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Reproducibility of thermal effects within the glass transition region

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The sensitivity of DSC-traces to controlled ageing in successive heating/cooling cycles within the glass transition region was studied. The effects of cooling rate both of the melt and of the supercooled liquid, as well as of the heating rate, were considered. It was concluded that within the transformation region the cooling rate of supercooled liquid exerts the predominant effect on the reproducibility of the DSC-curves. It was demonstrated that the thermal history of a sample during glass formation may be erased by only one heating/cooling cycle within the transformation region.

1. Introduction

The glass transition temperature, T_g, is a parameter of the reversible glass-to-supercooled-liquid transition, the latter being a typical rate process [1]. Therefore, T_g is not, in general, a thermodynamic parameter, and depends on the thermal history of glass [2–6]. The aim of this study was to find an experimental means of assessing the thermal characteristics near T_g being the most representative of the material studied. So far, stabilization by annealing for several hours at a temperature just above T_g has been recommended with respect to kinetically stable glasses, such as amorphous selenium [7, 8] and some polymers [6, 9]. In the present study, the sensitivity of both T_g and the shape of the DSC-curve near the glass transition to the number of heating/cooling cycles within the transition region was considered, using the cooling rate of the melt, R_m, and the supercooled liquid, R, and the glass heating rate, β, as the variables. The temperature interval below and above T_g was maintained constant during successive cycling.

The experiments were performed with a ternary chalcogenide glass of composition $Te_{80}Ge_{15}Pb_5$ (in at %), being sufficiently stable. The range of thermal stability is described by the difference between the crystallization temperature, T_x, and the glass transition temperature, T_g [10], and amounts to nearly 50 degrees for this glass (Fig. 1). The material studied is a typical example of a polymer-like glass with a chain structure, i.e. with covalent bonds dominating [11–14]. Therefore, the conclusions to be drawn on the basis of the present experiments are expected to hold true for the whole class of these materials. The initial glassy samples were obtained by rapid cooling of the melt, and thus the results ought to be representative of all glasses prepared by similar methods.

2. Experimental details

The alloy $Te_{80}Ge_{15}Pb_5$ (at %) was prepared from high-purity elemental solids [10]. The glassy samples were obtained by rapid cooling of the melt using the gun technique [15], or by much slower melt cooling in a DSC-unit. A Perkin-Elmer DSC-2 apparatus was used, at a sensitivity as high as 0.5 mcal sec^{-1}. The sample weight was 10 mg. The temperature scale was calibrated against standards. In order to detect any very slight changes in the thermal effects resulting from different treatments of the sample, the paper shift rate was made to be twice the recorded rate of the rise of temperature.

Two kinds of experiments were performed.

2.1. Experiment A: effect of cooling rate of the melt R_m .

The initial sample of as-splatted glass was remelted during the first run in a calorimeter by heating to temperature T_0 (100 K above the melting temperature), whereupon it was cooled at a cooling rate R_m to temperature T_1 (30 K below T_g). Next,

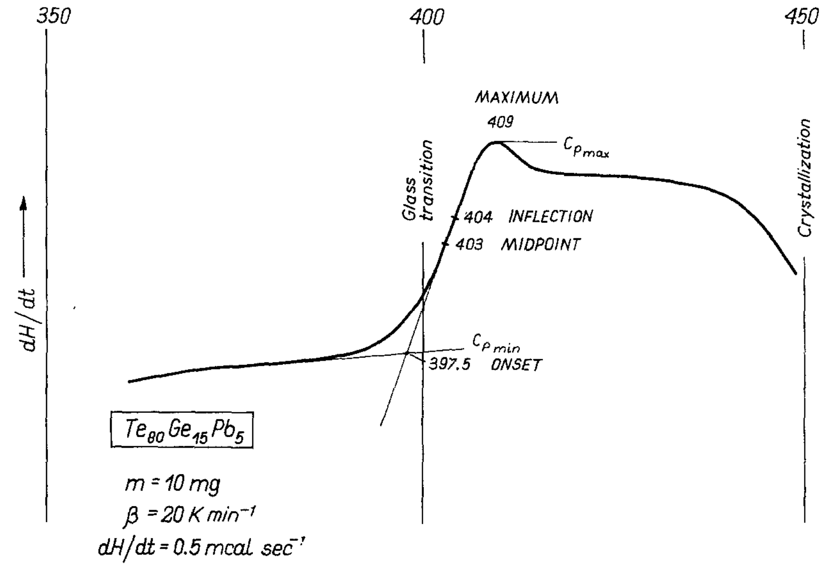


Figure 1 Reading of the glass transition temperature, T_g, from the DSC-trace: at $C_{p\max}$: $T_g = 409$ K; at inflection point: $T_g = 404$ K; at the mid-point (i.e. at the point corresponding to $1/2\Delta C_p$, where $\Delta C_p = C_{p\max} - C_{p\min}$): $T_g = 403$ K; at onset temperature, at the point of intersection of the base-line with a tangent to the rising part of the curve: $T_g = 397.5$ K.

