Certificate

ICTA Certified Reference Material Polystyrene

Certified by the
International Confederation for Thermal Analysis

distributed by the
United States National Bureau of Standards
as
GM – 754

This Certified Reference Material is certified for measurement of the glass transition temperature by differential thermal analysis or differential scanning calorimetry.

The National Bureau of Standards distributes a number of materials certified by recognized standards organizations, professional societies, or other government agencies.

The National Bureau of Standards has ascertained that the certifying organization is a recognized non-profit professional society one of whose objectives is to improve the reliability of measurements. The sponsoring organization is solely responsible for the quality of the material and for the accuracy of the statements and data related to this certified reference material.

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ICTA Certified Reference Material Polystyrene
for glass transition measurements

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GM-754

This certificate describes the testing and evaluation program of this Certified Reference Material. It also provides an analysis of the data as an aid to the user of the CRM in interpretation of his own data. The mean values for the defined points are given in Tables 1 & 2.

The certificate was prepared for the ICTA by
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of the

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1. INTRODUCTION

1.1 Background

In this certificate information is presented to enable the user of the ICTA's Certified Reference Material, a glass transition polystyrene standard, to obtain optimum accuracy in measurement of dynamic thermal tystems. It is a continuation of the effort of the Standards Committee of ICTA to provide dynamic temperature standards needed in several fields of thermal analysis. These vary in character and cover a wide temperature range.

A dynamic temperature standard fiffers from an equilibrium temperature standard in that, based on empirical studies, it exhibits the following characteristics; (a) it has an easily detected and reproducible thermal effect (i.e., provides an easily measureable and sensitive signal); (b) undergoes its thermal change rapidly enough to be measured in commercially available dynamic instruments; (c) is stable enough to permit its convenient use under the normal cooperating conditions of the instrument. These materials are not intended and may not meet the criteria for equilibrium temperature standards. Their values are based on dynamic measurements and incorporate the errors associated with them.

Dynamic temperature standards are needed in several fields of thermal analysis. These needs are quite different in character and cover a wide temperature range. The first completed task of supplying Standard Reference Materials resulted in the issuance of SRMs 758, 759, and 760 for differential thermal analysis between 100 and 1000 ¼C. The development was carried out by the International Confederation for Thermal Analysis (CTA) through its Committee on Standardization, in liaison with the National Bureau of Standards through O. Menis and J. P. Cali, and is described in the NBS Special Publication 260-40 [1].

These materials will continue to be issued through the National Bureau of Standards Special Reference Materials program, listed as GM 758, GM 759, and GM 760 respectively.

The present effort was carried out by the same committee. This program was initiated because of requests for high polymer standards from persons in that field. These included responses to questionnaires by members of the American Society for Testing and Materials (ASTM), ICTA, and the North American Thermal Analysis Society (NATAS), who felt a need for a DTA-DSC temperature standard for use under the dynamic conditions characteristic of these techniques.

1.2 Rationale

In the field of polymer technology, glass transition temperature data serve an important role in characterizing polymers. The data specify the temperature region in which the physical properties of the specific polymeric preparation will change. These reflect the increased mobility of some part of the macromolecule which changes a brittle or hard polymer to a rubbery material, or a resilient polymer to a leathery one. If the polymer is highly crystalline, the glass transition will not occur. On the other hand, by the addition of plasticizers or stabilizers to a polymer, the existing glass transition can be changed. Hence, glass transition temperatures are used widely in specifying or describing blends of polymers or modified polymers. For this reason, in fabrication of polymeric products, a precise method of identification and measurement of glass transition temperatures is needed. In differential thermal analysis (DTA), the glass transition temperature appears as a discontinuity in the ΔT versus T curve; this arises from the discontinuous change in heat capacity of the amorphous material. The corresponding change is observed in differential scanning calorimetry (DSC). The Certified Standard Reference Material Polystyrene is provided to: (1) yield a clearly discernible glass transition; and (2) yield a homogeneous and reproducible temperature standard compatible with the dynamic measuring conditions customarily employed in instrumental analysis of polymers.

1.3 Historical Development

The consideration of candidate materials began in 1970. Discussions in the committee and with other experts in the field led to the decision, in 1971, to assess samples of polystyrene and polypropylene. A number of members volunteered and formed a subcommittee for this preliminary test.

At the 1972 meeting of the ICTA Committee on Standardization, this sub-committee reported that the test samples of polypropylene did not show adequate storage stability to warrant further consideration as a temperature standard. However, a particular sample of polystyrene showed both good stability and good homogeneity.

This polystyrene was selected not only because of its stability, but also because the glass transition can be discerned easily on apparatus used in polymer studies. The material had been developed by the Polymer Supply and Characterization Center (PSCC) of the Rubber and Plastics Research Association (RAPRA) in the United Kingdom. The data presented by J. Maisey on the methods of preparation were discussed. This, along with a thorough testing of the material by other than thermoanalytical methods, convinced the committee of its suitability.

2. THE FOURTH INTERNATIONAL TEST PROGRAM

2.1 Preparation of the Sample Material

The material purchased from RAPRA was taken in part from each of the several containers of the material held by RAPRA. The total quantity was blended.

2.2 Selection of Participants

The designated members of the Committee on Standardization contacted persons in their country or geographic area who were known to be active and proficient in the field. Enough people to provide valid statistics and a variety of equipment agreed to participate. These are listed in Appendix A.

2.3 The Protocol

2.3.1 General plan of operation

Test procedures and report forms were drafted by H. Kambe and were approved at the 1973 meeting of the Committee. These are given in Appendix B. The samples were then distributed to Committee members for further distribution to the cooperating investigators in their areas. The reporting schedule was prepared by H. G. McAdie and circulated subsequent to the meeting.

Data from the participating laboratories were forwarded by the National Delegates to the Chairman (H. G. McAdie) for coding. The computer code previously used for the SECOND ITP was modified to enable use of the same programming.

The values given by the individual investigators were used as received, except where inspection of the charts indicated any obvious discrepancies. These discrepancies or uncertainties were clarified or resolved by correspondence.

A preliminary analysis of the data was prepared by H. G. McAdie. These data were examined in Akron, Ohio, on April 7, 1974, by a subcommittee comprised of P. D. Garn, H. Kambe, and O. Menis. This subcommittee has been authorized by the Committee on Standardization to determine the course of action to be recommended to the Council of the ICTA. The subcommittee then recommended that the Council certify this batch of polystyrene.

