Thermal diffusivity of polymers by flash radiometry: correlation between thermal diffusivity and fine structure of poly(ethylene terephthalate)

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The thermal diffusivity D of poly(ethylene terephthalate) (PET) film is measured by flash radiometry and the correlation between thermal diffusivity and supramolecular structure of PET is discussed. It is found that D increases stepwise with increasing temperature of heat treatment in the range 100–240°C for 1 h, corresponding to the stepwise increase of crystallite size. Also D increases with increasing time of heat treatment in the range 20–80 min at 220°C, reflecting a change of crystallite form from the thermodynamically unstable one to the more stable one. The *in situ* measurement of D on isothermal crystallization shows that the large increase of D due to first-order crystallization is followed by the gradual and small increase of D due to second-order crystallization. The value of D measured at room temperature for the sample whose D was levelled out on isothermal crystallization has a specific feature: the plot of D against isothermal crystallization temperature has a distinct sharp peak around 107°C and this result is explained as relating to the Avrami exponent calculated from the initial slope of the variation of D on isothermal crystallization. Boiling of a film sample in aqueous phenol solution gives rise to increasing D up to 50 vol% of phenol content, but above this content D decreases. The increase of D is mainly due to the progress of crystallinity by liquid-induced crystallization and the decrease of D is ascribed to the larger contribution of microvoids, which causes phonon scattering.

(Keywords: thermal diffusivity; flash radiometry; poly(ethylene terephthalate); crystallization; fine structure)

INTRODUCTION

A new flash radiometry (pulsed photothermal radiometry) has recently been developed to measure thermal diffusivity of solid materials by a non-contact mode[1–3]. In flash radiometry, a thermal gradient (i.e. thermal non-equilibrium state) is initially produced on the surface of a solid sample by a short-duration pulsed laser or flash, and the subsequent transient infra-red radiation from the heated surface (back-scattering mode) or that from the rear of the heated surface (transmission mode) is detected by an infra-red detector. The transient variation of the surface temperature of the sample can be measured in the range of microseconds to milliseconds, because the response time of the infra-red detector is of the order of microseconds or submicroseconds. This method provides an accurate and non-contact method to measure thermal diffusivity in a thin polymer film. We have applied this technique to the measurement of thermal diffusivity in polymer solids[4,5]. The thermal diffusivity of a solid polymer sensitively reflects the chemical, molecular and supramolecular structures of the polymer. Thus, it can be expected that the method of measuring thermal diffusivity by flash radiometry offers a new technique to analyse the structure of polymer solids.

In this paper, we report results of thermal diffusivity measurements of poly(ethylene terephthalate) (PET) film

by flash radiometry. The correlation between thermal diffusivity and the supramolecular structure of PET will be discussed based on the observed effects on thermal diffusivity of temperature and time of heat treatment, isothermal crystallization temperature and liquid-induced crystallization.

EXPERIMENTAL

Flash radiometry

Figure 1 shows the schematic diagram of the flash radiometry. The flash radiometric system consists of three blocks: (1) optical device block involving a light source for pulse heating and an aluminium-coated Herschelian mirror for concentrating infra-red radiation from the sample onto an infra-red detector; (2) electronic device block including a broad-band preamplifier, a transient memory, a microcomputer and a digital multimeter; and (3) sample chamber block in which the sample film is heated up to a given temperature under a nitrogen atmosphere.

