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THERMAL ANALYSIS OF POLYMER SAMPLES BY A ROUND ROBIN METHOD. I. REPRODUCIBILITY OF MELTING, CRYSTALLIZATION AND GLASS TRANSITION TEMPERATURES

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ABSTRACT

The reproducibility of transition temperatures (melting, crystallization and glass transition temperatures) of polymers determined by thermal analysis was examined by a round robin method, in which twenty three laboratories participated. Seven polymer samples were used for the test, which consisted of polyethylene pellet and film, two poly(ethylene terephthalate) fibers, poly(ether ether ketone) pellet, polystyrene sheet and poly(ether sulfone) pellet. Eight types of instrument were employed including 13 power-compensated type differential scanning calorimeters and 8 heat-flux type ones (quantitative differential thermal analyzers).

For the first-order transition such as melting and crystallization, the values of the peak melting and crystallization temperatures (T_{pm} and T_{pc}) and the extrapolated onset and end temperatures (T_{im} and T_{ic}, and T_{em} and T_{ec}) agreed well among laboratories. The standard deviations (σ_n) were smaller than 3.0 K for T_{pm}, T_{pc}, T_{im} and T_{em}, and T_{ic} and T_{ec} with a few exceptions. However, the onset and end temperatures (T'_{im} and T'_{em}, and T'_{ic} and T'_{ec}) are so scattered that it is reasonable to use T_{pm} and T_{pc}, and T_{im} and T_{em}, and T_{ic} and T_{ec} for the comparison of data obtained for polymers by thermal analysis in separate laboratories.

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For glass transition, the σ_n values were within 3.1 K for the extrapolated onset temperature (T_{ig}) and the midpoint temperatures (T_{mg}), but the onset and end temperatures (T'_{ig} and T'_{eg}) and the extrapolated end temperature (T_{eg}) were very scattered. Therefore, it is appropriate to use T_{ig} and T_{mg} to compare the data from different sources.

INTRODUCTION

Information on the thermal properties of polymers has been increasingly required in the various fields of polymer science and engineering including basic and developing researches, quality control and even commercial transactions. Thermal properties of polymers such as melting temperature (T_m), crystallization temperature (T_c) and glass transition temperature (T_g), decomposition temperature (T_d) of polymers can be determined most conveniently by thermal analysis. In the past twenty years, thermal analysis has shown remarkable progress and established its position as a tool for the evaluation of thermal properties of polymers coupled with the spread of the instruments. A questionnaire on the present status of the evaluation of thermal properties of polymer materials by thermal analysis was sent out by the Japan High Polymer Center to 46 organizations, of which 27 were private enterprises, 5 universities and 14 public institutions. According to the answers submitted to the questionnaire, not only the melting, glass transition and decomposition temperatures and thermal stability of polymers are determined by thermal analysis as routine work in these organizations, but the measurements of crystallization temperature, heats of melting (ΔH_m) and crystallization (ΔH_c), heat capacity (C_p) and heat conductivity (λ) are also carried out quite frequently [1]. However, there were few reports on the reproducibility of the data obtained by thermal analysis for polymers in different laboratories [2].

Therefore, a committee was set up to assess the reproducibility of the data of thermal analysis of polymers by a round robin method. Twenty three laboratories participated in the RRT, of which 15 were private enterprises, 3 universities and 5 public institutions (Table 1). Four programs, that is, (1) melting, crystallization and glass transition temperatures (T_m, T_c and T_g), (2) heats of melting and crystallization (ΔH_m and ΔH_c), (3) heat capacity (C_p) and (4) thermogravimetry (TG) were tested using 11 polymer samples.

The proper selection of the method and reference materials for the calibration of temperature are also essential to obtain better results in thermal analysis. Therefore, the melting and transition temperatures, and the Curie temperatures were determined by a round robin method for the temperature calibration of differential scanning calorimeter (DSC) and thermobalance, respectively, using 15 samples in total, which consisted of ICTA-NBS standard materials, pure metals and inorganic compounds.