A more detailed analysis of the data was performed by P. D. Garn, preparatory to presentation of the proposed certification to the Council and to the Fourth International Conference on Thermal Analysis held in Budapest in July 1974. Subsequent to that processing, a few more data sets were received. The entire set of data was used in preparation of this certificate.

2.3.2 Rationale for experimental procedure instructions

The instructions given to the participants are presented below with accompanying notes:

(1) The operating conditions of each instrument should be those normally employed.

In all cases, it is the instrument and its response to the thermal event which is under test. Hence, the conditions should not differ from those used for other samples.

(2) The accuracy of the temperature sensor should be known. Committee prefers use of recognized melting point standards, such as naphthalene and benzoic acid.

The accuracy of the thermocouples can be tested independently by standard equilibrium or near-equilibrium techniques; resistance thermometers will present a greater problem. If an equilibrium test measurement cannot be made, a large specimen and low heating-cooling rate will give the optimum approach to equilibrium conditions.

(3) All temperature data of T_a, T_b, and T_c, defined in the accompanying figure (See Figure 1), should be reported to the nearest 0.1 °C.

In most apparatus used for polymer studies, the temperature can be read to the nearest 0.1 °C. This precision will provide a better indication of instrument and laboratory reproducibility. It will enable a better interpretation of the deviation between instruments.

The identifications were changed in preparing the certificate to T_a, T_b, and T_c, to avoid inference of any imputation of thermodynamic significance to these points.

(4) The material should be examined at heating rates within four ranges, viz., 4-6, 8-12, 16-24, 30-50 °C. min^{-1}.

The known variation of polymer glass transitions with heating rate must be taken into account. In addition, the variation of point of measurement will show an independent contribution and, therefore, these effects must be delimited.

(5) A time-temperature curve (DTA) or data from the temperature sensor (DSC) should be included. If temperature is measured in the sample cell, this record should be obtained using alumina.

The existence of a very substantial slope will diminish the resolution of the glass transition measuring points. The "blank" with alumina provides an indication of the reliability of the reported data. See also (7).

(6) The reference alumina supplied for DTA use should be calcined to at least 1000 °C before use. The empty pan should be used as reference in the case of DSC.

Many samples of alumina chemisorb moisture slowly. Calcining the reference material is a good standard practice.

(7) One curve of the reference material against the reference material should be supplied, using the maximum sensitivity employed with the test material.

See also (5). This curve will disclose any inherent unbalance in the instrument.

(8) The material should be used strictly as received and not pretreated in any way.

In polymeric materials, the temperature and resolution of the glass transistion is dependent upon thermal history. This material in the condition issued is stable indefinitely at ambient temperatures. <u>Once the material has been heated, it is no longer a Certified Reference Material</u>.

(9) The material should not be diluted.

The maximum response under the normally-employed conditions is sought.

(10) Sample size and sensitivity will depend on the instrument used. It is recommended that sample weight be not greater than 50 mg.

Still, the normally employed conditions are to be used.

(11) A minimum of four runs of separate samples should be made at each heating rate. If any run is rejected, the rejected data should be forwarded with the other data together with the reason for rejection.

For polymeric materials, non-homogeneity is a possibility. This material has been homogenized by extended blending. Therefore, measurable variation in a many-particle sample should be rare. Calling for submission of rejected runs guarded against failure to detect an occasional real variation.

(12) Conditions of packing and/or enclosure of the sample within the sample holder should be specified.

Specific instructions were not given because the normally employed conditions are sought. The effects of sample-handling variables may be discernible from the data.

(13) The sample atmosphere should be oxygen-free nitrogen dried over $MgClO_4$ or its equivalent.

Moisture which may have been absorbed may affect the appearance of the curve.

(14) Results should be reported according to the recommendations for good practice defined by the Committee [*Anal. Chem.* 39, 543 (1969)].

Large numbers of data will be sent from many observers. A common terminology facilitates accurate assignment of parameters and, hence, interpretation.

3. DATA HANDLING AND PROCESSING

3.1 General

The processing involved the computation of the means and standard deviations of the defined points on the curve for:

(1) all data sets;

(2) all data sets from each investigation;

(3) sets of data sorted by heating rates;

(4) sets of data sorted by sample holder configuration;

(5) sets of data sorted by temperature sensor location;

(6) sets of data sorted by heating rate and temperature sensor location; and

(7) sets of data sorted by heating rate and sample holder configuration.

The means of the data sets of each sets from each investigator were further averaged to obtain the unweighted means reported in the certificate.

The defined points are shown in Figure 1.

3.2 The Unweighted Mean

The number of experiments reported was not the same for each investigator. The number of sets ranged from 6 to 30. Equal weighting for each set would favor the values obtained by the more active investigator.

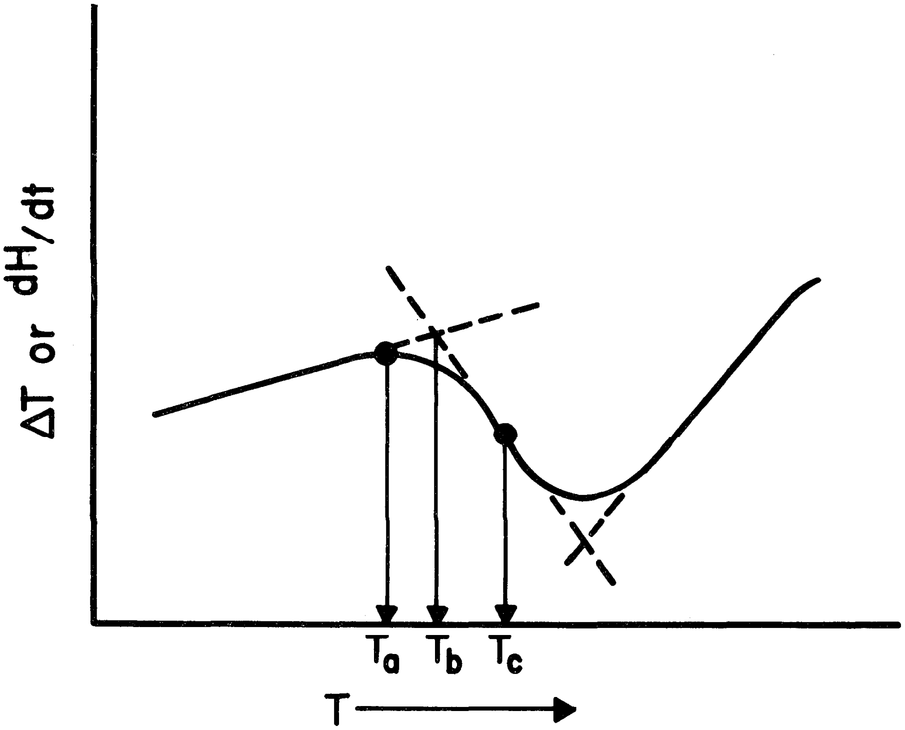


Figure 1. The measured points, T_a, T_b, and T_c, in the DTA or DSC curve for the glass transition.

