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Advances in Thermomicroscopy with Simultaneous DSC

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ABSTRACT

Four different substances, e.g. polyethylene terephtalate, azobenzene, trinitrotoluene and DDT were investigated with respect to crystallization kinetics, dimerization and purity by means of simultaneous thermomicroscopy/DSC. The advantages of this method will be shown with respect to the correlation of visually observed phenomena with the measured thermal data.

INTRODUCTION

Thermoanalytical results e.g. from DSC usually are reproducible and quantitative, but cannot always be correlated with the respective phase transformation or chemical reaction occuring in the substance. Therefore it has been tried to improve such thermoanalytical methods by correlating their results with physical or chemical changes of the substances being investigated.

Thermomicroscopy with DSC is also a very good teaching - method to introduce thermoanalytical investigations for 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 (see 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 sapphire 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. Table I gives a more detailed description of the instrumentation which is required for thermomicroscopic analysis.

CRYSTALLIZATION OF POLYMERS

The mobility of the macromolecules, of which polymers are composed, determines the tendency and degree of crystallinity. Depending on the type and position of the side groups, various transitions are possible from amorphous (atactic) to crystalline (isotactic and syndiotactic).

Polypropylene, polystyrene and polymethyl acrylate are examples for polymers, which are known in atactic and isotactic forms. For

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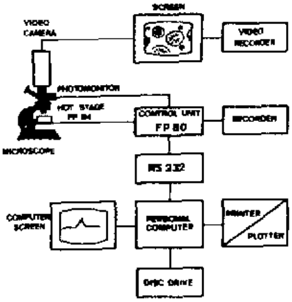

Fig.1 Instrumental set-up of the simultaneous hot stage microscopy

Table I

INSTRUMENTATION FOR THERMOMICROSCOPIC ANALYSIS

MICROSCOPE

OCULARS OBJECTIVES FILTERS LIGHT SOURCES

SIMULTANEOUSLY USED ACCESSORIES

HOT STAGE DSC-CELL PHOTOMETER IR-SPECTROMETER

SAMPLE HOLDERS

SLIDES CRUCIBLES SLIDE AND CRUCIBLE MATERIAL

FURNACES

TEMPERATURE RANGES HEATING PROGRAMS ATMOSPHERES

OPTICAL RECORDINGS

CAMERAS & FILM MATERIALS TV CAMERAS ACCESSORY ITEMS

COMPUTER EVALUATION OF THERMAL MEASUREMENTS

COMPUTERS INTERFACES HARDWARE SOFTWARE

the present crystallization studies polyethylene terephtalate was chosen. The samples for the measurement were prepared by melting and quenching a commercial granulate on the hot stage between microscopic slides. During heating the crystallization of PETP was recorded by DSC and optically, from 50 C to 275 C (see Fig.2). This could be correlated with the simultaneously observed spherulitic crystallization on the hot stage, which started also at 130 C and was complete at about 145 C. (Fig.3). Therefore the recorded DSC-peak corresponds to a 100% transformation from the glassy to the crystalline state. The heat of crystallization derived from this peak by integration was in the order of 115 J/g.

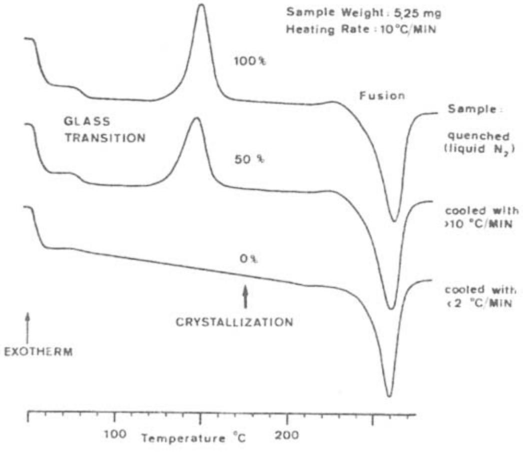

Fig.2 DSC curves of polyethylene-terephtalate (PETP)