As the first of a series of reports concerning the reproducibility of the

TABLE 1

Participants and items tested in round robin tests

Participant	Items tested								
	T_m	T_c	T_g	T_m(reference)	ΔH_m	ΔH_c	C_p	TG	Curie temp.
M. Adachi (Minolta Camera Co. Ltd.)	○	○		○	○	○			
S. Endo and F. Oishi (Railway Technical Research Institute, J.N.R.)	○	○	○	○	○	○			
T. Hatakeyama and T. Kurita (Research Institute for Polymers and Textiles)	○	○	○	○	○	○	○	○	○
M. Higuchi (Gunma-Ken Industrial Research Laboratory)	○	○	○	○					
K. Horiuchi (Sumitomo Bakelite Co. Ltd.)			○	○					
S. Imamura (Mitsubishi Plastics Industries, Ltd.)	○	○	○	○	○	○			
Y. Kawasaki (Tokuyama Soda Co. Ltd.)	○	○		○					
A. Kishi (Shinku-Riko Co. Ltd.)	○	○	○	○	○	○		○	
M. Momota (Rigaku Corporation)	○	○	○	○	○	○		○	○
K. Nakamura (Industrial Research Institute of Kanagawa Prefecture)	○	○	○	○	○	○	○	○	○
S. Nakamura (Kanagawa University)	○	○	○	○	○	○		○	
T. Okino (Shimadzu Corporation)	○	○	○	○	○	○		○	○
M. Ono and E. Jojima (Jissen Womens University)	○			○					
I. Sato (Kanegafuchi Chemical Industry Co., Ltd.)	○	○	○	○					
K. Sekine (Mitsubishi Rayon Co. Ltd.)			○	○					
Y. Shibasaki (Saitama University)	○	○		○	○	○			
M. Shimada (Toa Nenryo Kogyo Co. Ltd.)	○	○		○					
Suzuki (Government Industrial Development Laboratory, Hokkaido)	○	○	○	○	○	○		○	○
S. Takada (Mitsui Petrochemicals Co. Ltd.)	○	○	○	○	○	○		○	
T. Takahashi (Government Industrial Research Institute, Osaka)	○	○	○	○	○	○		○	○
Y. Teramoto (Seiko Instruments and Electronics Ltd.)	○	○	○	○	○	○	○	○	○
M. Todoki and T. Hosoi (Toray Research Center, Inc.)	○	○	○	○	○	○	○	○	○
S. Watanabe (Toyo Soda Manufacturing Co. Ltd.)	○	○	○	○	○	○	○		

data of thermal analysis for polymers, this article describes the results on the determination of melting, crystallization and glass transition temperatures.

EXPERIMENTAL

Samples

Polyethylene (PE) pellet and film, two poly(ethylene terephthalate) (PET) fibers, polystyrene (PS) sheet, poly(ether ether ketone) (PEEK) pellet, and poly(ether sulfone) (PES) pellet were used as polymer samples for the examination of reproducibility of melting, crystallization and glass transition temperatures. A detailed description of polymer samples is given in Table 2. These polymers were selected from a consideration of the following factors: (1) wide ranges of melting temperature (PE, PET and PEEK) and glass transition temperature (PS and PES) and (2) different shape (PE pellet and film) and thermal history (PET fibers). The samples were cut to the appropriate size according to the method recommended by ASTM standard D3418-82.

