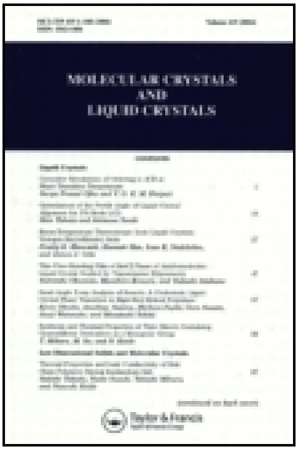

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Thermal Stabilizing Properties of Maleimidophenylmethacrylate Derivatives with Substitutes of Various Molecular Arhitectures in the Imide Cycle

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Thermal oxidative degradation of polystyrene doped with maleimidophenylmethacrylate derivatives which are succinimidophenylmethacrylates with substitutes of various molecular architectures in the imide cycle has been studied by dynamic thermogravimetry in air. The doping monomers (0.5–7 mol.%) have been built into polystyrene macromolecular chains by means of the copolymerization reaction. Succinimidophenylmethacrylates containing spatially non-hindered double bonds or bulky substitutes in the amide cycle show both inhibiting and retarding effects. The m- or p-substitutes have practically identical effect on the polystyrene resistance. The increase of the dopant content up to 5 mol.% results in a regular increase of the thermal stability of polystyrene.

Keywords: doped polystyrene; inhibitor; retarder; stabilizer; succinimidophenylmethacrylate; thermal oxidative degradation

INTRODUCTION

Thermal degradation in the presence of oxygen can be an influential factor on the deterioration of the mechanical properties of polymers during their processing. Protection against their thermal oxidative degradation, therefore, has been extensively studied, and a variety of antioxidants have been developed and widely used [1–4]. But there

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are very few effective thermal oxidative stabilizers which are satisfactory for ensuring the thermal resistance for such a polymer as polystyrene (PS) considering its main applications. Polystyrene is used mainly in consumer electronics and packaging (both foamed and foils one) due to good mechanical properties and a low gas permeability [5,6]. In such an application, the reduced migration of a stabilizer is often required. For that purpose, a stabilizer may be grafted on polystyrene macromolecules. Another effective way of polymer stabilization can be the introduction of a small quantity of a doping monomer into polymer chains through the copolymerization.

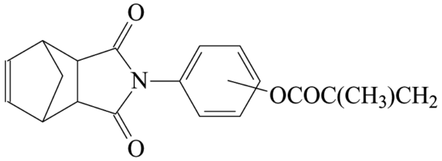
Recently [7], we have reported on the increased stability of polystyrene doped with maleimidophenylmethacrylates (1 mol.%) containing double bonds of different spatial hindrances. The subject of the present paper is the study of stabilizing properties of condensation products of maleimidophenylmethacrylate prepared by the Diels–Alder reaction [8] which are succinimidophenylmethacrylates with substitutes of various molecular architectures in the imide cycle. The influence of the substitute position (m- or p-isomer) and the dopant content (in the range 0.5–7 mol.%) is considered as well.

EXPERIMENTAL

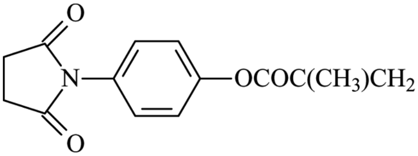
Substituted succinimidophenylmethacrylates have been prepared by the Diels–Alder reaction [8]. The structures of m- and p-methacryloiloxyphenylimide-bicyclo-[2,2,1]-5-heptene-2,3-dicarbonic acid (m- and p-endikimidophenylmethacrylate; m- and p-ENDPMA), p-succinimidophenylmethacrylate (p-SIPMA) and (9,10-dihydroanthracene-9,10-endoα, β-succinimido)phenylmethacrylate (p-ANTRIPMA) are illustrated with the following formulas:

Polystyrene and its copolymers with different contents of the mentioned doping monomers were synthesized by the radical copolymerization of styrene (Aldrich) thermally initiated with azo-bis-isobutyronitrile (AIBN) (1 wt.%) at 351 K for 20 h.

