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INVESTIGATIONS OF SOLID PHASE TRANSITIONS OF LOW MOLECULAR ORGANIC COMPOUNDS BY DIFFERENTIAL SCANNING CALORIMETRY

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For the purpose of finding temperature standards for DTA at the temperature below 150°, some solid transitions of low molecular organic compounds were measured by differential scanning calorimetry. Among fourteen materials, we have concluded to select transitions for hexachloroethane (71°) and hexamethylbenzene (110°) as candidates for such standards.

For calibrating the temperature scale of thermal analysis instruments, transition temperatures of standard materials are used by many workers. The Committee on Standardization, I. C. T. A., has carried out a cooperative international program for defining standard materials for the use in DTA [1]. They are composed of the melting points of In and Sn, and solid-solid transitions in several inorganic salts, that is KNO_3, $KClO_4$, Ag_2SO_4, SiO_2, K_2SO_4, K_2CrO_4, $BaCO_3$, and $SrCO_3$ covering the temperature range of 125−940°. However, for the study of organic materials, particularly of polymers, the temperature range below 125° is very important, and the standard materials covering this range are eagerly wanted. For this purpose, we have selected out from materials tables some solid transitions of organic compounds between 0 and 150°, measured their transition temperatures by differential scanning calorimetry (DSC), and checked their capability to be used as standard materials at the low temperature range. The Committee on Standardization is now investigating the solid transitions of hexachloroethane, the melting of several organics, and the glass transition of polystyrene for the same purpose [2]. Plato and Glasgow [3] has measured the heat of fusion of 95 kinds of organic compounds by DSC and obtained the method of evaluation of their purity. The melting points of pure substances have been generally used in the past as temperature standards. Reasons for the Committee on Standardization limiting their standards to the solid transitions have been precisely pointed out by McAdie [1], the Chairman of the Committee. We simply follow the same idea without further criticisms.

Experimental

The apparatuses used are Perkin-Elmer DSC-I and Rigaku Denki DSC-8001. A DTA equipment, Shimadzu DTGA-2B was used as comparison. Heating rates were 4 ~ 8°/min. Except for the case of specially large heat of transition,

Table 1

Samples

Material	Chemical formula	Transition point,* °C	Melting point,** °C
Trimethyl acetic acid	$(CH_3)_3CCOOH$	6.8	35.5
β-Methyl naphthalene	$C_{10}H_7(CH_3)$	15.3	35.1
d-Sodium potassium tartrate	$\begin{matrix}CH(OH)COONa\\ \vert \qquad\qquad \cdot 4H_2O\\ CH(OH)COOK\end{matrix}$	25	$(-4H_2O)$ 70~80
Ethylene diiodide	ICH_2CH_2I	26.8	81~82
Cetyl alcohol	$CH_3(CH_2)_{15}OH$	34	50~51
Eicosane	$CH_3(CH_2)_{18}CH_3$	36.2	36.8
Hexachloroethane	CCl_3CCl_3	45; 72	(in sealed tube) 187
Tetracosane	$CH_3(CH_2)_{22}CH_3$	48.1	51.1
Octacosane	$CH_3(CH_2)_{26}CH_3$	58	61.6
Acetamide	CH_3CONH_2	70	82
d,l-Borneol	$C_{10}H_{18}O$	71	207.2
Resorcinol	$C_6H_4(OH)_2$	74.1	110
Hexamethylbenzene	$C_6(CH_3)_6$	110.4	166
P ntaerythritol	$C(CH_2OH)_4$	187.7	260.5

* Landolt—Börnstein, Zahlenwerte und Funktionen, Vol. 2, Part 4, Springer-Verlag, Berlin, 1961.

** Chemical Tables, Chemical Society of Japan (1966).

the measurements were conducted at the highest sensitivity for the stable operation. The atmosphere of the sample was streaming nitrogen at a flow rate of 10 ~ 20 ml/min. Measurements during cooling were carried out only with the Perkin-Elmer instrument.