Apparatus

The apparatus used in the determination of melting, crystallization and glass transition temperatures were 13 power-compensated type differential

TABLE 2

Polymer samples used

Sample and specification	Items tested
Polyethylene, "Yukalon" EY-40L	
pellet	T_m, T_c, ΔH_m, ΔH_c
film (inflation film)	T_m, ΔH_m, TG
Polystyrene, HIPS	
sheet	T_g, C_p
Poly(ether sulfone)	
pellet	T_g, TG
Poly(ethylene terephthalate), Toray "Tetoron"	
fiber A, T-702C (150d, 288f)	T_m, ΔH_m
fiber B, T-210 (75d, 36f)	T_m, ΔH_m
Poly(ether ether ketone)	
pellet	T_m, T_c, ΔH_m, ΔH_c
Epoxy resin (specimen from shaped article)	
A, with filler	TG
B, with filler and glass fiber	TG
Polyacetal	
pellet A	TG
pellet B	TG

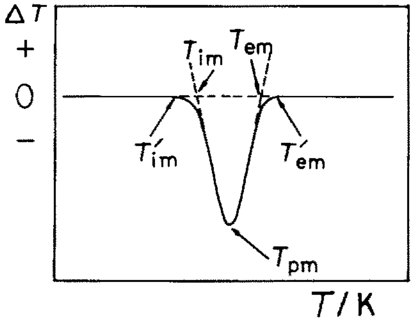

Fig. 1. Typical melting curve for polymer.

scanning calorimeters (DSCs) and 8 heat-flux type DSCs (quantitative differential thermal analyzers (q-DTAs)) consisting of eight types of instrument.

Calibration of temperature

The temperature scale of the apparatus was calibrated using the same heating rate used for the measurement of samples according to the method conventionally used in each laboratory.

Melting temperature

The samples used for the RRT of melting temperature were polyethylene pellet and film as general-purpose plastics, poly(ethylene terephthalate) fibers A and B as fibers with different thermal history and poly(ether ether ketone) as engineering plastics. The measurements were carried out by the test methods described in ASTM standard D3418-82, except that the cooling rate of 5 K min^{-1} was used instead of 10 K min^{-1} and the flow rate of nitrogen was kept at 50–100 ml min^{-1}.

The following corrected temperatures were determined in Kelvin as shown in Figs. 1 and 2.

T'_{im} onset temperature
T_{im} extrapolated onset temperature
T_{pm} melting peak temperature
T_{em} extrapolated end temperature
T'_{em} end temperature

Figure 1 shows a single melting peak, whereas the melting peak is divided into two peaks in Fig. 2. T_{im} and T_{pm} are used as recommended by the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA) [3]. T_{em} is the temperature at which the extrapolated base line intersects the tangent drawn at the point of greatest slope on the succeeding edge of the peak. T'_{im} is the temperature at which the leading

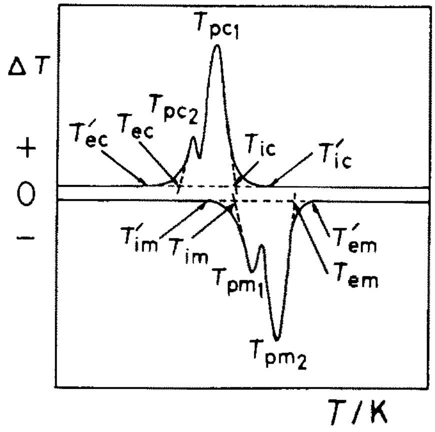

Fig. 2. Typical melting and crystallization curves for polymer with a double peak.

edge of the peak starts to depart from the base line and T'_{em} is the one at which the succeeding edge of the peak starts to deviate from the base line.

Crystallization temperature

Polyethylene pellet and poly(ether ether ketone) were used for the RRT of crystallization temperatures. The measurements were performed in the same procedure as ASTM D3418-82 except for the cooling rate of 5 K $\min^{-1}$ and the flow rate of nitrogen of 50–100 ml $\min^{-1}$. The following corrected temperatures were obtained as in Fig. 2, where a double peak of crystallization appears:

T'_{ic}	onset temperature
T_{ic}	extrapolated onset temperature
T_{pc}	crystallization peak temperature
T_{ec}	extrapolated end temperature
T'_{ec}	end temperature

T_{ic} and T_{pc} are as recommended by ICTA. T_{ec}, T'_{ic} and T'_{ec} are defined as melting temperatures.

