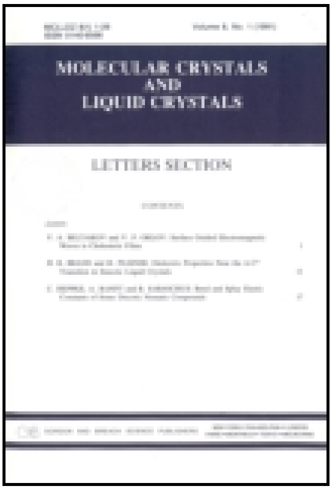
This article was downloaded by: [Xian Jiaotong University]
On: 11 December 2014, At: 13:22
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Brominating of Oxyphenylimides for Enhancement of Stabilizing Properties of their Derivatives

Yu. Karabets [a], A. Kolendo [a], O. Demchenko [a] & N. Iukhymenko [a]
[a] Macromolecular Chemistry Department, Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

Published online: 28 Mar 2014.

To cite this article: Yu. Karabets, A. Kolendo, O. Demchenko & N. Iukhymenko (2014) Brominating of Oxyphenylimides for Enhancement of Stabilizing Properties of their Derivatives, Molecular Crystals and Liquid Crystals, 590:1, 90-96, DOI: 10.1080/15421406.2013.873852

To link to this article: http://dx.doi.org/10.1080/15421406.2013.873852

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 590: pp. 90–96, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.873852

Brominating of Oxyphenylimides for Enhancement of Stabilizing Properties of their Derivatives

YU. KARABETS, A. KOLENDO, O. DEMCHENKO, AND N. IUKHYMENKO*

Macromolecular Chemistry Department, Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

New bromine-containing oxyphenylimides are synthesized by the Diels–Alder condensation from commercial products. The effect of the bromination of oxyphenylimides on their thermal behavior as comparing with the thermal stability of polystyrene in air is assessed by dynamic thermogravimetric analysis and differential scanning calorimetry. The bromination of oxyphenylimides has different influences on their thermal properties subject to the diene building. The perspectives of the usage of bromine-containing oxyphenylimides for the creation of new polystyrene-stabilizing systems are discussed.

Keywords oxyphenylimide; bromine derivative; melting; thermal decomposition; polystyrene

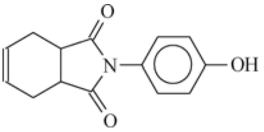
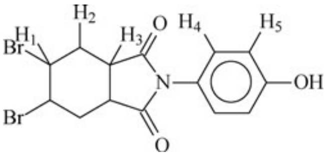
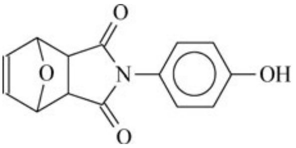
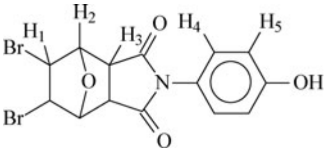
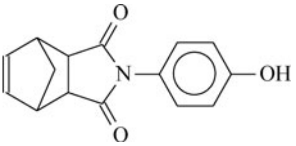
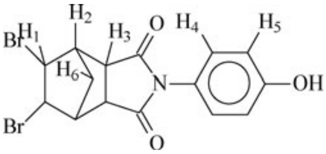
Introduction

Polystyrene (PS) is widely used in a number of commercial products, so the stabilized forms of this polymer are of importance. Imidophenyl(meth)acrylates were showed to be high-performance thermal stabilizers of polystyrene due to their properties to inhibit and to retard its thermal decomposition [1–3]. The stabilizing properties of imidophenyl(meth)acrylates can be tailored through changing the building of their imide fragment. Of special interest in this field are acylated oxyphenylsuccinimide derivatives which are products of the Diels–Alder condensation of oxyphenylmaleimide [4] with dienes containing a spatially non-hindered double bond and obtained from commercial products. In the earlier work, while investigating the thermal properties of model oxyphenylimides, we have revealed that the more effective PS stabilizers are those, whose thermal decomposition begins at temperatures near the same for the polymer [5]. To affect the thermal stability of oxyphenylimides, which is supposed to be the important characteristic at the creation of polystyrene-stabilizing systems, we decide to synthesize new brominated samples of oxyphenylimides. The scope of this paper is to realize the bromination of some anhydrides, obtain the appropriate oxyphenylimides, investigate their thermal behavior in air as compared with the thermal stability of polystyrene, and conclude about the suitability of

