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DERIVATOGRAPH IN THE THERMOCHEMISTRY OF POLYMERS

Yu. N. Sazanov
Institute of Macromolecular Compounds of the Academy of Sciences of the USSR, Leningrad, USSR

In the last two decades the derivatograph, a thermoanalytical instrument of the MOM Company (Hungary), became widely used as a convenient and informative apparatus for the determination of many thermophysical and thermochemical properties ofpolymers. At present it is impossible to study thermally stable polymers without employing the methods of thermal analysis and hence derivatograph has been widely applied to this field of investigation.

This paper presents generalized data on the application of a derivatograph to the study of the most thermally stable class of polymers. These data were obtained for the last 15 years in the thermochemical laboratory of the Institute of Macromolecular Compounds of the Academy of Sciences of the USSR. At the moment when this work started, many unsolved problems existed in the chemistry of polyimides. The solution of these problems was important both for the development of new thermally stable polymers and for the understanding of the mechanism of synthesis of polyimides and that of their high-temperature degradation. The application of derivatograph to the solution of these problems has made it possible to elucidate many relationships determining the course of chemical reactions of the formation of polyamic acids, the prepolymers of polyimides, and the process of their transformation into polyimides as well as various degradation reactions occurring in polyimides at high temperatures.

The effect of the solvent on the course of all these reactions was established, and optimum conditions of the preparation of polyimide films depending on many technological factors were determined. The most favourable conditions for the cyclodehydration of polyamic acids were established. These conditions ensure the preparation of polyamic films with high thermochemical and mechanical characteristics.

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Comparison of a number of thermal stability characteristics obtained by analyzing polyimides with a derivatograph during high-temperature degradation has made it possible to establish the dependence of thermal stability of these polyimides on their chemical structure. The experiments carried out with a great number of polyimides synthesized from 30 anhydrides of aromatic tetracarboxylic acids and 70 aromatic diamines showed that the most thermally stable samples are obtained by using condensed and highly aromatized systems: compounds containing nitrogen, sulphur and phosphorus atoms in the main chain. The effect of "defective" fragments of the polyimide chain on the thermochemical characteristics and the kinetics of degradation and structurization of polyimides was demonstrated. The influence of the quantitative and qualitative composition of the initial materials in the synthesis of copolyimides of the types of polyamidoimides, polyesterimides, polyoxazoles, etc. on the thermal stability of these compounds was tested.

In a series of experiments on the study of thermal stability of low molecular weight substances imitating individual fragments of the polyimide chain the conditions of thermal degradation of these compounds ensuring the application of the modelling method in the study of thermal stability of polyheterocyclic compounds were determined for the first time. In combination with other methods of thermal analysis, the analysis of model compounds with the aid of a derivatograph made it possible to evaluate the contribution of the structure of the initial chemical compound to the thermal stability of the polymer. These results also make it possible to establish the reverse relationships between the stages of degradation (analysis) and preparation (synthesis) of thermally stable polymers with predetermined properties, whereas the use of various procedures of analysis with the aid of a derivatograph provides possibilities of the modelling of directed thermochemical synthesis of the products being modelled. These concepts are supported by the data on the analysis of polyimides subjected to thermal treatment during a prolonged period of time under isothermal conditions in the atmosphere of a static inert gas and under the conditions of self-generated atmosphere. A valuable property of the derivatograph permitting the extension of the ranges of problems to be solved with its aid in the field of polymer chemistry is the possibility of effecting various modifications of its

individual assemblies for the specific needs of organic and polymer chemistry. The variety of shapes of sample holders, the wider ranges of programmed heating, the development of better methods of recording, the introduction of additional communication lines for ensuring a controlled gas atmosphere, the possibility of collecting gas samples in the course of experiments, the automatization of data control and processing and other modifications of the industrially manufactured apparatus - all these factors enable us to analyze more thoroughly many thermochemical transformations proceeding in the polymer over a wide temperature range.

This may be illustrated taking as an example our investigations of thermal stabilization of polyimides with the aid of triphenylphosphate. By combining various methodological approaches in the analysis it was possible to establish the qualitative and partly quantitative effect of this compound on the mechanism of formation of polyimide from polyamic acid and on the properties of the polymers formed. These measurements permitted some suggestions to be made on the mechanism for the initiation of thermo-hydrolytic reactions, the cyclodegradation of polyimide, the increase in the cyclization rate, the decrease in the oxidative activity of oxygen at high temperatures and other reactions ensuring the preparation of polyimides with high thermal stability characteristics.

A number of investigations of the thermal degradation of polyimides with a derivatograph provided information on the effect of the aggregate state, the shape and pre-history of the preparation of articles, supermolecular structure and other physical factors on the behaviour of polyimides at high temperatures. The first experiments on the high-temperature pyrolysis of polyimides under the conditions close to those under which other polymers are carbonized, stimulated the study of processes occurring with the rearrangement of the polyimide structure and provided a possibility of studying the mechanism of profound transformations of condensed heteroaromatic structures on the level of thermochemical reactions in a solid body occurring according to the "microreactor" principle.