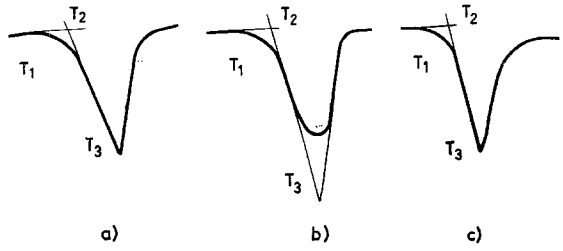


Fig. 1. Determination of transition temperatures

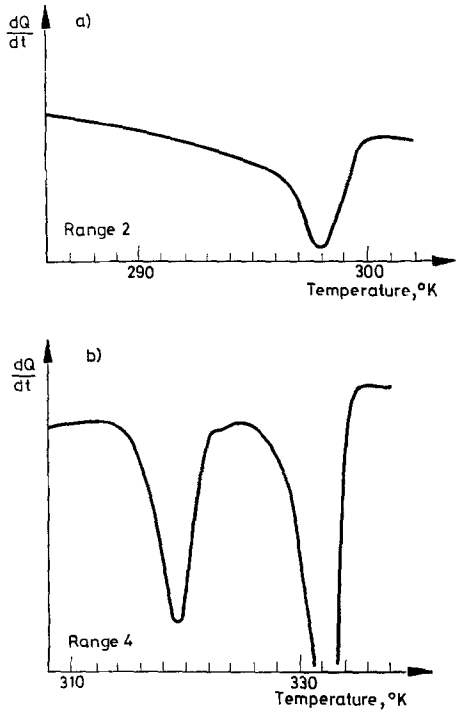
The transitions examined were selected from the materials tables, as shown in Table 1. The samples were commercially supplied. The size of the sample was determined to be 3 ~ 8 mg for DSC instruments and 60 ~ 180 mg for DTA, in order to give about the same size peak of transition for each instrument. The

sample was packed into the aluminium pan or the platinum cell, and covered by the lid. The reference pan was used vacant for the Perkin-Elmer DSC, and calcined alumina was used as the reference for the other instruments.

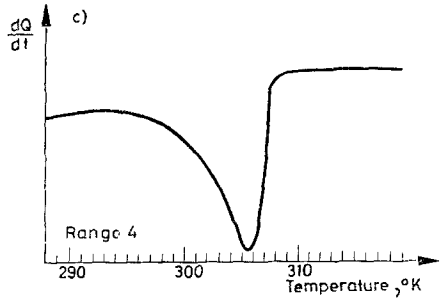
The transition temperatures were determined by the onset point (T_1), the extrapolated onset point (T_2), and the peak point (T_3), as shown in Fig. 1a, following the same procedure as adopted by the Committee on Standardization. In the case of the very blunt peak, the intersection of two extrapolated lines was taken as T_3 as in Fig. 1b. When the base line was considerably displaced after the transition, the initial base line was referred to determine the T_2, as in Fig. 1c.

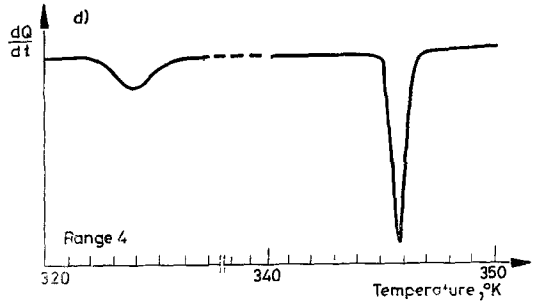
Results and discussion

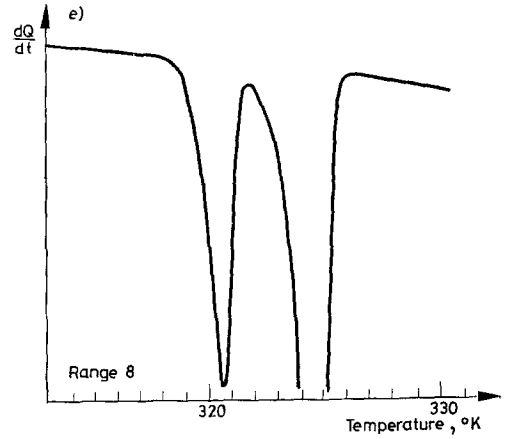
The DSC curves of the samples were taken as received and after purification by recrystallization. The transition peaks generally seemed to be sharpened by purification. The DSC peak for the transition of d-sodium potassium tartrate (Rochelle salt) was quite small and difficult to obtain even with the highest range of DSC. Peaks for trimethyl acetic acid, β-methyl naphthalene, and acetamide were very broad and not adequate to be standardized. Therefore, these four materials were excluded at first from the list of candidate standards.

