Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermal Analysis of Polypropylene Hydroperoxide

K. Kishore[a]

[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

To cite this Article Kishore, K.(1983) 'Thermal Analysis of Polypropylene Hydroperoxide', Journal of Macromolecular Science, Part A, 19: 6, 937 — 942

To link to this Article: DOI: 10.1080/00222338308060787

URL: http://dx.doi.org/10.1080/00222338308060787

J. MACROMOL. SCI.–CHEM., A19(6), pp. 937-942 (1983)

SHORT COMMUNICATION

Thermal Analysis of Polypropylene Hydroperoxide

K. KISHORE

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012, India

INTRODUCTION

Studies on the low temperature oxidation of polyolefins have been the subject matter of several investigations because of interest in understanding the aging and weathering of polymers. One of the key steps in such an oxidation is the formation of hydroperoxide. Estimation of the hydroperoxide in oxidized samples, which is conventionally done by iodometric titrations, is quite important to gain knowledge about the kinetics and mechanism of the process. The present investigation is the first report of the thermal analysis of polypropylene hydroperoxide samples from two angles: (1) the thermal behavior of its decomposition and (2) whether such an analysis leads to knowledge of the concentration of hydroperoxide in the sample.

EXPERIMENTAL

Polypropylene hydroperoxide samples of varying hydroperoxide content were prepared by a method described earlier [1]. –OOH estimations in the samples were carried out by iodometric titrations [1]. The average molecular weight (M_n) was obtained from gel permeation chromatograph (GPC-200, Waters). TG, DTG, and DTA traces were obtained on a MOM Derivatograph. DSC studies, both in the isothermal and scanning modes, were carried out on a DSC-1B

0022-233X/83/1906-0937$3.50/0

TABLE 1. Peroxide Concentration and Exothermic Heat of Decomposition of Polypropylene Hydroperoxide (PPHP) and Polyethylene Hydroperoxide (PEHP)

PPHP Sample	M_n	mmole OOH/mole monomer	-ΔH (decomposition) cal/g	cal (mol of monomer)$^{-1}$	kcal (mol OOH)$^{-1}$
PPHP 002	19,155	3.44	17.86	743.0	216.0
PPHP 004	-	6.97	20.66	868.0	124.5
PPHP 003	3,965	15.10	33.12	1,391.0	92.1
PEHP 007	4,834	3.81	10.21	286.0	75.1

Perkin-Elmer instrument. The details of the operation of the instrument and the method to obtain enthalpy from the thermograms are available elsewhere [2]. Sealed pans were used in all runs. Isothermal thermograms were obtained at several temperatures from 395 to 413 K and the enthalpy was calculated from them. The errors in enthalpy measurements were not more than 12% between runs at different temperatures.

The results are summarized in Table 1.

RESULTS AND DISCUSSION

DTA, DTG, dynamic, and isothermal DSC traces of polypropylene hydroperoxide (PPHP) are exhibited in Figs. 1 and 2. Figure 2 also

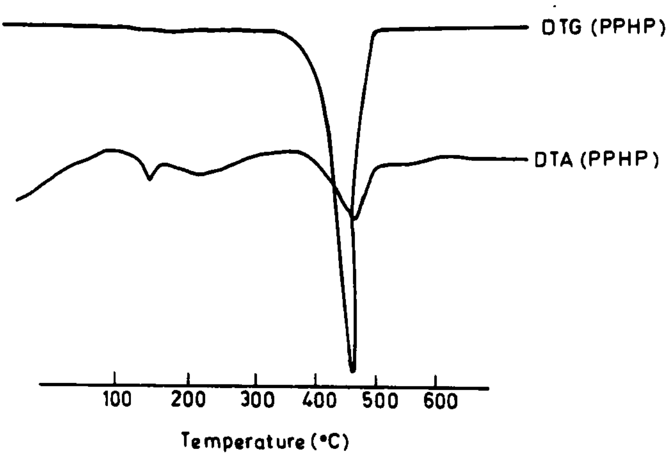

FIG. 1. DTA and DTG traces of PPHP.