Glass transition temperature

Polystyrene sheet and poly(ether sulfone) pellet were used as general-purpose polymer and engineering plastics. The procedure of ASTM D3418-82 was followed with the preliminary thermal cycle raising the temperature to 50 K above the glass transition temperature and 5–10 mg sample mass. The following temperatures were determined as given in Fig. 3.

T'_{ig}	onset temperature
T_{ig}	extrapolated onset temperature
T_{mg}	midpoint temperature
T_{eg}	extrapolated end temperature
T'_{eg}	end temperature

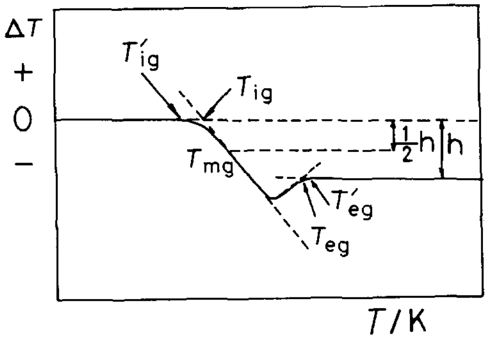

Fig. 3. Typical glass transition curve for polymer.

T'_{ig}, T_{ig} and T_{mg} are defined by the Committee on Standardization of ICTA [4]. T_{eg} is the temperature at which the extrapolated base line at the higher temperature side intersects the tangent drawn at the point of greatest slope on the step of glass transition. When a peak appears at the higher-temperature side of the step as in Fig. 3, T_{eg} is the temperature at the intersection of the extended base line at the higher temperature side with the tangent drawn at the point of greatest slope on the succeeding edge of the peak. T'_{eg} is the temperature at which the succeeding edge on the step of glass transition starts to deviate from the extrapolated base line.

RESULTS AND DISCUSSION

Melting temperature

In Tables 3–7, the mean value ($\bar{x}$), the standard deviation (σ_n), the maximum value (x_{max}), the minimum value (x_{min}) and the width between maximum and minimum (x_{max}–x_{min}) of reported values are tabulated for the onset (T'_{im}), extrapolated onset (T_{im}), peak (T_{pm}), extrapolated end (T_{em}) and end (T'_{em}) temperatures for each sample. In these tables, n represents the number of reported values.

The amount of scatter in the measured values of melting temperature varied from sample to sample. Without preliminary heating the values of T_{im}, T_{pm} and T_{em} agreed well among laboratories. The standard deviation σ_n values were within ± 3.0 K except for the T_{im} values of PET fiber A (6.1 K) and of PEEK (3.4 K). On the other hand, the values of T'_{im} and T'_{em} varied widely from laboratory to laboratory except for the T'_{em} value of PET fiber B (2.8 K). Namely, the values of σ_n for T_{im} were 13.6 K and 12.1 K for PET pellet and PEEK pellet, respectively. The widths $x_{max} - x_{min}$, which were also indication of the amount of scatter in measured values, were within ± 10 K for T_{im}, T_{pm} and T_{em} with a few exceptions, but those for T'_{im} and

TABLE 3

Melting temperatures (in K) of polyethylene film

	T'_{im}	T_{im}	T_{pm}	T_{em}	T'_{em}
x	364.0	395.2	403.6	407.0	411.2
σ_n [a]	10.6	2.6	1.5	2.5	4.4
x_{max}	377	398.7	408.0	414.0	422
x_{min}	339	387	400	403.9	405.0
$x_{max} - x_{min}$	38	11.7	8.0	10.1	17.0

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$, $n = 19$.

[b] When a double peak appeared, an average of peak temperatures was used.

