THERMAL AND THERMO-OXIDATIVE DEGRADATION OF POLYSTYRENE IN THE PRESENCE OF BROMINE-CONTAINING FLAME RETARDANTS

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The kinetic of thermal and thermo-oxidative degradation of polystyrene in the presence of bromine-containing flame retardants was investigated. It was shown that the kinetics is limited by diffusion in air and by the processes occurring at the interface in helium.

The flame retardants affect the degradation of polystyrene both chemically and physically, and change the mechanism of the limiting stage to some extent.

The thermal degradation of polystyrene (PS) has been studied in great detail. Thus, it may be considered as established that in the thermal degradation of PS the main process is its depolymerization, with the predominant isolation of the monomer, styrene [1, 2]. The reaction proceeds by a free-radical mechanism [2, 3]. The process of thermal degradation of PS is endothermic [4]. A detailed review of the data of thermogravimetric analysis [5] has led to the conclusion that the thermal degradation of PS proceeds as a first-order reaction with an activation energy of 250 ± 20 kJ mol^{-1}. In the thermal oxidation of PS, apart from styrene, which remains the main degradation product, benzaldehyde, benzene, toluene and, in the later degradation stages, carbon oxides are also isolated [6].

The aim of th present paper was to elucidate the effects of a number of bromine-containing flame retardants on the processes of thermal and thermo-oxidative degradation of PS, and to establish the correlation between this effect and the mechanism of action of the flame retardant.

Experimental

The polystyrene (PS-S) was obtained by suspension polymerization and purified by reprecipitation with methanol from CCl_4 solution.

The bromine-containing flame retardants decabromodiphenyl oxide

(DBDPO), hexabromodiphenyl, (HBDP) and hexabromocyclododecane (HBCD) were prepared and purified at the Iodine-Bromine Research Institute.

Thermal analysis was carried out with a Q-derivatograph (MOM, Hungary) at a heating rate of 10 deg min^{-1} in an atmosphere of air or in a helium stream (flow rate 25 l h^{-1}). The sample mass was 50 mg. The sample holders were ceramic or platinum crucibles without covers, forming part of the standard set for the derivatograph.

The activation energy (E_a) of the degradation process was calculated from the TG and DTG curves in the parts of the curves corresponding to a mass loss in the range of 20 to 40 mass %. The Gorbachev criterion method [8] was used to determine the type of kinetic function, the value of the mass at the moment of the maximum process rate being taken as a criterion.

Pyrolysis gas chromatography (PGC) was carried out with a Tswett-102 chromatograph supplied with a funace-type pyrolyser manufactured by the Dzerzhinsk Special Design Bureau of Biological Automatics. The conditions of pyrolysis were as follows: sample mass 0.5 mg, column size 3000×3 mm, packing 10 mass% of neopentylglycol succinate on chromatone N, flow rate of carrier gas (helium) 44 cm^3 min^{-1}, heat conductivity detector, current of detector bridge 190 mA, temperature of detector thermostat 150°, and temperature of column thermostat 107°.

Hydrogen bromide was sorbed with a 0.02 N solution of potassium hydroxide and determined by a mercurometric method [9].

Discussion of results

When the DTA and TG data on PS are compared, attention is immediately drawn to a marked effect of the experimental conditions on the shape of the DTA curves (Fig. 1, curves 1−3). This fact has previously been considered in detail [10], and here it will only be pointed out that these differences are associated with a considerable contribution of secondary processes to the DTA peaks, viz. oxidation (catalytic oxidation in the case of platinum holders) of products of PS degradation. These secondary processes have virtually no effect on the shape of the TG curves (Fig. 1, curves 2' and 3'). It follows that the degradation of PS in air is evidently limited by diffusion of degradation products in the sample. The same can be said about atmospheric oxygen acting in the well-known scheme [2] as an initiator of free-radical degradation processes. The replacement of a static air atmosphere by a flow of 25 l h^{-1} increases the removal of degradation products
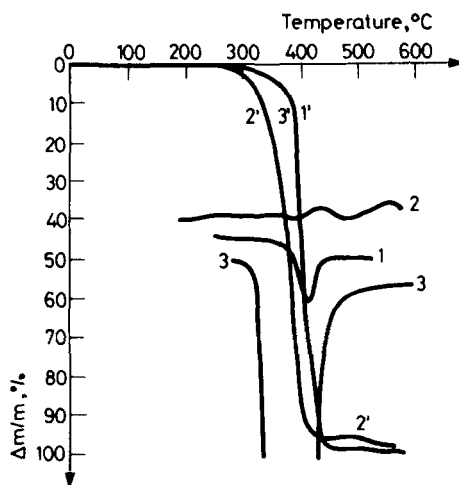
Temperature,°C