the sample was scanned at constant heating rate $\beta = 20\,\mathrm{K\,min^{-1}}$ to temperature T_2 (30 K above T_g). After reaching temperature T_2, the sample was immediately cooled to temperature T_1 at cooling rate $R = 20\,\mathrm{K\,min^{-1}}$. This procedure of heating/cooling within the temperature range T_1-T_2 was repeated several times, and referred to as "cycling". As a result of cycling, the heating curves became reproducible. After attainment of reproducibility, the same sample was remelted and cooled at a cooling rate R_m, lower than that previously used, from temperature T_0 to temperature T_1. Next, after thermal equilibration for a few minutes, the sample was cycled until attainment of fully reproducible scans. Experiments were repeated using increasingly lower cooling rates, R_m, of the melt, amounting to 320, 160, 80, and 20 K min^{-1}, respectively. For the composition studied, R_m = 80 K min^{-1} seems to be the critical cooling rate. At lower R_m no glass can be obtained.

2.2. Experiment B: effect of the cooling/heating rate within the transformation region

The initial glassy sample (splat) was heated in a calorimeter to temperature T_2 within the metastable liquid region (50 K above T_g), whereupon the sample was cooled to temperature T_1 (50 K below T_g). The heating/cooling cycle was repeated three or four times. Two variants of this experiment, B-1 and B-2, were realized:

variant B-1 – constant heating rate $\beta = 20$ K min^{-1}, various cooling rates R (320, 80, and 20 K min^{-1}, respectively). For each R a new sample was taken and cycled several times.

variant B-2 – variables: heating rate β and cooling rate R. In each experiment the heating rate was equal to the cooling rate. For each value of $R = \beta$ a new sample was taken, and the effect of cycling within the transition region was studied. In this variant both the heating and cooling curves were recorded.

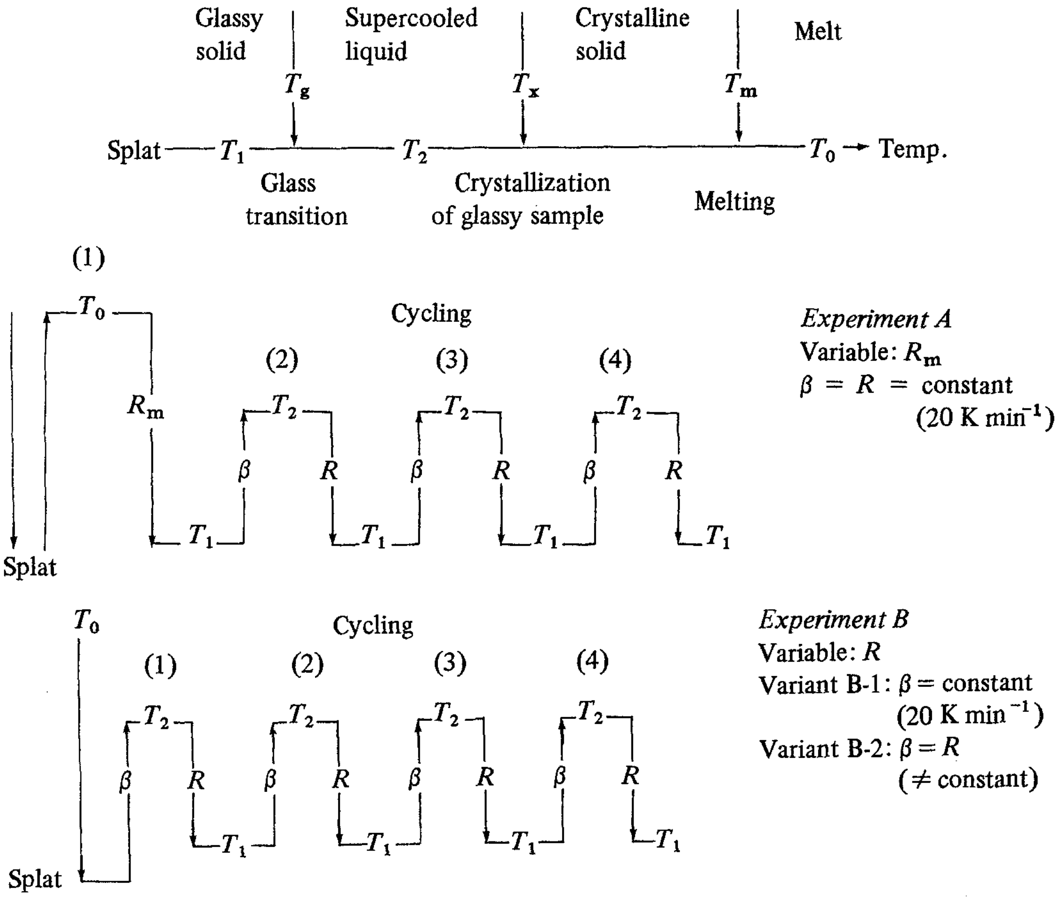
The thermal histories characteristic of Experiments A, B1 and B2 are illustrated schematically at top of following page.

