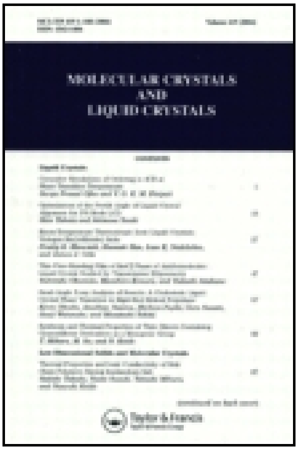

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Maleimidophenylmethacrylates and their Derivatives as Polystyrene Thermal Stabilizers

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Effects of maleimidophenylmethacrylates on thermal stability of polystyrene have been examined by dynamic thermogravimetric analysis in air conditions. The maleimidophenylmethacrylates with substitutes of various molecular architecture in imide cycle have been built in polystyrene macromolecular chains (as much as 1 mol %) by means of copolymerization reaction. The thermal stabilizing effects depend on the structure features of the used compounds. Some of the additives show the inhibiting effect only whereas other ones show combined inhibiting and retarding effects. The last ones revealed as very effective stabilizers of polystyrene against thermal oxidative degradation.

Keywords: inhibitor; maleimidophenylmethacrylate; polystyrene; retarder; stabilizer; thermal oxidative degradation

INTRODUCTION

Polystyrene is a large scale production polymer with a broad range of uses. Due to good mechanical properties and low gas permeability the main applications of polystyrene are packaging materials, extruded sheets and consumer electronics. Commercial polystyrene formulations usually contain additives acting as thermal stabilizers under polymer processing.

In many applications such as single-use kitchen a reduced stabilizer migration is required. For that reason the stabilizer may be grafted on

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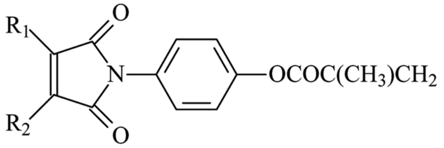
or copolymerized into polystyrene macromolecules. The introduction of small quantity (up to 5 mol %) of stabilizing additives into polymer chain through copolymerization is known as an effective way of polymers stabilization. In particular, amines and their alkyl and acyl derivatives are very perspective for this purpose because sp^2-hybridized nitrogen atom reacts with free radicals and inhibit the radical processes of polymers degradation.

This work proceeds from our interest in capabilities of maleimidophenylmethacrylates containing double bond of different spatial difficulty and of their derivatives, prepared by Diels-Alder reaction, with substitutes of various molecular architecture in imide cycle to stabilize polystyrene in the process of thermal oxidative degradation.

EXPERIMENTAL

The following maleimidophenylmethacrylates were applied: p-maleimidophenylmethacrylate (p-MAFMA), p-(3,4-dichloromaleimido)phenylmethacrylate (p-DCMAFMA) and p-(3-methylmaleimido)-phenylmethacrylate (p-MMAFMA). The maleimidophenylmethacrylates have been prepared by acylation of corresponding p-hydroxyphenylmethacrylates with chloroanhydride of methacrylic acid in the presence of 3-ethylamine [1] and were investigated as polystyrene stabilizers. The structures of the investigated additives are illustrated with the following formulas:



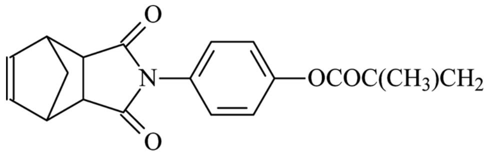
where

$R_1 = R_2 = H$ (p-MAFMA)

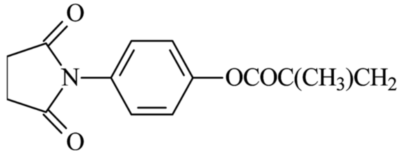
$R_1 = R_2 = Cl$ (p-DCMAFMA)

$R_1 = H,\ R_2 = CH_3$ (p-MMAFMA)

