Thermochimica Acta, 19 (1977) 141–145

COMPARATIVE THERMAL ANALYSIS OF THERMALLY STABLE POLYMERS AND MODEL COMPOUNDS

1. POLYPHENYLENE AND RELATED COMPOUNDS

Y. N. SAZANOV, L. A. SHIBAEV, B. A. ZAITSEV and G. I. KHRAMOVA
Institute of Macromolecular Compounds of the Academy of Sciences of the U.S.S.R., Leningrad 199004 (U.S.S.R.)
(Received 29 July 1976)

ABSTRACT

It has been established by comparative thermal analysis (CTA) of poly phenylene and model compounds that polyphenylene prepared by oxidizing cationic polymerization contains defective structures in the amount of approximately 2% of the polymer weight. They determine its low temperature thermooxidative degradation. At the same time the main polyphenylene structure exhibits higher thermooxidative stability than the corresponding model compounds.

INTRODUCTION

Processes of thermooxidative degradation of thermally stable polymers are very complex and, therefore, the results of investigation of similar processes for model compounds should be used. It may be expected that some fragment of the polymer chain exhibits higher thermal stability than the corresponding low molecular weight compound because its entropy value is lower. In some cases the thermal stability of a low molecular weight model may be considered as a guaranteed minimum of thermal stability expected for the polymer. However, in practice the polymer does not exhibit even this minimum thermal stability[1-3]. This is caused by the presence of defective structures in the polymer: functional end groups, structures produced as a result of incomplete reaction of polymer formation or side reactions. These defects decrease the thermostability of the polymer as compared to a polymer exhibiting a perfect structure and to the corresponding model compounds. This problem may be solved only if we take into account defective structures in investigations of the relationship between thermal stability and the structure of the polymers under investigation and use CTA of compounds modelling a perfect cell of a thermally stable polymer and of samples of the polymer itself. High vapor pressure of model compounds makes it difficult to carry out CTA of model compounds and limits the possibilities of studying thermooxidative degradation of these compounds with standard thermoanalytical instruments such as a derivatograph, Mac Ben or Statton thermobalances, etc. At the same time it is well known that thermal characteristics obtained vary with the slightest changes in experimental conditions[4]. Consequently, it is necessary to select such conditions for CTA which would be maintained both in the analysis of the polymers and in that of the corresponding model compounds. An ampoule method was used in this work (see below).

EXPERIMENTAL

Thermal oxidation of samples of the polymer and of model compounds in the amounts of 0.010–0.040 g was carried out in sealed glass ampoules 22 ml in volume under oxygen. The initial pressure of O_2 in the ampoule was ~0.25 atm at 20 °C. Each ampoule was maintained for 1 h at a certain temperature in the range from 270 to 450 °C and the amounts of CO and CO_2 evolved as a result of thermooxidative degradation of the sample were determined chromatographically[1].

The following compounds were chosen for investigations: polyphenylene (I) prepared by benzene polymerization according to Kovacic[5,6], benzene (II), diphenyl (III), p-terphenyl (IV) and *p*-quaterphenyl (V). We will briefly consider the characteristics used for evaluating the thermal stability of organic compounds. Usually we mean by thermal stability the limiting temperature or the temperature of the start of degradation, T_0, above which the compound begins to undergo chemical changes accompanied by the evolution of volatile products and, hence, by mass loss. Evidently, T_0 depends not only on the nature of the substance under investigation but also on some other factors: the concentration of the sample (see Table 1), the sensitivity of the instrument measuring the amount of volatile substances, the presence of impurities, the aggregate state of the sample, its size and shape etc. For the isothermic oxidation process the following relationship may be written based on the Arrhenius' equation:

$$T_0 = \frac{E_0/R}{\ln A_0 + n \ln [c] + m \ln [O_2] + \ln t - \ln B_0} \qquad (1)$$

where E_0 A_0, R are the activation energy, the pre-exponential factor in the Arrhenius' equation and the gas constant, respectively.

$[c]$, $[O_2]$ are the concentrations of the substance investigated and of oxygen, respectively.

n, m are the reaction orders in substance and in oxygen, respectively,

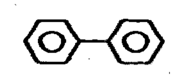
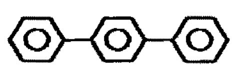
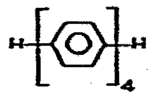
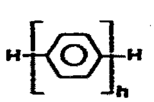
t is the time of thermal oxidation,

B_0 is the minimum amount of degradation products determined with the aid of this method.

This equation may be rewritten for a temperature characterized by the loss of a certain percentage of mass. T_{B_i}, e.g., in the range from 1 to 10%.

TABLE 1

THERMOOXIDATIVE STABILITY OF POLYPHENYLENES

Compound	*Sample weight*		*Temp. (°C) of mass loss (%)*			*Reaction order in hydrocarbon*	
	g	*mole x10⁵*	*0*	*3*	*5*	*Temp. range (°C)*	*n*
	0.010 0.020	12.8 25.6	382 345	408 397	412 403	390–420	2.0
	0.010 0.020	6.5 13.0	365 340	402 402	410 410	380–420	1.0
	0.013 0.020	5.8 8.7	345 325	401 385	411 398	390–420	2.3
	0.020 0.040	6.5 13.0	345 335	403 —	414 —	360–380	1.0
	0.020 0.040	— —	270 270	426 —	456 —	400–420	0.7

Evidently, these characteristics depend to a lesser extent on such factors as the presence of impurities and the instrument sensitivity. The equations shows that the dependence of T_0 on the chemical structure of the substance can be completely revealed only when all the parameters in this equation (except E_0 and A_0) are constant. Constancy of B_0, t and O_2 can be maintained by using appropriate experimental conditions. As to the concentration of the sample c and the order of reaction n, the strict fulfilment of the requirement of their constancy is difficult because the compounds under investigation are polyfunctional, i.e., under conditions of their complete degradative oxidation, concentrations of reaction centers for one molecule differ and also because the aggregate states of some models and of the polymer are different. We assume that the most satisfactory approach for comparing thermal stabilities of the compounds under investigation is the equality of their weight concentrations.