From the DSC-traces the values of T_g were read (Fig. 1), using the recommendations available in the literature. Namely, T_g was read at the onset of the specific heat step (onset), at the point corresponding to $1/2\Delta C_p$, where $\Delta C_p = C_{p_{max}} - C_{p_{min}}$ (midpoint), at inflection point (inflection), and at the maximum of specific heat curve $C_{p_{max}}$ (maximum).

3. Results

Representative scans are presented in Figs. 2 to 6. Numerical data are shown in Table I.

The effect of the cooling rate of the melt on



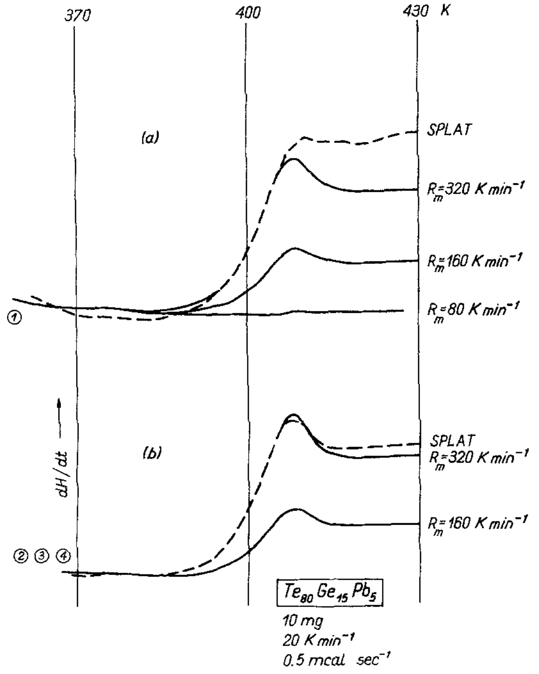


Figure 2 Results of experiment A: effect of melt cooling rate, R_m, on the DSC-traces recorded for the first run (a) and after the cycling procedure (b).

glass stabilization was studied in experiment A, and it is illustrated in Figs. 2 and 3. In the first run, i.e. when the as-quenched sample is scanned, the DSC-traces are most differentiated (Fig. 2a), as a result of using various melt cooling rates, R_m. After cycling within the glass transition region, the curves become more similar. Differentation of the scans after cycling (Fig. 2b) decreases with a rise of the melt cooling rate, as is evident from the similarity of traces in Fig. 2b for $R_m \geqslant 320\,\text{K}\,\text{min}^{-1}$. On the other hand, the higher the melt cooling rate, the more pronounced is the primary stabilization by one thermal cycle within the glass transition region (Fig. 3).

The effect of the parameters of thermal stabilization on DSC-characteristics of glassy samples was studied in experiment B. The higher the cooling rate, R, within the glass transition region, the more similar are the heating curves recorded for increasing cycle numbers. In other words, the higher the cooling rate, the smaller the number of cycles required to achieve glass stabilization (Fig. 4). At the same time, the larger the cycle number, the

TABLE I Changes in glass transition temperature as a result of cycling. T_g read from the heating (a) and cooling (b) curves. R_m, R and β denote the cooling rate of the melt, the cooling rate of supercooled liquid and the heating rate, respectively (K min^{-1})