Infra-red radiation was detected by a liquid-nitrogen-cooled HgCdTe detector operating in photoconductive mode with germanium window (Fujitsu model MC-A). The detector is sensitive to 6–12 μm infra-red radiation and has a response time within 2 μs. The light source was a photographic xenon flash lamp (Sunpak Auto-Zoom 4800) whose pulse duration changes from 100 to 1000 μs according to the light intensity, and the light was concentrated onto the sample by means of a light guide.
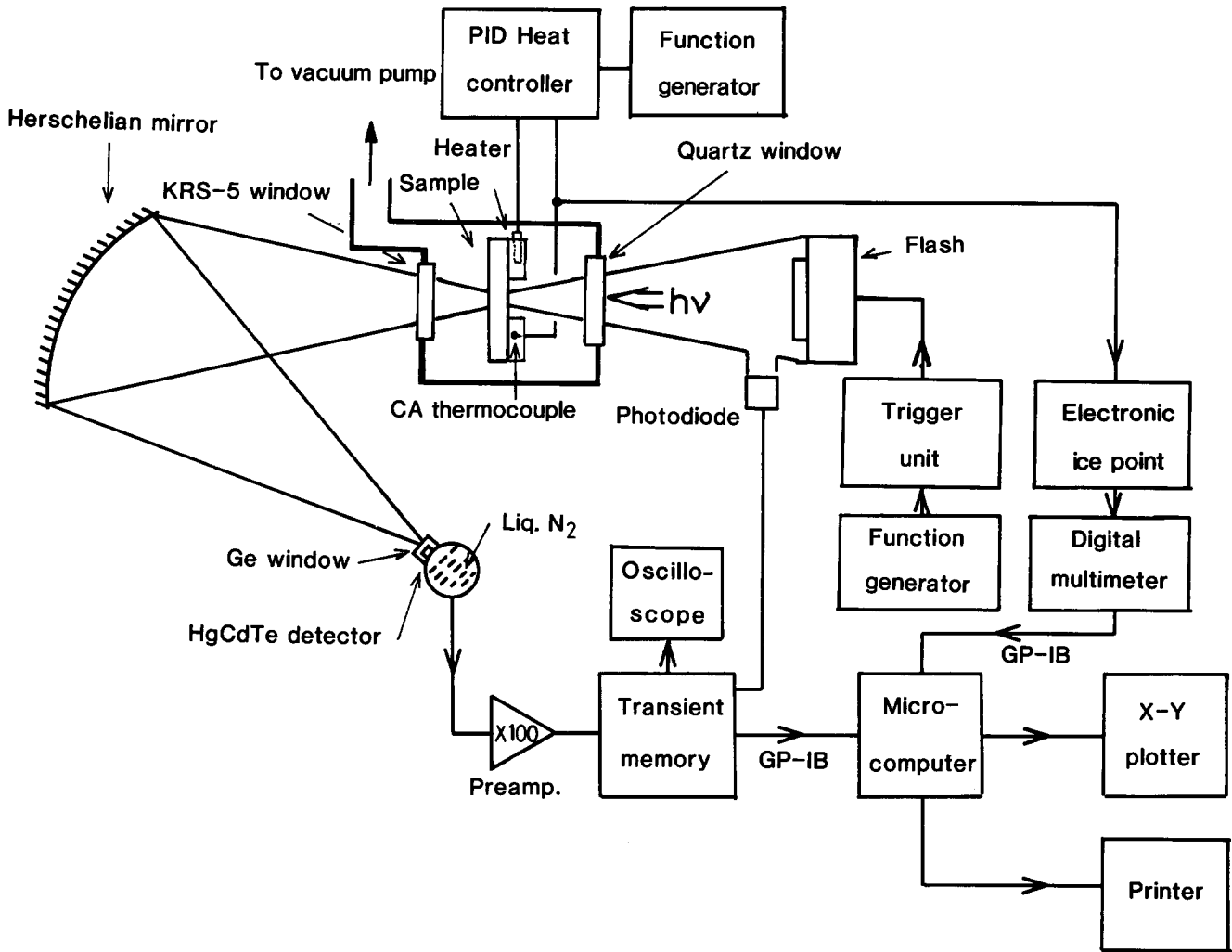
Figure 1 Schematic diagram of flash radiometry

(a) Backscattering mode   (b) Transmission mode
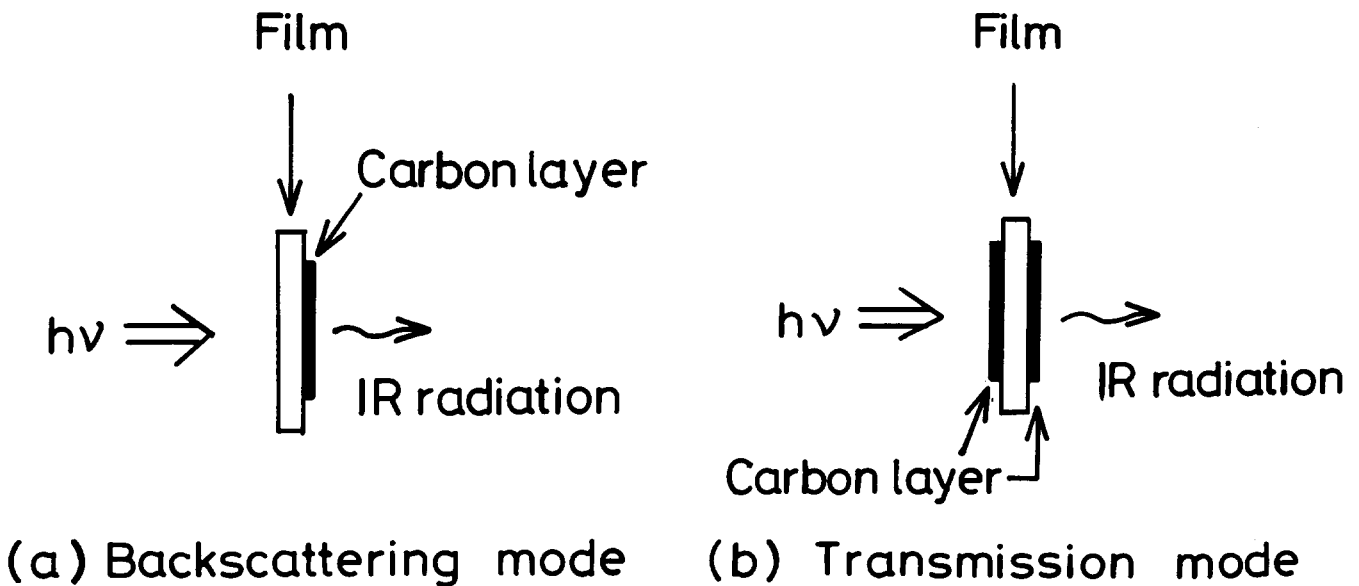
Figure 2 Schematic diagram of two measurement modes: back-scattering mode and transmission mode

