}}$[a]
Toluene (l)	0.88	420	1.5	0.13	0.13
$C_{12}H_{26}$ (l)	0.75	440	1.6	0.12	0.14
$C_{17}H_{36}$ (l)	0.75	430	1.6	0.12	
$C_{33}H_{68}$ (s)	2.0	804	1.8	0.36	
PE (s)	3.5	880	1.5	0.53	0.46 ~ 0.53
PI (s)	1.7	610	1.5	0.26	0.29
Epoxy (s)	1.6	450	1.1	0.18	0.20

[a] Japan Society of Thermophysical Properties (1990).

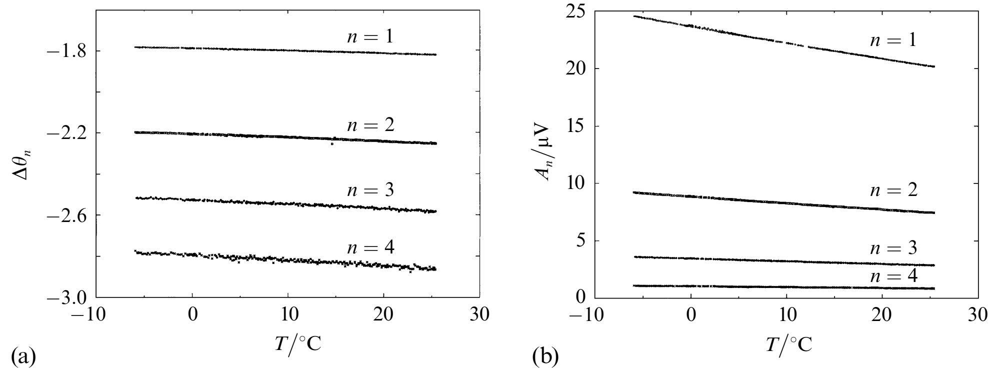

Figure 5. (a) The phase delay ($\Delta\theta$) and (b) the amplitude (A_n) of each harmonic in the simultaneous measurement of $C_{12}H_{26}$ on heating and cooling: $f = 18$ Hz, $a = 0.2$, $n = 1 \sim 4$, scan rate is $\pm 0.2\ \mathrm{K\,min^{-1}}$.

is used as a reference. A comparison of measured thermal properties by this Fourier transform thermal analysis technique with published values at room temperature is also shown in table 1.

The advantage of this technique is the application for the temperature scan under the simultaneous measurement of harmonics. Figure 5 shows the phase delay ($\Delta\theta$) and the amplitude (A_n) of each harmonic propagated in $C_{12}H_{26}$ on heating and cooling. The fundamental frequency, f, is 18 Hz, the duty factor a, is 0.2, the order of the harmonic, n, is $1-4$, and the scan rate is $\pm 0.2\ \mathrm{K\,min^{-1}}$. As can be seen in figure 5, the signal is extremely stable and good precision is assured.

The dependence of thermal diffusivity α, heat capacity per unit volume c, and thermal conductivity λ on temperature derived from figure 5 is shown in figure 6.

6 Summary

A new piece of apparatus based on the Fourier transform thermal analysis technique has been developed to measure thermophysical properties, both static and during controlled heating and cooling. Experiments show that it can also be used for thermal analysis applications by simultaneous measurement of thermal properties and their dependences on frequency and temperature during melting, solidification, and phase transition. Such property information is required for processing and application of materials.

The major advantages of this technique are summarised as follows: (i) a very small temperature gradient is established across the thickness direction of the film specimen; (ii) measurement can be made over a broad temperature range covering the solid and