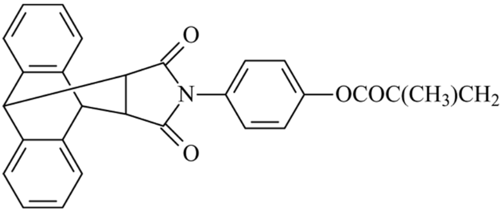
Thermal analysis experiments were performed in the air atmosphere using an F. Paulik, G. Paulik, and L. Erdey Q-1500D instrument in the non-isothermal regime (the temperature range 25 to 500°C and a heating rate of 5°C/min). All the prepared polymer samples were used in weights of 80–100 mg. The weight loss and the weight loss rate were recorded simultaneously. The initial (T_{in}) and final (T_{f}) temperatures [9] of thermal oxidative degradation, temperature of the maximum rate of weight loss ($T_{\max}$), and temperatures which corresponds to 10% and 50% of the weight loss ($T_{10\%}$ and $T_{50\%}$) have been determined from the experimental data.



m- and p-ENDPMA



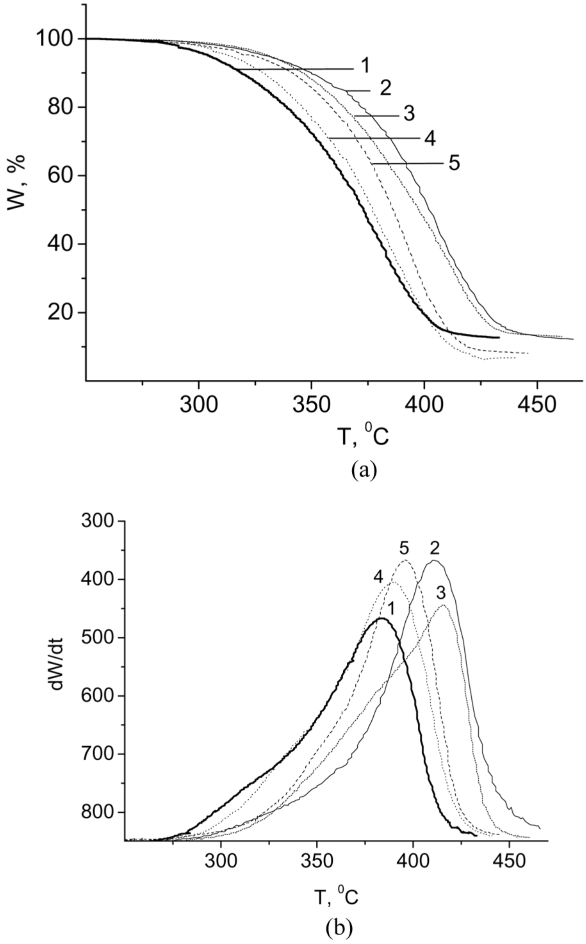
p-SIPMA



p-ANTRIPMA

RESULTS AND DISCUSSION

Both the weight loss curves (TG) and the weight loss rate curves (DTG) recorded as a function of the temperature for the polystyrene samples doped with 1 mol.% of succinimidophenylmethacrylates with substitutes characterizing by various molecular architectures in the imide cycle are presented in Figure 1. The characteristic temperature values for thermal oxidative degradation of the doped polymer samples are presented in Table 1. The thermal oxidative degradation of both the virgin polymer and doped polystyrenes occurs in one stage. One can see in Table 1 that the thermal degradation for all the doped PS samples started several degrees later than those for the virgin PS – approximately 22°C for PS-m-ENDPMA, PS-p-ENDPMA, PS-p-ANTRIPMA and 13°C for PS-p-SIPMA. The initial temperature of degradation (T_{in}) evidences clearly that all the studied dopants inhibit the PS thermodegradation. The temperatures of 10% and 50% weight loss ($T_{10\%}$, $T_{50\%}$) evidenced that the dopants retard the thermal degradation as well. The order of the retarding effectivenesses is as following: m-ENDPMA > p-ENDPMA > p-ANTRIPMA > p-SIPMA. Comparing the temperatures of the maximum weight loss rate ($T_{\max}$), one can obtain such an order: p-ENDPMA > m-ENDPMA > p-ANTRIPMA > p-SIPMA. The temperature interval of thermal