Figure 2 shows the schematic diagrams of the two measurement modes: back-scattering mode and transmission mode. For the back-scattering mode, the transient infra-red radiation from the carbon layer coated onto the front surface of the polymer film was measured after the carbon layer was heated by a pulse flash of light passing

through the polymer film. In this mode, transient heat transport into bulk polymer from the carbon layer was observed. For the transmission mode, both surfaces of the polymer film were coated by carbon layers. The carbon layer at the rear surface of the film was heated by a pulsed light and the subsequent transient heat

transport in the bulk polymer was observed via the infra-red radiation from the carbon layer coated onto the front surface of the polymer film. Since the thermal diffusivity in the thin carbon layer is much larger than that in the polymer film and the thermal contact between polymer surface and carbon layer is good, the transient infra-red radiation from the carbon layer directly represents the heat transport in the polymer film.

Infra-red radiation intensity for the back-scattering mode, $S_B(t)$, and that for the transmission mode, $S_T(t)$, can be expressed as:

$$S_B(t) = G\varepsilon\sigma\alpha \int_0^\infty \{[T_0 + \theta(x, t)]^4 - T_0^4\} \exp(-\alpha x)\, dx \quad (1)$$

$$S_T(t) = G\varepsilon\sigma\alpha \int_0^\infty \{[T_0 + \theta(x, t)]^4 - T_0^4\} \exp[-\alpha(L-x)]\, dx$$

$$(2)$$

where G is a geometrical factor, ε is the emissivity averaged over the detection spectral bandwidth, σ is the Stefan–Boltzmann constant, α is the infra-red absorption coefficient of carbon layer averaged over the detection spectral bandwidth, L is film thickness, T_0 is the temperature around the sample before pulse heating and $[T_0 + \theta(x, t)]$ is the temperature in the sample at a distance x ($0 \leqslant x \leqslant L$) from the irradiated surface at a time t after the irradiation of pulsed light. Under the condition $\theta(x, t) \ll T_0$, equations (1) and (2) can be written, respectively, as follows:

$$S_B(t) = K\alpha \int_0^\infty \theta(x, t) \exp(-\alpha x)\, dx \quad (3)$$

$$S_B(t) = K\alpha \int_0^\infty \theta(x, t) \exp[-\alpha(L-x)]\, dx \quad (4)$$

where $K = 4G\varepsilon\sigma T_0^3$.

If the initial temperature of the sample is $\theta(x, 0)$, the temperature at a time t is given by Carslaw and Jaeger[6] as:

$$\theta(x, t) = \frac{1}{L} \int_0^L \theta(x, 0)\, dx$$

$$+ \frac{2}{L} \sum_{n=1}^\infty \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \cos\left(\frac{n\pi x}{L}\right)$$

$$\times \int_0^L \theta(x', 0) \cos\left(\frac{n\pi x'}{L}\right) dx' \quad (5)$$

where D is the thermal diffusivity of solid polymer. Since the carbon layer on the polymer film is heated by a pulse of light, the temperature distribution at $t = 0$ is given by:

$$\theta(x, 0) = Q/Cg \qquad (0 \leqslant x \leqslant g)$$
$$\theta(x, t) = 0 \qquad (g < x \leqslant L) \quad (6)$$

where Q is the total energy absorbed by the carbon layer in small depth g and C is the heat capacity of the sample. With the condition of equation (6), equation (5) can be written as:

$$\theta(x, t) = \frac{Q}{CL}\left[1 + 2 \sum_{n=1}^\infty \frac{\cos(n\pi x/L) \sin(n\pi g/L)}{n\pi g/L} \right.$$

$$\left. \times \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \right] \quad (7)$$

In the present case, αL is much larger than unity and $\sin(n\pi g/L) \sim (n\pi g/L)$ is satisfied since g is much smaller than the film thickness L. Thus, using equation (7), $S_B(t)$ and $S_T(t)$ are written as follows:

$$S_B(t) = \frac{KQ}{CL}\left[1 + 2 \sum_{n=1}^\infty \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \right] \quad (8)$$

$$S_T(t) = \frac{KQ}{CL}\left[1 + 2 \sum_{n=1}^\infty (-1)^n \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \right] \quad (9)$$

In equations (8) and (9), thermal diffusivity D and heat capacity C are variables depending on the structure of solid polymer. In the actual simulation, however, the value of (KQ/CL) was used as a variable instead of the C value, because the Q value and values of G and ε in K were not determined in this work.

