BUTTERWORTH
HEINEMANN

*Polymer* Vol. 36 No. 23, pp. 4439–4443, 1995

0032-3861/95/$10.00+0.00

# Study of change in thermal diffusivity of amorphous polymers during glass transition

**Junko Morikawa*, Junji Tan and Toshimasa Hashimoto**
*Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan*
*(Received 4 April 1995)*

The thermal diffusivity of amorphous polymers was investigated by the newly developed a.c. joule heating technique in the practical temperature range including the melt state, glass transition and glassy state. The temperature dependence of thermal diffusivity was measured both in the glassy state and the melt state and its discontinuous change at the glass transition was clearly observed. $\Delta\alpha$, defined as the change of thermal diffusivity during the glass transition, was closely related to the glass transition temperatures and to the change in heat capacity, $\Delta C_p$. It is confirmed that the thermal diffusivity is one of the basic thermophysical properties which can connect the chemical structure and molecular weight of polymer to the glass transition.

**(Keywords: thermal diffusivity; amorphous polymers; glass transition)**

## INTRODUCTION

The thermophysical properties of polymers, such as heat capacity at constant pressure $C_p$, thermal diffusivity $\alpha$, thermal conductivity $\lambda$, and density $\rho$, are closely related according to the formula[1]:

$$\lambda = \alpha C_p \rho \tag{1}$$

Hence, in polymer processing the thermal transport properties such as thermal diffusivity $\alpha$ and thermal conductivity $\lambda$ are important both from the theoretical and practical points of view. However, because of the difficulty in measuring $\alpha$ and $\lambda$ over a wide temperature range, there have been few discussions of $\alpha$ and $\lambda$ based on detailed experimental data.

A new a.c. joule heating technique has been developed to measure thermal diffusivity[2,3]. The main advantages of this technique are as follows: (1) small temperature gradient across a small part of the sample; (2) wide temperature range including the melt state; (3) short measurement period; and (4) high temperature resolution. By this technique it is possible to measure the temperature dependence of thermal diffusivity of polymers over a temperature range including the glass transition and crystallization.

In this paper we studied the thermal diffusivity of amorphous polymers, including engineering plastics, in which the glass transition temperatures are higher than 250°C, and the changes of thermal diffusivity during the glass transition.

## THEORY

The heat flow in polymer films, with thickness $d$ and attached by the substrate at $x = 0$ and $x = d$ as depicted in *Figure 1*, is described by the one-dimensional heat diffusion equation (the thermal flow vertical to the sample thickness is neglected because the area of the gold-sputtered sensor, 1 mm × 6 mm, is much larger than the sample thickness, 50 $\mu$m):

$$\begin{aligned} \frac{\partial T}{\partial t} &= \alpha \frac{\partial^2 T}{\partial x^2} \quad (0 < x < d) \\ \frac{\partial T}{\partial t} &= \alpha_s \frac{\partial^2 T}{\partial x^2} \quad (x < 0 \text{ and } d < x) \end{aligned} \tag{2}$$

where $T$ is temperature, $\alpha$ is the thermal diffusivity of the polymer and $\alpha_s$ is that of the substrate. It is assumed that the substrate is infinite (the substrate (glass slide, 0.9 mm, or epoxide resin) is much thicker than the sample, so the thermal wave is allowed to decay to be negligible), so the temperature oscillations at infinity are:

$$\begin{aligned} T(x \to -\infty, t) &= 0 \\ T(x \to +\infty, t) &= 0 \end{aligned} \tag{3}$$

The boundary conditions at $x = 0$ and $x = d$ are:

$$\begin{aligned} T(x \to -0, t) &= T(x \to +0, t) \\ T(x \to d_{-0}, t) &= T(x \to d_{+0}, t) \end{aligned} \tag{4}$$

(There is no contact resistance between the gold-sputtered layer (sensor and heater) and the sample or substrate. The sputtered layer is much thinner (~100 Å) than the sample, so the temperature is continuous at the boundary of sample and substrate.) The thermal balances at the interface of polymer and substrates are:

$$\begin{aligned} \kappa_s \frac{\partial T}{\partial x}\bigg|_{x\to -0} - \kappa \frac{\partial T}{\partial x}\bigg|_{x\to +0} &= q(t) = q_0 \exp(i\omega t) \\ \kappa \frac{\partial T}{\partial x}\bigg|_{x\to d-0} - \kappa_s \frac{\partial T}{\partial x}\bigg|_{x\to d+0} &= 0 \end{aligned} \tag{5}$$

