

Invariant Kinetic Parameters of Polymer Thermolysis. III. The Influence of a Fire-Retardant Additive on Polypropylene Thermolysis

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SYNOPSIS

The present paper analyzes the thermolysis gross-kinetics of polypropylene (PP) and a PP-based fire-resistant composition containing 10% of hexabrominecyclododecane (HBCD) as the fire-retardant additive. The kinetic parameters of thermolysis of an individual PP are calculated by the isoconversion method. The increasing dependence of the effective activation energy on the transformation degree has been established. This dependence is attributed to the competitive character of the processes of thermodestruction initiated by oxidation and to the PP pyrolysis. Thermolysis in the helium atmosphere leads to oxidation suppression and increases the effective activation energy at the initial stage of thermolysis. A similar effect can be attained by introducing HBCD into PP, which permits considering the ability of inhibiting the oxidation process proceeding in the condensed phase as one of the reasons of the fire-retardant activity of this additive.

INTRODUCTION

This paper is a sequel to our previous series.^{1,2} Since then, we have carried out investigations aimed at elucidating the methods of calculation that permit obtaining reliable values of the kinetic parameters (KP) of a process. In particular, it has been found³ that besides the method⁴ of invariant KP (IKP), reliable information about KP can also be obtained by other methods that do not use the discrimination of formal models in solving the inverse kinetic problem. In this case, the KP obtained by the nondiscrimination methods, like the parameters calculated by the IKP method, display the property of invariance with respect to the choice of the process model. This fact makes it possible to dissociate the concept "invariant KP" from a concrete method of calculation, thus giving it a broader sense, namely: parameters calculated without any assumptions about the concrete form of the process model.

Besides, it has been found⁵ that the application of the IKP method is limited by the gross-single-

stage processes (i.e., by processes whose kinetics can be described by one rate constant). To obtain information about complex processes, a special approach was proposed previously,⁵ which is based on the analysis of the shape of the transformation-degree dependence of the effective activation energy calculated by the isoconversion method. The isoconversion methods permit finding the values of KP that are not associated with the choice of the process model or, in other words, display the property of being invariant. Therefore, in this paper, which aims to study the kinetic features of thermolysis of pure polypropylene (PP) and a PP-based fire-resistant composition containing hexabrominecyclododecane (HBCD), all the kinetic information has been obtained from the viewpoint of the above-mentioned approach relying on one of the isoconversion methods.⁶

The urgency of our investigation is due to the necessity of elaborating theoretically substantiated approaches to the solution of the practically important problem of increasing the fire-resistance of polymeric materials, in particular, by means of directional control of the rate of processes proceeding in the condensed phase. Also, it should be noted that the literature⁷⁻¹³ gives ambiguous information

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on KP of PP thermolysis whose kinetics is very dependent on the experimental conditions and the characteristics of the PP itself. No information on the influence of fire-retardant additives on the kinetics of PP thermolysis has been found in the literature. As to the fire-retardant effect of HBCD, we investigated it earlier.¹⁴

EXPERIMENTAL

In our investigations, commercial isotactic PP of the grade 21060 (TU 6-05-1756-78) was used. As the fire-retardant additive, we chose 1,2,5,6,9,10-HBCD, the gross-formula— $C_{12}H_{18}Br_6$. Derivatograms were taken by a derivatograph "MOM" in the stationary air and dynamic helium atmosphere (flow rate, 120 mL/min) at heating rates 2.5, 5, 10, and 20 deg/min. Samples weighing 250 mg each were investigated in open platinum crucibles.

RESULTS AND DISCUSSION

The results of calculating the KP values by the isoconversion method are given in Figure 1. Curve 1

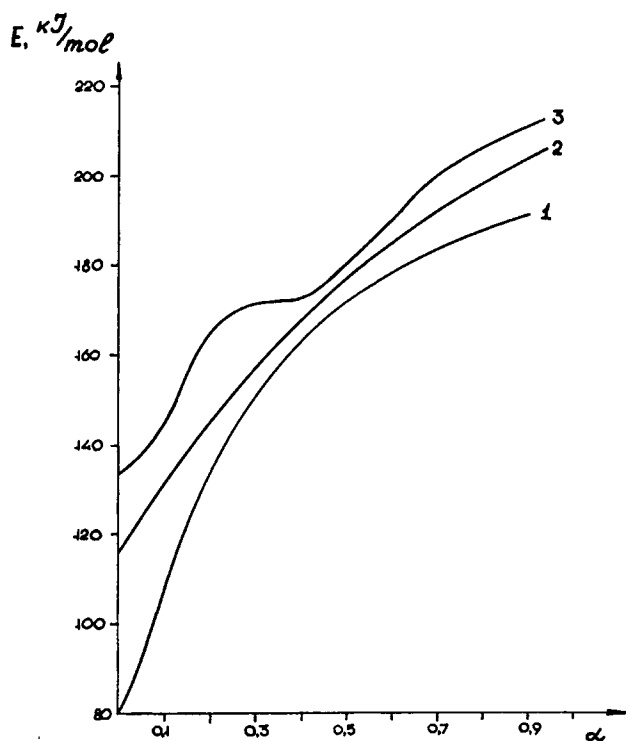


Figure 1 The transformation-degree dependencies of effective activation energy calculated by the isoconversion method for the thermolysis of PP in the air (1), PP in the helium flow (2), and PP-HBCD mixture in the air (3).