---

*Corresponding author, N. Iukhymenko. Tel.: +380442393411, Fax: +380442393100. E-mail: yukhimenko@mail.ru

Table 1. Oxyphenylimides under study

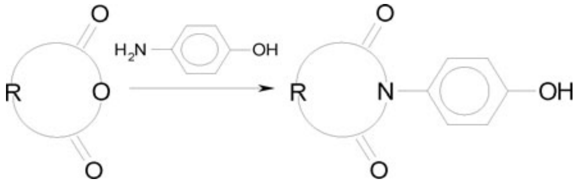
	2-(4-hydroxyphenyl)-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)dione	p-TGFTIPOH
	5,6dibrome-2-(4-hydroxyphenyl)hexahydro-1H-isoindole-1,3(2H)dione	p-BrTGFTIPOH
	2-(4-hydroxyphenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3-dione	p-FURIPOH
	5,6-dibromo-2-(4-hydroxyphenyl)hexahydro-1*H*-4,7-epoxyisoindole-1,3-dione	p-BrFURIPOH
	2-(4-hydroxyphenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3-dione	p-ENDIPOH
	5,6-dibromo-2-(4-hydroxyphenyl)hexahydro-1*H*-4,7-methanoisoindole-1,3-dione	p-BrENDIPOH

the use of their methacrylated derivatives for the creation of new polystyrene-stabilizing systems.

Experimental

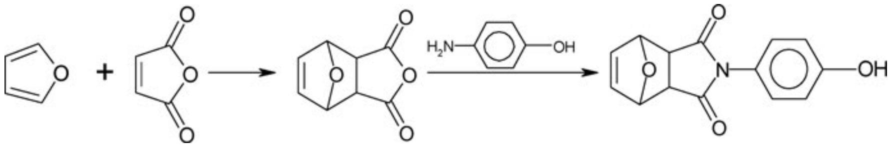
The range of synthesized and investigated oxyphenylimides and their bromine derivatives are presented in Table 1.

Oxyphenylimides were synthesized by the condensation of appropriate commercial anhydrides with p-aminophenol:



(1)

p-FURIPOH was obtained from furan by the following scheme:



(2)

The brominated oxyphenylimides were obtained by Eqs. (1) and (2), but using the appropriate bromine derivatives of anhydrides.

p-BrTGFTIPOH (table 1): white solid: ^{1}H NMR (DMSO-d$_6$, 400 MHz, TMS), ppm: 9.46 (s, OH), 4.60 (s, 2H, H$_1$), 3.25 (s, 2H. H$_3$), 2.55 (m, 4H, H$_2$), 7.02 (d, 2H, H$_4$), 6.81 (d, 2H, H$_5$).

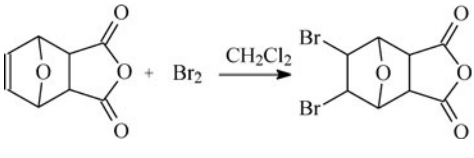
p-BrFURIPOH (table 1): white solid: ^{1}H NMR (DMSO-d$_6$, 400 MHz, TMS), ppm: 9,52 (s, OH), 4.81 (s, 2H, H$_1$), 3.37 (s, 2H, H$_2$), 3.07 (s, 2H, H$_3$), 6.94 (d, 2H, H$_4$), 6.79 (d, 2H, H$_5$).

p-BrENDIPOH (table 1): white solid: ^{1}H NMR (DMSO-d$_6$, 400 MHz, TMS): ppm: 9.50 (s, OH), 4.38 (s, 2H, H$_1$), 3.40 (s, 2H, H$_2$), 3.10 (s, 2H, H$_3$), 7.07 (d, 2H, H$_4$), 6.79 (d, 2H, H$_5$), 2.40 (d, 2H, H$_6$).

The bromination of anhydrides was carried out in acetic acid as

(3)

(where x = CH_2, n = 0; 1) or dichlormethane:



(4)

Polystyrene was synthesized by the radical copolymerization of styrene (Aldrich) thermally initiated with azo-bis-isobutyronitrile (AIBN) (1 wt.%) at 78°C for 20 h.