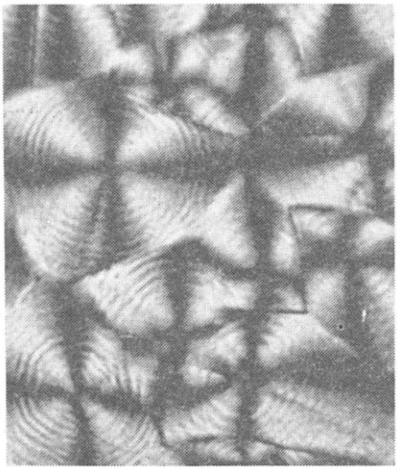

Fig.3 Spherulitic crystallization of PETP

Dimerization of azobenzene

An example for dimerisation is the highly unstable cis-azobenzene, which was gradually transformed from the cis- to the stable trans-isomer by illumination with a polychromatic light source. The decreasing concentrations of cis-azobenzene may be seen from DSC curves which are shown in Fig.4. The curve on the top corresponds to pure cis-azobenzene (99.5 Mole%) and the curve at the bottom was taken after almost complete transformation to the trans isomer (97 Mole%). The melting points are 71,6 C for the cis- isomer and 68,3 C for the trans- isomer respectively. These two isomers form an eutectic system with a melting point of 40,6 C for the eutectic composition with 52 Mole% trans- isomer.

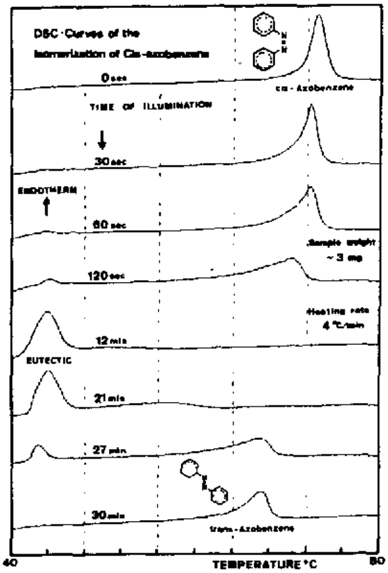

Fig.4 Isomerization of cis- to trans-azobenzene

2,4,6 Trinitrotoluene (TNT)

In production of explosive materials, a mixture of TNT and 4 weight% hexogene is used to give a castable melt to fill cartridges. Fig.5 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.6 shows the crystallite formation of pure TNT (above) and the mixture with 4 Mol% hexogene (below) (magnification 200x). A slow cooling rate produced small crystallites in pure TNT, whereas the mixture gives big ones having much less phase boundaries.

Fast cooling changes the results and the mixture gives irregular crystal shapes and even a segregation.

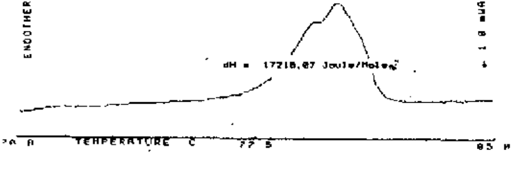

Fig.5 DSC- curve of TNT with 4 Mole% hexogene

Fig.6 Different crystallization of TNT

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 molecular 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 to study the crystal growth under isothermal conditions (TV or photography). The evolution of the growth rate under isothermal conditions is shown in Fig.7. For the sample preparation the substance, e.g. DDT is molten on 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 in 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 to calculate the activation energy of crystallization. According to Avrami (1) the crystallization rate of disc-like particles can be described in terms of the equation $\bar{v}_i = 1/3(\pi d k_i^2 t^2)$. In the case of DDT Fig.8 shows a diagram of ln k versus 1/T which allows to derive the activation energy of crystallization.

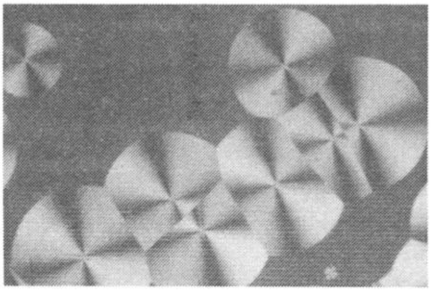

Fig.7 Microphotograph showing the growth of DDT- spheriulites (23 C)

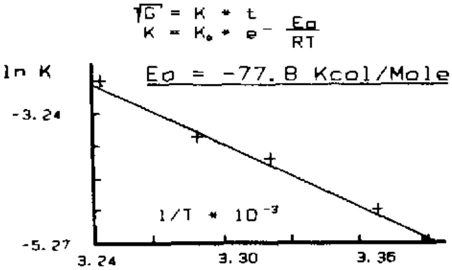

Fig.8 Derivation of the activation energy of crystallization for DDT

CONCLUSIONS

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

REFERENCES

(1) H.G. Elias, Makromoleküle, Hüthig & Wepf Verlag, Basel 1971