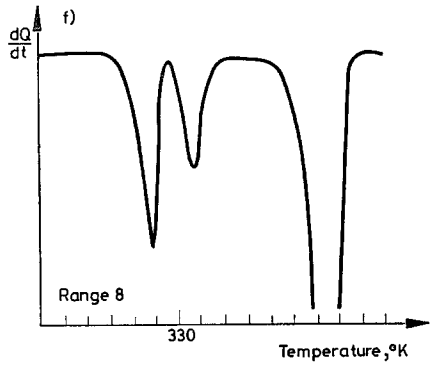


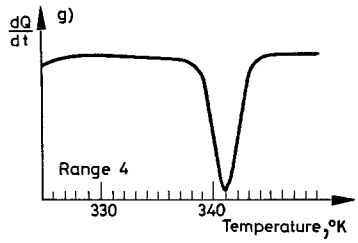
The DSC curves for the other ten materials were taken with Perkin-Elmer instrument, and are shown in Fig. 2(a) – (j). Among them, diiodoethane shows the sublimation overlapped with the transition, while pentaerythritol shows a very broad peak. Normal paraffins, i.e. eicosane, tetracosane, and octacosane

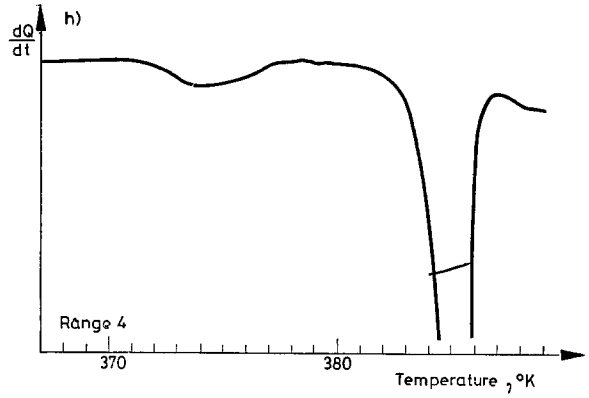


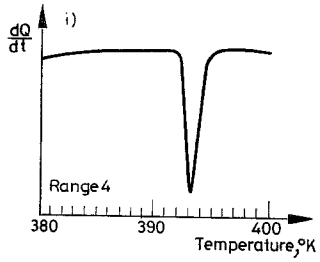





f)
dQ/dt
Range 8
330
Temperature, °K


g)
dQ/dt
Range 4
330
340
Temperature, °K


h)
dQ/dt
Range 4
370
380
Temperature , °K


i)
dQ/dt
Range 4
380
390
400
Temperature, °K

show a transition peak closely followed by melting peak. The peaks for cetyl alcohol and resorcinol show the same feature as the paraffins. Borneol is a mixture of d- and l-forms. These also seem to be unsuitable as standards.

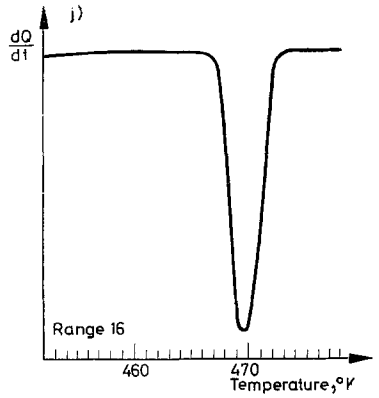


Fig. 2. a—j. DSC curves (Temperature scales are uncorrected)