Dynamic thermogravimetric analysis (TG and DTG curves) of the investigated oxyphenylimides and PS has been carried out on a TA Q 600 STD thermo-analyzer (TA Instruments). The thermal behavior of oxyphenylimides and their bromine derivatives was studied by differential scanning calorimetry (DSC) with the help of a Du Pont

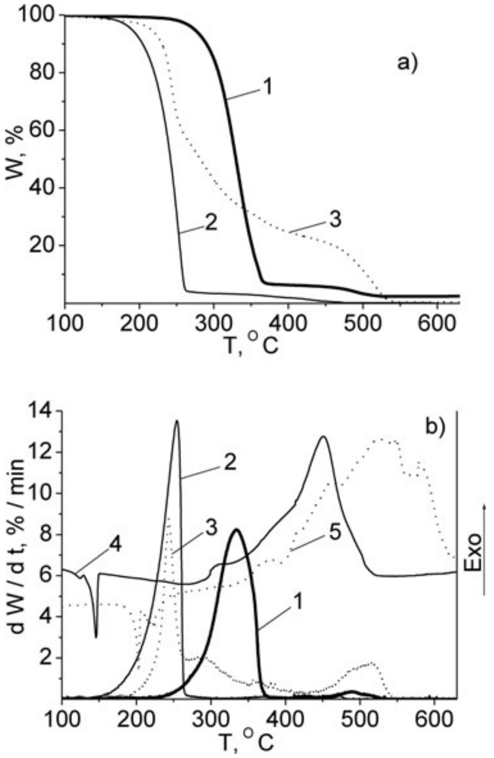


Figure 1. TG (a) and DTG (b) curves for PS (1); p-TGFTIPOH (2); p-BrTGFTIPOH (3), and DSC curves (b) for p-TGFTIPOH (4) and p-BrTGFTIPOH (5).

DTA/DSC-910 on a Du Pont 1090 thermo-analyzer. 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 melting temperature (T_m), temperature interval of melting (ΔT_m), enthalpy of melting (ΔH_m), initial and final temperatures of thermal decomposition (T_{in}, T_f), and temperature of the maximum rate of weight loss (T_{max}) have been determined from the experimental data.

Results and Discussion

The results of thermal properties investigations of oxyphenylimides and their bromine derivatives in air are presented in Figs. 1–3, the melting parameters and the characteristic temperatures of thermal decomposition comparing to polystyrene are in Table 2.

The thermal decomposition behavior of oxyphenylimides and PS suggests a two-step process, where the sample loses at first near 90% of the weight and then the remaining weight at higher temperatures (Figs. 1–3, curves 1, 2). The last is interpreted by the decomposition of peroxides which are formed during the thermal oxidative decomposition of a sample [6,7]. In what follows, we will consider the first step, where the thermal decomposition of a sample actually occurs.

The thermal decompositions of p-TGFTIPOH and p-FURIPOH do not differ by characteristic temperatures and occurs for PS in one stage (Figs. 1 and 2, Table 2). This process is accompanied firstly by the endothermic effect which may be attributed to the

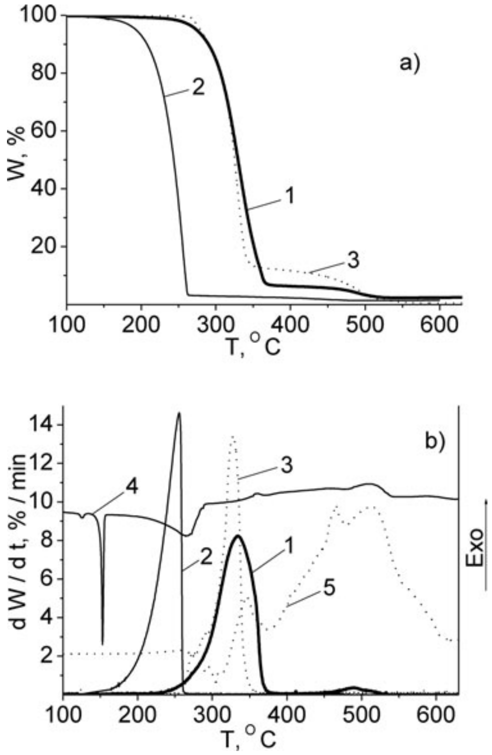


Figure 2. TG (a) and DTG (b) curves for PS (1); p-FURIPOH (2); p-BrFURIPOH (3), and DSC curves (b) for p-FURIPOH (4) and p-BrFURIPOH (5).