In this work, a transmission mode expressed by equation (9) was employed to determine the D value. The D value obtained by flash radiometry was in good agreement with that reported by Chen *et al.*[7].

Sample preparation and characterization

Poly(ethylene terephthalate) film (Toyobo Co. Ltd) was used. Film thickness was in the range 140–180 μm. Heat treatment of film was performed in an electric furnace under a flow of nitrogen gas. Measurement of thermal diffusivity on isothermal crystallization was carried out in a cell equipped with PID thermal controller, which enables one to attain a given temperature within 5 min. Liquid-induced crystallization was performed by immersing a film sample in boiling aqueous phenol solution. Then, the film was dried *in vacuo* for 1–2 days, soaked in methanol for 1 day to remove residual phenol and water from the film, and further dried *in vacuo* for 1–2 days.

The density of the sample film was measured in a heptane–carbon tetrachloride gradient column at 30°C. Crystallinity of the sample film was determined using the measured density ρ, densities of amorphous phase ρ_a of 1.335 g cm^{-3} and of crystalline phase ρ_c of 1.455 g cm^{-3} (ref. 8).

X-ray diffraction patterns were determined with a Toshiba model ADG X-ray diffractometer with nickel-filtered Cu K$_\alpha$ radiation. Differential thermal analysis (d.t.a.) was carried out on a Shimadzu model DT-30 differential thermal analyser at a heating rate of 20°C min^{-1} in nitrogen atmosphere.

RESULTS AND DISCUSSION

Heat-treatment dependence of thermal diffusivity

Figure 3 shows the thermal diffusivity D of PET film measured at room temperature after heat treatment at various temperatures in the range 100–240°C for 1 h. In this figure, the D value at a heat treatment temperature of 20°C represents that of the untreated sample. It can be seen that D increases stepwise with increasing temperature of heat treatment. Crystallinity, which is also shown in *Figure 3*, increases from 5% of untreated PET to 40% of PET treated at 140°C. Thus, the large increase in D of PET treated at 140°C is due to crystallization of PET. Since heat transfer in the crystalline region is faster than that in the non-crystalline (amorphous) region, crystallization increases D. Although crystallinity increases linearly with increasing temperature of heat treatment in
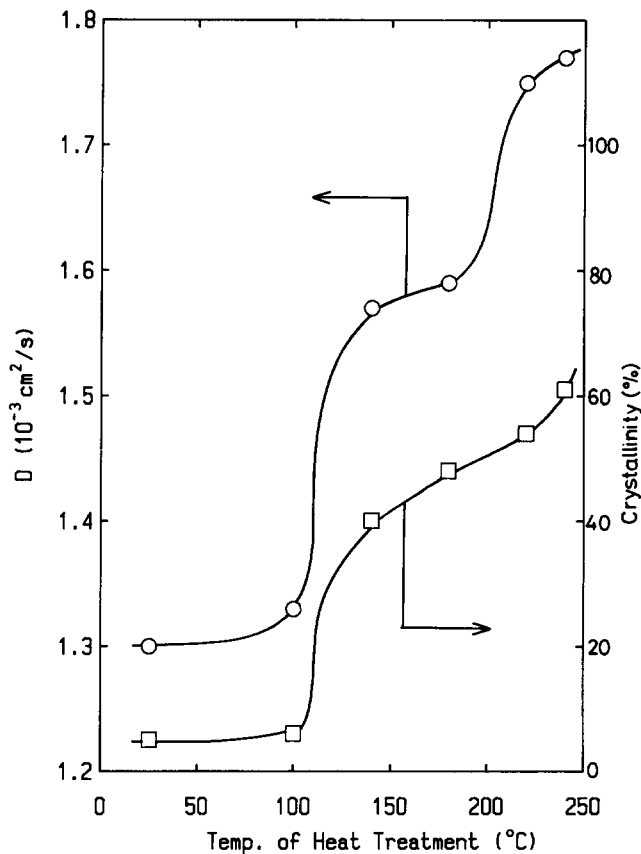
Figure 3 Dependence of thermal diffusivity (O) and crystallinity (□) on the temperature of heat treatment for 1 h