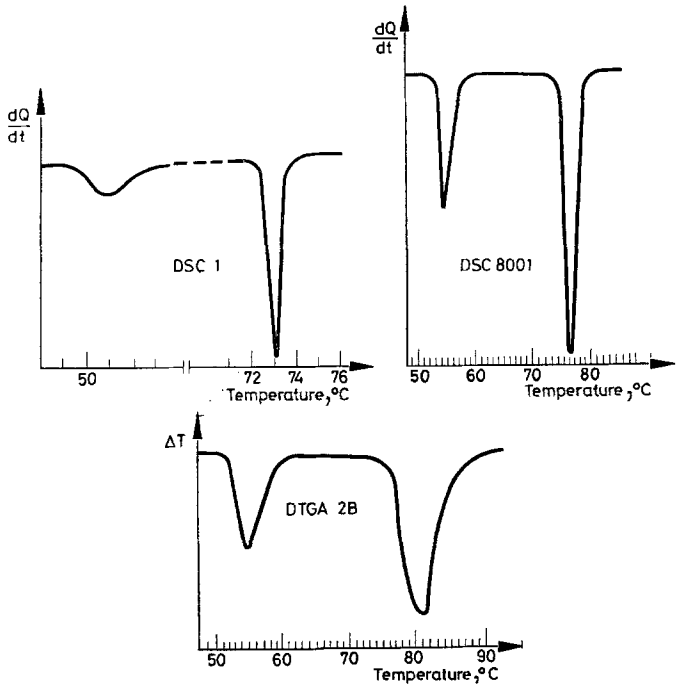


Fig. 3. DSC curves for hexachloromethane. DSC 1: Perkin-Elmer, range 4, 4°C/min; DSC 8001: Rigakudenki, range ±1, 5°C/min; DTGA 2B: Shimadzu, range ±25, 5°C/min

Table 2

Transition temperatures

(a) Hexamethylbenzene (Literature value 110.4 °C)

Apparatus	Heating rate (°/min)	T_1 (°C)	T_2 (°C)	T_3 (°C)
DSC-1 (Perkin-Elmer)	4	112.7 ± 0.1	112.8 ± 0.0	113.2 ± 0.0
		*(109.8 ± 0.1)	(109.5 ± 0.1)	(109.0 ± 0.2)
	8	113.3 ± 0.1	113.3 ± 0.1	113.9 ± 0.1
		*(110.7 ± 0.1)	(110.6 ± 0.1)	(109.7 ± 0.0)
DSC-8001 (Rigaku Denki)	3	112.8 ± 0.4	112.8 ± 0.4	114.4 ± 0.1
	5	115.6 ± 0.2	115.6 ± 0.2	116.7 ± 0.1
	10	114.7 ± 0.2	114.7 ± 0.2	117.5 ± 0.1
DTGA-2B (Shimadzu)	5	117 ± 1	118 ± 1	120 ± 1
	10	114 ± 0	117 ± 2	120 ± 2

(b) Hexachloroethane (Literature value 71.4 °C)

Apparatus	Heating rate (°/min)	T_1 (°C)	T_2 (°C)	T_3 (°C)
DSC-1 (Perkin-Elmer)	4	72.2 ± 0.0	72.4 ± 0.0	73.2 ± 0.0
		*(69.6 ± 0.1)	(69.5 ± 0.0)	(68.8 ± 0.1)
	8	74.6 ± 0.1	74.7 ± 0.2	76.1 ± 0.2
		*(71.2 ± 0.1)	(71.1 ± 0.1)	(70.0 ± 0.2)
DSC-8001 (Rigaku Denki)	3	73.3 ± 0.4	73.3 ± 0.4	76.2 ± 0.7
	5	75.3 ± 0.2	75.3 ± 0.2	78.0 ± 0.0
	10	74.5 ± 0.1	74.5 ± 0.1	77.9 ± 0.1
DTGA-2B (Shimadzu)	5	76 ± 1	78 ± 2	83 ± 1
	10	76 ± 1	79 ± 0	84 ± 1

(c) Hexachloroethane (Literature value 45.0 °C)