Table 2. Parameters of melting and characteristic temperatures of thermal decomposition of PS and oxyphenylimides

Sample code	$T_m{}^a$, °C	$\Delta T_m{}^b$, °C	$\Delta H_m{}^c$, kJ/mol	$T_{in} \div T_f{}^d$, °C	$\Delta T_d{}^e$, °C	$T_{max}{}^f$, °C
PS				240–369	126	334
p-TGFTIPOH	124, 146	104–150	24	140–262	122	255
p-BrTGFTIPOH	203, 222	179–237	106	140–538	398	244, 286, 364
p-ENDIPOH	246	236–252	40	228–540	312	274, 493
p-BrENDIPOH	288	271–292	41	260–540	280	320, 492
p-FURIPOH	125, 153	116–158	38	140–262	122	255
p-BrFURIPOH	291, 305	264–345	188	260–355	95	327

[a] Melting temperature,
[b] Temperature interval of melting,
[c] Enthalpy of melting,
[d] Initial and final temperatures of thermal decomposition,
[e] Temperature interval of thermal decomposition,
[f] Temperature of the maximum rate of weight loss.

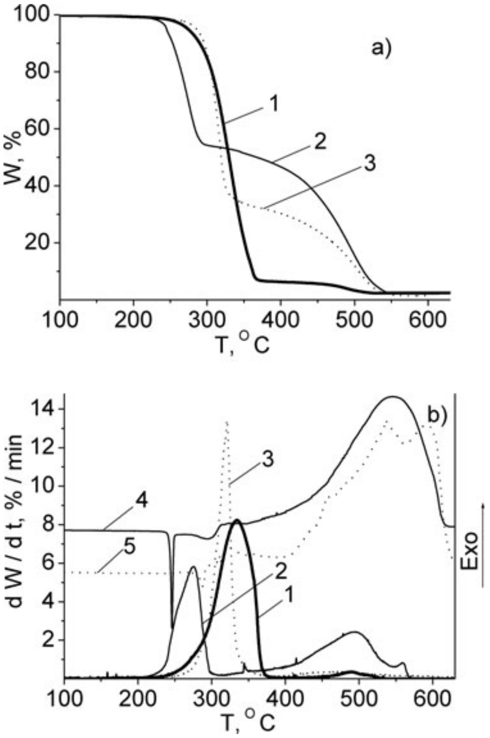


Figure 3. TG (a) and DTG (b) curves for PS (1); p-ENDIPOH (2); p-BrENDIPOH (3), and DSC curves (b) for p-ENDIPOH (4) and p-BrENDIPOH (5).

retro Diels–Alder reaction behavior and then by the exothermic effect, where the thermal oxidative decomposition of a sample occurs (Fig. 1b, 2b, curves 4). The thermal stability of p-TGFTIPOH and p-FURIPOH is revealed rather poorly in comparison to that of polystyrene (Fig. 1a, 2a). The thermal decomposition of these oxyphenylimides starts during the melting by 100° below than that for PS and is almost finished at the point of the onset of thermal decomposition of the polymer (Table 2). Two melting peaks in the DSC curves for p-TGFTIPOH and p-FURIPOH can be seen (Fig. 1b, 2b, curves 4). This is interpreted as follows: the inclusion complexes yielded during the Diels–Alder condensation of oxyphenylmaleimide can exist in the form of endo- and exoisomers [8,9], the latter being usually more thermodynamically stable [8].

The TGA results in Fig. 3 indicate that the thermal stability of p-ENDIPOH remarkably differs from that of the above-considered samples. This oxyphenylmaleimide starts to decompose still during the melting nearly before the onset of thermal decomposition of PS, and this process occurs in two stages in a relatively wide temperature interval (Table 2). The thermal decomposition of p-ENDIPOH is accompanied firstly by the endothermic effect, which may be attributed to the retro Diels–Alder reaction, and then by the exothermic effect, where the thermal oxidative decomposition of a sample occurs (Fig. 3b, curve 4).