In consultation with statisticians at the NBS, the decision was made to weight the data of each investigator equally since differences between investigators are the major sources of error [2]. Means and standard deviations were computed for each investigator. The mean values from the investigators' means were computed with their respective standard deviations. These are given in Table 1 with the investigators' means.

3.3 The Initial Deflection, T_a

Examination of the data by the Committee on Standardization led to the conclusion that the measurement of the initial deflection was too subjective. Graphical methods lead to low reproducibility and the probable variation of the measured value with a change of instrument sensitivity introduces a source of error which is not encountered in the measurement of points T_b and T_c. During its Tenth Meeting, September 1975, the Committee decided to include the data for information only. Discussions of instrumental effects, etc., for that reason, will be confined also to the measured points T_b and T_c.

4. RESULTS

4.1 General

The data display a high degree of reproducibility within a laboratory. The variations observed are, therefore, related to differences in handling, in procedure, or in apparatus design. The sortings and computations by selected parameters enable some hypotheses to be formulated concerning the origins of some of these variations. The limited sets of combinations of sample holder and temperature sensor positions may prevent complete isolation of effects, but does not prevent a reasonably detailed interpretation of these effects.

The earlier NBS Special Publication 260-40 set forth a series of conclusions carefully limited to those which could be documented by accepted statistical methods. These were extended by Garn [3] to include deductions and inferences based upon experience. In this present report, the magnitude of the standard deviations for a single heating rate is taken as a measure of significance. For this purpose, the means and standard deviations for each investigator were computed and the standard deviations for points T_b and T_c at each of the four heating rates were averaged for each investigator. These 24 mean standard deviations ranged from 0.24 to 1.27°, with an average of 0.53° ± 0.28°. From this value, differences or increments of 0.8° can be looked upon as evidence, but not firm proof, of a real difference in measured temperature. Standard deviations of larger sets of data are greater because of variations due to experimental parameters, but these are precisely the variations which are to be analyzed.

The method having been stated and the data having been independently obtained and completely reported, the conclusions which are reached may be critically examined.

SAMPLE HOLDER TYPE

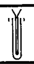
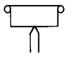
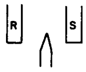
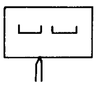
SENSOR LOCATION	412 SHALLOW CUP, LOOSELY COVERED, BOTTOM UNIFORMLY = WALL	422 SHALLOW CUP, SEALED, BOTTOM UNIFORMLY = WALL	602 DEEP CUP, UNCOVERED BOTTOM, UNIFORMLY = WALL	614 DEEP CUP, LOOSELY COVERED, BOTTOM UNIFORMLY > WALL	700 CAPILLARY, OPEN	701 CAPILLARY, LOOSELY COVERED
00 IN THE SAMPLE AXIALLY						
03 IN CONTACT WITH SAMPLE HOLDER, AXIALLY						
13 IN CONTACT WITH REFERENCE HOLDER, AXIALLY						
21 LOCATION GEOMETRICALLY EQUIVALENT TO S AND R, AXIALLY						
30 LOCATION GEOMETRICALLY MIDWAY BETWEEN S AND R, AXIALLY						
40 SHIELD SURROUNDING S AND R IN A THERMALLY EQUIVALENT WAY						

Figure 2. The Physical Relationships between Sample Holder and Temperature Sensor in the Experimental Arrangements used in the Fourth International Test Program.

Table 1

Unweighted mean values for all data at all heating rates for the defined points T_a, T_b, and T_c for the polystyrene certified Reference Material. The standard deviations of the unweighted means are given with the means.

	T_a	T_b	T_c
Means	97.2	104.4	107.5
S.D.	3.7	1.5	1.7

T_a	±	T_b	±	T_c	±	N
99.2	0.8	104.9	2.5	107.7	2.6	17
98.8	1.7	105.2	3.4	107.5	3.6	6
96.8	3.0	104.1	2.4	107.3	2.6	20
97.8	1.9	103.9	3.1	106.8	3.0	16
98.7	1.8	103.6	2.2	106.6	2.0	16
100.0	3.0	107.4	3.3	110.3	3.6	20
95.8	2.9	105.1	3.0	108.0	2.8	16
93.4	4.4	101.9	1.4	105.4	1.4	8
95.6	3.3	104.3	2.5	107.4	2.7	16
95.5	1.8	101.5	0.8	104.5	1.0	16
95.0	0.4	102.4	3.2	104.9	3.0	16
101.0	1.0	103.8	1.6	106.3	1.7	15
99.2	2.6	103.9	3.6	106.7	4.0	20
98.9	1.8	103.3	2.3	106.0	2.3	19
97.8	3.8	105.0	2.2	108.8	2.2	12
93.1	6.1	105.1	3.0	109.0	3.9	16
93.6	4.6	103.3	1.4	106.3	1.8	13
102.0	3.1	106.4	4.6	108.9	4.7	16
99.4	3.5	105.8	4.0	108.4	4.2	16
86.1	2.2	104.1	0.3	109.3	1.0	13
100.0	1.4	103.4	1.5	105.4	1.6	16
105.0	2.8	106.4	2.9	108.2	3.0	30
96.3	2.1	104.9	3.6	107.7	3.7	17
94.8	3.4	106.6	3.3	112.7	3.7	8

The order of listing is randomized and is not related to the order of listing of contributors.

4.2 Special Test For Homogeneity

At the time of distribution of the samples of the national delegates, six packages were taken at random for a homogeneity test of the batch of material to be certified. These were tested by Bruce Cassell (Perkin-Elmer Corp.) at a single heating rate. For this instrument rate, thirteen measurements on the six samples yielded standard deviations of 0.30 and 0.44 for T_b and T_c, respectively. It is important to note also that the values were in excellent agreement with preliminary values obtained on the same material three years earlier.

4.3 All Data

There is *prima facie* reason to treat each experiment equally. If all experimental conditions are identical or if all investigators reported the same number of experiments, the means and standard deviations for all data would be the appropriate values to obtain. The values computed with equal treatment are shown in Table 2.

From the standard deviations, it is clear that at least one low datum for T_a and at least one high datum for T_c have deviations exceeding three standard deviations; discarding of these data would be acceptable by common rules of data evaluation. Because of the variations in experimental parameters, however, all data were retained for the more intensive comparisons.

