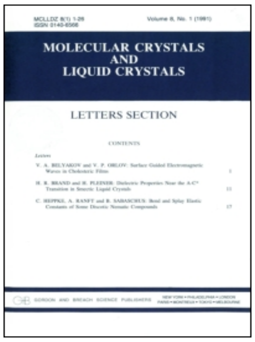

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Synthesis and investigation of bromine containing oxy- and propionoxyphenylimides for polymers thermostabilization

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ABSTRACT

The new bromine containing oxyphenylimides are synthesized by Diels-Alder condensation from commercial products. From the bromine containing oxyphenylimides were obtained corresponding imidophenylpropionates. The brominating of oxyphenylimides has different influence on their thermal properties subject to diene building. The possible routes of thermal decomposition of the brominated oxyphenylimides and imidophenylpropionates were studied with the help of thermal desorption analysis coupled with mass spectrometry. The perspectives of bromine containing oxyphenylimides usage for creation of new polystyrene stabilizing systems are discussed.

KEYWORDS

oxyphenylimide; imidophenylpropionate; bromine derivative; thermal decomposition

Introduction

Polystyrene (PS) 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 depends on formation of dienes and the products of the decomposition of phenylmaleimide units [5–6] 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 polysterene [7]. 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 oxyphenylpropionates and examine their thermal stability and the products of their thermal decomposition. Corresponding imidophenylpropionates were obtained because they are nearest analogue of chain in modified polystyrene:

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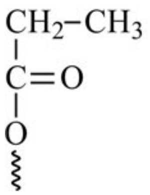
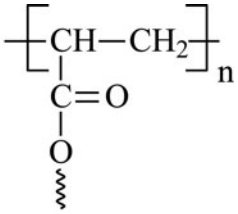
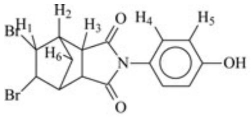




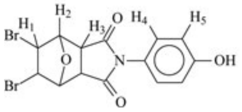
Experimental

In the present work we report data on synthesis and thermal decomposition of the brominated oxyphenylimides containing bridges in imide cycle:



5,6-dibromo-2-(4-hydroxyphenyl)hexahydro-1*H*-4,7-methanoisoindole-1,3-dione

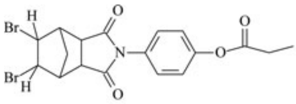
p-BrENDIPOH



5,6-dibromo-2-(4-hydroxyphenyl)hexahydro-1*H*-4,7-epoxyisoindole-1,3-dione

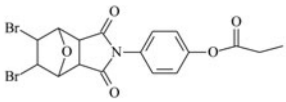
p-BrFURIPOH

From these oxyphenylimides were obtained corresponding imidophenylpropionates by acylation of propionate anhydride:



4-(5,6-dibromo-1,3-dioxooctahydro-2H-4,7-methanoisoindol-2-yl)phenyl propionate

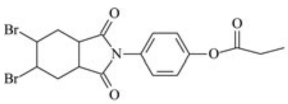
p-BrENDIPOPr



4-(5,6-dibromo-1,3-dioxooctahydro-2H-4,7-epoxyisoindol-2-yl)phenyl propionate

p-FURIPOPr

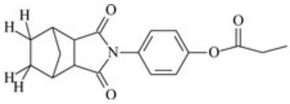
For comparison the imidophenylpropionate which does not contain bridge in imide cycle was investigated:



4-(5,6-dibromo-1,3-dioxooctahydro-2H-isoindol-2-yl)phenyl propionate

p-BrTGFTIPOPr

Also the hydrated sample of p-BrENDIPOPr was obtained with a help of it hydration in the solution of methanol – DMFA + 10% Pd/C catalyzer:



4-(1,3-dioxooctahydro-2H-4,7-methanoisoindol-2-yl) phenyl propionate

p-HENDIPOPr

The thermal decomposition products of the bromine containing compounds have been investigated by TPD-MS (Thermally programmed desorption with mass spectrometry)