Fig. 1 DTA (1–3) and TG curves (1'–3') of polystyrene
— 1,1' — ceramic crucibles, helium flow, 25 h $^{-1}$
— 2,2' — ceramic crucibles, static air
— 3,3' — platinum crucibles, static air

from the sample surface and the supply of oxygen to the surface, but does not result in any change in the TG curve. It should be noted that PS melts below the temperature of the start of degradation, and therefore the processes of thermal degradation occur in the liquid phase, and the aggregate state of the initial sample is negligible.

Hence, the TG data correspond to the thermal degradation of PS to a greater extent than the observed DTA effects; this fact is taken into account in the further discussion.

The kinetic parameters were calculated from the data of thermal analysis by using the well-known equation:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

where $f(\alpha)$ is the "kinetic" function, the form of which is determined by the mechanism of a one-stage process.

It is shown above that the main process in the thermal degradation of PS is its depolymerization. Hence, an attempt may be made to determine the mechanism of thermal degradation by selecting the form of the kinetic function that is in best agreement with the experimental data. The methodological procedure of this analysis was described in detail earlier [8]. The results are given in Table 1.

Table 1 Kinetic parameters of thermal degradation of PS composition with bromine-containing flame retardants (content − 1 mass % based on bromine, calculation − from the TG-DTG data)

Flame retardant	Atmosphere	Activation energy E_a, kJ mole^{-1}	Type of kinetic function $f(\alpha)$	Mechanism of the process
−	air	242	$[(\frac{1}{1-\alpha})^{1/3}-1]^{-1}$	three-dimentional diffusion
HBCD	air	316	$[-\ln(1-\alpha)]^{-1}$	two-dimentional diffusion
DBDPO	air	215	$[(\frac{1}{1-\alpha})^{1/3}-1]^{-1}$	three-dimensional diffusion
HBDP	air	295	$1-\alpha$	first order equation
−	helium	262	$(1-\alpha)^{2/3}$	2/3 order
HBCD	helium	301	$(1-\alpha)^{2/3}$	2/3 order
DBDPO	helium	289	$(1-\alpha)^{2/3}$	2/3 order
HBDP	helium	444	$(1-\alpha)^{2/3}$	2/3 order

First, it should be noted that, unlike the authors of previously published papers, we could not confirm the assumption that the thermal degradation of PS proceeds as a first-order reaction. On the contrary, it follows from the analysis of the DTA data given above that this process in air is limited by the diffusion of degradation products (and, possibly, of atmospheric oxygen) in the sample. The thermal degradation of PS in helium obeys another mechanism: the reaction order is 2/3, which generally indicates that the reaction proceeds at the interface. It may be assumed that in this case the process is limited by the evaporation of degradation products from the sample surface. As indicated above, in the case of thermo-oxidative degradation secondary processes of oxidation of the degradation products develop on the surface of the sample, and the evaporation stage no longer plays an importanat role in the kinetics of the process.

The values of E_a for the thermal degradation of PS are not outside the ranges reported in the literature [5]. If these values are compared with those obtained for thermo-oxidative degradation in the presence of flame retardants, the following serie is obtained: PS+DBDPO < PS < PS+HBDP < PS+ +HBSD. The fact that the introduction of DBDPO into the polymer sligthly decreases E_a for the thermal degradation in air, at first sight corresponds to the results published in [7], although, since diffusion remains the limiting stage, it might be assumed that DBDPO decreases the viscosity of the melt, thereby facilitating the diffusion of the monomer (or oxygen) in it, rather than accelerating the processes of free-radical degradation of PS. In the

case of the other two flame retardants, a certain retardation of the thermal degradation occurs, as indicated by an increase in E_a and changes in the mechanism of the limiting stage. Only in the case of the system containing HBDP is a first order observed for the thermal degradation of PS in air.