			T_g (K)					
			(a) Heating				(b) Cooling	
Experiment			Onset	Inflection	Midpoint	Maximum	Onset	Inflection
Exp. A	R_m	Cycle						
Melt	Splat	Number						
cooling	cooling	1	396.5	403		409.5		
(const.)		2	396.5	402.5		407		
		3	396.5	402		407.5		
		4	396.5	402.5		407.5		
	320	1	397	403		408		
		2	397	403		408		
		3	397	403		408		
		4	397	403		408.5		
	160	1	398	403		408.5		
		2	398	403		409		
		3	398	403		409		
		4	398	403		408.5		
	80	1				408		
		2				408.5		
Exp B-1	R	Cycle						
Cooling		number						
within	5	1	391.5	398	398	406.5	380	393
transform-		2	396.5	400	400	406		
ation		3	401	403	403	404		
region	20	1	394	400.5	399	407.5	383	392
β = const.		2	394.5	399.5	399	406	384	392
		3	395.5	400	400	406	384	396
		4	395	400	400	406		
	80	1	393	400	400	407		
		2	394	400	399.5	406.5		
		3	394	399	399.5	407		
		4	394.5	400	400	407		
	320	1	394.5	400	400	408		
		2	394	399.5	399.5	406		
		3	394	399.5	399.5	406.5		
		4	394	399.5	399.5	406.5		
		5	394.5	400	400	407		
Exp B-2	R	Cycle						
Cooling		number						
within	5	1	391.5	397.5	396	403	380.5	394
transform-		2	391.5	397	396.5	401	380	393
ation		3	391.5	397	396.5	401	380	394
region	10	1	391.5	400	399	407	380	395
$\beta = R$		2	394	400	399.5	405	380	394
($\neq$ const.)		3	394	400	400	405.5	380.5	394.5
	20	1	396	404.5	403	411	373	394
		2	397	403.5	402.5	409	373	395
		3	397.5	404	403	409	372.5	395

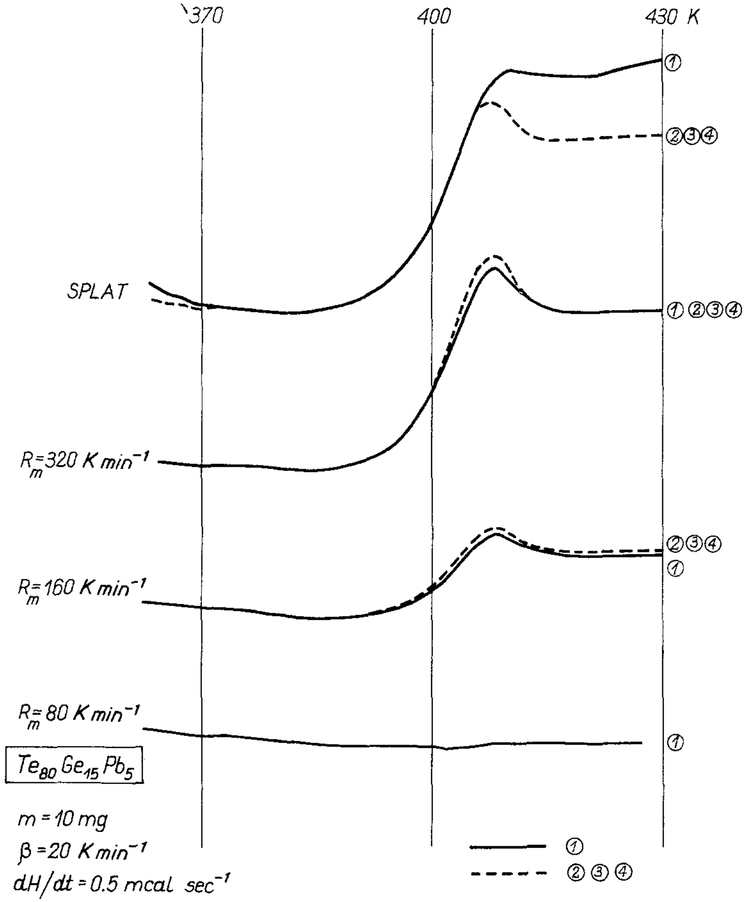


Figure 3 Another presentation of the results of experiment A: effect of cycling on the DSC-curves at various melt cooling rates, R_m. Arabic numerals denote the successive cycle number.

