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The Influence of the Volatility of Reaction Products on Thermogravimetric Results of Polymer Degradation

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To Prof. C.I. Simionescu's 60th birthday

Summary

It is evidenced that the volatility of reaction products may alter the results of thermogravimetric measurements of polymers. Not only kinetic computation is influenced, but also the evaluation of thermal stability if larger fragments are formed during degradation.

Introduction

Thermogravimetry, besides DTA and DSC, seems to be one of the most used methods to characterize the thermal behaviour of polymers. Generally three major aspects were in the attention of the research workers: Determination of the thermal stability, degradation steps and intermediates and kinetic evaluation of TG-results.

In studies of polymer degradation, however, little attention is paid to the fact that thermogravimetric measurements are connected to the volatility of the degradation products, although, depending on the reaction mechanism, during thermal degradation of polymers fragments of different length may occure, which not necessary are also volatile at the respective temperature.

To exemplify, the thermogravimetric degradation of a linear poly(ethylene) - SRM 1475 NBS - will be discussed here.

Results and Discussion

Thermogravimetric curves of the degradation of 20 mg samples, obtained with a Derivatograph MOM-Budapest, always show a bend in the weight loss at about 670K at lower heating rate, simulating a modification of the reaction mechanism (Fig.1). This typical behaviour is observed both for the degradation in nitrogen and in air.

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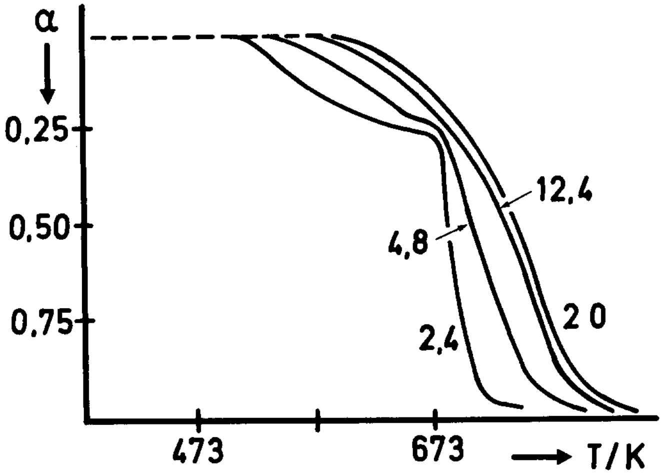

Fig.1 Thermogravimetric curves of linear PE.
Heating rate: 2.4, 4.8, 12.4 and 20°/min.

Such TG-curves can hardly be used for kinetic computation. Accounting, however, for the linear portions in a COATS-REDFERN (1964) - plot only, the "apparent activation energy" values presented in Table I were obtained.

Even if these values have no signification, there is no reason for such dramatically change in the energetic values at lower heating rates.

TABLE I. Thermogravimetric degradation in air of 1-PE.

h.r., [°/min]	transformation degree,	$E_{a,app}$ [KJ/mol]
2.4	.30 - .70	332
4.8	.25 - .70	108
12.4	.20 - .70	91
20	.15 - .70	84

Taking into account that during PE-degradation even at 123°C changes in viscosity are observed (HOLMSTRÖM, SÖRVIK) and that fragments of 30-C atoms (SEEGER, CANTOW) and possibly of higher dimensions are formed, the observed thermogravimetric curves may be explained by the reduced volatility of such higher boiling fragments.

As the boiling temperature of fragments larger than 25-C atoms are above 670K, their accumulation at lower temperatures will increase with decreasing heating rate. They will volatilize then at higher temperatures only, simulating an excessive increase of the thermogravimetric weight loss.

It seems recommendable therefore to use higher heating rates under such conditions, to assure the elimination of larger fragments formed during the thermal degradation of polymers. This accumulation of higher boiling products will influence not only kinetic computations, but also the evaluation of the thermal stability of polymers.

The statement, however, to use higher heating rates to assure the volatilization of higher boiling products is in contradiction to the general accepted recommendation in thermogravimetry to apply lower heating rates to prevent a dramatic influence of the reaction heat, which will increase with the heating rate used.

Therefore it seems to be hardly believeable that thermogravimetry will offer useful data for polymer splitting into larger fragments during thermal degradation.

References

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