

**Thermal decomposition of the bromine containing oxyphenylimides**

Yu. Karabets, A. Kolendo, O. Demchenko, A. Byeda, B. Mischanchuk

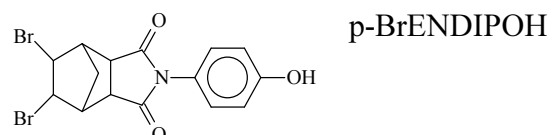
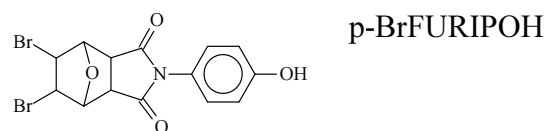
*Kiev National Taras Shevchenko University, Faculty of Chemistry, Department of Macromolecular Chemistry, 64 Vladimirska St, 01033 Kiev, Ukraine*[y.karabets@gmail.com](mailto:y.karabets@gmail.com)

The new bromine containing oxyphenylimides are synthesized by Diels-Alder condensation from commercial products. The effect of brominating of oxyphenylimides on their thermal stability on air is assessed by dynamic thermogravimetric analysis. The possible routes of thermal decomposition of the brominated oxyphenylimides are researched with the help of thermal desorption analysis coupled with mass spectrometry and  $^1\text{H}$  NMR spectroscopy.

**Introduction**

Polystyrene is a large-volume commercial polymer used in a variety of applications. Imidophenyl(meth)acrylates were showed to be high-performance polystyrene thermal stabilizers [1-3]. Their properties can be tailored through changing molecular structure of substitutes in the imide cycle. Of the special interest are represented acylated oxyphenylsuccinimide derivatives which are the products of oxyphenylmaleimide Diels-Alder condensation [4] with dienes containing spatially non-hindered double bond and obtained from the commercial products. Previously it was ascertained that stabilizing effect of succinimidophenylmethacrylate derivatives prepared by the Diels-Alder reaction covalently introduced to PS is conditioned by formation of dienes and the products of the decomposition of phenylmaleimide units [5] and stabilizing effectiveness of an addition are determined by the nature of imide cycle and thermal stability of imidophenyl(meth)acrylate

which should be near the same for polystyrene [6]. To effect on the thermal stability of imidophenyl(meth)acrylates from this range it was interesting to realize their brominating. The first step in these investigations was to synthesize brominated oxyphenylimides and examine their thermal stability and the products of their thermal decomposition. In the present work we report data on synthesis and thermal decomposition of the brominated oxyphenylimides containing bridges in imide cycle:

**Results and discussion**

The results of thermo gravimetric investigations of p-BrFURIPOH and p-

BrENDIPOH comparing to non brominated samples are presented on Fig.1.

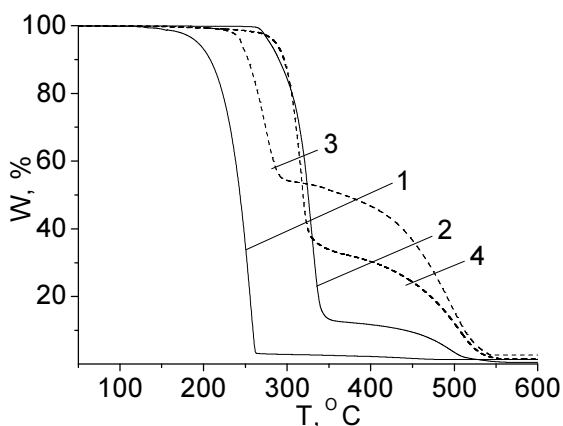
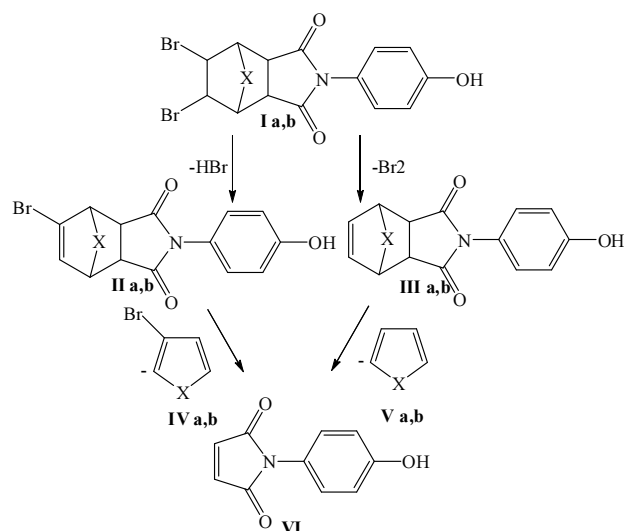


Figure 1. TG curves for p-FURIPOH (1), p-BrFURIPOH (2), p-ENDIPOH (3), and p-BrENDIPOH (4).

Thermal stability of p-FURIPOH is revealed rather poorly. The difference in thermal stability of p-ENDIPOH is remarkable in comparison to above considered sample. The brominating of oxyphenylimides has different influence on their thermal properties subject to diene building. For p-BrFURIPOH the onset temperature of thermal decomposition significantly shifted to the higher temperatures region - by 120°. The brominating of p-ENDIPOH is result in enhancement of oxyphenylimide thermal stability by 32°.

The thermal decomposition of bromine containing p-hydroxyoxyphenylimides (**Ia** and **Ib**) may occurs through firstly dehydrohalogenation with formation of **IIa** or **IIb** or dehalogenation with formation of **IIIa** or **IIIb** processes then retro Diels-Alder reaction passing with formation of corresponding dienes (**IVa,b** or **Va,b**) and dienophile -

phenylmaleimide (**VI**) with subsequent their decomposition (Fig 2).