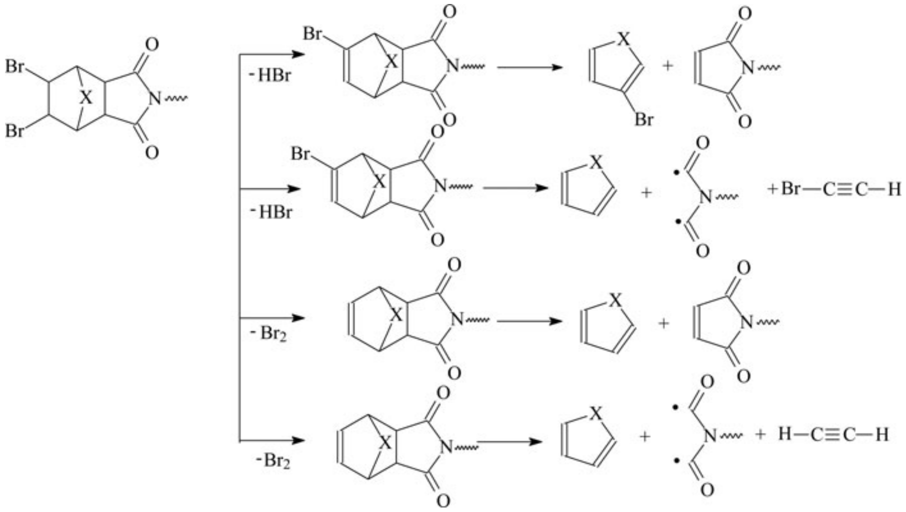


Figure 1. Where X = -O-; -CH_2-.

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.

Results and discussion

The thermal decomposition of bromine containing compounds may occur through different routs and firstly dehydrohalogenation or dehalogenation (Fig 1).

The TPD-MS for p-BrENDIPOH does not contain masses indicating on the release of Br^+ or HBr^+ probably because their particles are not charged. But we can observe the ions with *m*/*z* 66 and *m*/*z* 40 which indicates the possibility that $C_5H_6^+$ (cyclopentadiene) and its fragment $C_3H_4^+$ is released [8]. This indicates that thermal decomposition of p-ENDIPOH occurs through dehalogenation (IIIb). As in the case of above considered oxyphenylimide the ions with *m*/*z* 54, 79 can appear due to the decomposition process of phenylmaleimide fragment (VI) with formation of $C_3H_2O^+$ and $C_5H_5N^+$ (pyridine).

On TPD-MS for p-BrENDIPOPr we observe *m*/*z* 80, 82 which indicates than HBr^+ can be released [8] (Fig 2).

The ions with *m*/*z* 66, 39 can appear due to cyclopentadiene $C_5H_6^+$ and its fragment $C_3H_3^+$ is releasing. In comparison with oxyphenylimide the fragmentation for p-BrENDIPOPr occurs differently. The products of phenyl ring are absent.

The thermal decomposition of hydrated sample of p-HENDIPOPr occurs as alkanes. On TPD-MS for this sample the products of imide fragment decomposition are absent.

On the TP-DMS for p-BrFURIPOH we observe the ions with *m*/*z* 80 (Fig. 3, curve 4) which indicates that HBr^+ can be released [8].

The ions with *m*/*z* 82 for 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

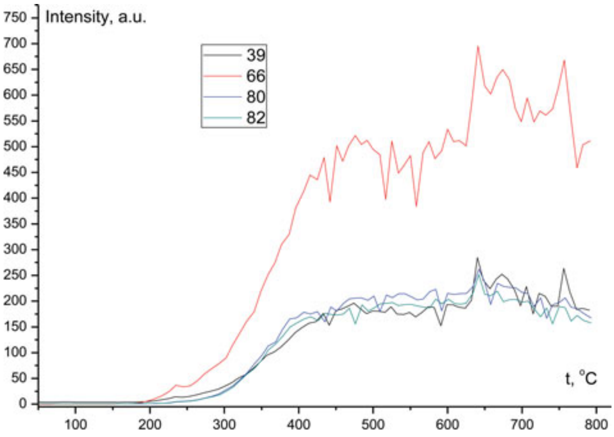


Figure 2. TPD-MS profiles of p-BrENDIPOPr, for the ions with *m*/*z* 39 (1), *m*/*z* 66 (2), *m*/*z* 80 (3), *m*/*z* 82 (4).

on TPD-MS profiles probably because their particles are not charged. The products of the fragmentation of phenylmaleimide unit are detected on Fig. 3. During TPD-MS measurements the CO^+ ions with *m*/*z* 28 are released from the phenol fragment due to ionization process. The ions with *m*/*z* 54, 79 can appear due to the decomposition process of phenylmaleimide fragment with formation of $C_3H_2O^+$ and $C_5H_5N^+$ (pyridine) [8].