Thermal diffusivity on isothermal crystallization

Figure 7 shows typical results of time variation of thermal diffusivity on isothermal crystallization at 97 and 107°C. The onset time of increasing D was around 100 h for the sample isothermally crystallized at 89°C and decreased greatly on raising the temperature of isothermal crystallization. The change of crystallinity is also plotted against the time of isothermal crystallization in *Figure 7*. The profile of D is in good agreement with that of the crystallinity. The rapid increase of D in these curves is due to the first-order crystallization process in which the
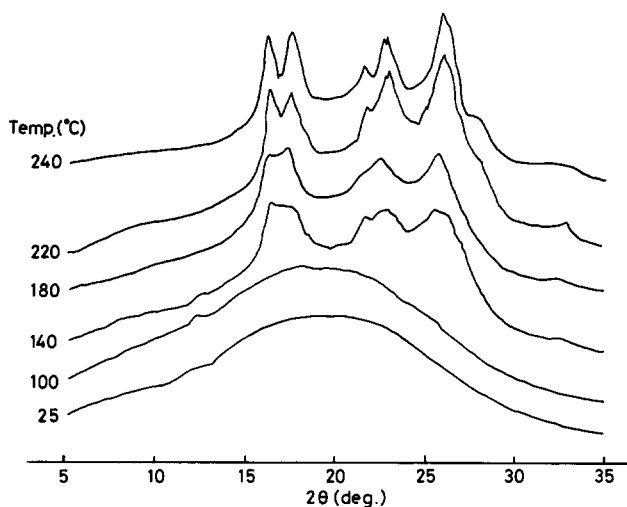

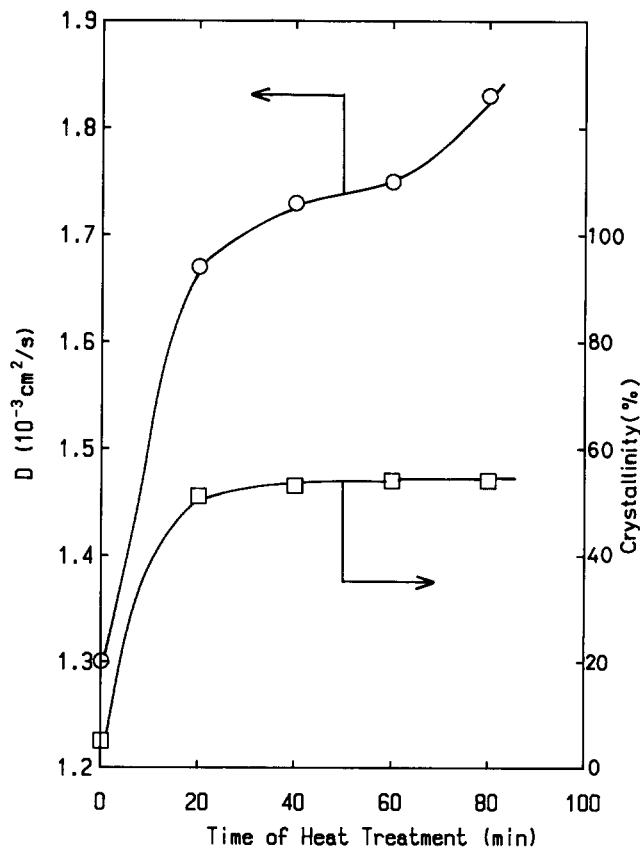**Figure 4** X-ray diffraction intensity curves after heat treatment at various temperatures for 1 h

the temperature range 140–240°C, D shows a stepwise increase. X-ray diffraction patterns became sharper in stepwise fashion with increasing temperature of heat treatment, as shown in *Figure 4*, which implies a stepwise increase of crystallite size. Therefore, it is considered that the stepwise increase of D reflects the difference of crystallite size between the samples treated at 140 and 180°C and those treated at 220 and 240°C.

Figure 5 shows D values measured at room temperature and crystallinity of PET treated at 220°C for various times in the range 20–80 min. In this figure, D and crystallinity at zero heat treatment time represent those of the untreated sample. The large increase in D of PET treated for 20 min is also due to polymer crystallization, corresponding to an increase of crystallinity from 5% of untreated PET to 51% of PET treated for 20 min. D increases further with increasing time of heat treatment above 20 min, while the crystallinity is almost constant and the X-ray diffraction pattern does not change, irrespective of the time of heat treatment. Thus, the increase of D is considered to imply other changes in the supramolecular structure of PET with increasing time of heat treatment. The d.t.a. curve shown in *Figure 6* shows two endothermic peaks, at 234°C (lower peak) and 251°C (upper peak) for PET treated for 20 min, and the area of the lower peak and its temperature increase with increasing time of heat treatment. This change in the d.t.a. curves corresponds well with the increase in D. Consequently, the increase in D is considered to reflect a change of crystallite form from the thermodynamically unstable one to the more stable one[9,10].