TABLE 4

Melting temperatures (in K) of polyethylene pellet

Experimental details [a]		T'_{im}	T_{im}	T_{pm}	T_{em}	T'_{em}
I	x	363.3	395.5	404.1	408.0	412.9
	σ_n [b]	13.6	2.1	2.1	2.0	4.9
	x_{max}	383	398	410.0	413.0	424
	x_{min}	332	390	401.4	404.7	406.5
	$x_{max} - x_{min}$	51	8	8.6	8.3	17.5
II	x	360.9	396.8	406.5	410.0	414.4
	σ_n [b]	13.8	2.2	1.3	2.0	4.0
	x_{max}	379.2	399.4	409.0	413.0	421
	x_{min}	333	391	404.0	406.2	408.0
	$x_{max} - x_{min}$	46.2	8.4	5.0	6.8	13.0

[a] I, without preliminary thermal cycle, $n = 18$; II, with preliminary thermal cycle, $n = 17$.

[b] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$.

TABLE 5

Melting temperatures (in K) of poly(ethylene terephthalate) fiber A

	T'_{im}	T_{im}	T_{pm} [b]	T_{em}	T'_{em}
x	501.1	518.0	528.2	532.5	537.7
σ_n [a]	8.1	6.1	2.9	2.0	3.6
x_{max}	513.0	527.5	533.0	538	547
x_{min}	481	506.2	523.0	530.0	534
$x_{max} - x_{min}$	32	21.3	10.0	8.0	13

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 19$.

[b] When a multiple (double or triple) peak appeared, the main peak temperature was used.

TABLE 6

Melting temperatures (in K) of poly(ethylene terephthalate) fiber B

	T'_{im}	T_{im}	T_{pm} [b]	T_{em}	T'_{em}
x	500.7	520.2	525.9	532.2	536.9
σ_n [a]	7.7	2.2	2.4	1.7	2.8
x_{max}	517	523.4	530.2	536	545
x_{min}	486	513.1	521.2	528.5	534
$x_{max} - x_{min}$	31	10.3	9.0	7.5	11

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 19$.

[b] When a double peak appeared, the main peak temperature was used.

T'_{em} were larger, i.e., the width for T'_{im} of PE pellet was 51 K and that of PEEK 42.2 K.

As for PET fibers, the scattering was smaller for fiber B than for fiber A irrespective of characteristic temperatures measured.

When the melting temperature is measured not for end products but for polymer materials themselves, the sample should be heated at a constant rate to an appropriate temperature above the melting temperature to erase the previous thermal history, held at that temperature for a predetermined time and cooled to sufficiently below its melting temperature at a constant rate before measurement.

After the preliminary thermal cycle, the scattering in measured values for PE pellet was a little smaller than before the thermal cycle. The values of σ_n for T_{pm} and T_{em} varied from 2.1 K to 1.3 K and from 4.9 K to 4.0 K, respectively. The width $x_{max} - x_{min}$ became narrower from 8.6 K to 5.0 K for T_{pm}, from 8.3 K to 6.8 K for T_{em} and from 17.5 K to 13.0 K for T'_{em} as a

TABLE 7

Melting temperatures (in K) of poly(ether ether ketone) pellet

Experimental details [a]		T'_{im}	T_{im}	T_{pm}	T_{em}	T'_{em}
I	x	577.4	595.7	612.6	620.9	626.7
	σ_n [b]	12.1	3.4	2.1	2.3	4.3
	x_{max}	598.0	602.1	616.1	625	636
	x_{min}	555.8	590	608	615.5	618.4
	$x_{max} - x_{min}$	42.2	12.1	8.1	9.5	17.5
II	x	569.3	595.3	613.9	619.2	623.7
	σ_n [b]	25.2	14.1	1.5	1.8	2.9
	x_{max}	601	605.3	617	623	629.0
	x_{min}	527	557.0	610.5	615.5	618
	$x_{max} - x_{min}$	74	48.3	6.5	7.5	11.0

[a] I, without preliminary thermal cycle, $n = 17$; II, with preliminary thermal cycle, $n = 16$.

[b] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$.