On the TPD-MS for p-BrFURIPOPr we observe the ions with *m*/*z* 39, 68 (Fig. 4, curves 1,2) which indicates than $C_4H_4O^+$ (furan) and its fragments can be released.

Obviously the thermal decomposition of p-BrFURIPOPr begins from the decomposition of heterocyclic fragment with furan releasing. The traces of imide fragments decomposition on TPD-MS for p-BrFURIPOPr are absent.

p-BrTGFTIPOPr has not the bridge in the imide cycle. This is the reason that it is decomposed as bromoalkanes. When the termoenergy becomes close to C-C bond energy the statistical destruction of the C-C bonds will begin.

The TPD-MS for all investigated samples does not contain masses indicating on the release of Br^+ probably because their particles are not charged.

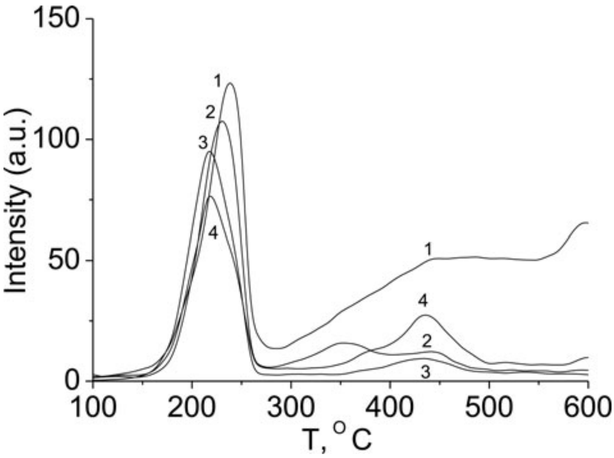


Figure 3. TPD-MS profiles of p-BrFURIPOH for the ions with *m*/*z* 28 (1), *m*/*z* 54 (2), *m*/*z* 79 (3) and *m*/*z* 80 (4).

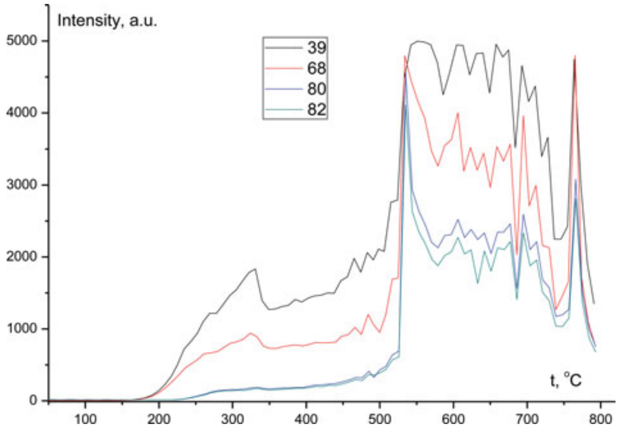


Figure 4. TPD-MS profiles of p-BrFURIPOPr for the ions with *m/z* 39 (1), *m/z* 68 (2), *m/z* 80 (3) and *m/z* 82 (4).

New bromine containing methacrylated derivatives of oxyphenylimides with bridges in imide cycle can be used for creation of new effective polystyrene stabilizing systems by adding them in to the chain.

Conclusions

The brominating of oxyphenylimides and imidophenylpropionates has different influence on their thermal properties according to diene structure. The thermal decomposition of bromine containing oxyphenylimides with bridges in imide cycle occurs through dehydrohalogenation or dehalogenation whis later passing Diels-Alder reaction with formation of corresponding dienes and dienophile - phenylmaleimide fragment. In comparison with oxyphenylimide the fragmentation for imidophenylpropionates occurs differently. For imidophenylpropionates on the TPD-MS profiles the traces of imide fragments decomposition are not observed. The thermal decomposition of hydrated sample occurs as for alkanes. The sample without bridge in the imide cycle is decomposed as bromoalkanes.

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