Figure 5 Dependence of thermal diffusivity (O) and crystallinity (□) on the time of heat treatment at 220°C

Time(min)
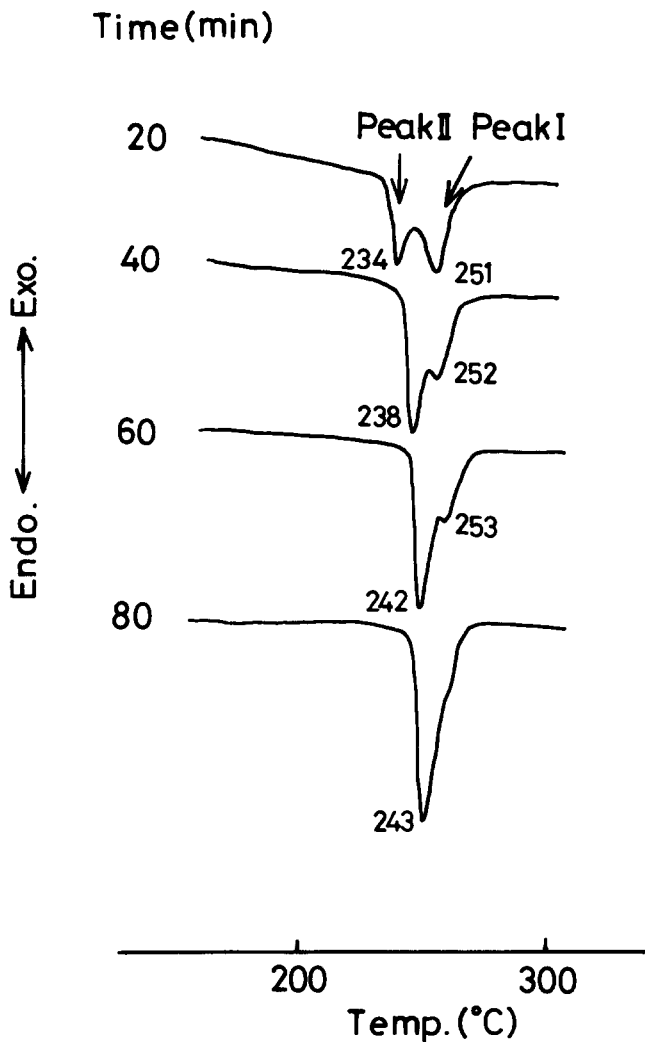
Figure 6 D.t.a. curves of after heat treatment for various times at constant temperature of 220°C

where w_c is the weight fraction of polymer crystallized, k is the constant describing the rate of crystallization, n is the Avrami exponent (varying with the type of nucleation and growth process), D_0 is D value at the initial stage of isothermal crystallization, D_t is D value at time t and D_∞ is D value after levelling out. The Avrami exponent n was determined by the slope of $\ln\{-\ln[(D_t-D_\infty)/(D_0-D_\infty)]\}$ vs. $\ln t$ and is listed in *Table 1* for the temperature of isothermal crystallization.
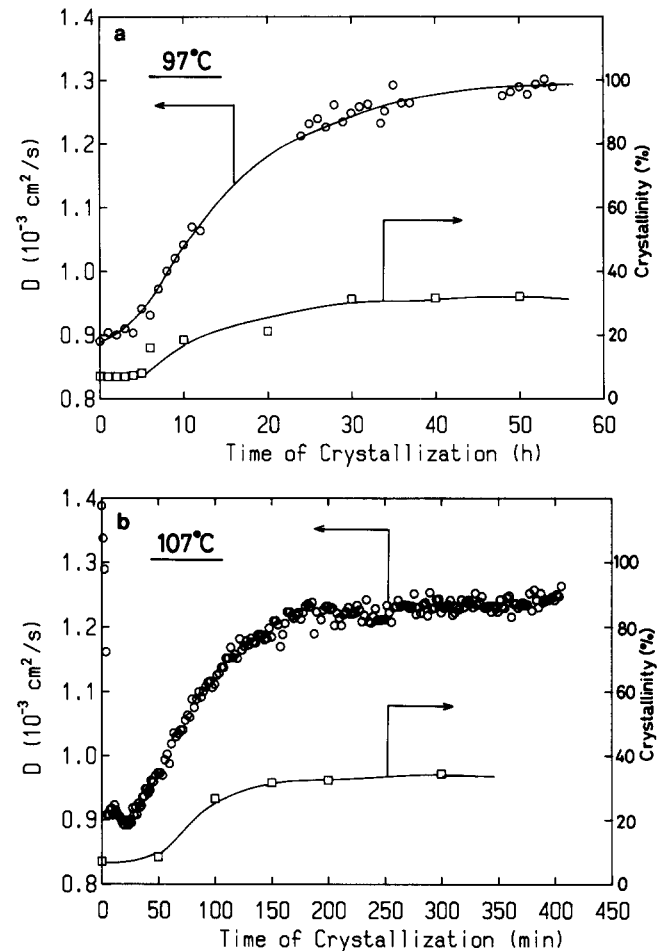