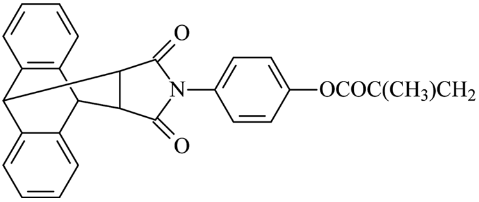
Some maleimidophenylmethacrylate derivatives have been also prepared by Diels-Alder reaction [2], namely p-endikimidophenylmethacrylate (p-ENDFMA), p-succinimidophenylmethacrylate (p-SIFMA) and (9,10-dihydroanthracene-9,10-endoα,β-succinimido)-phenylmethacrylate (p-ANTRIFMA) of following structures:



p-ENDFMA



p-SIFMA



p-ANTRIFMA

Polystyrene (PS) and its copolymers with the mentioned additives (1 mol %) were synthesized by radical copolymerization of styrene (Aldrich) thermally initiated with AIBN (1 weight %). Considering the copolymerization constants of styrene with phenylmethacrylates are less than one [3] we assume that all the used additives are completely copolymerized with styrene. The introduced maleimidophenylmethacrylate additives have been shown as that having no apparent effect on the PS molecular weight ($\bar{M}_v = 114000$) measured by means of viscosimetry [4].

Thermal analysis experiments were performed in air atmosphere using a F. Paulik, G. Paulik and L. Erdey Q-1500D instrument in the non-isothermal regime (temperature range 25 to 500°C and heating rate 5°C/min). All the prepared polymer samples were used in weights of 80–100 mg. A computer processing of TG/DTG experimental data has been applied using Arrhenius equation in the matrix form [5] and the least square method [6]. The four formal kinetic parameters of thermal oxidative degradation have been determined for all the polymers samples namely activation energy (*E*), reaction order (*n*), frequency factor (*Z*) as well as kinetic constant (*k*) [7].

RESULTS AND DISCUSSION

Both the weight loss curves (TG) and the weight loss derivative curves (DTG) were recorded as a function of temperature for the polystyrene samples stabilized with maleimidophenylmethacrylates and their derivatives. The example TG and DTG curves are presented in Figures 1 and 2, respectively. The characteristic temperature values for thermal oxidative degradation of the polymer samples are shown in Table 1. The thermal oxidative degradation of both virgin polystyrene and stabilized polystyrenes occurs in one stage. As shown

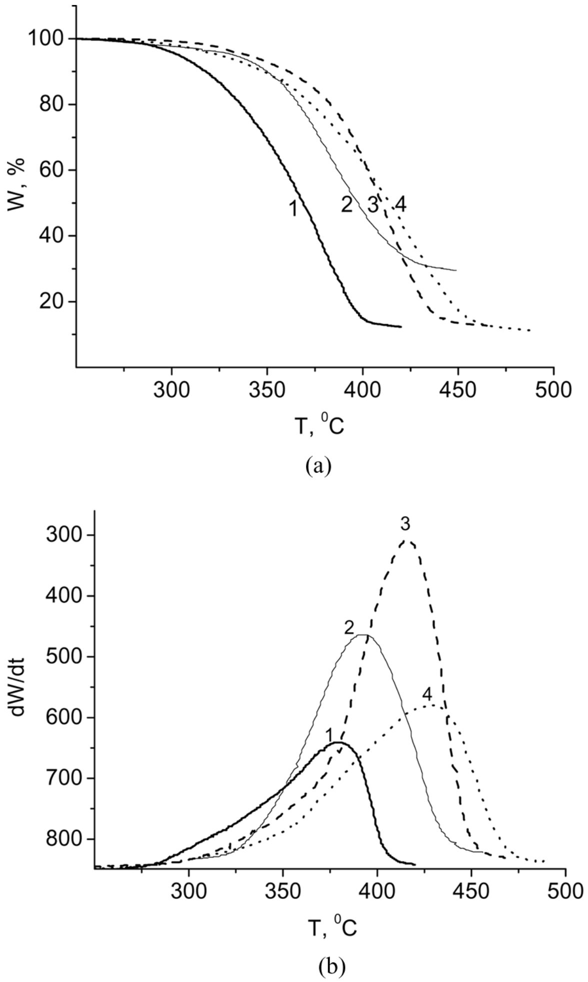
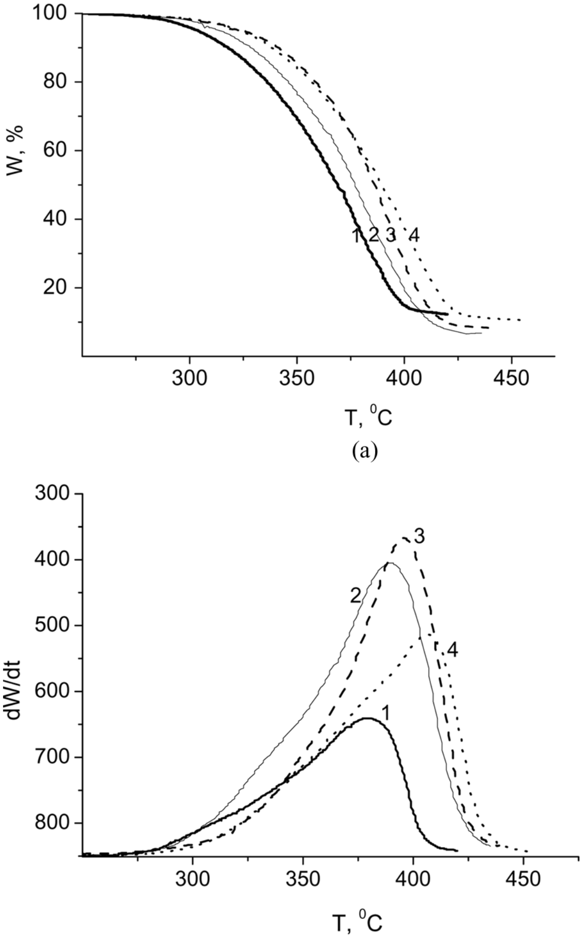