Table 2

Means, standard deviations, spread, and number of data points, T_a, T_b, and T_c for all data for GM 754. ICTA Certified Reference Materials, polystyrene.

Measured Point	Mean	S.D.	Spread	Number
T_a	97.8	4.7	82-110	378
T_b	104.5	3.1	98-113	378
T_c	107.5	3.3	101-118	378

These values differ slightly from the values, in Table 1 because each datum, rather than each investigator, is regarded as equal in value for the purpose of the treatments described in the following sections.

4.4 Heating Rate

It is generally accepted that the measured temperature of the glass transition varies with heating rate. The preliminary tests of this polystyrene indicated a relatively low dependence upon heating rate. Nevertheless, the variation in data is real and warrants further examination. The means for all data are shown in Table 3.

Table 3

The Measured Points, T_a, T_b, T_c, at the prescribed heating rates 1 (4-6° C/min), 2 (8-12°/min), 3 (16-24°.min), and 4 (30-50°/min).

Heating Rate	T_a	T_b	T_c	N
1	97.2	101.5	104.2	109
2	96.0	103.8	106.8	104
3	98.0	105.6	108.5	86
4	100.7	108.4	111.6	79
		Standard Deviations		
1	3.2	1.4	1.4	
2	4.9	1.2	1.8	
3	4.8	1.7	1.9	
4	4.6	2.8	3.0	
		Range of Reported Temperatures		
1	89.6-103.9	97.6-104.2	100.6-108.8	
2	82.0-103.8	99.5-107.0	103.7-111.6	
3	82.0-105.0	102.4-109.5	105.0-113.6	
4	92.7-109.7	100.8-113.2	104.8-117.8	

It is clear from Table 3 that measured points T_b and T_c have systematic variations with heating rate. The <u>increments</u> in temperature are greatly in excess of the single observer-single heating rate standard deviations. In addition, and more important, there is a continuous upward trend with heating rate; hence, the trend can be assumed to be real.

The data in Table 3 include the several groups of instrument variables. Any special characteristics of a particular set of parameters cannot be uniquely identified. Moreover, the computed values are dominated by the most common type of apparatus. For these reasons more detailed examinations of the heating rate dependence of the measured points by sample holder and by temperature sensor position are presented.

4.5 Sample Holder Configuration

The shape and design of a sample holder affect the measured rate of melting or phase transition or any process requiring the movement of thermal energy. This arises because this energy must pass through a series of interfaces and/or materials having a variety of thermal resistances. The breadth of the major heat path and the firmness of mechanical contact are two of the more obvious parameters which are fixed by sample holder and furnace design. Similar sample holders may be associated with different support devices and, hence, the thermal environments of specimens in the same kind of sample holder, but in differing apparatus, may be strikingly different.

It is to be expected, therefore, that sorting out the effect of the sample holder alone will not provide, by itself, a clearly delineated effect. The thermocouple or sensor location must be examined as well. The types of sample holder and sensor location used by the participants in this test program are shown in Figure 2.

The effects of variations in sample holder configuration are shown in Table 4.

Table 4

Effect of the type of sample holder on the measured points in the glass transition of the Certified Reference Material polystyrene.

A. Means

Sample Holder Code(1)	T_a	T_b	T_c	No. of data Points	No. of Observers
All data	97.8	104.5	107.5		
412	99.1	103.4	106.1	19	1
422	98.0	104.8	107.7	266	17
602	95.2	104.4	108.1	28	2
614	97.6	105.9	108.8	33	2
700	95.6	101.6	104.4	16	1
701	97.8	105.0	108.8	16	1

B. Standard Deviations

Sample Holder Code(1)	T_a	T_b	T_c
All data	4.7	3.1	3.3
412	1.9	2.2	2.3
422	4.9	3.2	3.4
602	4.7	3.3	3.9
614	4.8	3.5	3.6
700	1.7	0.7	1.0
701	3.8	2.2	2.2

The standard deviations are large because of inclusion of all heating rates. No systematic variations can be identified with certainty. Still a further separation of variable is needed.

(1) see figure 2.

4.6 Temperature Sensor Location

Even with the same kind of sample holder, the measuring point used to indicate the sample temperature may differ. The difference may be intrinsic in the design of a commercial apparatus or, in some apparatus by choice of the user. For example, a simple change in connection of one wire can shift the temperature measuring point from the sample (or sample thermocouple) to the reference (or its thermocouple). In other instruments, the design fixes the temperature measuring point to an extent which leaves the user no option. See Figure 2.

The transport of energy from the heater to the sample requires a temperature gradient. The position of the thermocouple with respect to the sample determines also its position within the temperature field. The results were noted in the SECOND ITP and discussed in general terms in Special Publication 260-40. One of us (PDG) has made an independent analysis of the data presented in the Special Publication to give a more detailed interpretation of the differences and the apparatus factors which caused them [3].

Variations with temperature measuring point are also apparent in the present set of data. See Table 5.

Table 5

Effect of type of sample holder on the measured points in the glass transition of the Certified Reference Material polystyrene.

Sensor Location Code	T_a	T_b	T_c	N	No. of Observers
00	97.8	102.5	104.9	32	2
03	98.3	104.7	107.6	237	15
13	97.8	105.0	108.8	12	1
21	97.4	105.8	108.7	33	2
30	93.2	104.1	107.8	24	2
40	98.0	104.0	107.0	40	2
		Standard Deviations			
00	2.8	1.5	1.4		
03	4.8	3.1	3.3		
13	3.8	2.2	2.2		
21	4.8	3.4	3.6		
30	5.5	3.0	3.7		
40	3.0	3.0	3.4		

The data in Table 5 suggest a real variation due to variation in the position of measurement. The reality is obscured by the large standard deviation caused by use of data from the several heating rates. Separations by heating rate, discussed in the following section, verify the trends.

4.7 Data Sorted By Heating Rate and Temperature Sensor Location

The variation of the measured temperatures (a) with heating rate for each temperature sensor location and (b) with temperature sensor location at the given heating rates are shown in Table 6.

Now the relatively small variations with properly matched experiments stand out. For some sensor positions, particularly where only one sample holder type is involved, the small standard deviations and continued incremental trend with heating rate render the authenticity of the variation indisputable.

At this stage, it is possible to perform a further analysis.

4.8 Data Sorted By Heating Rate and Sample Holder

In the same manner as in the previous section, the data may be separated to show the heating rate variation for each type of sample holder as well as the differences between sample holders at any given heating rate. The data are shown in Table 7.