---

* To whom correspondence should be addressed

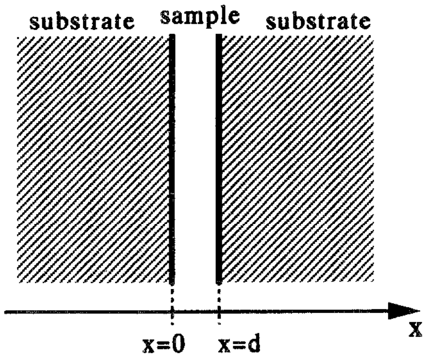

**Figure 1** Schematic diagram of a sample, a heater and a sensor, and an infinite substrate

where $\kappa$ and $\kappa_s$ are the thermal conductivities of the polymer and substrates, and $q(t)$ is a periodical heat flow.

The heat diffusion equation (2) can be solved by the boundary conditions in equations (3)–(5). The temperature oscillation at $x = d$ is[4,5]:

$$T(d,t) = \frac{[q_0 \exp(i\omega t)/(1+i)] \exp[-(1+i)kd]}{\{(\kappa k + \kappa_s k_s)^2 - (\kappa k - \kappa_s k_s)^2 \exp[-2(1+i)kd]\}/2\kappa k} \tag{6}$$

where $k = (\omega/2\alpha)^{1/2}$ and $k_s = (\omega/2\alpha_s)^{1/2}$. If $kd > 1$, the second term in the denominator is much smaller than the first term and then equation (6) becomes:

$$T(d,t) = \frac{\sqrt{2} q_0 \kappa k \exp(-kd)}{(\kappa k + \kappa_s k_s)^2} \exp\left[i\left(\omega t - kd - \frac{\pi}{4}\right)\right] \tag{7}$$

The condition $kd > 1$ means that the sample is thermally thick. On the other hand, the voltage across the resistance $R$ in *Figure 2* is obtained as:

$$V_R = \frac{RE}{R + R_s(t)} \tag{8}$$

$$R_s(t) = R_s + aR_s T(d,t) \tag{9}$$

where $R_s$ is the resistance of the sputtered gold sensor at a measured temperature, $a$ is a temperature coefficient, and $E$ is a d.c. voltage. (The second term in equation (9), the change term of $R_s(t)$ by the temperature oscillation, is much smaller than $R_s$.) When equation (9) is substituted into equation (8), $V_R$ is obtained as:

$$V_R = \frac{RE}{R_s + R} - \frac{aR_s RE}{(R_s + R)^2} T(d,t) \tag{10}$$

The second term in equation (10) is the signal voltage $V_{signal}$:

$$V_{signal} = \frac{aR_s RE}{(R_s + R)^2} T(d,t) = AT(d,t) \tag{11}$$

That is, the signal voltage is proportional to the temperature oscillation at the rare surface of the samples. From equations (7) and (11) the signal voltage is derived as:

$$V_{signal} = A \frac{\sqrt{2} q_0 \kappa k \exp(-kd)}{(\kappa k + \kappa_s k_s)^2} \exp\left[i\left(\omega t - kd - \frac{\pi}{4}\right)\right] \tag{12}$$

The amplitude of the signal voltage and the phase delay to the reference are determined by the lock-in amplifier. The phase delay $\Delta\theta$ is determined as:

$$\Delta\theta = \sqrt{\frac{\pi f}{\alpha}} d + \frac{\pi}{4} \tag{13}$$

where $f$ is the frequency of the generated heating wave ($f = \omega/2\pi$) and $\alpha$ is determined by the slope in the linear plot of $\Delta\theta$ and $\sqrt{f}$.