The values of E_a for the thermal degradation of PS in helium in the absence and presence of flame retardants form the following series: PS < PS+ +DBDPO < PS+HBCD < PS+HBDP. In all these cases it is possible to assume the same mechanism of the limiting stage. Flame retardants have a certain influence on the surface effects for the PS melt, and in this case there is no reason to associate their action with participation in the degradation process.
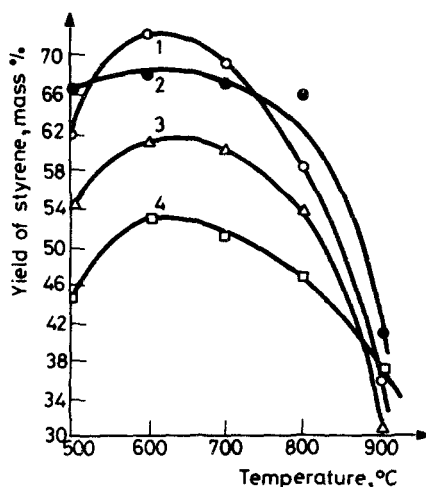

Fig. 2 Formation of styrene upon heating polystyrene pure or containing 15 mass % flame retardant (based on bromine) to various pyrolysis temperatures
1) PS, 2) PS + HBDP, 3) PS + DBDPO, 4) PS + HBCD.

Comparison of the curves of the temperature-dependence of the styrene yield in pyrolysis (Fig. 2) with those of the isolation of hydrogen bromide from the composition of PS with bromine-containing flame retardants (Fig. 3) reveals a marked correlation in the following series: for styrene yield PS>PS+HBDP>PS+DBDPO>PS+HBCD, and for hydrogen bromide evolution PS+HBCD>PS+DBDPO>PS+HBDP. These data suggest that the stabilizing effect is in all cases related to the isolation of hydrogen bromide, and all the flame retardants considered here are stabilizers of the thermal degradation of PS.
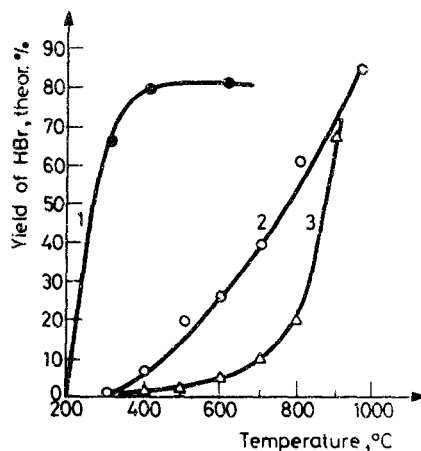
Fig. 3 Formation of hydrogen bromide upon heating polystyrene containing 15 mass % flame retardants
(based on bromine) to various pyrolysis temperatures
1) PS + HBCD, 2) PS + DBDPO, 3) PS + HBDP.

However, these series do not quite coincide with those obtained from thermal analysis. The overall process of thermal degradation of PS both in air and in helium in the presence of flame retardants is presumably affected both by the chemical factors, which are probably related to the direct participation of the hydrogen bromide evolved in the free-radical degradation process, and by the physical factors changing some characteristics of the polymer melt.

Conclusions

1. The thermal degradation of PS in air and in an inert atmosphere is limited by diffusion processes occurring at the interface, respectively.
2. The introduction of bromine-containing flame retardants into PS affects the kinetics of its thermal degradation.
3. The influence of a flame retardant on the thermal degradation of PS is a complex process, the chemical aspects of which are related to inhibition of the chain reaction with the participation of free radicals by hydrogen bromide, while the physical aspects are related to the changes in some characteristics of the polymer melt.

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Zusammenfassung – Die Kinetik des thermischen und thermo-oxidativen Abbaus von Polystyren in Gegenwart bromhaltiger Flammschutzmittel wurde untersucht. Es wird gezeigt, dass die Reaktion durch die Diffusion in Luft bzw. durch die Grenzflächenvorgänge in Helium begrenzt wird.

Die Flammschutzmittel beeinflussen den Abbau von Polystyren sowohl chemisch als auch physikalisch und verändern im gewissen Masse auch den Mechanismus des geschwindigkeitsbestimmenden Schritts.

РЕЗЮМЕ — Изучена кинетика термического и термоокислительного распада полистирола в присутствии бромсодержащих ингибиторов пламени. Установлено, что кинетика таких процессов в атмосфере воздуха определяется диффузией, а в отмосфере гелия — процессами протекающими на границе раздела. Ингибиторы пламени затрагивают физически и химически распад полистирола и до некоторой степени изменяют механизм определяющей стадии.