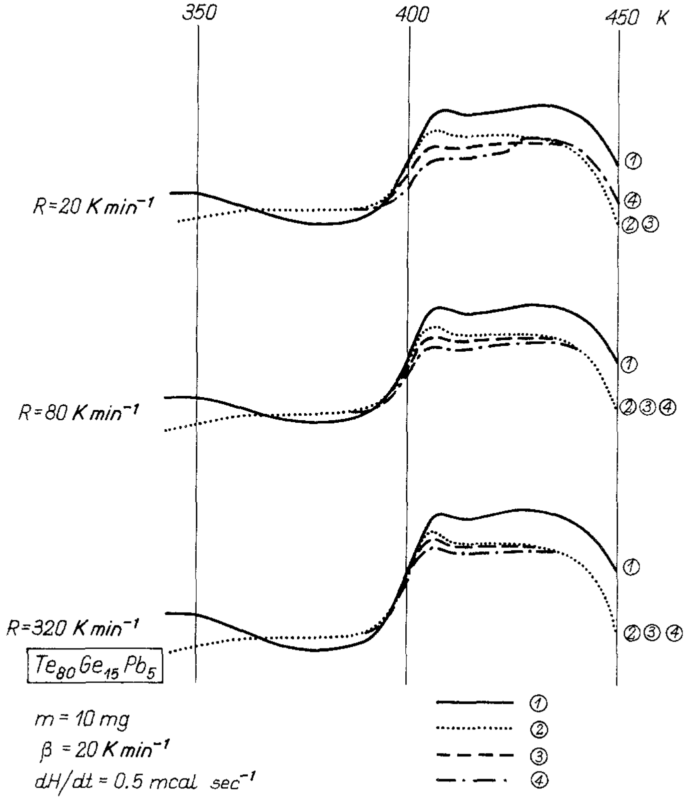


Figure 4 Results of experiment B1: effect of cycling on the DSC-traces, at various cooling rates, R, within the transformation region. Arabic numerals denote the seccessive cycle number.

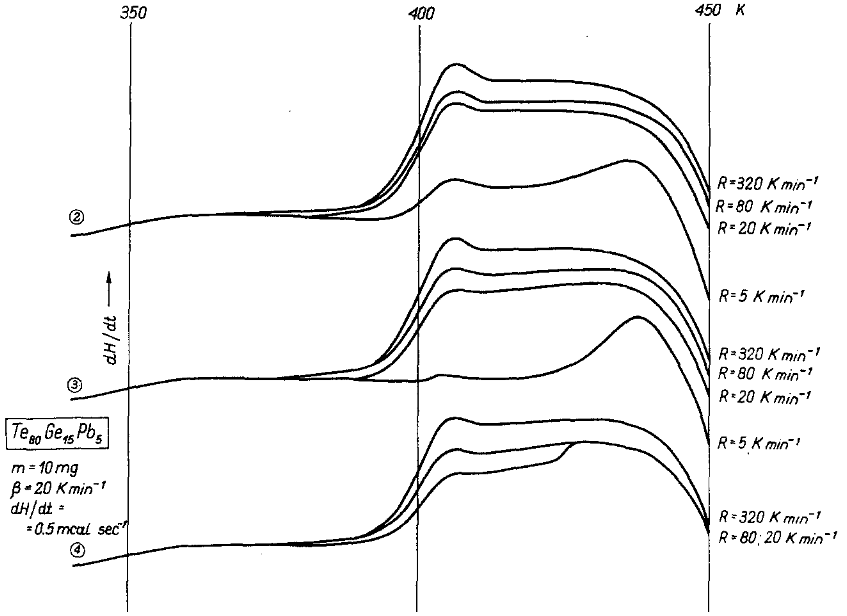


Figure 5 Another presentation of the results of experiment B1: effect of cooling rate R within the transformation region on the DSC-traces recorded for successive cycle number.

more sensitive is the DSC-trace to the cooling rate, R, of the metastable liquid (Fig. 5).

As far as the effect of the glass heating rate, β, is concerned (Fig. 6), an increase in β results in enhanced responsiveness of both heating and cooling curves to the cycle number. The higher the heating rate β within the transformation region, the greater the distance between the initial DSC-trace and the next ones, recorded after cycling. The sensitivity of the cooling curves to thermal treatment is much lower than that of the heating curves.

