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Advances in Thermomicroscopy with Simultaneous DSC

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ABSTRACT

Various organic substances, e.g. poly diethyl siloxane, (PDES), tetratriacontane, trinitrotoluene (TNT) and DDT were investigated with respect to crystallization kinetics and purity by means of simultaneous thermomicroscopy/DSC. The advantage of this method is that it allows the correlation of visually observed phenomena with the measured thermal data.

INTRODUCTION

Results obtained from thermoanalytical measurements like DSC are generally reproducible and quantitative, but they cannot always be correlated to the respective phase transformations or chemical reactions occurring in the substance. The present paper will demonstrate the usefulness of simultaneous DSC and hot stage microscopy. Effects which don't show any significant enthalpy change in DSC often can be detected with microscopy. On the other hand thermomicroscopic investigations sometimes require to estimate heats of transformation, fusion or crystallization.

Besides, the combination of thermomicroscopy with DSC is also a very good teaching method to introduce thermoanalytical investigations to beginners. This is because one can see changes in the investigated substance together with the course of the measured curve.

INSTRUMENTAL

The simultaneous measurements are based on a commercial microscope and the hot stage of the Mettler Thermosystem FP800. The schematic picture (Fig.1) shows the microscope with the hot stage and the control unit FP80, which can be connected with a RS 232C to a personal computer system, wherein the evaluation programs are accessible. The sample is filled directly into the crucible. In the case of low-viscosity substances and of liquid crystals, three sapphire balls act as spacers and help to maintain a uniform sample distribution and thickness during the measurement.

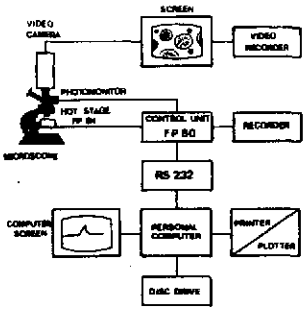

Fig.1 Instrumental set-up of simultaneous hot stage microscopy

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1. Poly (diethyl siloxane) PDES

An other investigated sample is the poly (diethyl siloxane) PDES, a liquid polymer (1).

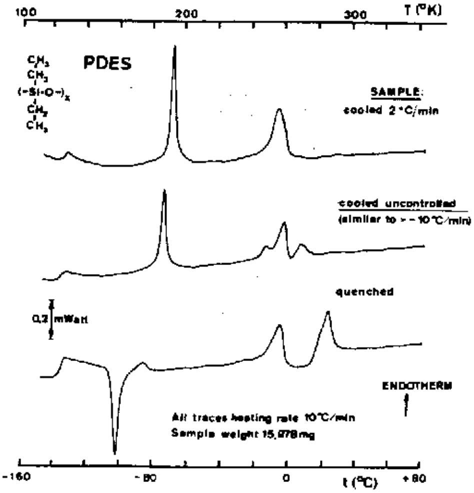

Fig.2 DSC-curves of PDES

Fig.2 shows three curves of the same sample of poly (diethyl siloxane) which has had different cooling treatment before reheating with 10 C/Min from -160 to +80 C.
The sample of the first curve was cooled down to -160 C with 2 C/Min. During heating up with 10 C/Min it shows a glass transition at -130 C and a first order transformation at -80 C to a condis crystal (that means a conformationally disorderd crystal). Melting takes place at -16 C. The sample of the second curve was uncontrolled cooled to -160 C, that means faster than 10 C/Min. The curve shows a similar glass transition at the same temperature and a smaller heat of transformation to the condis crystal, followed by an incongruent melting behavior. The sample of the third curve was quenched in liquid nitrogen before heating up. This curve is different from the others. Only the glass point looks similar and is followed by a recrystallization and a very small transformation. The melting process shows two melting peaks the first peak is due to a reorientation of the condis crystal whereas the second peak corresponds to the melting. Simultaneously recorded DSC/thermomicroscopy runs allowed the correlation between the enthalpy changes and the morphological changes when going from the melt to the crystallized and liquid crystalline state. This is shown by the DSC curve (Fig.3) which was recorded during cooling of molten PDES. The corresponding thermomicroscopyc pictures were recorded on a video - tape, Fig.4a and 4b are taken from the video screen.