FIGURE 1 The TG (a) and DTG (b) curves for PS (1); PS-p-DCMAFMA (2); PS-p-MMAFMA (3) and PS-p-MAFMA (4).

in Table 1, thermal degradation for all the stabilized PS samples except PS-p-MAFMA started several degrees later than those for PS – about 44°C for PS-p-MMAFMA, 32°C for PS-DCMAFMA, 22°C for PS-p-ENDFMA and PS-p-ANTRIFMA, 13°C for PS-p-SIFMA. The order of inhibiting effectiveness of the studied additives is the following: p-MMAFMA, p-DCMAFMA, p-ENDFMA, p-ANTRIFMA, p-SIFMA, as evidenced by values of initial temperature of degradation (T_{in}) and temperature of 10% weight loss ($T_{10\%}$). Comparing the



(a)

(b)

FIGURE 2 The TG (a) and DTG (b) curves for PS (1); PS-p-SIFMA (2); PS-p-ANTRIFMA (3) and PS-p-ENDFMA (4).

values of temperature of maximum weight loss rate ($T_{\max}$) one can obtain another order: p-MMAFMA, p-ENDFMA, p-ANTRIFMA, p-DCMAFMA, p-SIFMA. The temperature interval of thermal oxidative degradation has been registered to be slightly shortened (p-DCMAFMA and p-ANTRIFMA additives) or somewhat enlarged (p-MMAFMA, p-ENDFMA, p-SIFMA additives). The highest values of $T_{\max}$ temperature have been registered for p-MMAFMA and p-ENDFMA stabilized polystyrene samples (Table 1). The experimental

TABLE 1 Characteristic Temperatures of Thermal Oxidative Degradation

Sample	$T_{\mathrm{in}} \div T_{\mathrm{f}}{}^{a}$, °C	ΔT^{b}, °C	$T_{10\%}{}^{c}$, °C	$T_{50\%}{}^{d}$, °C	$T_{\max}{}^{e}$, °C
PS	284–405	121	318	369	384
PS-p-MAFMA	284–490	204	345	415	434
PS-p-DCMAFMA	316–434	118	350	398	393
PS-p-MMAFMA	328–450	122	361	410	416
PS-p-ENDFMA	306–433	127	338	390	407
PS-p-SIFMA	297–421	124	328	377	390
PS-p-ANTRIFMA	306–425	119	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.

results indicate that the applied additives have a different influence on the kinetics of PS thermal degradation process. Apparently, p-DCMAFMA and p-ANTRIFMA additives while inhibiting thermal oxidative degradation of PS, may also accelerate this process at the certain temperatures. Others additives (p-MMAFMA, p-ENDFMA) exhibit a combined action (as inhibitor + retarder). In that case thermal oxidative degradation starts at higher temperatures and proceeds with lower rate comparing with virgin polymer. PS-p-MAFMA has the same onset temperature of thermal oxidative degradation than PS, but TG/DTG curves are different with respect to the characteristic temperatures ($T_{10\%}$, $T_{50\%}$) and the position of DTG peaks ($T_{\max}$). The p-MAFMA additive results in considerable widening (about 83°C) of temperature interval of PS thermal oxidative degradation. The reason could be that p-MAFMA is effectively slow down the PS degradation process.