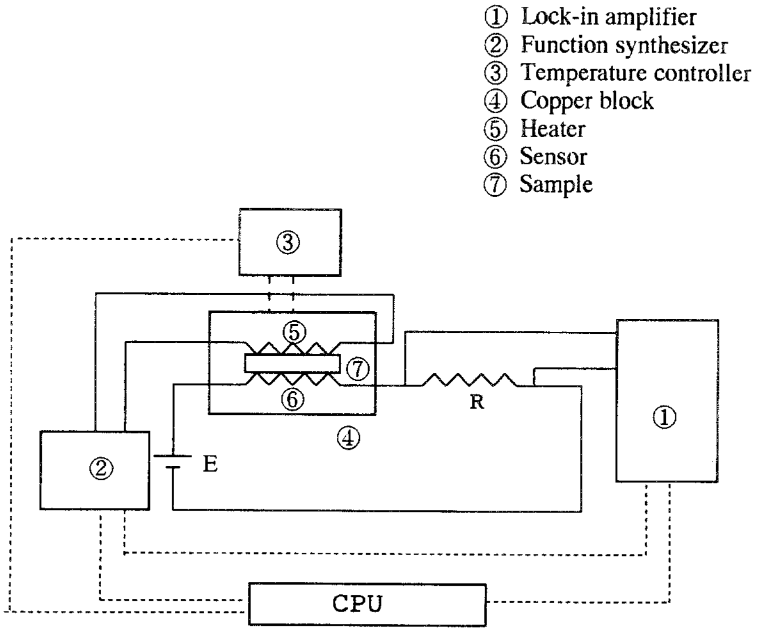

**Figure 2** Schematic diagram of the measurement apparatus: function generator, lock-in amplifier, resistance $R$ and $r$, and d.c. voltage E

**Table 1** The commercial grade of the amorphous polymers and the results of the thermal diffusivity measurement

| Amorphous polymer[a] | Grade | $\alpha$ (40°C) ($10^{-7}\,m^2\,s^{-1}$) | $\alpha$ ($T_g + 30$°C) ($10^{-7}\,m^2\,s^{-1}$) | $T_{g_m}$ (°C) | $\Delta\alpha$ ($10^{-7}\,m^2\,s^{-1}$) | $d\alpha/dT$ (40°C) ($10^{-7}\,m^2\,s^{-1}$) |
|---|---|---|---|---|---|---|
| PS | Topolex 55051 | 1.15 | 0.69 | 105.0 | 0.23 | −0.0019 |
| SAN33 | Laitac A 180PC | 1.11 | 0.65 | 124.0 | 0.16 | −0.0027 |
| PMMA | Parapet GF | 1.08 | 0.66 | 93.0 | 0.12 | −0.0030 |
| PES | Victrex 4800 | 1.42 | 0.79 | 242.0 | 0.46 | −0.0013 |
| PSF | Udel | 1.33 | 0.67 | 198.0 | 0.34 | −0.0014 |
| PI | Larc | 1.61 | 0.71 | 258.0 | 0.38 | |
| PEI | Ultem | 1.39 | 0.58 | 231.0 | 0.52 | −0.0013 |
| PC | Panlite 1250 | 1.73 | 1.15 | 165.0 | 0.38 | −0.0012 |
| mono. PS1 | $M_w = 2200$ | 1.20 | 0.76 | 78.0 | 0.22 | |
| mono. PS2 | $M_w = 10\,000$ | 1.29 | | 110.0 | 0.23 | |
| mono. PS3 | $M_w = 200\,000$ | 1.43 | | 129.0 | 0.36 | |

[a] PS, polystyrene; SAN33, poly(styrene-*co*-acrylonitrile); PMMA, poly(methyl methacrylate); PES, poly(ether sulfone); PSF, poly(arylether aryl)sulfone; PI, polyimide; PEI, poly(ether imide); PC, polycarbonate; mono. PS1, monodispersed polystyrene ($M_w = 2200$); mono. PS2, monodispersed polystyrene ($M_w = 10\,000$); mono. PS3, monodispersed polystyrene ($M_w = 200\,000$)