The isolation by sample holder types does not disclose any strikingly new information, but does enable separation of data from types 700 and 701. Data disclose that the 701-type temperatures are in all cases higher than for 700-type, but lower than for any other sample holder type (except for two points at the lowest heating rate, but these exceptions are by only 0.2 and 0.0°, respectively).

5. DISCUSSION

5.1 Reproducibility of the Glass Transition

From the data presented in this report, one can note that the ICTA's Certified Reference Material (CRM), Polystyrene, undergoes a glass transition over a highly reproducible temperature range. For example, the standard deviation of individual observations at a single heating rate from 0.24 to 1.02 °C with an average of 0.51 °C. Also, tests of homogeneity yield standard deviations of only 0.30 and 0.44 °C for T_b and T_c, respectively.

The known homogeneity and reproducibility should enable the user of the CRM to evaluate the response of his instrument with respect to others of a similar type and make useful deductions relative to the significance of observed variation in the response of different instruments. The subsequent discussion relates to the variables encountered

Table 6

Effect of sensor location (SL) and heating rate on the measured values. The sample holder types (SH 700, 701) are listed for cross reference. See Figure 2.

Heating Rate	T_a	T_b	T_c	N
1	98.0	101.2	103.3	8
2	98.2	102.2	104.4	8
3	97.5	103.2	105.6	8
4	97.1	103.2	106.5	8
	Standard Deviations			
1	2.2	0.6	0.4	
2	2.1	0.6	0.3	
3	2.6	0.7	0.3	
4	4.1	2.4	1.4	
	SL 03, SH (412, 422)			
1	97.7	101.4	104.1	61
2	95.7	103.6	106.7	65
3	99.0	105.7	108.3	58
4	101.3	108.9	111.8	53
	Standard Deviations			
1	3.4	1.6	1.5	
2	5.5	0.8	1.8	
3	3.3	1.4	1.6	
4	4.8	2.3	2.6	
	SL 13, (SH 602)			
1	94.5	102.8	106.3	4
2	97.0	105.0	109.0	4
3	102.0	107.3	111.0	4
	Standard Deviations			
1	3.4	0.5	0.5	
2	0.8	0.8	0.0	
3	1.4	1.7	1.6	
	SL 21 (SH 614)			
1	97.7	102.1	104.8	8
2	98.7	104.6	107.4	11

3	94.8	107.1	110.2	8
4	98.2	111.0	114.3	6
	Standard Deviations			
1	2.7	1.1	0.6	
2	3.6	1.6	1.6	
3	7.7	2.2	1.8	
4	3.9	0.8	0.6	
	SL 30 (SH 422, 602)			
1	93.6	101.7	104.5	8
2	92.5	103.2	106.8	8
3	85.5	105.0	109.8	4
4	101.6	109.7	114.8	4
	Standard Deviations			
1	2.9	0.4	0.3	
2	3.7	1.6	1.0	
3	1.8	0.2	0.2	
4	1.6	0.5	0.4	
	SL 40 (SH 422)			
1	97.3	101.5	104.1	20
2	95.0	105.3	108.3	8
3	100.3	106.0	109.3	4
4	101.7	108.0	111.6	8
	Standard Deviations			
1	2.0	1.6	1.6	
2	2.0	0.7	0.4	
3	0.5	0.0	0.5	
4	2.3	1.8	1.8	

Table 7

Effect of sample holder configuration (SH---) and heating rate on measured points.

Heating Rate	T_a	T_b	T_c	N
SH 412 (SL 03)				
1	98.6	101.4	103.9	8
2	97.0	103.6	105.8	4
3	100.4	105.4	108.4	7
Standard Deviations				
1	1.7	1.7	1.4	
2	1.1	1.6	1.2	
3	1.0	0.8	0.9	
SH 422 (SL 03, 40)				
1	97.4	101.4	104.2	77
2	95.3	103.7	107.0	73
3	98.8	105.7	108.4	55
4	101.4	108.8	111.8	61
Standard Deviations				
1	3.1	1.5	1.5	
2	5.4	1.0	1.7	
3	3.4	1.4	1.7	
4	4.6	2.3	2.5	
SH 602 (SL 13, 30)				
1	92.9	102.3	105.5	8
2	95.5	104.6	108.1	8
3	93.7	106.1	110.2	8
4	101.6	109.7	114.8	4
Standard Deviations				
1	2.9	0.6	0.9	
2	1.8	0.7	1.0	
3	9.0	1.7	1.4	
4	1.6	0.5	0.4	

SH 614 (SL 21)

1	97.7	102.1	104.8	8
2	98.7	104.6	107.4	11
3	94.8	107.1	110.2	8
4	98.2	111.0	114.3	6

Standard Deviations

1	2.7	1.1	0.6
2	3.6	1.6	1.6
3	7.7	2.2	1.8
4	3.9	0.8	0.6

SH 700 (SL 00)

1	96.7	100.8	103.1	4
2	96.3	101.7	104.2	4
3	95.5	102.5	105.5	4
4	93.3	101.1	105.2	4

Standard Deviations

1	1.9	0.2	0.2
2	0.6	0.3	0.4
3	1.4	0.2	0.2
4	0.4	0.3	0.4

SH 701 (SL 00)

1	99.3	101.6	103.5	4
2	100.0	102.8	104.7	4
3	99.6	103.8	105.7	4
4	100.9	105.4	107.8	4

Standard Deviations

1	1.8	0.5	0.4
2	1.1	0.1	0.1
3	1.7	0.3	0.4
4	0.6	0.6	0.1

in this program and to the evaluation of their effects on the reported unweighted mean value.

5.2 The Basis for Variation with Heating Rate

The glass transition is carefully given a time-related definition by polymer scientists, who describe it as the temperature at which a measurable change in physical properties occurs within the time interval of the experiment. In the DTA experiment, the dynamic heating is progressively reducing the time interval necessary to observe the change in properties.

We may assume for simplicity that the degree of change is linear with time (constant rate); but, of course, the transition rate constant increase with temperature. (Whether or not this linearity is a good approximation for polystyrene is not important; illustration of the principle requires only an increasing rate constant with temperature).

As an example, if at a temperature T_1, the change can be observed in 300 sec., during that 300 sec. the temperature is advancing, hence decreasing the time interval required for the observation (see Figure 3). If, at a low heating rate, say 2.0 °C/min., the first detectable change is at T_1, the temperature increase during the isothermal completion interval would be 10 °C. But the temperature reached during that time, T_2, would be associated with a much smaller time interval, perhaps 60 sec. By this time the process is complete at the low heating rate, so that the measured points in the process will lie between T_1 and T_2.