(a)

(b)

FIGURE 1 TG (a) and DTG (b) curves for PS (1); PS-m-ENDPMA (2); PS-p-ENDPMA (3); PS-p-SIPMA (4), and PS-p-ANTRIPMA (5) at a dopant content of 1 mol.%.

oxidative degradation has been registered to be slightly shortened for the p-ANTRIPMA and p-SIPMA dopants, and the one is somewhat enlarged for the m-ENDPMA and p-ENDPMA dopants. The highest values of $T_{\max}$ have been registered for p-ENDPMA and m-ENDPMA doped polystyrene samples (Table 1). The presented experimental results indicate that the applied dopants exhibit a combined action (both as inhibitors and retarders) on the PS thermal degradation kinetics. However, the dopants have different effectivenesses. The

TABLE 1 Characteristic Temperatures of Thermal Oxidative Degradation of Polystyrene Doped with 1 mol.% of Succinimidophenylmethacrylates

Sample	$T_{in} \div T_f{}^a$, °C	ΔT^b, °C	$T_{10\%}{}^c$, °C	$T_{50\%}{}^d$, °C	$T_{max}{}^e$, °C
PS	284–413	129	319	373	384
PS-m-ENDPMA	306–447	141	350	402	411
PS-p-ENDPMA	306–441	135	346	398	415
PS-p-SIPMA	297–421	124	328	377	390
PS-p-ANTRIPMA	306–427	121	341	386	395

[a] Initial and final temperatures.
[b] Temperature interval.
[c] Temperature of 10 wt.% of weight loss.
[d] Temperature of 50 wt.% of weight loss.
[e] Temperature of the maximum rate of weight loss.

data in Table 1 indicate clearly that the p-ENDPMA and m-ENDPMA dopants retard more efficiently the degradation process than the p-ANTRIPMA dopant, while the p-SIPMA one has almost insignificant effect on the degradation rate. One can infer that, among succinimidophenylmethacrylates, the more efficient PS thermal stabilizers are the dopants containing spatially non-hindered double bonds (p-ENDPMA and m-ENDPMA) as well as the dopant with a bulky substitute in the imide cycle (p-ANTRIPMA).

It should to note that the substitute position (m- or p-isomer) in succinimidophenylmethacrylate (m-ENDPMA and p-ENDPMA dopants) has no significant effect on the polystyrene stabilization (Table 2). Both isomers reveal the same inhibiting properties, while

TABLE 2 Characteristic Temperatures of Thermal Oxidative Degradation of PS-m-ENDPMA and PS-p-ENDPMA at Different Dopant Contents

Sample	Content, mol.%	$T_{in} \div T_f{}^a$, °C	ΔT^b, °C	$T_{10\%}{}^c$, °C	$T_{50\%}{}^d$, °C	$T_{max}{}^e$, °C
PS-m-ENDPMA	1	306–447	141	350	402	411
	3	306–475	169	375	426	433
PS-p-ENDPMA	1	306–441	135	346	398	415
	3	306–470	164	377	428	435

[a] Initial and final temperatures.
[b] Temperature interval.
[c] Temperature of 10 wt.% of weight loss.
[d] Temperature of 50 wt.% of weight loss.
[e] Temperature of the maximum rate of weight loss.

m-ENDPMA retards somewhat strongly the process of PS thermal oxidative degradation in the temperature range up to $T_{50\%}$. At the same time, the value of $T_{\max}$ for p-ENDPMA is higher than that for m-ENDPMA. So the studied isomers have somewhat different effects on the polystyrene thermal oxidative degradation rate.