Apparatus	Heating rate (°/min)	T_1 (°C)	T_2 (°C)	T_3 (°C)
DSC-1 (Perkin-Elmer)	4	49.0 ± 0.1	49.5 ± 0.1	51.0 ± 0.1
	8	49.7 ± 0.0	50.4 ± 0.1	51.6 ± 0.1
DSC-8001 (Rigaku Denki)	3	48.5 ± 0.2	49.0 ± 0.1	51.2 ± 0.1
	5	52.1 ± 0.0	53.2 ± 0.1	55.2 ± 0.1
	10	51.1 ± 0.1	51.3 ± 0.2	53.9 ± 0.3
DTGA-2B (Shimadzu)	5	53 ± 1	54 ± 1	57 ± 1
	10	53 ± 1	54 ± 1	58 ± 1

* Parenthesized values were determined in the cooling condition.

Therefore, only two candidates for standard materials remain: hexachloroethane and hexamethylbenzene. Figs 3 and 4 show transition peaks for hexachloroethane and hexamethylbenzene, respectively, with different instruments. Transition temperatures were determined as shown in Table 2 (a) – (c) with standard deviations.

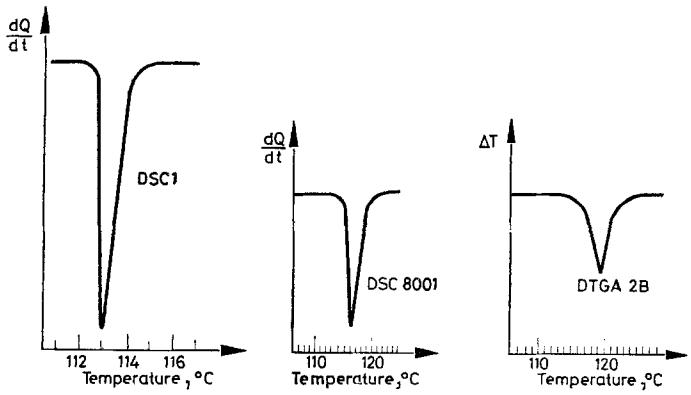


Fig. 4. DSC curves for hexamethylbenzene (conditions are the same as shown in Fig. 3)

The transition temperature for hexamethylbenzene is rather high for the low temperature standard, but it is very sharp and reproducible.

The transition peaks for hexachloroethane have been already investigated by the Committee on Standardization [2]. The upper peak is very appropriate to be the standard, but the lower one is rather diffuse and seems not useful as a standard.

The effects of the heating rates and the instruments are not yet clear in these measurements. However, the measured values of T_1 at smaller heating rates with Perkin-Elmer DSC I seem to be closest to the existing literature values.

*

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References

1. H. G. McAdie, Thermochim. Acta 1 (1970) 325.
2. Private communication.
3. C. Plato and A. R. Glasgow, Jr., Anal. Chem., 41 (1969) 330.

Résumé — Pour le but de trouver des étalons de température au-dessous de 150°C pour l'ATD, on a examiné les transitions en phase solide de différents composés organiques de bas poids moléculaire à l'aide d'un analyseur enthalpique différentiel. Sur les 14 échantillons étudiés, on propose l'hexachloroéthane (71°) et l'hexaméthylbenzène (110°) comme étalons.

ZUSAMMENFASSUNG — Zur Temperaturnormung unter 150° die DTA Methode wurden verschiedene organische Verbindungen von niedrigem Molekulargewicht und geeigneten Umwandlungen in fester Phase durch Differential Scanning Kalorimetrie geprüft. Von 14 verschiedenen Substanzen wurden Hexachloräthan (71°) und Hexamethylbenzol (110°) zum gesuchten Zweck geeignet gefunden.

Резюме — С целью нахождения температурных стандартов для ДТА ниже температуры 150°С изучены некоторые переходы в твердой фазе органических соединений с низким молекулярным весом. Найдено, что из 14 изученных соединений переходы двух веществ — гексахлорэтана (71°) и гексаметилбензола (110°), удовлетворяют требованиям стандартов.