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# NON-ISOTHERMAL INVESTIGATIONS ON POLYMER DEGRADATION AT LOW CONVERSION

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## ABSTRACT

By example of the thermal and thermooxidative degradation of PVC, polyphenylene and PET the possibilities and advantages of using the non-isothermal thermoanalytical technique to investigate the degradation of polymers at low degrees of conversion are shown.

## INTRODUCTION

There are mainly two reasons to limit investigations on polymer degradation to low degrees of conversion:

- in many cases polymeric materials lose essential properties important for application (e.g. mechanical properties, colour) at the very beginning of degradation processes;
- at higher degrees of conversion often the influence of secondary reactions increases and the interpretation of TA data became more and more difficult or impossible at all.

For these reasons methods to evaluate kinetic data from non-isothermal TA results must be applicable to low conversions contrary to other TA applications (e.g. inorganic materials) where it is usual to investigate the whole range of conversion. Flynn /1/ dealt with such problems especially in connection with life time prediction of polymers. This paper will discuss some other possibilities of kinetic evaluation of TA results in investigations on polymer stability.

## EXPERIMENTAL

TG and DTA measurements were carried out using a Mettler Thermoanalyzer TA1. In the case of the degradation of PET a sample weight of 20 mg, a flow rate of air or $N_2$ of 7 l $h^{-1}$, Al sample holder and NiCr/Ni-thermocouple were used. The investigations on PVC and polyphenylene were carried out with a sample weight of 80 mg, a flow rate of $N_2$ of 15 l $h^{-1}$ and of air of 7 l $h^{-1}$ (polyphenylene), a Pt sample holder and Pt Rh/Pt-thermocouple. The dehydrochlorination of PVC was measured by a conductometer connected to the thermoanalyzer.

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## RESULTS AND DISCUSSION

PVC and polyphenylene are examples for a group of polymers the thermal stability of which depend strongly on small amounts of structural defects in the macromolecular chain. Let us make the assumptions that the activation energy of initiation of a degradation process caused by defect structures is different from that on regular chain segments and secondly that these two processes proceed indepently from each other. Then from the point of view of non-isothermal reaction kinetics it is possible to separate the two processes qualitativly and finally also quantitativly.
In the case of thermooxidative degradation of polyphenylene the TG data could be explained by the model of two independent overlapping reactions of zero-order /2/. Fitting the model-curve to the experimental TG curve, the kinetic parameters of the two processes and the parts of sample weight responsible for the individual reaction steps could be evaluated. Relating the lower conversion range to the initiation on more easy degradable structures the following data for this step were calculated: activation energy 82 ± 4 kJ $mol^{-1}$, frequency factor $10^2$ $sec^{-1}$ and 8 % of sample weight.
Because of the very small amount of defect structures in PVC and the essential deterioration of material properties (colour) already at conversions $< 1$ %, investigations on the presence of defect structures and on their influence on the dehydrochlorination kinetics are rather complicated. Even in this case non-isothermal investigations present advantages over isothermal measurements, because the dehydrochlorination can be measured under well defined conditions from the very beginning of the experiment. As figure 1 shows the kinetics of dehydrochlorination depends strongly on the nature of the defect structures. Because of their consumption by reaction there is a change in the over-all activation energy indicated by a "breakpoint" in the slope of the curves. The value of log $\alpha$ at this breakpoint allows an estimation of the defect structure concentration /3/. The values got from such non-isothermal investigations are in a good correlation with those got from other analytical methods. They are in the order of magnitude of $1 \cdot 10^{-4}$ mol ketochlorallylic groups/mol PVC (e.g. $2{,}0 \cdot 10^{-4}$ mol/mol PVC for the sample B) and $1 \cdot 10^{-3}$ mol tertiary chlorine /mol PVC (e.g. $3{,}1 \cdot 10^{-3}$ mol/mol PVC for sample A).

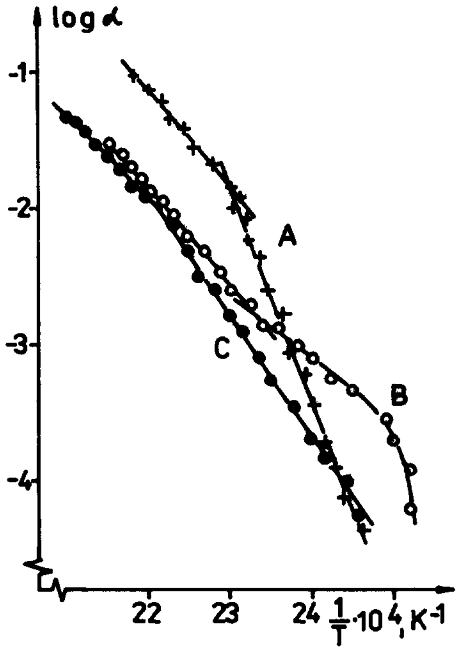

Figure 1
Satava-plot of non-isothermal measurements (0,2 K•min$^{-1}$) of thermal dehydrochlorination of a commercial PVC (C) and of PVC with high amounts of tertiary chlorine (A) or ketochlorallylic groups (B).

PET: The extent of thermal and thermooxidative degradation of PET depend mainly on chemical modifications (e.g. ether links) of the polymer chain caused by side reactions or by addition of cocomponents as well as on the transesterification catalysts retained in the polymer. Already small amounts of additives or byproducts may led to essential differences in the degradation behaviour of various PET samples especially in the temperature range of preparation and processing. This can be detected in an easy manner by DTA and TG. However the degree of conversion to be investigated must be limited to a few percents because of the increasing formation of other volatile degradation products than acetaldehyd caused by secondary reactions and random scission of increasingly shorter polymer chains. Using a modified Kissinger method /4/ and an integral method according to Zsako kinetic parameters were evaluated from DTA and TG data describing the thermal stability of PET in a quantitativ manner.

To examine the validity of these non-isothermal results, they were compared with kinetic data evaluated from isothermal investigations of the increase in carboxyl end-groups in PET caused by chain scission. The results presented in Table 1 prove the data obtained from isothermal and non-isothermal measurements to be in very good agreement.

Table 1 Comparison of the energies of activation, E, the frequency factors, A, and the rate constants, k, of thermooxidative degradation of PET calculated a) from non-isothermal DTA data, using a modified Kissinger method, and b) from the increase of carboxyl end-groups by isothermal heating

| PET sample | | $k \cdot 10^5$, $s^{-1}$ | | | E<br>kJ $mol^{-1}$ | lnA<br>in $s^{-1}$ |
|---|---|---|---|---|---|---|
| | | 207 °C | 217 °C | 227 °C | | |
| I | a) | 0,6 | 1,5 | 3,5 | 179 | 32,79 |
| | b) | 0,6 | 1,6 | 3,5 | 177 | 32,56 |
| | | 212 °C | 222 °C | 232 °C | | |
| II | a) | 0,2 | 0,6 | 2,1 | 270 | 53,49 |
| | b) | 0,1 | 0,7 | 2,2 | 265 | 52,26 |

## CONCLUSIONS

The examples demonstrate non-isothermal TA investigations and the evaluation of kinetic data with limitation to low degrees of conversion to be useful

- to get meaningful informations about the kinetics of polymer degradation and the factors influencing it, provided that sufficient knowlegde on the chemical mechanism of degradation and the nature of the volatile products exist;
- to characterize those influencing factors quantitativly, e.g. to determine the amount of defect structures.

## REFERENCES

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