The bromination of oxyphenylimides has different influences on their thermal properties subject to the diene building (Figs. 1–3, curves 3 and 5). Concerning the melting process, the bromination of oxyphenylimides results in a rising of their T_m especially considerably for p-BrFURIPOH (Table 1). Meanwhile ΔT_m for the last is extended, but it is restricted for p-BrTGFTIPOH and p-BrENDIPOH. The bromination affects differently ΔH_m: it practically does not vary for p-BrENDIPOH, but increases more than by four times for p-BrTGFTIPOH and p-BrFURIPOH.

The thermal decomposition onset temperature for p-BrTGFTIPOH does not change as compared with that of not brominated oxyphenylimide, whereas ΔT_d is significantly extended, and the process occurs in three stages (Fig. 1, Table 2). The bromination of p-TGFTIPOH results in retarding and varying the character of the thermal decomposition of oxyphenylimide. For p-BrFURIPOH, the initial temperature of the thermal decomposition significantly shifts to the higher-temperature region, by 120°. The interval ΔT_d is somewhat restricted, but the process occurs in one stage as for not brominated oxyphenylimide (Fig. 2, Table 2). The bromination of p-ENDIPOH results in the enhancement of its thermal stability by 32°, ΔT_d is somewhat restricted, but the process occurs in two stages as for not brominated oxyphenylimide (Fig. 3, Table 2).

Previously, it was ascertained that the stabilizing effect of succinimidophenylmethacrylate derivatives prepared by the Diels–Alder reaction and covalently introduced to PS is caused by the formation of decomposition products of the corresponding dienes and the dienophile - phenylmaleimide fragment [10]. The stabilizing effectiveness of methacrylated derivatives of oxyphenylimides is determined by the nature of the imide cycle and the thermal stability of oxyphenylimide comparing with addition-free polystyrene [5]. The methacrylated derivatives of p-TGFTIPOH and p-FURIPOH without a further chemical modification will not reveal, probably, the stabilizing effect toward PS. The methacrylated derivative of p-ENDIPOH showed to be a high-performance thermal stabilizer of polystyrene [1–3]. The bromination of oxyphenylimides with bridges in the imide cycle, p-FURIPOH and p-ENDIPOH, results in an enhancement of their thermal stability. Probably, it may be explained by the dehalogenation or dehydrohalogenation processes foregoing the retro Diels-Alder reaction passage. Hence, the bromine derivatives of such oxyphenylimides can be used for the creation of new effective polystyrene-stabilizing systems.

Conclusions

The bromination of oxyphenylimides has different influences on their thermal properties subject to the diene building. The bromination of oxyphenylimides containing bridges in imide cycle results in an enhancement of their thermal stability. Such new bromine-containing methacrylated derivatives of oxyphenylimides can be used for the creation of new effective polystyrene-stabilizing systems.

References

[1] Kolendo, A. Yu., *et al.* (2009). *Ukr. P. 40865. Promyslova Vlastnist'*, 8.
[2] Kolendo, A. Yu., *et al.* (2009). *Ukr. P. 41029. Promyslova Vlastnist'*, 8.
[3] Nestorak, Iu. S., *et al.* (2011). *Vopr. Khimii i Khim. Tekhn.*, *3*, 63.
[4] Kolendo, A. Yu., Syromyatnikov, V. G., & Paskal, L. P. (1990). *Ukr. Khim. Zh.*, *56*, 647.
[5] Karabets, Yu. M., *et al.* (2012). *Vopr. Khimii i Khim. Tekhn.*, *6*, 56.
[6] Rose, N., *et al.* (1996). *Polym. Degrad. Stab.*, *54*, N 2–3, 355.
[7] Cheng, S. Z. D. (2002). *Handbook of Thermal Analysis and Calorimetry*, Elsevier: Amsterdam.
[8] Chemical Encyclopedia, edited by I. L. Knunyants. (1998). Moscow: Sovets. Entsyklop., Vol. 2 (in Russian).
[9] Ponomar'ov A. A. (1960). Synthesis and Reactions of Furan Substances. Saratov: Saratov Univ. (in Russian).
[10] Nestorak, Iu., *et al.* (2011). *Mol. Cryst. Liq. Cryst.*, *536*, 208.