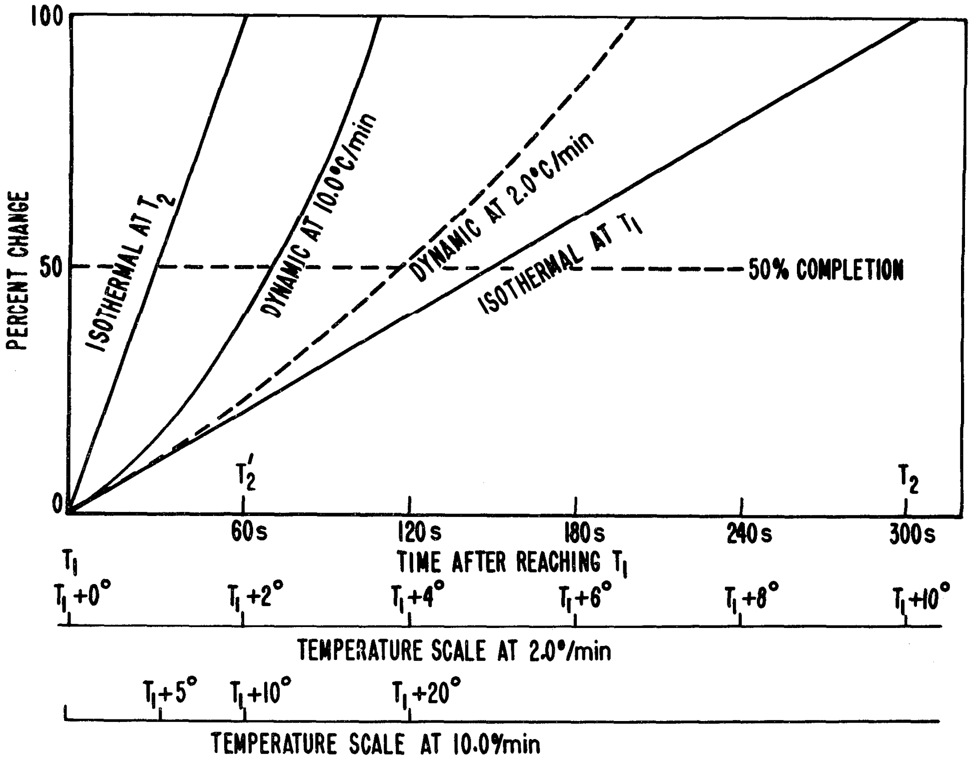


Figure 3. An arbitrary representation of the percent change of properties during the glass transition as a function of time and temperature at two heating rates. Linear change during isothermal experiments is assumed for ease of illustration.

Now carry out the same process at 10.0°/min. The process is initiated at T_1 but in 1.0 min., the temperature has reached T_2 ($>T_1$) but the change is not yet complete. Hence, some part of the curve by which the change is measured will be above T_2.

From the arbitrarily chosen values of Figure 3, the 50 percent and 100 percent points for the two heating rates can be read as:

	T_{50}	T_{100}
2°/min	T_1+4°	T_1+7°
10°/min	T_1+12°	T_1+18°

In general, any chosen degree of completion will be reached at a higher temperature, if the heating rate is increased.

Whether or not the chosen points to be measured on the experimental curve are precisely analogous to T_b and T_c, it should be clear that the chosen points will demonstrate the same general behavior as do these, only-somewhat-exaggerated curves.

It is reasonable to infer that any measured point on the curve except the initial departure (if that can be measured well) will be at a higher temperature for a given heating rate than the corresponding measured point at the lower heating rate. The glass transition, then, appears as a heating-rate-dependent process. This behavior is common to all processes in which there is a chemical or physical step which is slow enough to exert a measurable influence upon the rate of the overall process.

The real rate dependence may be obscured, however, by an apparent heating rate dependence arising from other factors. This apparent heating rate dependence arises from the manner in which the sample is contained and the temperature measured. These influences are discussed in the following sections.

5.3 Variation of Measured Temperatures Arising from the Point of Measurement

In an analysis of the data from the second ITP, one of us has shown [2] that the measured temperature in a DTA apparatus was influenced substantially by the comparative position of the sample and the measuring point within the field of thermal flux. When the temperature measuring point was in intimate contact with the sample, the temperature interval during which the transition took place was smaller. Heating and cooling temperatures were in better agreement and the spread of data was smaller than for other arrangements. These other arrangements are more susceptible to error because there is no way to place the measuring point so that it will have the same temperature as the specimen itself both

1. during steady state heating and
2. during a thermal event in which the specimen is absorbing energy in the process of changing its state.

The same sources of error are operative in this program.

Figure 2 shows general relationships used by the participants in this program. They typify the commercial apparatus in common use for these measurements. They also show significant differences in the comparative positions of the measuring point and the sample holder with respect to the heat path. This positioning is an important cause of the large apparent heating rate dependence of the glass transition temperature.

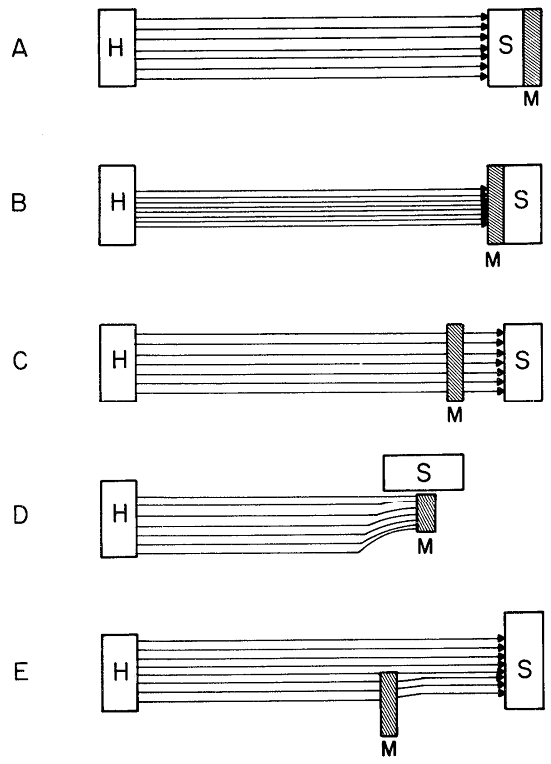


Figure 4. Representations of the relationships between the heat source and path, the sample and the measuring point in differential thermal analysis.