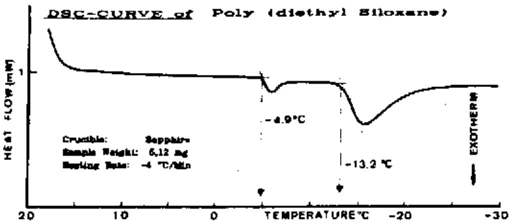

Fig.3 DSC-curve of PDES

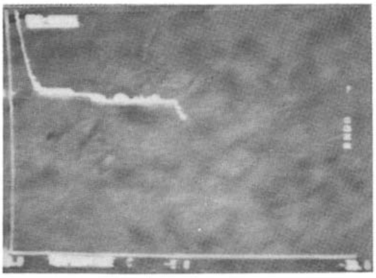

Fig.4a Crystallization

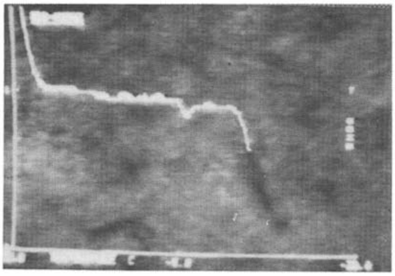

Fig.4b Liquid crystalline state

2. ALCANES

Another application of DSC and hot stage microscopy can be demonstrated with alcanes. Fig.5 shows a DSC curve of tetratriacontane (C H) with two transitions, the first at 69 C and the second at 72 C. Earlier interpretation defined the first to be a premelting effect and the second as a fusion. But simultaneous observation of the sample in the hot stage as well as with heating X-ray proved the first transition to be a solid-solid transition, called "odd-even effect". This effect is caused by rotation and bending of the chain of the molecules and gives a volume change which is visible by fissures and cracks in the sample (see Fig.6, left and right).

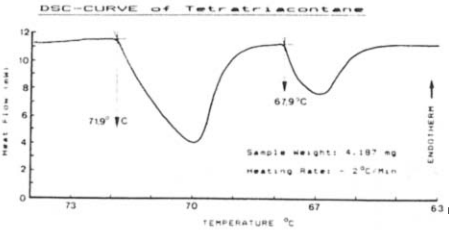

Fig.5 DSC-curve

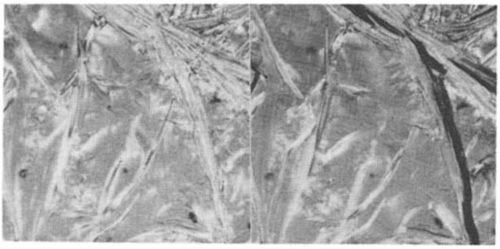

Fig.6 Crystallization behavior

3. 2,4,6 Trinitrotoluene (TNT)

In production of explosive materials, a mixture of TNT and 4 Mole% hexogene is used to give a castable melt to fill cartridges. Fig.7 shows in a DSC-curve the melting behaviour of TNT with 4 Mole% hexogene. Addition of too much of the hexogene gives a poor product, which may show ignition failures, due to the cracks and exudates.

With thermomicroscopy, the crystallization process can be investigated. Fig.8 shows micrographs of pure TNT (above) and of the mixture with 4 Mol% hexogene (below). A slow cooling rate produced small crystallites in pure TNT, whereas the mixture gives big ones having fewer phase boundaries. Fast cooling changes the results and the mixture gives irregular crystal shapes and even a segregation.