Figure 7 Typical results of time variation of thermal diffusivity (○) and crystallinity (□) on isothermal crystallization at (a) 97°C and (b) 107°C
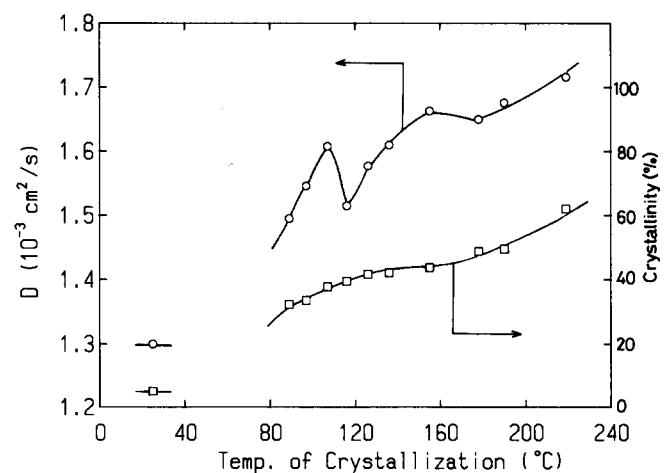
formation of the nucleus of a crystallite is followed by the growth of a spherulite. The following gradual and small increase of D corresponds to the second-order crystallization process in which the crystallite form changes from the thermodynamically unstable one to the more stable one, which is in good agreement with the result shown in *Figure 5*.

Figure 8 shows the changes of D and crystallinity for the sample cooled down to room temperature after the D value levels out on isothermal crystallization, i.e. after apparent crystallization at that temperature is completed. D increases with increasing isothermal crystallization temperature, with a distinct peak at 107°C and a broad peak around 150°C. Crystallinity increases monotonically with a small peak around 150°C corresponding to a peak around 150°C on the D profile. X-ray diffraction patterns of these samples show the continuous change in the profile, and there was no significant change around 107°C. Furthermore, photographs of sample films by scanning electron microscopy did not show any specific change around 107°C.

The variation of D against crystallization time is replotted according to the modified equation for the Avrami relation[11]:

$$\ln[(D_t-D_\infty)/(D_0-D_\infty)] = -(k/w_c)t^n \qquad (10)$$

Figure 8 Plots of thermal diffusivity (○) and crystallinity (□) against isothermal crystallization temperature

Table 1 Avrami exponent n for various isothermal temperatures T_i

T_i (°C)	n
89	1.6
97	1.5
107	2.2
116	3.2
126–219	_[a]_

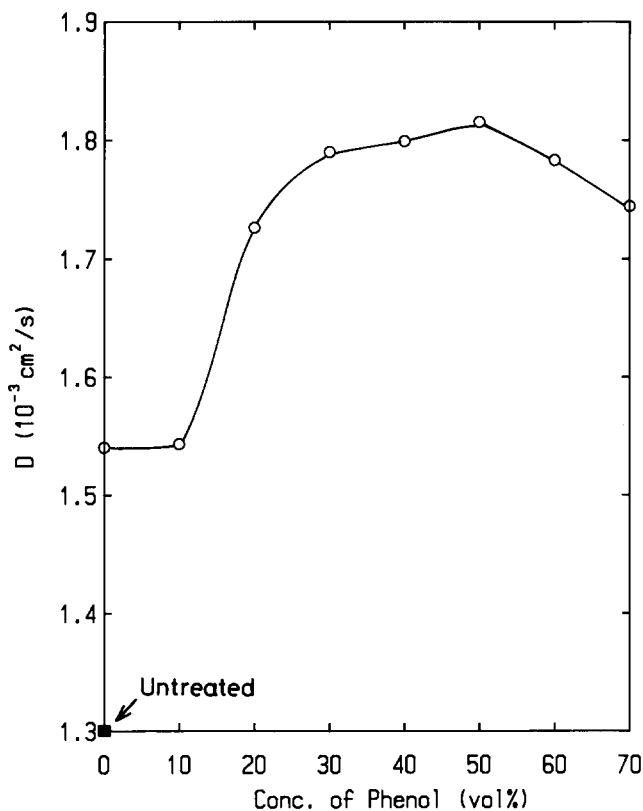[a] Increase of D is too rapid to obtain n value

Figure 9 Phenol concentration dependence of thermal diffusivity when crystallizing by soaking in a boiling aqueous phenol solution

The value of n is almost the same at 89 and 97°C but at 107°C it increases, which implies that the type of growth of the crystallite changes between 97 and 107°C. This difference in type of growth of crystallite may also affect the aggregation state of the amorphous region, and thus results in the specific variation of D at about 107°C.