TABLE 8

Reproducibility of melting temperatures

Sample	T_{im}			T_{pm}			T_{em}		
	±1.0 K	±2.0 K	±3.0 K	±1.0 K	±2.0 K	±3.0 K	±1.0 K	±2.0 K	±3.0 K
Polyethylene									
film	9/19 (47%)	13/19 (68%)	16/19 (84%)	14/19 (74%)	17/19 (89%)	17/19 (89%)	7/19 (37%)	13/19 (68%)	17/19 (89%)
pellet I	7/18 (39%)	13/18 (72%)	16/18 (89%)	5/17 (29%)	13/17 (76%)	16/17 (94%)	7/18 (39%)	15/18 (83%)	17/18 (94%)
pellet II	5/17 (29%)	13/17 (76%)	15/17 (88%)	10/17 (59%)	14/17 (82%)	17/17 (100%)	6/17 (35%)	11/17 (65%)	15/17 (88%)
Poly(ethylene terephthalate)									
fiber A	4/19 (21%)	5/19 (26%)	5/19 (26%)	2/19 (11%)	7/19 (37%)	13/19 (68%)	7/19 (37%)	14/19 (74%)	18/19 (95%)
fiber B	8/19 (42%)	14/19 (74%)	17/19 (89%)	6/19 (32%)	13/19 (68%)	14/19 (74%)	11/19 (58%)	15/19 (79%)	17/19 (89%)
Poly(ether ether ketone)									
pellet I	7/17 (41%)	9/17 (53%)	10/17 (59%)	7/17 (41%)	11/17 (65%)	14/17 (82%)	8/17 (47%)	13/17 (76%)	13/17 (76%)
pellet II	0/17 (0%)	1/17 (6%)	2/17 (12%)	11/17 (65%)	13/17 (76%)	14/17 (82%)	7/17 (41%)	12/17 (71%)	14/17 (82%)

TABLE 9

Crystallization temperatures (in K) of polyethylene pellet

	T'_{ic}	T_{ic}	T_{pc}	T_{ec}	T'_{ec}
x	394.7	392.6	390.7	387.4	363.1
σ_n [a]	3.3	1.5	2.0	2.0	16.0
x_{max}	407.0	395	395	391	385
x_{min}	390.5	389.5	386.0	384	330.3
$x_{max} - x_{min}$	16.5	5.5	9.0	7.0	55.3

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 19$.

result of the preliminary thermal cycle.

The melting peak of PEEK pellet was made somewhat sharper by the preliminary thermal cycle. The values of σ_n were smaller for T_{pm} and T'_{em} but became remarkably larger for T_{im} and T'_{im}, that is they increased from 3.4 K to 14.1 K and 12.1 K to 25.2 K. The same tendency was also observed for $x_{max} - x_{min}$. The scattering of T'_{im} became wider from 42.2 K to 74 K.

From the above results, it is concluded that the scattering among laboratories is larger for T'_{im} and T'_{em} than for T_{im}, T_{pm} and T_{em}.

To examine the reproducibility of measurements in different laboratories, the number of reported values of T_{im}, T_{pm} and T_{em} which lie within ± 1.0 K, ±2.0 K and ± 3.0 K from the mean values are given in Table 8 for each sample, where the denominator is the total number of reported values and the nominator is the number of reported values within ± 1.0 K, ± 2.0 K and ± 3.0 K from the mean values. In any sample, the number of reported values was increased remarkably by widening the range from $\bar{x} \pm 1.0$ K to $\bar{x} \pm 2.0$ K and then to $\bar{x} \pm 3.0$ K. As an example, the value of 6/19 (32%) at $\bar{x} \pm 1.0$ K became 13/19 (68%) at $\bar{x} \pm 2.0$ K and 14/19 (74%) at $\bar{x} \pm 3.0$ K for T_{pm} of PET fiber B. The T_{pm} value of the PE pellet after the preliminary thermal cycle was most reproducible and was 10/17 (59%) at $\bar{x} \pm 1.0$ K increasing to 17/17 (100%) at $\bar{x} \pm 3.0$ K.