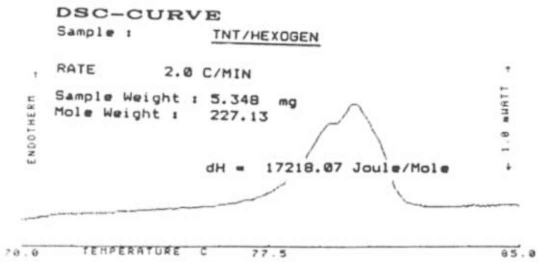

Fig.7 Melting behavior of TNT with 4 Mole% hexogene

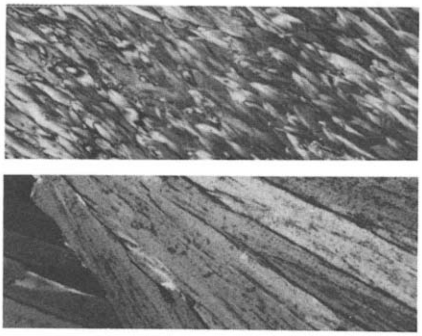

Fig.8 Different crystallization of TNT

4. Crystallization kinetics of DDT

For the primary crystallization of macromolecules, three cases may be distinguished, depending on the macroconformation of the molecules: The crystallization of spherical molecules (e.g. globulines) or particles (latex spheres) leads to ordered packings. If rod-like molecules (e.g. helices) are crystallized from solutions, a statistical isotropic arrangement of the molecules is no longer possible. Therefore a parallel ordering takes place which leads to the necessary increase in density with formation of ordered, anisotropic phases. Finally in the case of macro coil-shaped molecules (e.g. nylon) their crystallization depends strongly on the solvent and on the temperature. The coil-molecules are built in individually by the growing crystal which usually causes a folding of chains. In most such cases, lamellar packings crystallize from the melt which are interlaminarly connected. For the thermomicroscopic determination of the rate of crystallization, one usually starts with a premelted sample. This allows the study of crystal growth under isothermal conditions (TV or microphotography, see Fig.9). The evolution of the growth rate under isothermal conditions is shown in Fig.10. For the sample preparation, the substance, e.g. DDT, is molten onto the sample holder using spherical spacers and a cover in order to get a defined thickness, in the present case 0,06 mm. If the density of the substance as a function of the temperature is known, one can calculate the increase in weight from the shapes of the growing crystals. These data, the linear rate of crystallization and increase in weight as function of the temperature, allow the calculation of activation energy of crystallization. According to Avrami, the crystallization rate of disc-like particles can be described in terms of the equation $\overline{V_i} = 1/3(\pi d k_2^2 t^2)$. In the case of DDT, Fig.11 shows a diagram of ln k versus 1/T which allows the derivation of the activation energy of crystallization.

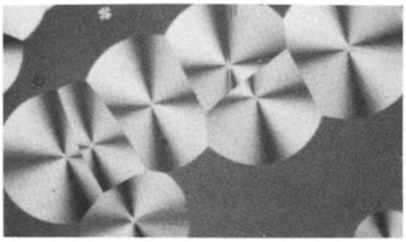

Fig.9 Growth of DDT-spherulites

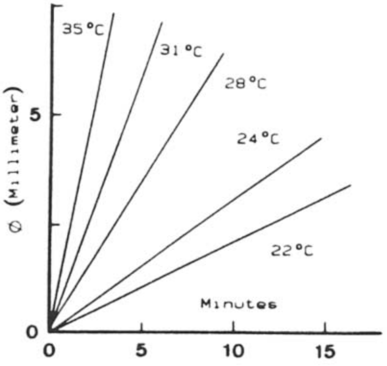

Fig.10 Isothermal growth

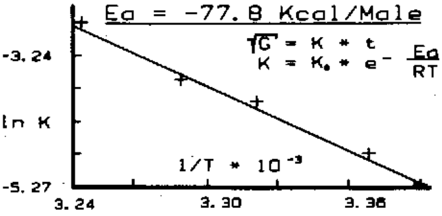

Fig.11 Derivation of the activation energy

CONCLUSIONS

The results presented in this paper prove that simultaneous thermomicroscopy/DSC is very useful for studies on liquid polymers, alcanes, and crystallization of various organic materials.

REFERENCES

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