4. Discussion

Substances able to form a glass are known in all cases of materials [16, 17]. The experimental

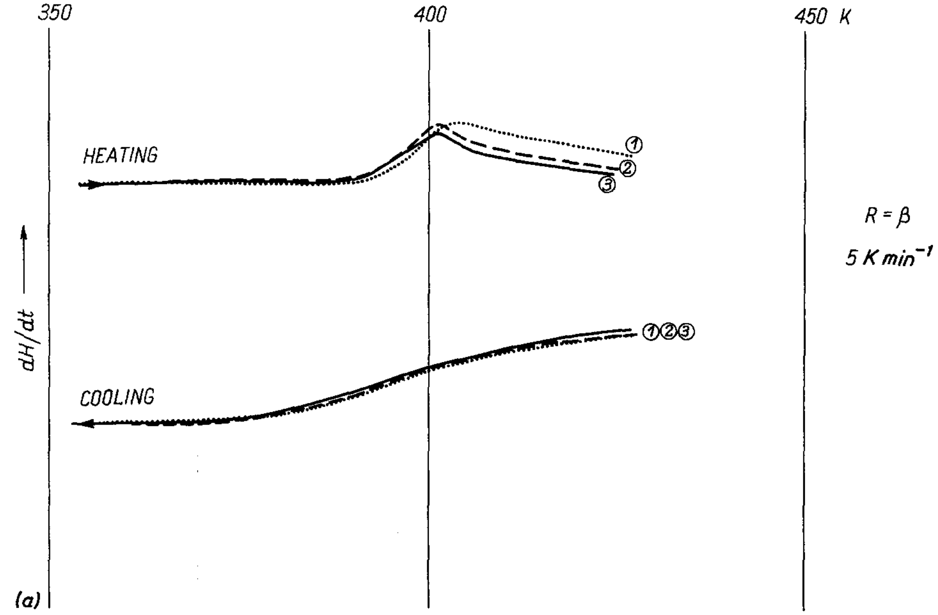


Figure 6 Results of experiment B2: effect of cycling within the transformation region on both the heating and cooling curves at various scanning rates (heating rate β equals cooling rate R).