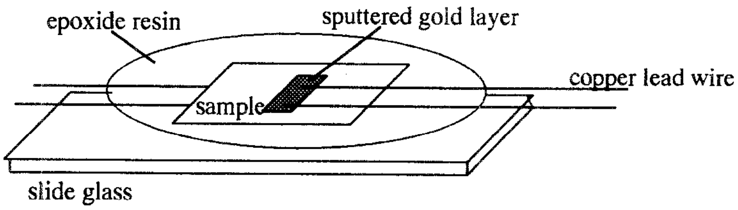

**Figure 3** Schematic diagram of the sample, thin gold layers, copper leads and epoxy adhesive

## EXPERIMENTAL

The polymer specimens used in this study were commercial polymers and are listed in *Table 1*. Samples were melt-hot-pressed into films about 50 $\mu$m thick, and thin gold layers were sputtered onto both surfaces across an area 1–6 mm wide, as shown in *Figure 3*. These layers on the front and the rear surfaces were used for a heater producing the thermal wave by a.c. joule heating and a sensor detecting the temperature wave, respectively. The electrical resistance of the gold layer was controlled at approximately 50 $\Omega$. Copper lead wires were attached to both surfaces of the gold layers. Samples were enveloped in the epoxide resin or imide powder to avoid deformation by shrinkage or melting.

The frequency of the temperature wave varies by twice as much as that of the applied voltage. The thermal wave diffused across the sample in a vertical direction to the rear surface. The temperature variations on the rear surface were detected by the signal voltage $V_{\text{signal}}$ which was analysed using an NF-type lock-in amplifier.

The range of frequency for the measurement was selected as:

$$1.5\sqrt{f_c} < \sqrt{f} < 2.5\sqrt{f_c} \tag{14}$$

where $f_c$ is defined as:

$$d = \sqrt{\frac{\alpha}{\pi f_c}} \tag{15}$$

*Figure 4* shows typical data on the relationship between the square root of $f$ and the phase shifts at 50 and 270°C, which correspond to the glassy and melt state of poly(ether sulfone). The gradient and thermal diffusivity can be obtained from equation (13). This method is based on the phase-shift measurement, hence the influence of the backing material, e.g. glass plate, can be neglected.

$C_p$ was measured by differential scanning calorimetry (d.s.c.) (TAS200-DSC 8230D, Rigaku Electric Co. Ltd).

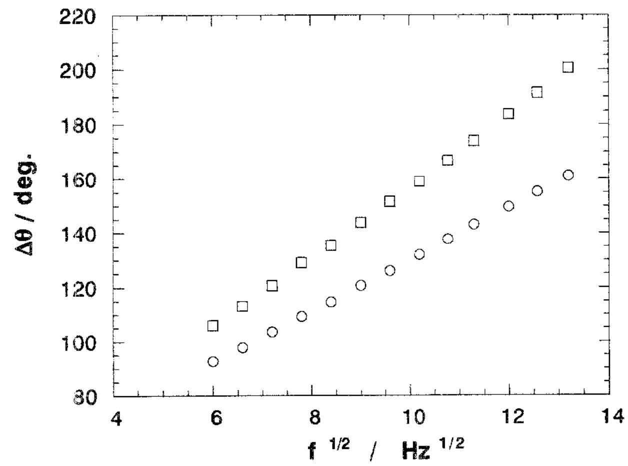

**Figure 4** Phase shift ($\Delta\theta$) vs. square root of frequency ($\sqrt{f}$) for poly(ether sulfone) (PES) obtained at 50°C (○) and 270°C (□)

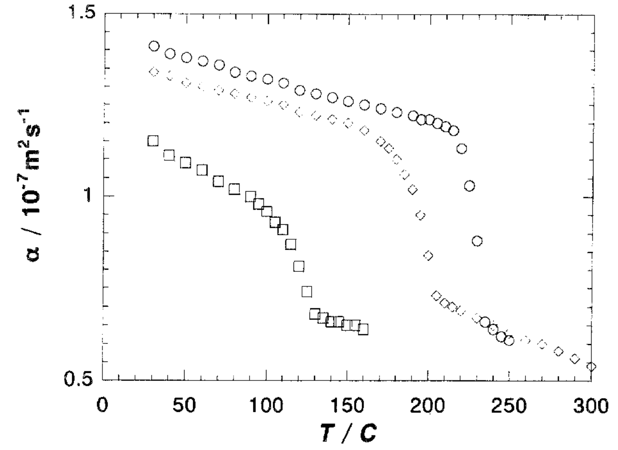

**Figure 5** Temperature dependence of thermal diffusivity for poly(ether imide) (PEI) (○), poly(arylether aryl)sulfone (PSF) (◇) and poly(styrene-*co*-acrylonitrile) (SAN) (□)

The samples were pre-melted at a temperature above the transition temperature for 5 min and then cooled at 5°C min$^{-1}$. $C_p$ was measured at a heating rate of 10°C min$^{-1}$ under an atmosphere of nitrogen.