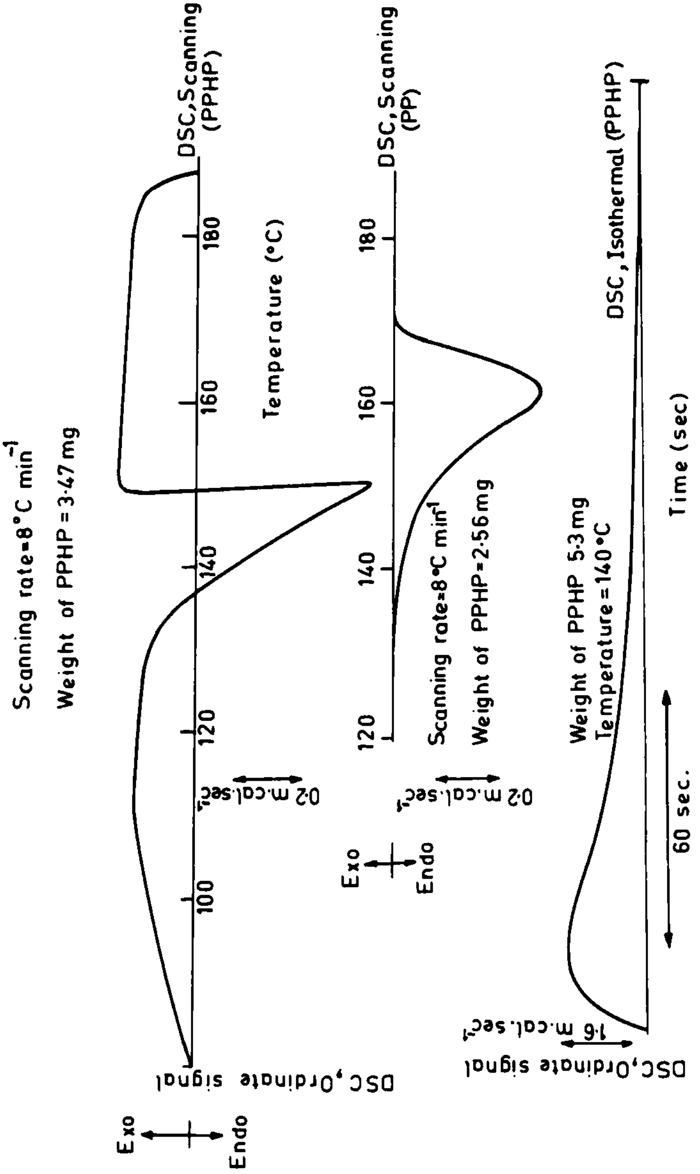

FIG. 2. DSC traces of PP and PPHP.

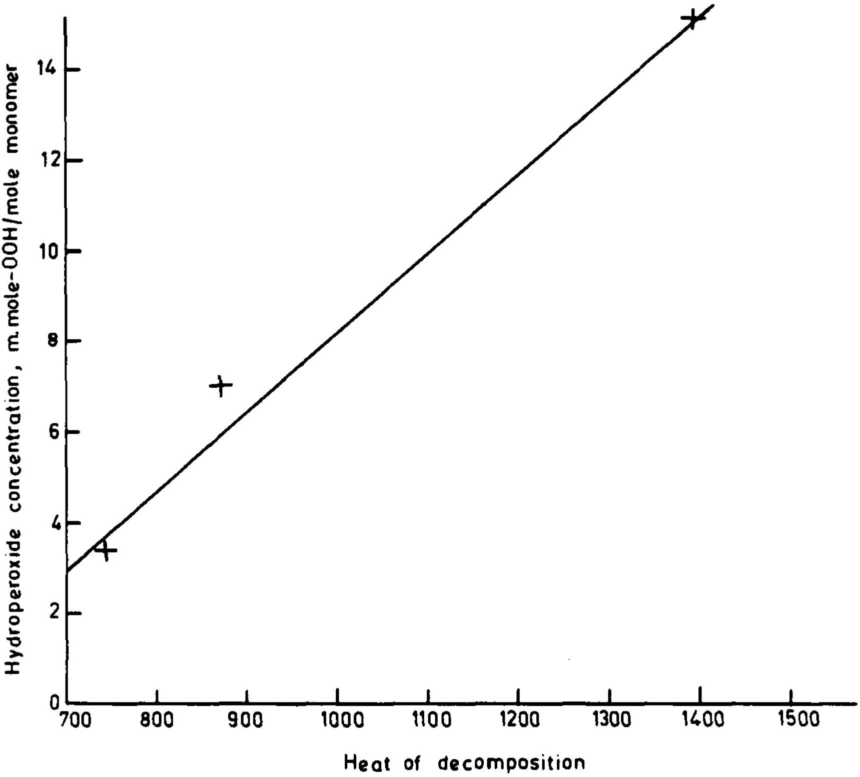

FIG. 3. Dependence of exothermic heat of decomposition on peroxide content of the PPHP samples.