Variation of thermal diffusivity by liquid-induced crystallization

Boiling a film sample in aqueous phenol solution gave rise to the progress of crystallinity due to liquid-induced crystallization[12]. D increased drastically by soaking a film sample for 5 min in boiling aqueous phenol solution and almost levelled out for 240 min. This treatment did not change the reduced specific viscosity of a film sample. *Figure 9* shows the variation of D with the change of phenol concentration. All values of D were values after boiling in aqueous phenol solution for 240 min. Below 50 vol% of phenol content, increase of phenol concentration causes the increase of D. This increase is due to the increase of crystallinity of PET. The decrease of D above 50 vol% of phenol content is probably attributed

to generation of microvoids, corresponding to the larger increment of intensity in the smaller angle of X-ray diffraction patterns shown in *Figure 10*. Namely, microvoids may cause phonon scattering and decrease of D.

CONCLUSIONS

This study is concerned with the measurement of thermal diffusivity of PET by flash radiometry based on the flash heating and detection of the time dependence of the surface temperature using infra-red radiation, and the resulting discussion of correlation between thermal diffusivity and the micro- and fine structures of PET.

It was found that the D value sensitively reflects the changes in the supramolecular structure, such as crystallite size, crystallite form, type of growth of crystallite, which affects the aggregation state of the amorphous region, and microvoids. Therefore, flash radiometry is considered to be a useful tool to estimate the supramolecular structure of polymers.

ACKNOWLEDGEMENTS

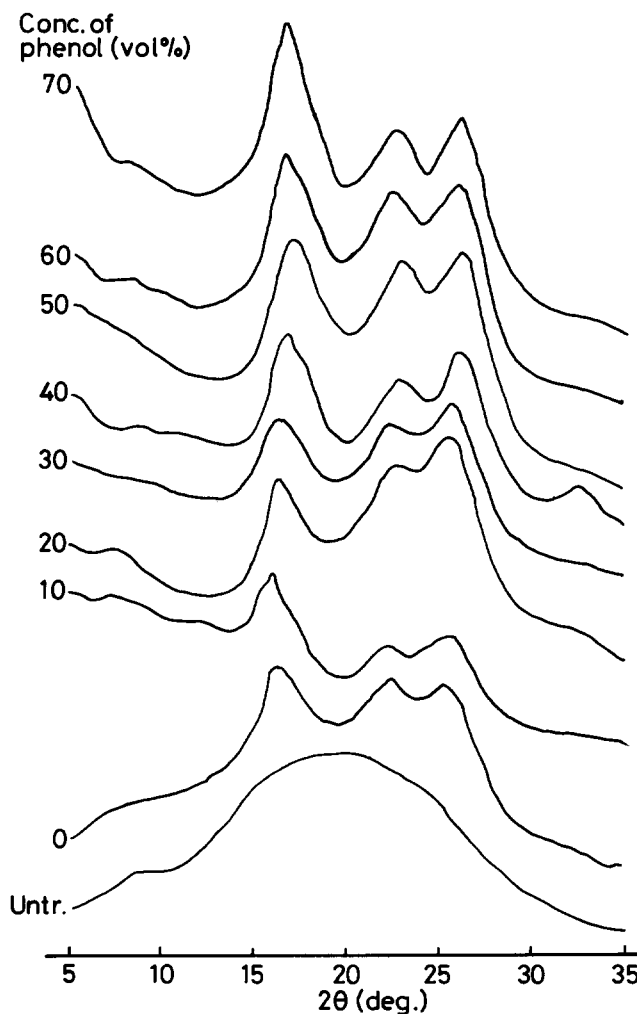**Figure 10** X-ray diffraction intensity curves after soaking in various concentrations of aqueous phenol solution

REFERENCES

1   Tam, A. C. and Sullivan, B. *Appl. Phys. Lett.* 1983, **43**, 333
2   Leung, W. P. and Tam, A. C. *Opt. Lett.* 1984, **9**, 93
3   Leung, W. P. and Tam, A. C. *J. Appl. Phys.* 1984, **56**, 153
4   Tsutsumi, N. and Kiyotsukuri, T. *Appl. Phys. Lett.* 1988, **52**, 442
5   Tsutsumi, N., Takizawa, T. and Kiyotsukuri, T. *Polym. Commun.* 1988, **29**, 28
6   Carslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids', 2nd Edn., Clarendon, Oxford, 1959, p. 101
7   Chen, F. C., Poom, Y. M. and Choy, C. L. *Polymer* 1977, **18**, 129
8   Daubeny, R. P., Bunn, C. W. and Brown, C. J. *Proc. R. Soc. Lond. (A)* 1954, **226**, 531
9   Bell, J. P. and Dumbleton, J. H. *J. Polym. Sci. (A-2)* 1969, **7**, 1033
10   Bell, J. P. and Murayama, T. *J. Polym. Sci. (A-2)* 1969, **7**, 1059
11   Avrami, M. *J. Chem. Phys.* 1939, **7**, 1103; *ibid.* 1940, **8**, 212
12   Lin, S. and Koenig, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1539