TABLE 10

Crystallization temperatures (in K) of poly(ether ether ketone) pellet

	T'_{ic}	T_{ic}	T_{pc} [b]	T_{ec}	T'_{ec}
x	582.2	578.8	573.4	566.7	550.3
σ_n [a]	2.8	3.7	3.2	4.3	13.3
x_{max}	586.5	582.8	578.0	576.0	572.0
x_{min}	577.2	573.1	567.7	558	522.2
$x_{max} - x_{min}$	9.3	9.7	10.3	18.0	49.8

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 17$.

[b] When a double peak appeared, an average of peak temperatures was used.

TABLE 11

Reproducibility of crystallization temperatures

Sample	T_{ic}			T_{pc}			T_{ec}		
	±1.0 K	±2.0 K	±3.0 K	±1.0 K	±2.0 K	±3.0 K	±1.0 K	±2.0 K	±3.0 K
Polyethylene pellet	10/19 (53%)	15/19 (80%)	17/19 (89%)	11/19 (58%)	14/19 (74%)	16/19 (84%)	10/19 (53%)	11/19 (58%)	16/19 (84%)
Poly(ether ether ketone) pellet	8/17 (47%)	10/17 (59%)	12/17 (71%)	4/17 (24%)	7/17 (41%)	11/17 (65%)	2/17 (12%)	6/17 (35%)	11/17 (65%)

TABLE 12

Glass transition temperatures (in K) of polystyrene sheet

	T'_{ig}	T_{ig}	T_{mg}	T_{eg}	T'_{eg}
x	357.6	364.9	368.7	376.6	380.0
σ_n [a]	7.5	2.2	1.4	4.1	6.4
x_{max}	368.0	369.2	371.4	383.1	392.6
x_{min}	340.0	360.0	366.0	369.0	370.0
$x_{max} - x_{min}$	28.0	9.2	5.4	14.1	22.6

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 18$.

Crystallization temperature

The values of $\bar{x}$, σ_n, x_{max}, x_{min} and $x_{max} - x_{min}$ are shown in Tables 9 and 10 for T'_{ic}, T_{ic}, T_{pc}, T_{ec} and T'_{ec} of each sample. The different scattering among samples was observed for crystallization temperature. For PE pellet, the σ_n values were small for T_{ic} (1.5 K), T_{pc} (2.0 K), and T_{ec} (2.0 K), but those for T'_{ic} and T'_{ec} were 3.3 K and 16.0 K, respectively. The difference $x_{max} - x_{min}$ was also large for T'_{ic} (16.5 K) and T'_{ec} (55.3 K). The same tendency was observed for PEEK even though the σ_n values were generally somewhat larger. The $x_{max} - x_{min}$ values were 58.5 K and 49.8 K for T'_{ic} and T'_{ec}, respectively.

The T'_{ic} and T'_{ec} values varied more widely than those of T_{ic}, T_{pc} and T_{ec}. The reproducibility of end temperature T'_{ec} was especially poor among laboratories.

The number of reported values of T_{ic}, T_{pc}, and T_{ec} which lie between $\bar{x} \pm 1.0$ K, $\bar{x} \pm 2.0$ K and $\bar{x} \pm 3.0$ K is listed in Table 11 for each sample. For crystallization temperatures, the number of reported values included also increased remarkably by varying the range from $\bar{x} \pm 1.0$ K, to $\bar{x} \pm 2.0$ K and then to $\bar{x} \pm 3.0$ K. The value of 11/19 (58%) at $\bar{x} \pm 1.0$ K became 16/19 (84%) at $\bar{x} \pm 3.0$ K for T_{pc} of PET pellet.

TABLE 13

Glass transition temperatures (in K) of poly(ether sulfone) pellet

	T'_{ig}	T_{ig}	T_{mg}	T_{eg}	T'_{eg}
x	489.8	495.2	499.8	509.6	512.3
σ_n [a]	12.1	3.1	2.0	8.3	7.7
x_{max}	498.7	498.5	505.2	532.6	533.1
x_{min}	481.0	487.0	496.5	499.0	502.0
$x_{max} - x_{min}$	17.7	11.5	8.7	33.6	31.1

[a] $\sigma_n = [\Sigma(x_i - x)^2/n]^{1/2}$; $n = 18$.

