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DSC OF AMORPHOUS MATERIALS

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SUMMARY

Most solid materials are crystalline, some are semicrystalline with amorphous fractions while very few are completely amorphous.

This work deals with the preparation of undercooled melts by using cooling rates around 100 K/s, the determination of their glass transition temperature and the study of the devitrification behavior (cold crystallization).

The following amorphous solids were prepared and studied: acetyl salicylic acid, ethanol, selenium, methanol, sulfapyridine, vanillin, p-nitrobenzene and polyethylenterephthalate (PET).

INTRODUCTION

Non polymeric materials such as metals or rocks are of crystalline nature in their solid state. The same applies for most inorganic and organic chemicals. In absence of decomposition they all melt at a characteristic temperature, T_f, when heated. Polymers on the other hand can not be completely crystalline because of the insufficient order along the chain of linear macromolecules (e.g. polypropylene, cellulose). In case of atactic, branched and crosslinked polymers the crystallinity (fraction of crystallized areas) approaches to zero, i.e. such materials can be completely amorphous. Mineral glasses and natural resins including amber are other examples of amorphous substances. They undergo glass transition at a characteristic temperature, T_g. Above T_g some of them show a tendency to form crystals, which is called devitrification or "cold crystallization".

It is known from the production process of metallic glasses, that virtually all substances can be obtained in the amorphous state by quenching the melt with high enough cooling rate to a temperature well below the expected T_g. For metallic glasses the required cooling rate is ca. 10^4 K/s.

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EXPERIMENTAL

The amorphous samples are prepared by melting the crystalline initial substance in the DSC cell for the quenching methods B and C or in an oven or an additional DSC cell for method A.

The DSC pan with the molten specimen is quench cooled by any of the techniques mentioned in the table.

To avoid crystallization the samples were heated to a temperature 10°C higher than melting point for about 30 s. This pretreatment obviously distroys some surviving nuclei of crystallization.

Newton's law of cooling ($\beta = \Delta T/\tau$) allows to estimate the cooling rate, β, as a function of the temperature difference, ΔT, between the specimen and the heat sink and the time constant τ. For small ΔT values and with a thin thermocouple in the specimen τ can be determined previously. The following table indicates the obtained time constants and the calculated cooling rates at 200 and 100°C for the Mettler Standard Aluminum pan of 40 µl volume:

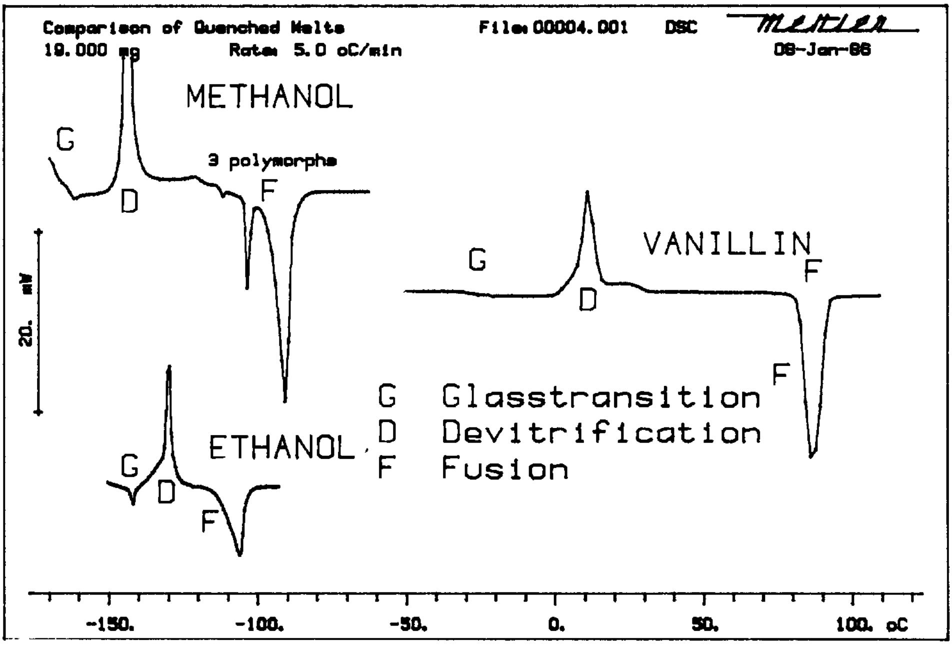
	Quenching Method	$T_{\text{heat sink}}$	τ s	β at 200°C K/s	β at 100°C K/s
A:	Pan placed in precooled DSC cell	-170	7	53	39
B:	Pan pressed on ice cube	0	0.9	220	110
C:	Pan immersed in liquid nitrogen	-195	1.2	330	250

The elegant method A is sufficient for samples which do not crystallize easily: PET, sulfapyridine, sulfur and vanilline. Method B is ideal for all samples with a T_g higher than room temperature (or $T_f > 125°C$) e.g. for selenium and many polymers. The only disadvantage is that the pan has to be dried with some filter paper or similar before the DSC measurement . Method C sometimes failes due to Leidenfrost's phenomenon (bad heat transfer through the layer of insulating nitrogen gas formed). This can be avoided to a certain extent by shaking and tilting the pan while dipping into liquid nitrogen with tweezers. As soon as there is no more boiling nitrogen around the pan, the latter is rapidly transferred into the precooled DSC cell purged with ca. 100 ml dry nitrogen per minute to counteract the condensation of humidity.