## RESULTS AND DISCUSSION

*Figure 5* shows the thermal diffusivity $\alpha$ of poly(ether imide) (PEI), poly(arylether aryl)sulfone (PSF) and poly(styrene-*co*-acrylonitrile) (SAN). The temperature dependence of $\alpha$ in the melt state can be measured even in the temperature range above 250°C. The $\alpha$ decreases with increasing temperature and a discontinuous drop is observed at around the glass transition temperature. The glass transition temperatures ($T_g$) are shown in *Table 1*. $T_g$ is defined as the middle point of the glass transition in this measurement.

*Figure 6* shows the $\alpha$ of polycarbonate (PC), polyimide (PI) and poly(ether sulfone) (PES). It is also possible to observe the glass transition above 250°C. The $\alpha$ decreases with increasing temperature in the glassy state and melt state. The absolute values of $\alpha$ in the glassy state (40°C) and melt state ($T_g + 30$°C) are also shown in *Table 1*.

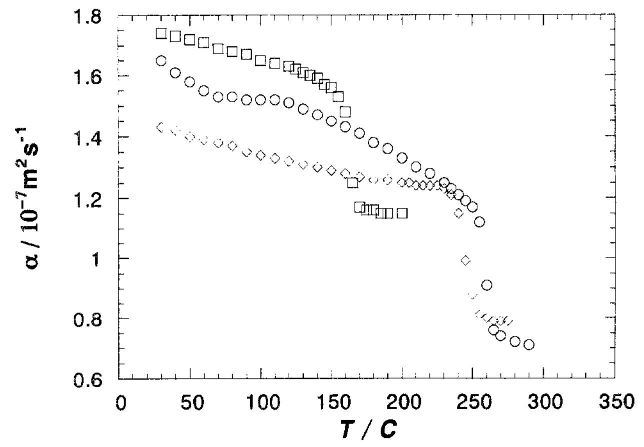

**Figure 6** Temperature dependence of thermal diffusivity for polycarbonate (PC) (□), polyimide (PI) (○) and poly(ether sulfone) (PES) (◇)

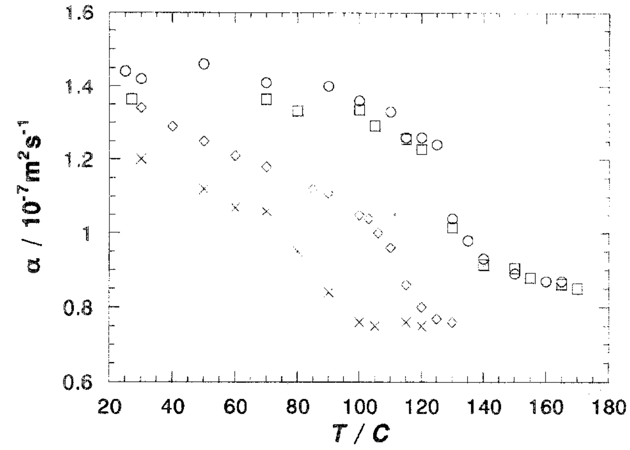

**Figure 7** Dependence of the thermal diffusivity on the molecular weight of monodispersed polystyrene: ○, $M_w = 200\,000$; □, $M_w = 110\,000$; ◇, $M_w = 10\,000$; ×, $M_w = 2200$

In *Figures 5* and *6* it is characteristic that the temperature dependence of $\alpha$ is observed both in the glassy state and in the melt state. For the engineering plastics, the slope of $\alpha$, $d\alpha/dT$, in the glassy state is almost constant (−0.0012 to −0.0014) for PES, PEI, PSF and PC.