The effect of the succinimidophenylmethacrylate content in the range up to 7 mol.% has been studied with the p-ENDPMA dopant. The characteristic temperatures of thermal oxidative degradation for PS-p-ENDPMA at different dopant contents are gathered in Table 3. One can observed that the dopant content has marked influence on the onset temperature of PS degradation. The inhibiting effect of p-ENDPMA starts to reveal at 1 mol.% and is not changed up to 3 mol.% of the dopant content. The most significant increase of the onset temperature of PS degradation (about 21°C) occurs at the p-ENDPMA content from 3 to 5 mol.%. The further increase of the dopant content does not affect this parameter. The retarding properties of p-ENDPMA are illustrated by the data presented in Figure 2 and Table 3. The characteristic temperatures of thermal oxidative degradation ($T_{10\%}$, $T_{50\%}$, and $T_{\max}$) for PS-p-ENDPMA are increased with the dopant content up to 5 mol.% and then remain almost constant. A comparison of the characteristic temperatures ($T_{10\%}$, $T_{50\%}$ and $T_{\max}$) of thermal oxidative degradation of doped polystyrene with those of the virgin polystyrene leads to the inference that the p-ENDPMA dopant slightly retards the thermal oxidative degradation of PS at 0.5 mol.% of the dopant content. The increase of the dopant content from 1 to 3 mol.% results in the significant retardation of

TABLE 3 Characteristic Temperatures of Thermal Oxidative Degradation of PS Doped with p-ENDPMA at Different Dopant Contents

Content, mol.%	$T_{in} \div T_f{}^a$, °C	ΔT^b, °C	$T_{10\%}{}^c$, °C	$T_{50\%}{}^d$, °C	$T_{\max}{}^e$, °C
0	284–413	129	319	373	384
0.5	284–435	151	336	390	401
1	306–441	135	346	398	415
2	306–460	154	361	413	430
3	306–470	164	377	428	435
5	327–480	153	399	442	444
7	327–490	163	399	446	448

[a] Initial and final temperatures.
[b] Temperature interval.
[c] Temperature of 10 wt.% of weight loss.
[d] Temperature of 50 wt.% of weight loss.
[e] Temperature of the maximum rate of weight loss.

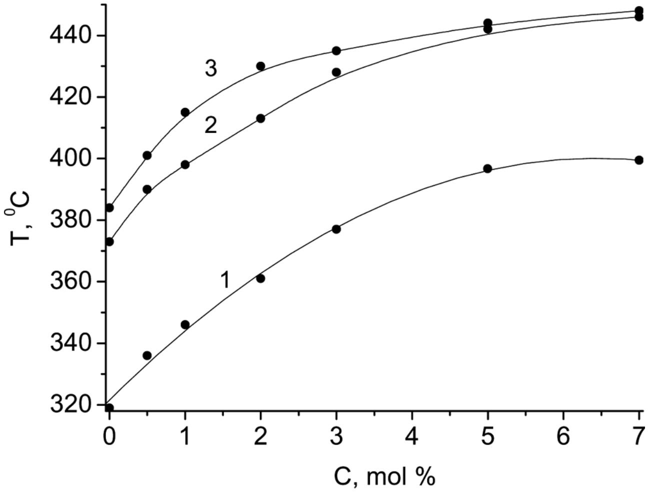


FIGURE 2 Characteristic temperatures of thermal oxidative degradation: $T_{10\%}$ (1), $T_{50\%}$ (2), and $T_{\max}$ (3) for PS-p-ENDPMA *vs* the dopant content.

the PS thermal oxidative degradation, while it does not affect the inhibiting properties (the onset temperature remains the same). The introduction of 5 mol.% and 7 mol.% of p-ENDPMA to PS affects mostly the rate on the initial stage of thermal oxidative degradation of PS ($T_{10\%}$ increases by 80°C, while $T_{\max}$ increases by 60°C and 64°C for 5 mol.% and 7 mol.% content of the dopant, respectively). So, the inhibiting and retarding properties of p-ENDPMA reveal in different ways depending on the dopant content.

CONCLUSIONS

All the studied dopants exhibited the substantial stabilizing action and reveal the combined effect (both as inhibitors and retarders) on the thermal degradation of polystyrene. The dopant effectiveness depends on the dopant molecular structure. The most effective stabilizers are succinimidophenylmethacrylates containing spatially nonhindered double bonds or bulky substitutes in the imide cycle. The substitute position in succinimidophenylmethacrylates (m- or p-isomer) has practically no effect on the polystyrene resistance against thermal oxidative degradation. The rise of the dopant content up to 5 mol.% results in a significant increase of the stabilizing effect.

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