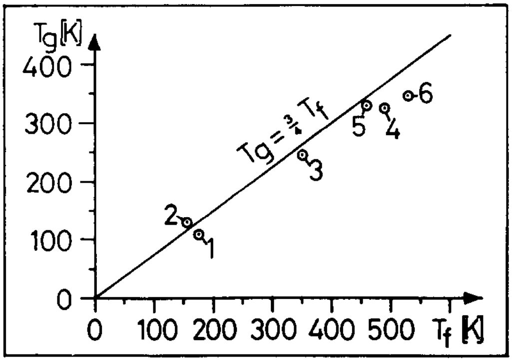
The subsequent DSC measurements were performed in the Mettler TA3000 System using the low temperature cell (-170°C to +600°C). The new GraphWare TA70 is applied for curve comparison and graphical presentations.

RESULTS

Many of the tested substances can be obtained in the glassy state using a cooling rate of 20 to 300 K/s. Others crystallize despite the fast cooling, e.g. benzoic acid, naphtaline, phenacetine, polyethylene, stearic acid.



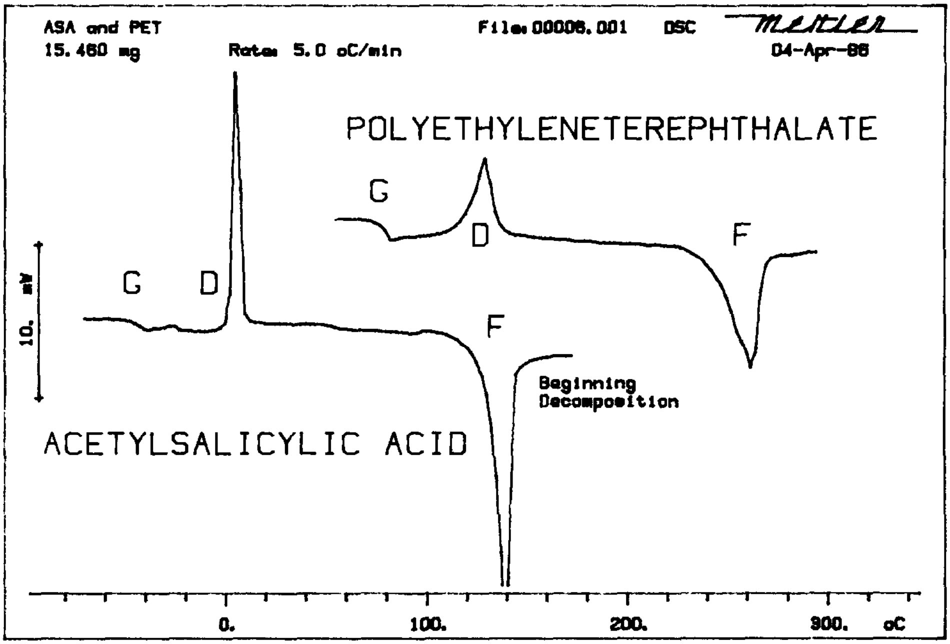
Up to 4 curves in 4 colors can be drawn on a diagram by the new METTLER GraphWare TA70.



Glass transition temperature as a function of the temperature of fusion

1 Methanol	108 K,	175 K
2 Ethanol	128 K,	156 K
3 Vanillin	243 K,	353 K
4 Selen	323 K,	490 K
5 Sulfapyridine	331 K,	463 K
6 PET	344 K,	529 K

The thumb rule $T_g \sim 3/4\ T_f$ (straight line in diagram) obviously is quite good.



CONCLUSION

The tendency to crystallize from melt varies from substance to substance. With the described simple quenching methods a lot of materials are obtained in the amorphous state. Such glasses are relatively stable below T_g. On heating most of the substances begin to crystallize above Tg. Quite often a metastable plymorph is appearing first (Ostwald's step rule) which would not be formed from melt directly. Thus this procedure is helpfull to check polymorphism of substances (ref. 1). It seems, that nuclei formation is promoted by the application of a cyclic temperature program between T_g and T_g + 20 K. The maximum crystal growth rate occurs at about T_g + 40 K. These empirical facts also hold in absence of polymorphism.

On the other hand quenched samples allow an accurate determination of T_g by supressing crystallization.

Last but not least the obtained curve is of an aesthetic value too. Indeed it is accepted as the logogram of thermal analysis.

REFERENCE

1 W. McCrone Fusion Methods in Chemical Microscopy, Interscience Publishers New York