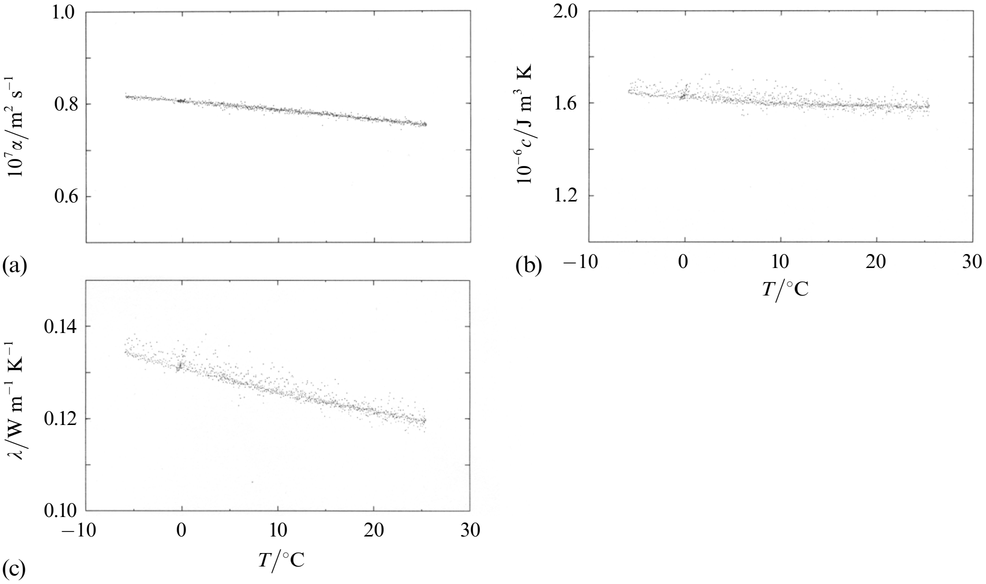

Figure 6. The temperature dependence of (a) thermal diffusivity α, (b) heat capacity per unit volume c, and (c) thermal conductivity λ, derived from figure 5.

molten state; (iii) a short measurement period; (iv) a high temperature resolution; (v) no special specimen pretreatment, for example coating the surface; (vi) simultaneous measurements of thermal diffusivity, specific heat capacity per unit volume, and thermal conductivity from an analysis of high-order harmonics of the temperature wave which is really propagated in the specimen; (vii) thermal diffusivity, specific heat, and thermal conductivity measurements while heating or cooling at constant rate of 0.2 K $\mathrm{min^{-1}}$ to 10 K $\mathrm{min^{-1}}$; (viii) property dependences on temperature and frequency from only one run with a fundamental frequency.

References

Adams M J, Kirkbright G F, 1977 *Analyst* **102** 678 – 682
Birge N O, Nagel S R, 1985 *Phys. Rev. Lett.* **54** 2674 – 2677
Carslaw H S, Jaeger J C, 1959 *Conduction of Heat in Solids* second edition (Oxford: Oxford University Press)
Hashimoto T, 1993 *Handbook of Thermal Properties of Polymers* (Tokyo: Yu-tes)
Hashimoto T, Tsuji T, 1992, presented at the Tenth International Congress on Thermal Analysis, Hatfield, UK, 24 – 28 August
Hashimoto T, Tsuji T, 1993 *J. Therm. Anal* **40** 721 – 726
Hashimoto T, Hagiwara A, Miyamoto A, 1990 *Thermochim. Acta* **163** 317 – 324
Hatta I, Sakakibara K J, Suzuki J, Yao H, 1988 *Jpn. J. Appl. Phys.* **27** 2156 – 2159
Japan Thermophysical Society, 1990 *Thermophysical Properties Handbook* (Tokyo: Yoken-do)
Kato R, Maesono A, Hatta I, 1993 *Jpn. J. Appl. Phys.* **32** 3653 – 3655
Morikawa J, Hashimoto T, 1998 *Jpn. J. Appl. Phys.* **37** L1484 – L1487
Morikawa J, Hashimoto T, 2000 *Thermochim. Acta* **352 – 353** 291 – 296
Morikawa J, Hashimoto T, Maesono A, 2001 *High Temp. – High Press.* **33** 000 – 000
Morikawa J, Tan J, Hashimoto T, 1995 *Polymer* **36** 4439 – 4443
Parker W J, Jenkins R J, Butler C P, Abbott G L, 1961 *J. Appl. Phys.* **32** 1679 – 1687
Reading M, Elliott D, Hill V L, 1992, presented at the Tenth International Congress on Thermal Analysis, Hatfield, UK, 24 – 28 August
Reading M, Elliott D, Hill V L, 1993 *J. Therm. Anal.* **40** 949 – 955
Rosencwaig A, Gersho A, 1976 *J. Appl. Phys.* **47** 64 – 69
Sullivan P F, Seidel G, 1968 *Phys. Rev.* **173** 679 – 685