The influence of position can best be understood by looking in more detail at a generalized view (Figure 4) of the path of heat from the source to the specimen and to the measuring point, remembering that our goal is to measure at Point M (in Figure 4) the temperature at which an event actually occurs in Area S. These illustrations are incomplete in that Type A would ordinarily be radially symmetric about the measuring point, for example, a thermocouple on the axis of a cylindrical sample; Type B may be radially symmetric about the sample; Type D may have the sample at any position including in part directly over the measuring point and including then the possibility of radial symmetry. Discussion of all possible combinations is not fruitful.

The path of heat is through materials which display both a heat capacity and a thermal resistance; consequently, there will be a temperature gradient in the system--positive toward the left side. Types A & B, in which M is in direct contact with S, will yield the closest relationship of the measured temperature to the sample temperature because there is no intervening gradient. Type C, with its separation and intervening heat flux, will show an apparent temperature dependence because the need to convey a greater quantity of heat at the higher rates requires a larger gradient between the measuring point and the sample. For either D or E, the heat flux will tend to heat the measuring point more or less independently of the sample, yielding a very poorly resolved relationship between the sample temperature and the measured temperature. In steady state heating, the two temperatures may be very close, but during extra absorption of heat by the sample, or even during a discontinuous increase of heat capacity (that is, at a glass transition) this relationship will change. The magnitude of the change can be expected to be heating rate dependent. Table 6 showed that variation of the measured values with heating rate were common to all sensor locations. It also showed that the variations were not the same.

For some thermocouple positions, particularly where only one sample holder type is involved, the standard deviations are small enough that the reality of the temperature increment with heating rate is indisputable.

At this stage, it is possible to perform a further analysis. If the very common heating rate range of 8-12 °C/min. is shown arbitrarily, a new table can be constructed for points T_b and T_c. Comparing these values for the several temperature sensor locations and comparing the temperature increments from heating rate one (lowest) to the higher heating rates three and four, some relationships can be deducted. The data are given in Table 8 where the identifications refer to the measured temperatures and the numbered heating rates of Table 6 as shown below.

Heating Rate	Measured Points	
	T_b	T_c
1	T_{b1}	T_{c1}
2	T_{b2}	T_{c2}
3	T_{b3}	T_{c3}
4	T_{b4}	T_{c4}

Table 8

Variation of the measured points at one heating rate and the trends with heating rate as functions of the sensor location.

Sensor Location	T_{b2}	T_{c2}	$T_{b3} - T_{b1}$	$T_{b4} - T_{b1}$	$T_{c3} - T_{c1}$	$T_{c4} - T_{c1}$
00	102.2±0.6	104.4±0.3	2.0	2.0	2.3	3.2
03	103.6±0.8	106.7±1.8	4.2	7.5	4.2	7.7
13	105.0±0.8	109.0±0.0	4.5	*	4.7	*
21	104.6±1.6	107.4±1.6	5.0	8.9	5.4	9.5
30	103.2±1.6	106.8±1.0	3.7	8.0	5.3	10.3
40	105.3±0.7	108.3±0.4	4.5	6.5	5.2	7.5

First, we can see that in several cases the mean values are separated by amounts in excess of the sum of the individual standard deviations and, more important, show a continuous trend. This is particularly true for point T_c. These criteria serve to point out that these differences are real.

It is of special significance that thermocouple position 00 is distinctive in the difference between its measured temperatures and those of every other position in at least one of the measuring points T_b or T_c. The data on temperature increment with heating rate are even more instructive, it is very clear that every other thermocouple position has a much greater variation with heating rate than does position 00. The proper deduction is that most of this apparent heating rate dependence is due to the separation of the measuring point from the sample, rather than to a real variation in the glass transition temperature with heating rate.

5.4 Variation of the Measured Temperatures Arising from the Type of Sample Holder

The data in Table 7 showed that sample holders also varied in their apparent heating rate dependences. A table similar in form to Table 8 can be derived from Table 7. These relationships are shown in Table 9.

Here again it is clear that sample holders 700 and 701 are different, not only having lower temperatures but also much smaller temperature increments with heating rate.

It is also clear that sample holder type 700 has a significantly lower increment with heating rate than does 701, but the increment for 701 is substantially lower than for any of the others. The common characteristic is, of course, measurement of temperature directly in the sample. Reference back to table 7 may suggest a lowering of the glass transition temperature with heating rate. From the limited data, however, no conclusion can be drawn except a near-zero temperature dependence upon heating rate.

Table 9

Variation of the measured points at one heating rate as functions of the sample holder configuration.

SH	T_{b2}	T_{c2}	$T_{b3} - T_{b1}$	$T_{b4} - T_{b1}$	$T_{c3} - T_{c1}$	$T_{c4} - T_{c1}$
412	103.6	105.8	4.0	--	4.5	--
422	103.7	107.0	4.3	7.4	4.2	7.6
602	104.6	108.1	3.8	7.4	4.7	9.3
614	104.6	107.4	5.0	8.9	5.4	9.5
700	101.7	104.2	1.7	0.3	2.4	2.1
701	102.8	104.7	2.2	3.8	2.2	4.3

T_{b2} is Point T_b at 2nd heating rate.

$T_{b3} - T_{b1}$ is the increase in Point T_b in going from the first (slowest) heating rate to the third.

6. CONCLUSIONS

6.1 The Glass Transition as a Standard Reference Point

The reproducibility within laboratories of the measured points T_b and T_c and the reasonably systematic variation from one sample holder type to another indicate that the glass transition itself occurs over a small range of temperature.

This temperature interval is difficult to define because of its small but real variation with the kind of measurement made and, for dynamic-temperature measurements, with the rate of temperature increase. Nevertheless, estimates of the interval and some separation of the apparatus contribution can be made.

6.2 The Heating Rate Dependence of the Glass Transition

The measured points on the recorded curve by dynamic temperature methods will appear to be heating rate dependent because of the intrinsic time dependence of the phenomenon.

There is, in addition, an apparatus contribution which arises from the separation of the measuring point from the sample. The measured temperature and the heating rate dependence of the defined points is determined in part by the position of the temperature sensor with respect to the sample and the furnace assembly.

6.3 The Significance of the Measured Heating Rate Dependence

The intrinsic time dependence of the glass transition is a useful measurement related to the properties of the polymer but the apparatus factors may introduce a large enough apparent heating rate dependence to conceal the intrinsic variation.

For those uses in which knowledge of the intrinsic dependence is required, selection of a sample holder assembly with a low apparatus contribution is appropriate. The lowest apparatus contributions arises from measurement at the center of the sample.