contains the scanning DSC thermogram of pure polypropylene (PP). An examination of the DSC thermogram (scanning of PPHP) reveals that it starts decomposing exothermically around 80° C and ends at about 185° C. This exothermic decomposition is characteristic of peroxide decomposition. In between the exothermic decomposition, an endotherm also appears around 140° C. This endotherm is due to melting of PPHP. Pure PP does not decompose exothermically but it melts around 160° C (see Fig. 2). It may be possible that the melting temperature of PPHP is lower than that of PP. The DTA trace of PPHP (Fig. 1) complies with that of the corresponding DSC picture (Fig. 2). DTG of PPHP (Fig. 1) shows that there is no weight loss during the decomposition and melting process below 200° C. PPHP samples during DSC operations (both isothermal and scanning mode) were weighed after crystallization was over, and it was observed that the weight loss was less than 2%, thus supporting the DTG results.

Due to the appearance of the endothermic process during exothermic decomposition, it was not possible to calculate accurately the enthalpy change associated with the exothermic decomposition of PPHP in a dynamic run. Thus recourse was taken to follow the isothermal runs below the melting of PPHP for enthalpy calculations. It may be mentioned here that isothermal decomposition of PPHP below the melting point is quite fast and goes to completion. Three samples of PPHP having different hydroperoxide contents (Table 1) were chosen. The hydroperoxide concentrations of the samples were checked by iodometric titration. A plot of hydroperoxide concentration (iodometric estimation) versus the enthalpy of hydroperoxide decompositions is shown in Fig. 3. The resulting linear correlation suggests that DSC enthalpy measurements could be used to estimate hydroperoxide concentration in oxidized PP samples. The DSC technique, in addition to its easy operation, has the advantage of consuming only small amounts of sample.

Figure 3 was used to calculate the enthalpy associated with the hydroperoxide decomposition: 55-60 kcal/mol of hydroperoxide. This value is about twice the reported value for the activation energy (E) for the decomposition of many peroxide compounds [3]. Situations where the E value and the enthalpy of decomposition for the same process are different are quite numerous in the literature. Since the purpose of the present communication is to report the thermal analysis results, an in-depth discussion of the significance of the enthalpy value is not included.

An attempt was made to estimate the enthalpy of the polyethylene hydroperoxide (PEHP), but due to the closeness of the temperature of decomposition to its melting point, no reliable results could be obtained. Another sample, a copolymer of styrene and oxygen, where the peroxide groups are bonded in the polymer backbone [4], was also analyzed, but in this case the proportion of the concentration of the peroxide groups to that of the enthapy value was widely different. No reliable method is available for the chemical estimation of bonded peroxy groups. Therefore the data are not reliable enough to be included.

ACKNOWLEDGMENTS

The author wishes to thank the authorities of the Indian Institute of Science, Bangalore, the University Grants Commission, New Delhi, and the Institute for Cultural Relations, Budapest, for arranging a visit to Hungary under the Indo-Hungarian Cultural Exchange Programme. He is grateful to Dr (Mrs) M. Iring and Dr Z. Fodor, Department of Macromolecular Chemistry, Central Research Institute of Chemistry, Budapest, for providing the facilities necessary to carry out the present work.

REFERENCES

[1] M. Iring, T. Kelen, F. Tüdős and Zs. Laszlo-Hedvig, J. Polym. Sci., Polym. Symp., 57, 89-99 (1976).
[2] K. Kishore, Anal. Chem., 50, 1079-1083 (1978).
[3] K. Kishore, V. R. Pai Verneker, and V. Gayathri, J. Anal. Appl. Pryolysis, 1, 315-322 (1980).
[4] K. Kishore, V. Gayathri, and K. Ravindran, J. Macromol. Sci.–Chem., A16(8), 1359-1383 (1981).

Accepted by editor August 14, 1982
Received for publication September 14, 1982