The kinetic analysis of thermal oxidative degradation has been carried out for the PS samples stabilized with maleimidophenylmethacrylates, which gave better results. The formal kinetic

TABLE 2 Formal Kinetic Parameters of Thermal Oxidative Degradation

Sample	E, kJ/mol	n	Z, s^{-1}	k^{a}, s^{-1}
PS	80	0.4	3.06×10^{5}	0.13
PS-p-MAFMA	88	0.8	5.27×10^{5}	0.15
PS-p-DCMAFMA	168	1.4	5.54×10^{12}	0.32
PS-p-MMAFMA	170	1	2.13×10^{12}	0.24

[a] Constant of maximum process rate.

TABLE 3 Kinetic Constant Values of Thermal Oxidative Degradation and Temperatures at Various Degree of Weight Loss

Sample	$k_{5\%}$, s^{-1}	$T_{5\%}$, °C	$k_{10\%}$, s^{-1}	$T_{10\%}$, °C	$k_{20\%}$, s^{-1}	$T_{20\%}$, °C	$k_{40\%}$, s^{-1}	$T_{40\%}$, °C
PS	0.017	304	0.026	318	0.042	336	0.076	360
PS-p-MAFMA	0.001	326	0.017	345	0.036	373	0.073	403
PS-p-DCMAFMA	0.016	333	0.039	350	0.089	366	0.24	387
PS-p-MMAFMA	0.006	340	0.018	361	0.054	383	0.13	402

parameters obtained are presented in Table 2. For the virgin PS sample the degradation reaction follows the kinetics of a 0.4 reaction order and the activation energy has been found to be 80 kJ/mol. Both the E and n values are nearly doubled when p-MAFMA is introduced into PS chain. The addition of p-DCMAFMA and p-MMAFMA to polystyrene changes these parameters more significantly – the activation energy was found to increase from 80 kJ/mol for PS to 168 kJ/mol for PS-p-DCMAFMA and to170 kJ/mol for PS-p-MMAFMA. The degradation reactions follow the kinetics of a 1.4 and 1 reaction orders, respectively. As the onset temperature for PS-p-DCMAFMA and PS-p-MMAFMA are higher than that for virgin polymer, we have calculated the kinetic constant for these samples at temperatures of various degree of weight loss (Table 3) in order to compare the effect of maleimidophenylmethacrylates on the rate of PS thermal oxidative degradation in wide temperature range. At the temperature of 5% of weight loss the addition of p-DCMAFMA practically not effect while the addition of p-MAFMA and p-MMAFMA reduce the kinetic constant of PS in 1.6 and 2.8 times, respectively. At the temperature of 10% of weight loss the value of kinetic constant of thermal degradation only for PS-p-DCMAFMA exceed the same for polystyrene. At the temperature of 20% of weight loss this parameter for PS-p-MMAFMA exceeds the same for polystyrene again. Only for PS-p-MAFMA the kinetic constant even on reaching the temperature of 40% of weight loss has been registered to remain somewhat smaller than that for PS. So, the p-MAFMA additive only retards the process of PS thermal oxidative degradation in wide temperature range.

CONCLUSIONS

All the compounds studied exhibited marked stabilizing action on thermal degradation of polystyrene. However, effectiveness of their influence depends on features of the additive structure. The most effective stabilizers proved maleimidophenylmethacrylates containing the least spatially hindered double bonds in imide cycle. The additive p-DCMAFMA exhibits the inhibiting properties during PS thermal oxidative degradation. The additive p-MMAFMA demonstrates a combine effect (inhibitor + retarder) and p-MAFMA is effective rate retarder of polystyrene thermal oxidative degradation. Among the maleimidophenylmethacrylate derivatives the more effective PS thermal stabilizers are the compounds, prepared by Diels-Alder reaction with bulky structural architecture of substitute in imide cycle namely p-ENDFMA and p-ANTRIFMA.

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