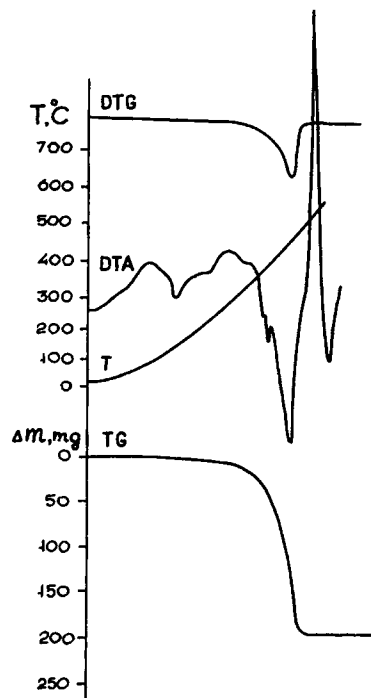


Figure 2 The derivatogram of the PP thermolysis in the air (heating rate 5°C/min).

represents the transformation-degree dependence of the effective activation energy value for the process of PP thermolysis in the stationary air atmosphere. This dependence is increasing, which, from the point of view of our approach⁵ to the analysis of complex processes, points to the presence of at least two competitive reactions. It should be noted that in the temperature range of PP conversion on the DTA curve (Fig. 2) two consecutive effects are observed: the exo- and the endothermic ones, which are likely to be associated with the oxidation-stimulated destruction and PP pyrolysis, respectively. The connection between the exo-effect and the oxidation process is testified by the fact that at PP thermolysis in a helium flow the area of the exo-effect on the DTA curve decreases by a factor of 10–15. Comparison of the effective activation energy values corresponding to the initial and the final stage of conversion with those given in the literature also permits interpreting competitive processes as oxidation-stimulated destruction and pyrolysis. In particular, proceeding from the results of the works^{7–13} devoted to the investigation of the PP thermolysis kinetics in an oxidation atmosphere and of those^{9–13} presenting KP of PP thermolysis in an inert atmosphere, we may conclude that the activation energy value of the oxidation-stimulated process of thermodestruction lies in the 59–105 kJ/mol range, whereas that of pyrolysis in an inert atmosphere is

in the range of 214–251 kJ/mol. Therefore, curve 1 of Figure 1 shows that the effective activation energy value increases from 80 to 190 kJ/mol because of the growth, with increasing temperature (transformation degree), of the partial contribution of the pyrolysis process, compared to the oxidation-stimulated process, to the total PP pyrolysis rate.

Figure 1 (curve 2) shows the transformation-degree dependence of the effective activation energy calculated by the isoconversion method for PP thermolysis in a helium flow. The shape of this dependence is similar to that of the dependence corresponding to thermolysis in the stationary air atmosphere, but it is characterized by larger values of the effective activation energy, especially at the initial stage of conversion (117 instead of 80 kJ/mol). The increase in the activation energy is likely to be due to the suppression of the oxidation process at PP thermolysis. However, the constancy of the shape of the transformation-degree dependence of activation energy and the presence of a small exo-effect on the DTA curve point to incomplete suppression of oxidation when experiments are carried out in the dynamic helium atmosphere.

Thus, proceeding from the foregoing, we may assume that the kinetic features of PP thermolysis in the air are explained by the competitive character of processes of oxidation-stimulated thermodestruction and pyrolysis. Consider from this point of view the effect of introducing a fire-retardant additive (HBCD) on the kinetics of PP thermolysis in the stationary air atmosphere.

The thermolysis of a sample consisting of 90% of PP and 10% of HBCD has two consecutive stages (on the TG curve, two S-shaped portions are observed). The temperature range of the first stage coincides with that of pure HBCD thermolysis. This allows us to assume that the first stage of the PP–HBCD mixture thermolysis is largely associated with the conversion of the HBCD itself. Therefore, the activation energy was calculated for the second stage, which is associated with the thermolysis of the mixture of PP and the products of HBCD conversion formed during the first stage.

Figure 1 (curve 3) shows the transformation-degree dependence of the value of the effective activation energy calculated by the isoconversion method for the second stage of the PP–HBCD mixture thermolysis. This dependence increases like that corresponding to pure PP thermolysis in the air and helium atmosphere, but it is characterized by higher activation energy values throughout the range of transformation degrees compared to the above-mentioned ones. Comparing the transformation-degree dependencies of activation energy for

thermolysis of pure PP and PP modified by the products of HBCD thermolysis, it may be noted that the introduction of this component leads to changes in the gross-kinetics of the process similar to those caused by the replacement of the air atmosphere by the helium one.

The analogous change in the kinetic features of the process under the influence of different factors allows us to assume that there is a common mechanism of the effect of these factors on the process. In this case, it should probably be assumed that the introduction of HBCD into PP makes it possible to suppress the oxidation process at thermolysis. Also, most probably, the inhibition of oxidation occurs due to the interaction between the products of HBCD conversion and PP. Therefore, we deem it necessary to take into account the ability of HBCD to suppress the oxidation process proceeding in the condensed phase as one of the reasons explaining its fire-retardant efficiency.

CONCLUSION

Thus, based on the analysis of the gross-kinetic data, one of the possible reasons of the fire-retardant action of HBCD has been established. Of course, the establishment of the potential reason of the fire-retardant effect of the additive does not mean the elucidation of the mechanism, but the obtained information is valuable for its understanding, since it permits concretizing the direction of more thorough studies of the mechanism.

It should be noted that the above information has been obtained in terms of nonisothermal kinetics that are not recognized by many researchers as being able to provide reliable data (see, e.g., Ref. 15). In this connection, we wish to emphasize again that in obtaining reliable kinetic information the decisive role is played by the method of calculating KP rather than the regime (iso- or nonisothermal). In turn, the reliability of the method is fully determined by the methodology³ of solving the inverse kinetic problem underlying it. In this sense, most reliable are the methods based on the methodology of complementarity¹⁶ that permit calculating KP values invariant to the form of the process model.

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