This means that upon complete oxidation of any of these compounds (benzene, diphenyl, terphenyl etc.) an approximately equal total amount of moles of CO and CO_2 is evolved.

DISCUSSION OF RESULTS

Data in Fig. 1 and Table 1 show that compounds II–V are stable approximately to 330–340 °C and their intense degradation begins at 390–400 °C. It might be expected that in passing from diphenyl to *p*-quaterphenyl the thermostability would increase for two reasons. First, the angle between benzene rings decreases in passing from the gaseous state ($\theta = 42$ °C) to the liquid state ($\theta = 30$–35 °C)[7,8] and, hence, conditions for dissociation of the C–C bond between rings become less favorable. Secondly, the oxidation rate under heterogeneous conditions is lower than under homogeneous conditions. Nevertheless, this increase is not observed and the fact that curves of compounds II–V run close to each other in the 340–400 °C range indicates that the contribution of the dissociation and the aggregate state of the sample to the overall degradation process is relatively small. It should be noted that the order of the overall reaction (n) of oxidation of the substance alternates in accordance with the odd or even amount of aromatic nuclei contained in the molecule of model compounds (Table 1). Investigations of thermooxidation of I–IV showed that the logarithm of the thermooxidation rate constant decreases with increasing temperature. The exception is benzene for which the activation energy of thermooxidation in the initial part of the curve is 45 kcal mol^{-1}. This agrees well with the data in refs. 9 and 10, viz., 50–70 kcal mol^{-1} over the 400–500 °C temperature range.

In contrast to model compounds, in thermooxidative degradation of polyphenylene three temperature ranges are observed (Fig. 1, curve 5): (1) 270–360 °C; (2) 360–400 °C and (3) 400 °C and higher temperatures.

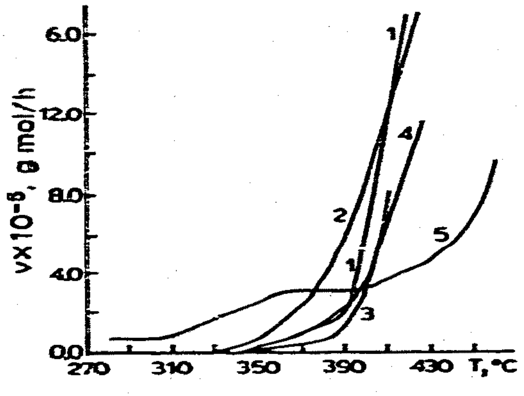


Fig. 1. Curves of formation rate of $CO+CO_2$ in thermal oxidation of benzene (1); *p*-terphenyl (2); diphenyl (3); *p*-quaterphenyl (4); and polyphenylene (5).

In the first range about 2% of the polymer is oxidized owing to defects in structure. And indeed, we could hardly suppose that the thermooxidation curve for benzene rings in polyphenylene would run at lower temperatures than curves for model compounds. Over the second range the amount of gaseous products remains at a constant level attained as a result of oxidation of defective structures in the first range. In the third range the amount of CO and CO_2 increases sharply; this shows that the main polymer structure is thermooxidated. Thus, it may be assumed that in polyphenylene one defective ring (e.g., a cyclohexadiene or cyclohexene ring) exists for every 50 benzene rings. Another peculiarity of thermooxidative degradation of polymer samples as compared to model compounds is the lower rate of gas evolution at temperatures above 400 °C. This is clearly seen in Fig. 1 and in values of $T_{3\%}$ and $T_{5\%}$ shown in Table 1. Higher thermal stability of polyphenylene as compared to model compounds at 400 °C and higher temperatures is related, first, to the coplanar arrangement of aromatic nuclei in the polymer chain ($\theta = 0\,°C^{7,8}$) which results in a stronger intra- and intermolecular interaction of chain fragments and, secondly, to the heterogeneous character of the oxidation reaction.

Thus, CTA of polyphenylene and related model compounds shows that polyphenylene contains defective structures amounting to approximately 2% of the polymer weight and determining the low temperature of its thermooxidative degradation. At the same time the main polyphenylene structure exhibits higher thermooxidative stability than the corresponding model compounds.

REFERENCES

1 M. M. Koton, Yu. N. Sazanov, L. A. Shibaev, L. M. Shcherbakova, *Dokl. Akad. Nauk SSSR*, 213 (1973) 594.

2 Yu. N. Sazanov and L. A. Shibaev, *Thermochim. Acta*, 15 (1976) 43.

3 Yu. N. Sazanov and L. A. Shibaev, *Thermal Anal. Proc. 4th Int. Conf. Thermal Anal., Budapest, 1974*, Vol. 2, Budapest, 1975, pp. 117–126.

4 Yu. N. Sazanov, *Therm. Anal.*, in press.

5 J. G. Speight, P. Kovacic and F. W. Koch, *J. Macromol. Sci. Rev. Macromol. Chem.*, C5(2) (1971) 295.

6 P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, 85 (1963) 454.

7 B. A. Zaitsev and G. I. Khramova, *Izv. Akad. Nauk, Ser. Khim.*, (1974) 2722.

8 H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, London, 1967.

9 J. H. Burgoyue, *Proc. Roy. Soc.*, A174 (1940) 394; A175 (1940) 539.

10 V. Ya. Stern, *Mekhanizm okislenuja uglevodorodov v gazovoi faze*, Moscow, 1960, p. 425–438.