6.4 The Significance of Variation from the Mean Temperatures

In any given apparatus, the measured temperatures of the defined points T_b and T_c for the Certified Reference Material Polystyrene may differ from the certified values by reason of differences in temperature sensor location or type of sample holder from the most common form. The existence of a significant difference does not, of itself, imply any untoward measuring error.

Furthermore, the existence of a significant difference does not vitiate the utility of the Certified Reference Material Polystyrene as a means for intercomparison of data. The certified values are the composite values from a range of instrument types. Therefore these values may differ measurably from those obtained on any specific instrument. However, based on the analysis of data in this report, the user should be able to interpret his results, evaluate the performance of his instrument, and compare his data with other results.

Substantial deviation from the certified values coupled with a substantial heating rate dependence of the measured points may result from deficiencies in design of the furnace assembly for use in measurement of glass transition temperatures.

7. Summary

The testing and evaluation program leading to the certification of a selected batch of polystyrene as Certified Reference Material GM 754 is described. Defined points from the glass transition curve were obtained first, in a preliminary program, then in 24 laboratories using eight kinds of apparatus. Data were obtained in four heating rate ranges, 4-6, 8-12, 16-24, and 30-50 °C/min. The initial departure was rejected for certification because of its relative lack of reproducibility and the comparatively subjective nature of its determination. The two defined points, T_b and T_c had unweighted mean values of 104.4 and 107.5 °C, respectively, with standard deviations of 1.5 and 1.7 °C, respectively. Data from individual investigation at a standard deviation of 0.53 °C, ±0.28 °C.

Separation of the data by heating rate, sample holder configuration, temperature sensor location and combinations of these disclosed that (a) the reproducibility under a given set of conditions warranted certification; (b) the apparent heating rate dependence of the measured point (sensor location) from the sample; and (c) the inherent time dependence of the glass transition leads to an intrinsic contribution to the apparent heating rate dependence whose upper limit is about 3 °C over the range of heating rates used.

The invaluable assistance of J. P. Cali and T. Mears, of the NBS Office of Standard Reference Material, in preparing for certification and distribution is gratefully acknowledged.

For the special support of one of us (PDG) in his participation in the planning and the computation of data, the authors are grateful to the University of Akron and to H. E. Kenessy and F. G. Tompkins for revising the computer program.

The authors further acknowledge the assistance of H. H. Ku of the Applied Mathmatics Division of NBS.

8. REFERENCES

[1] McAdie, H. G.; Garn, P. D.; Menis, O.; NBS Special Publication 26-40. U.S. Government Printing Office, Washington, D.C. 20402.

[2] Eisenhart, C., Contribution to Panel Discussion on Adjustments of the Fundamental Constants. *Precision Measurement and Fundamental Containments*, Proceedings of the International Conference held at the National Bureau of Standards, Gaithersburg, Maryland, August 3-7, 1970, edited by D. N. Langenberg and B. N. Taylor. (NBS Special Publication 343)

[3] Garn, P. D., *Journal of Thermal Analysis*, 7, 593-9 (1975).

The material contained in this report represents the labors of 24 laboratories, each of whom voluntarily contributed time and effort to participate in this Fourth International Test Program. The Committee on Standardization is grateful to them and to their supporting organizations.

LIST OF FIGURES

FIGURE NO.

LIST OF TABLES

APPENDIX A

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APPENDIX B

Instructions to Participants in the Fourth International Test Program

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS
COMMITTEE ON STANDARDIZATION

PROCEDURES

Fourth International Test Programme

Temperature Standards for DTA or DSC

Glass Transition in Polymers

(Sample: RAPRA, PSCC, Polystyrene PS 2)

1. The operating conditions of each instrument should be those normally employed.

2. The accuracy of the temperature sensor should be known. The Committee prefers use of recognized melting point standards, such as napthalene and benzoic acid.

3. All temperature data of T_i, T_p, and T_m defined in the accompanying figure should be reported to the nearest 0.1°C.

4. The material should be examined at heating rates within four ranges, viz. 4-6, 8-12, 16-24, 30-50 °C. min^{-1}.

5. A time-temperature curve (DTA) or data from the temperature sensor (DSC) should be included. If temperature is measured in the sample cell, this record should be obtained using alumina.

6. The reference alumina supplied for DTA use should be calcined to at least 1000°C before use. The empty pan should be used as reference in the case of DSC.

7. One curve of the reference material against the reference material should be supplied, using the maximum sensitivity employed with the test material.

8. The material should be used strictly as received and not pretreated in any way.

9. The material should not be diluted.

10. Sample size and sensitivity will depend on the instrument used. It is recommended that samples be not greater than 50 mg.

11. A minimum of four runs on separate samples should be made at each heating rate. If any run is rejected, the rejected data should be forwarded with the other data, together with the reason for rejection.

12. Conditions of packing and/or enclosure of the sample within the sample holder should be specified.

13. The sample atmosphere should be oxygen-free nitrogen dried over $MgClO_4$ or its equivalent.

14. Results should be reported according to the recommendations for good practice defined by the Committee [Anal. Chem. 39 543 (1969)].

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

COMMITTEE ON STANDARDIZATION

INSTRUMENT DESCRIPTION

Fourth International Test Programme
Temperature Standards for DTA or DSC
Glass Transitions in Polymers
(Sample: RAPRA, PSCC, Polystyrene PS 2)

Investigator ....

Thermal Analysis Method (DTA or DSC) ....

Instrument Manufacturer ....

" Model No. ....

ΔT Thermocouple* Material ....

ΔT Thermocouple* Wire Diameter (mm.) ....

T Thermocouple* Material ....

T. Thermocouple* Reference Temp. (°C) ....

Was T Thermocouple* Calibrated? Yes .... No .... If yes, how?....

....

Location of T Thermocouple* ....

Method of T Measurement ....

Sample Holder Material ....

Description of Sample Holder Size and Shape ....

Sample Atmosphere Flow Pattern ....

Sample Atmosphere Flow Rate (cc. min^{-1}.) ....

Please supply a small drawing or photograph of the sample holder or enclosure.

* If another temperature sensor was used please describe.

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

COMMITTEE ON STANDARDIZATION

DATA REPORT

Fourth International Test Programme

Temperature Standards for DTA or DSC

Glass Transitions in Polymers

(Sample: RAPRA, PSCC, Polystyrene PS 2)

Chart No.	Sample Weight (mg)	Sensitivity (°C.cm^{-1} or mcal. sec.$^{-1}$ cm^{-1})	Chart Speed (cm.min^{-1})	Heating Rate (°C. min^{-1})	Temperature (°C)		
					Initial (Ti)	Ext.Onset (Tp)	Midpoint (Tm)