*Figure 7* shows the $\alpha$ of monodispersed polystyrene with different molecular weights ($M_w = 2200$, 10 000, 110 000 and 200 000). The $\alpha$ shows molecular weight

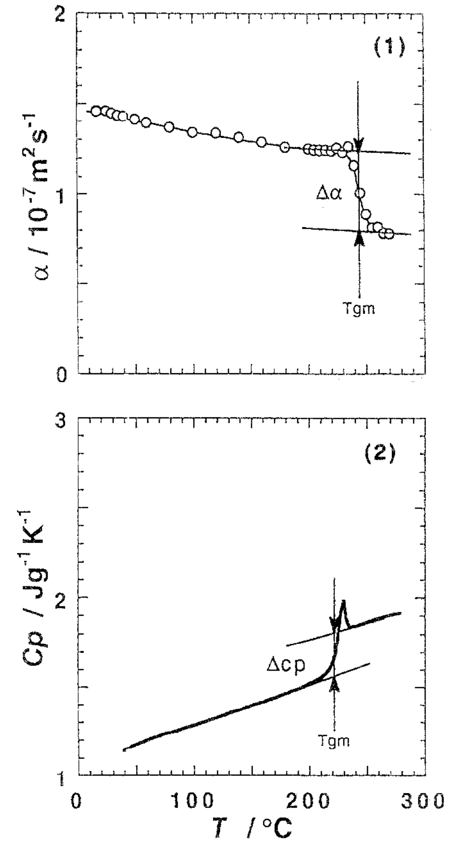

**Figure 8** (1) Definition of the glass transition temperature ($T_g$) and the change of thermal diffusivity ($\Delta\alpha$) during the glass transition in the thermal diffusivity measurement of PES. (2) Definition of the glass transition temperature ($T_g$) and the change of the specific heat ($\Delta C_p$) during the glass transition in d.s.c. measurement of PES

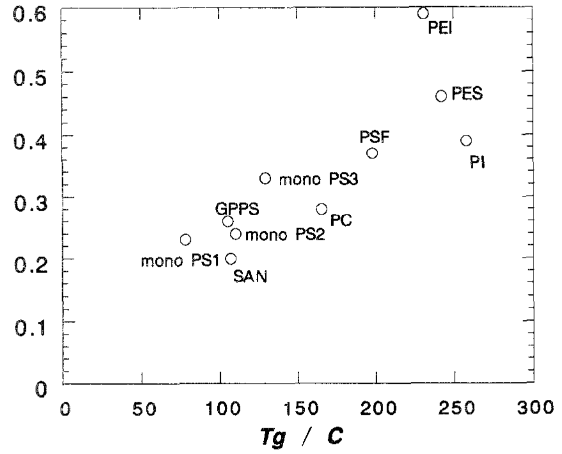

**Figure 9** Plot of $T_g$ and $\Delta\alpha$ of amorphous polymers

dependence. With increasing molecular weight, $\alpha$ and $T_g$ increase, but a saturation level is observed for $\alpha$ when the molecular weight is greater than 110 000. The saturation of thermal conductivity with increasing molecular weight has been observed by several authors[6–9].

The experimental results in *Figures 5–7* show that the thermal diffusivity is one of the thermophysical properties which characterizes the chemical structures and molecular weight of amorphous polymers. We applied this property to analyse the essentials of the glass transition of amorphous polymers. We introduce $\Delta\alpha$, defined as the change of $\alpha$ during the glass transition; it is shown in *Figure 8*. The $\Delta\alpha$ of each polymer is shown in *Table 1*.

*Figure 9* shows the relationship between $\Delta\alpha/\alpha$ (at $T_g$) and $T_g$ of amorphous polymers. $\Delta\alpha/\alpha$ means a change ratio of $\alpha$ at the glass transition of each polymer. The ratio $\Delta\alpha/\alpha$ increases with increasing $T_g$. In other words, at higher glass transition temperatures the thermal diffusivity of polymer changes more drastically.

It has been reported that the physical properties of polymers, such as thermal expansivity, compressibility at constant temperature and heat capacity at constant pressure, changed discontinuously at the glass transition[10,11]. The experimental results in *Figure 9* show that the thermal diffusivity is also one of the thermophysical properties which is connected to the glass transition.