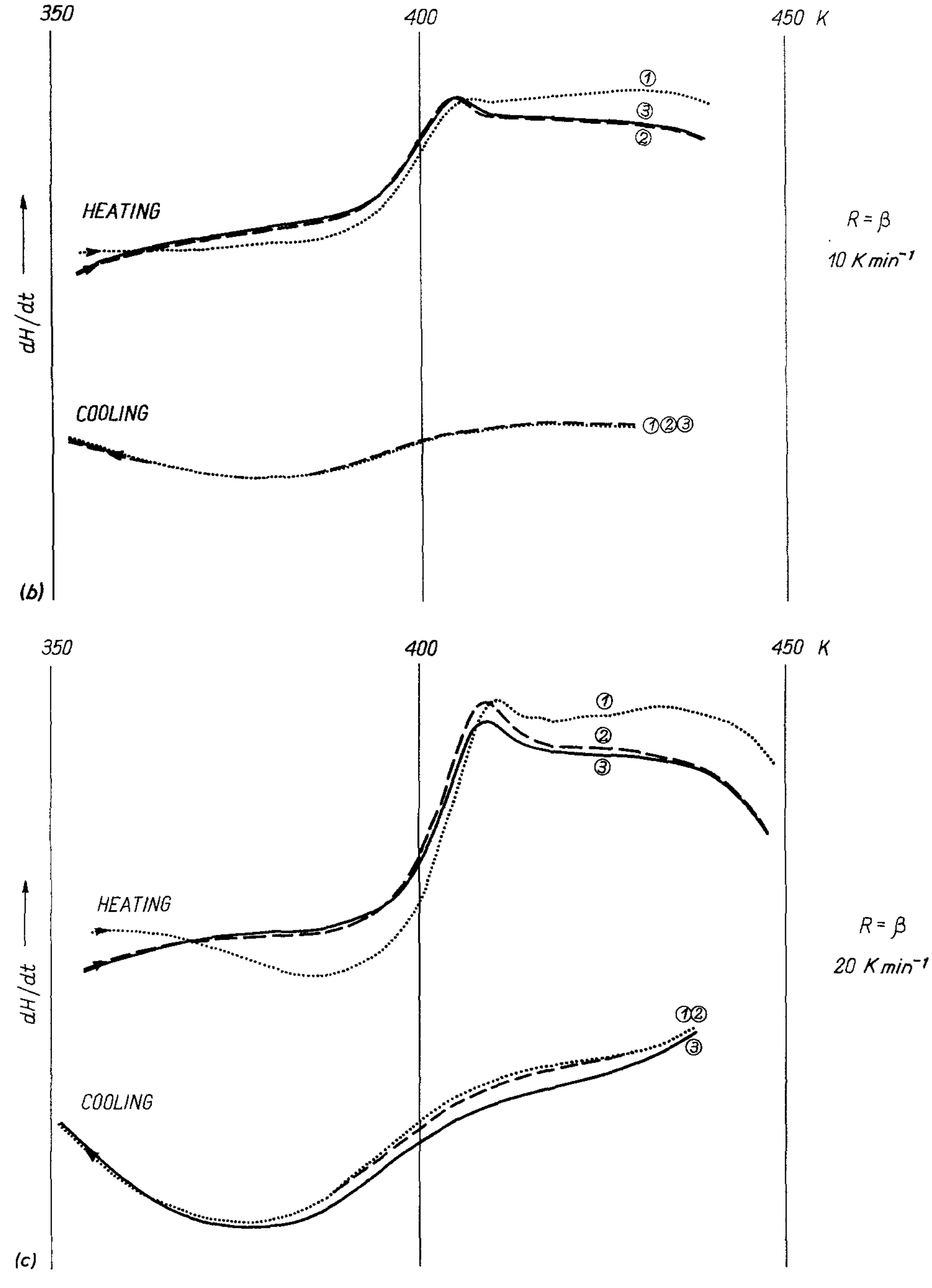


Figure 6 continued.

parameters governing glass formation depend on the chemical nature of the materials [18]. As far as the liquid-to-solid transition is concerned, the critical required cooling rate changes within as wide a range as 10^{-1} to 10^{10} K sec^{-1} [19]. Therefore, the glasses obtained differ markedly in relaxation power. Enthalpy or volume relaxation into the metastable supercooled-liquid state is considered to be the source of the observed changes in the properties of glass [9, 20, 21]. Theoretical considerations of the nature of transformations in the glassy state are based on the assumption of extremely low heating or cooling rates [22, 23]. However, it is not always possible to fulfil this requirement. For example, metallic glasses, or even many chalcogenide glasses, become crystalline on slow heating, whereas their melts do not form a glass if slowly cooled. In such materials the problem of experimental comparability of their glassy state is of special importance.

From the present results it may be deduced that the drastic changes in properties caused by the rate effect can fairly easily be erased by a simple stabilization procedure. Stabilization within the transformation region by way of controlled ageing of glass has so far been suggested for some polymeric glasses [6, 9]. Irrespective of whether the nature of the glass transition is kinetic [24] or thermodynamic [1, 25–28], the characteristics of the glassy state obtained from the DSC-method may be modified and made almost insensitive to the initial melt cooling rate by preliminary heating of glass within the glass transition region. An increase in the cooling rate of the melt results in a reduced kinetic stability of disorder, as illustrated by an increase in the separation between the first and second run of DSC-traces (Fig. 3). On the other hand, the higher the cooling rate of the melt, the closer are the respective DSC-traces after preliminary heating (Fig. 2b). Fig. 2b indicates that if the melt cooling rate exceeds 320 K min^{-1}, then glasses seem to be in corresponding states after only one thermal cycle of heating/cooling near T_g. Therefore, the thermal characteristics of glasses obtained by rapid melt cooling become reproducible as early as in the second run, irrespective of the melt cooling rate (if the cooling rate is high enough). It seems of interest that slight crystallization [2, 29], probably accompanying the stabilization by cycling, exerts no effect on the characteristics of glass since the DSC-traces after the 2nd, 3rd and 4th cycle are the same (Figs. 2b, 3).

The effect of the cooling rate within the transformation regions (Figs. 4 and 5) on DSC characteristics of glasses is more pronounced when the cycle number increases (Fig. 5), in contrast to the observed effect of the melt cooling rate. The curves corresponding to various cooling rates of the metastable liquid are closer, the smaller the cycle number. Successive heatings enable approaching of the ideal glass configuration, and that depends on the previous cooling rate of supercooled liquid. Therefore, in Fig. 5 for each cooling rate the final run seems to be most representative of the material studied. On the other hand, cooling within the transformation region at a higher cooling rate indicates that less time is available for the structural rearrangements [21, 30]. Thus, for example, the cycle number should be much greater than 4 in order to differentiate the DSC-traces recorded with heating at a constant rate of 20 K min^{-1} (Fig. 4).

The experiments in which the heating rate is equal to the cooling rate within the transformation region show (Fig. 6) that only the heating curves are sensitive to the cycle number, and this effect is stronger for higher scanning rates. Therefore, the time of heating is of importance. The slower the scanning rate, the longer the time of heating and the smaller the interval between the actual glassy state and ideal glass. Also in this experiment the unavoidable partial crystallization of the sample fails to affect the DSC-traces within the transformation region.