, where x = -O- (a); x = -CH<sub>2</sub>- (b)

Figure 2. Ways of bromine containing hydroxyphenylimides thermal decomposition.

The sample of p-BrENDIPOH (**Ib**) was heating on air at 290 °C during 10 minutes then cooled and examined by <sup>1</sup>H NMR spectroscopy. The maleimides protons of **VI** are revealed at 7.2 ppm in <sup>1</sup>H NMR spectra. So at heating of **Ib** sample the retro Diels-Alder reaction occurs with formation of diene and p-hydroxyphenylmaleimide.

For the detailed investigation of thermal decomposition and retro Diels-Alder reaction passage the mass spectral analysis of desorbed decomposition products (ionization method – electron impact) has been carried out. The thermal desorption profiles (TPD-MS) on the p-BrFURIPOH (**Ia**) decomposition are presented in Fig 3.

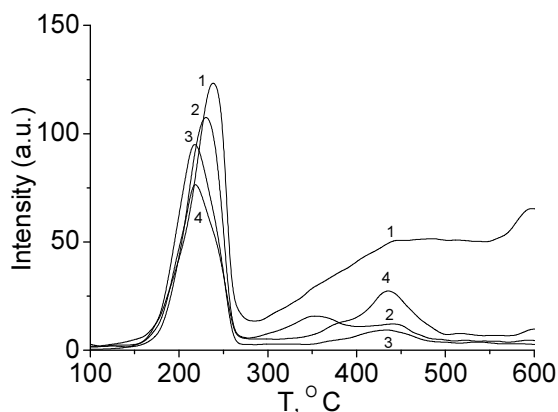


Figure 3. TPD-MS profiles of p-BrFURIPOH, for  $m/z$  28 (1),  $m/z$  54 (2),  $m/z$  79 (3) and  $m/z$  80 (4).

On the TP-DMS for p-BrFURIPOH we observe  $m/z$  80 (Fig. 3, curve 4) which indicates that  $\text{HBr}^+$  can be released [7]. The  $m/z$  82 for  $\text{HBr}^+$  containing second bromine isotope is also present on TPD-MS profiles. The masses corresponding to formation of diene or its fragments are not revealed on TPD-MS profiles probably because their particles are not charged. The products of the fragmentation of p-hydroxyphenylmaleimide unit (VI) are detected (Fig. 3). Due to ionization process occurs during measurements  $\text{CO}^+$  with  $m/z$  28 is released from the phenol fragment. The ions with  $m/z$  54, 79 can appear due to the decomposition process of phenylmaleimide fragment with formation of  $\text{C}_3\text{H}_2\text{O}^+$  and  $\text{C}_5\text{H}_5\text{N}^+$  (pyridine) [7].

The TP-DMS for p-ENDIPOH (Ib) does not contain masses indicating on the release of  $\text{Br}^+$  or  $\text{HBr}^+$  probably because their particles are not charged. But we can observe  $m/z$  66 and  $m/z$  40 which indicates the possibility that  $\text{C}_5\text{H}_6^+$  (cyclopentadiene) Vb and its fragment  $\text{C}_3\text{H}_4^+$  is released. This indicates that thermal

decomposition of Ib occurs through dehalogenation with formation of IIIb. As in the case of above considered p-hydroxyphenylimide the ions with  $m/z$  54, 79 can appear due to the decomposition process of phenylmaleimide VI with formation of  $\text{C}_3\text{H}_2\text{O}^+$  and  $\text{C}_5\text{H}_5\text{N}^+$ . So, at heating of bromine containing p-hydroxyphenylimides at first for p-BrFURIPOH dehydrohalogenation and in the case of p-ENDIPOH dehalogenation occurs. Later retro Diels-Alder reaction is passing with formation of corresponding dienes (for p-ENDIPOH - Vb) and dienophile - p-hydroxyphenylmaleimide. The products of the fragmentation of the last are observed on the TPDMS profiles for the both compounds.

### Conclusions

The brominating of oxyphenylimides containing bridges in imide cycle results in enhancement of their thermal stability. It may be explained by occurrence of the dehalogenation or dehydrohalogenation processes foregoing retro Diels-Alder reaction passage with formation of corresponding dienes and dienophile - phenylmaleimide. Such new bromine containing methacrylated derivatives of p-hydroxyphenylimides can be used for creation of new effective polystyrene stabilizing systems.

### Experimental part

New bromine containing p-hydroxyphenylimides were prepared by brominating of appropriate commercial anhydrides and condensation of obtained products with p-aminophenol. The effect of

brominating of hydroxyphenylimides on their thermal stability on air is assessed by dynamic thermogravimetric analysis with the help of TA Q 600 STD thermo-analyzer (TA Instruments). All measurements have been performed in the temperature range 20-650°C and a heating rate of 5°/min in the air atmosphere. Weights of all the prepared samples in use were 5-10 mg. The thermal decomposition products of the bromine containing oxyphenylimides have been investigated by TPD-MS. The sample (0.01 g) was placed into a quartz reactor connected with quadrupole mass-spectrometer (MX-7304 A), evacuated before the desorption runs and then heated using a linear heating regime with 14 °/min rate. The desorbed volatilized compounds were then ionized and filtered selectively in the quadrupole by  $m/z$ . The intensity of ions in the spectrum with  $m/z$  in the range of 15–100 was monitored with the mass spectrometer as a function of the temperature, at a total pressure of *ca.*  $1 \cdot 10^{-4}$  Pa. The thermal decomposition products were also examined by  $^1\text{H}$  NMR spectroscopy with the help of Varian Mercury-400 spectrometer.

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