TABLE 14

Reproducibility of glass transition temperatures

Sample	T_{ig}				T_{mg}				T_{eg}			
	±1.0 K	±2.0 K	±3.0 K	±4.0 K	±1.0 K	±2.0 K	±3.0 K	±4.0 K	±1.0 K	±2.0 K	±3.0 K	±4.0 K
Polystyrene pellet	7/18 (39%)	14/18 (78%)	16/18 (89%)	16/18 (89%)	10/18 (56%)	14/18 (78%)	18/18 (100%)	18/18 (100%)	1/17 (6%)	3/17 (18%)	9/17 (53%)	11/17 (65%)
Poly(ether sulfone) pellet	5/18 (28%)	10/18 (56%)	14/18 (78%)	15/17 (83%)	7/18 (39%)	13/18 (72%)	17/18 (94%)	17/18 (94%)	4/17 (24%)	6/17 (35%)	10/17 (59%)	11/17 (65%)

Glass transition temperature

The $\bar{x}$, σ_n, $x_{\max}$, $x_{\min}$ and $x_{\max}$–$x_{\min}$ values are given in Tables 12 and 13 for T'_{ig}, T_{ig}, T_{mg}, T_{eg} and T'_{eg} of PS sheet and PES pellet. The scattering of the midpoint temperature (T_{mg}) was smallest for both PS (1.4 K) and PES (2.0 K). The amount of scatter of T_{ig} was rather larger than that of T_{mg}, σ_n being 2.2 K for PS and 3.1 K for PES. The reported values of T'_{ig}, T_{eg} and T'_{eg} were very scattered.

The width $x_{\max} - x_{\min}$ had the same tendency and was smallest for T_{mg}, that is 5.4 K for PS and 8.7 K for PES. Then the width of T_{ig} is somewhat larger as observed from 9.2 K for PS and 11.5 K for PES. The widths for T'_{ig}, T_{eg} and T'_{eg} were much larger and that of T_{eg} for PES was 33.6 K.

Table 14 shows the ratios of the number of reported values lying within $\bar{x} \pm 1.0$ K, $\bar{x} \pm 2.0$ K, $\bar{x} \pm 3.0$ K and $\bar{x} \pm 4.0$ K of the total number of reported values. For the glass transition temperatures too, the reproducibility was increased by widening the range from $\bar{x} \pm 1.0$ K to $\bar{x} \pm 4.0$ K. Thus, the value of 7/18 (38%) for T_{ig} of PS increased to 16/18 (89%) and that of 10/18 (56%) for T_{mg} of PS to 18/18 (100%). From Table 14, the scattering of T_{mg} was smallest and then was followed by that of T_{ig}. The value of T_{eg} varied more widely.

CONCLUSION

From the examination of the reproducibility of the first-order transition temperatures (melting and crystallization temperatures), the values of T'_{im} and T'_{em}, and T'_{ic} and T'_{ec} reported by different laboratories are too scattered to compare. Therefore, it is reasonable to use T_{im}, T_{pm} and T_{em}, and T_{ic}, T_{pc} and T_{ec} for the report of first-order transition of polymers by thermal analysis. The reproducibility of within ± 3.0 K is considered to be practical for the first-order transition temperatures T_{im}, T_{pm}, T_{em}, T_{ic}, T_{pc} and T_{ec} of identical polymer samples determined by different laboratories using different instruments, because the standard deviations σ_n were smaller than 3.0 K for these temperatures with a few exceptions.

The onset and end temperatures T'_{ig} and T'_{eg} of glass transition are scattered remarkably among laboratories. The scattering of the extrapolated end temperatures T_{eg} is also not so small. Therefore, it is reasonable to use T_{ig} and T_{mg} alone for comparison. The values of T_{ig} and T_{mg} of glass transition should be reproducible within ± 4.0 K for the determination by different laboratories.

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