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Thermolysis kinetics of polypropylene on rapid heating

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Abstract

Using the system of rapid heating, the thermolysis kinetics of polypropylene (PP) was studied with heating rates in the 150–4760 K min^{-1} range. For the formation processes of fragments with $m/z = 41$, 42, 43, identical rising dependences of the effective activation energy on the transformation degree have been revealed. The shape of the obtained dependences is due to the occurrence of parallel, competing reactions, interpreted as the transformation processes of associated and non-associated macromolecules of PP. This mechanism also explains the kinetic laws for the overall thermolysis of PP at normal heating rates.

INTRODUCTION

The enhancement of fire resistance of polymeric materials necessitates the study of the polymer thermolysis at heating rates reached in the combustion wave. For these investigations, a system was developed on the basis of a time-of-flight MCX-4 mass spectrometer [1] which provides data on polymer thermolysis at heating rates up to 2000 K s^{-1}. A polymer sample in the form of a thin film is deposited onto a tape heater located near the ion source. The tape heater consists of two tantalum tapes (3 mm × 30 mm in size and 0.05 mm in thickness) to one of which is welded the junction of a chromel–alumel thermocouple. The mass spectrometer works on line with a computer which controls the heating and accumulates information on the intensity of the mass spectrum peaks and temperature.

This paper reports the thermolysis kinetics of polypropylene (PP) on rapid heating and compares the results with kinetic data obtained at normal heating rates.

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EXPERIMENTAL

Commercial isotactic 2106 PP was chosen for the investigation. PP thermolysis under conditions of rapid heating was carried out at heating rates of 150, 300, 600, 1180, 2350 and 4760 K min^{-1}. The mass of the sample, depending on the mass spectrometer sensitivity and the duration of the experiment, was varied from 0.1 to 2 mg. In the course of the experiment, the change in intensity of the peaks corresponding to the three main fragments arising from the PP thermolysis ($m/z = 41$, 42 and 43) was registered. PP thermolysis at normal heating rates (2.5, 5, 10, 20 K min^{-1}) was studied using thermogravimetric data recorded on a MOM derivatograph in a dynamic helium atmosphere (flow rate 120 ml min^{-1}). PP samples (250 mg) were investigated in open platinum crucibles.

RESULTS AND DISCUSSION

The kinetic processing of the thermoanalytical data was carried out using the software KINTOOL, written by Vyazovkin and Goryachko. KINTOOL is based on the analysis of the transformation degrees (w) dependence of the activation energy (E) calculated by the isoconversion method. This dependence can be used successfully both for identifying the kinetic scheme of a process [2–6] and for solving applied kinetic problems associated with the evaluation of the thermal stability of materials beyond the experimental temperature range [7–10]. The application and potential of KINTOOL are described in refs. 8 and 9.

Figure 1 (curves 1–3) shows the E versus w dependences for data on the thermolysis kinetics of PP on rapid heating. For comparison, this figure gives a similar dependence (curve 4) for the PP thermolysis at normal heating rates [5]. It should be noted that all four dependences are practically coincident accounting for the confidence interval for the calculated values of the activation energy, on average 10–15%.

It was shown in ref. 2 that the rising dependence of E on w is characteristic of complex processes incorporating parallel reactions. The similarity between the shapes of the dependences in curves 1–3 indicates a common mechanism for formation of fragments, each of which is likely to appear as a result of the same parallel reactions.

We shall attempt to formulate the nature of the parallel reactions from the viewpoint of the proposed mechanism for the thermolysis of linear polymers [11]. This mechanism implies that the depolymerization rate is determined by the competition between the processes of decomposition of individual macromolecules and of intermolecular associates, which are in equilibrium and whose rate of formation exceeds the rate of depolymerization. With increasing temperature the equilibrium is shifted

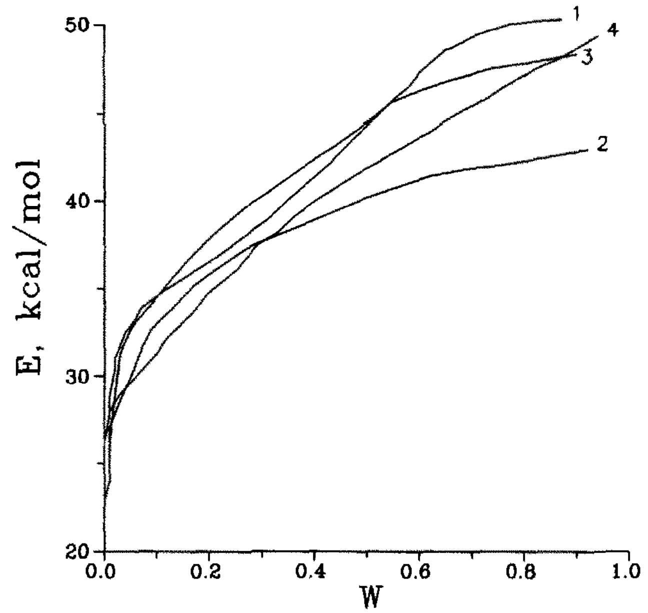

Fig. 1. Transformation-degree dependences of activation energy obtained from mass spectrometric data: 1, $m/z = 41$; 2, $m/z = 42$; 3, $m/z = 43$; and 4, thermogravimetric data.

towards the formation of non-associated molecules. Therefore, at low temperatures corresponding to the onset of transformation, the depolymerization rate is largely determined by the rate of transformation of intermolecular associates, while at high temperatures it is determined by the rate of transforming individual macromolecules.

It should be noted that not only the theoretical assumptions underlying this mechanism, but also the experimental results, indicate the possibility of using the mechanism for explaining the kinetic regularities of PP thermolysis. In particular, the concave Arrhenius dependence obtained in ref. 11 in the kinetic processing of data on polysterene thermolysis corresponds [2] to the rising dependence of E on w observed here for PP thermolysis. This means that both polymers have analogous kinetic regularities of thermolysis.

Taking into account the above mechanism, the kinetic scheme that we established can be described as a competition between the parallel reactions of transformation of associated and non-associated PP macromolecules. Consequently, the transformation-degree dependences of the effective activation energy (Fig. 1) reflect the temperature-rise-dependent transition of the PP thermolysis process from being predominantly the transformation of associated macromolecules to predominantly the transformation of non-associated macromolecules.

The information obtained gives a better insight into the mechanism of PP thermolysis. In our previous work [5], thermogravimetric investigations of PP thermolysis in air revealed that its kinetics was determined by the competition between the heating- and oxidation-stimulated processes. The above-described mechanism explains the kinetic regularities of the process stimulated by heating. The similarity between the shapes of the dependences 1–3 and 4 suggests a common kinetic scheme for PP thermolysis with rapid and normal heating rates. From this, it can be supposed that the overall kinetics of PP thermolysis in an inert atmosphere at normal heating rates is determined by the kinetics of formation of the fragments with $m/z = 41, 42, 43$.

Thus, appropriate processing of the experimental data obtained under rapid heating has made it possible to identify the kinetic scheme for the formation of the main fragments arising from PP thermolysis. In turn, comparison of this scheme with the gross-kinetic data has yielded information on the mechanism of the process of PP thermolysis at normal heating rates.

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