So far, the qualitative effects of stabilization by cycling have been considered. The shape of the DSC-curve is very sensitive to the parameters of stabilization, as a result of the sensitivity of the properties of glass to its thermal history. At the same time, however, T_g values read from the scans are almost the same in all experiments (Table I) performed at the same heating rate β, and this is the reason for the very good reproducibility of T_g. As far as the T_g values are concerned, the value corresponding to the maximum of specific heat, read at the $C_{p_{max}}$ on the heating curves, is most sensitive to the thermal history of the sample (Fig. 7). On the other hand, T_g values read from the cooling curves are almost insensitive to the thermal history and may, therefore, be considered to be material constants.

5. Conclusions

(1) As indicated by reproducibility of DSC-traces after successive cycling about the glass transition, the glassy state is more sensitive to the cooling rate of the supercooled liquid within the transformation region, than to the cooling rate of the melt during glass formation. The lower the cooling rate within the transformation region. the more pronounced the differences caused in scans by successive cyclings.

(2) The thermal history of glass formation can easily be erased by the cycling procedure. Representative scans may be obtained after only one cycle at 20 K min^{-1}, irrespective of the melt cooling rate.

(3) Stabilization by one heating/cooling cycle seems to be of special interest for glasses obtained by techniques for rapid cooling of melts. The lower the cooling rate of the melt, the closer to

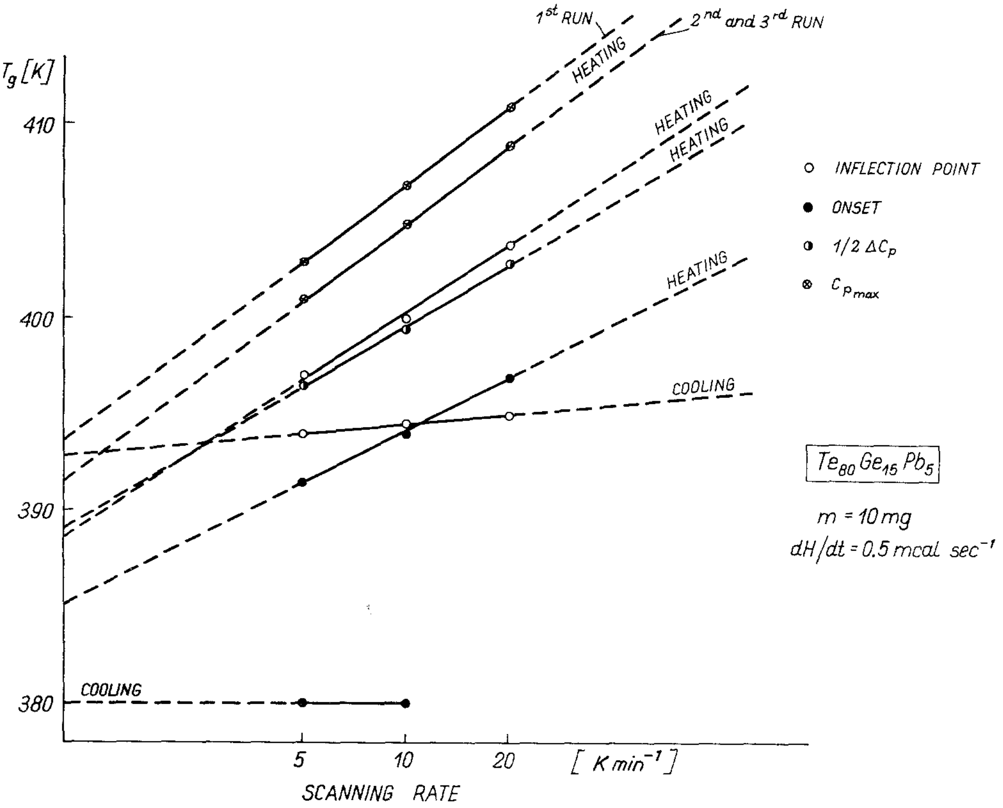


Figure 7 Glass transition temperature, T_g, read in four different ways from the heating and cooling curves, plotted as a function of the logarithm of the scanning rate. Only T_g read at $C_{p_{max}}$ is a function of the cycle number.

the initial DSC-trace is the scan obtained after the first cycle.

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