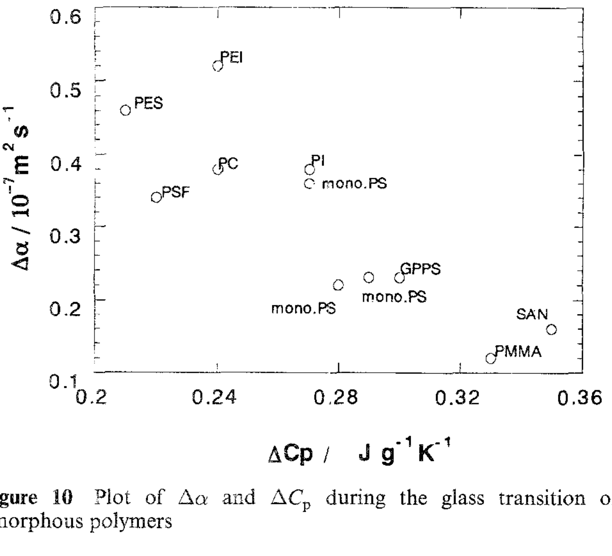

**Figure 10** Plot of $\Delta\alpha$ and $\Delta C_p$ during the glass transition of amorphous polymers

The relation between $T_g$ and $\Delta C_p$ has been discussed by several authors[12–14]. For example, $\Delta C_p$ was described as[14]:

$$\Delta C_p \propto (E_h/RT_g)^2 \exp(-E_h/RT_g) \qquad (16)$$

where $E_h$ is the molar excess energy over the 'no hole' situation, and $R$ is the gas constant. By considering the relationships in *Figure 9* and equation (16), it is possible to connect $\Delta\alpha$ to $\Delta C_p$. Experimentally it is observed that $\Delta\alpha$ is inversely proportional to $\Delta C_p$ (*Figure 10*). This means that the mode of thermal vibration in the amorphous polymer changes drastically during the glass transition, for example the change of the mean free path of a phonon[15–17] during the glass transition.

## CONCLUSION

The thermal diffusivity of amorphous polymers was investigated by the newly developed a.c. joule heating technique in the practical temperature range including the melt state, glass transition and glassy state. The temperature dependence of thermal diffusivity was measured both in the glassy state and the melt state, and its discontinuous change at the glass transition was clearly observed. It is confirmed that this technique is applicable to engineering plastics in which $T_g$ and the melt state are higher than 250°C. The change of thermal diffusivity during the glass transition was determined as $\Delta\alpha$ for the first time.

It was found that $\Delta\alpha/\alpha$ was closely related to the glass transition temperatures. This means that the thermal diffusivity is one of the basic thermophysical properties that can connect the chemical structure and molecular weight of a polymer to the glass transition. The relationship of $\Delta\alpha$ and $\Delta C_p$ was also examined experimentally. $\Delta\alpha$ was inversely proportional to $\Delta C_p$. It is confirmed that the thermal diffusivity is one of the basic thermophysical properties of amorphous polymers.

## REFERENCES

1 Godovsky, Y. K. 'Thermophysical Properties of Polymers', Springer-Verlag, 1992
2 Hashimoto, T. and Tsuji, T. *J. Thermal Anal.* 1993, **40**, 721
3 Hashimoto, T., Matsui, Y., Hagiwara, A. and Miyamoto, A. *Thermochim. Acta* 1990, **163**, 317
4 Birge, N. O. *Phys. Rev. B* 1986, **34**, 1631
5 Hatta, I., Sakakibara, K., Suzuki, J. and Yao, H. *J. Appl. Phys.* 1988, **27**, 2156
6 Uberrciter, K. and Laupenmuhlen, E. O. *Z. Naturforsch.* 1954, **8a**, 664
7 Lohe, P. *Kolloid-Z. Z. Polym.* 1965, **205**, 1
8 Hansen, D. and Ho, C. C. *J. Polym. Sci. Pt A.* 1965, **2**, 659
9 Hansen, D., Kantayya, R. C. and Ho, C. C. *Polym. Eng. Sci.* 1966, **6**, 210
10 Simha, R. and Boyer, R. F. *J. Chem. Phys.* 1962, **37**, 1003
11 Nose, T. *Polym. J.* 1967, **2**, 124, 427, 437, 445
12 Roe, R. J. and Tonelli, A. E. *Macromolecules* 1978, **11**, 114
13 DiMarzio, E. A. and Dowell, F. *J. Appl. Phys.* 1979, **50**, 6061
14 Wunderlich, B. *J. Chem. Phys.* 1960, **64**, 1052
15 Eiermann, K. *J. Polym. Sci. Pt C* 1963, **6**, 157
16 Kittel, C. *Phys. Rev.* 1949, **75**, 972
17 Debye, P. 'Vortage uber die kinetische Theorie der Materie und Elektrizitat Teubner', Berlin, 1914